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INNOVATIVE SITE REMEDIATION TECHNOLOGY

DESIGN & APPLICATION

Volume 1

Bioremediation

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INNOVATIVE SITE REMEDIATION TECHNOLOGY: DESIGN AND APPLICATION

BIOREMEDIATION

One of a Seven-Volume Series

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Air & Waste Management Association

The Air & Waste Management Association is a nonprofit technical and educational organization with more than 14,000 members in more than fifty countries. Founded in 1907, the Association provides a neutral forum where all viewpoints of an environmental management issue (technical, scientific, economic, social, political, and public health) receive equal consideration.

Qualified reviewers were recruited from the Waste Group of the Technical Council. It was determined that the monograph is technically sound and publication is endorsed.

American Society of Civil Engineers

The American Society of Civil Engineers, established in 1852, is the premier civil engineering association in the world with 124,000 members. Qualified reviewers were recruited from its Environmental Engineering Division.

ASCE has reviewed this manual and believes that significant information of value is provided. Many of the issues addressed, and the resulting conclusions, have been evaluated based on satisfying current regulatory requirements. However, the long-term stability of solidified soils containing high levels of organics, and potential limitations and deficiencies of current testing methods, must be evaluated in more detail as these technologies are implemented and monitored.

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The Hazardous Waste Action Coalition (HWAC) is the premier business trade group serving and representing the leading engineering and science firms in the environmental management and remediation industry. HWAC's mission is to serve and promote the interests of engineering and science firms practicing in multi-media environment management and remediation. Qualified reviewers were recruited from HWAC's Technical Practices Committee. HWAC is pleased to endorse the monograph as technically sound.

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Soil Science Society of America

The Soil Science Society of America, headquartered in Madison, Wisconsin, is home to more than 5,300 professionals dedicated to the advancement of soil science. Established in 1936, SSSA has members in more than 100 countries. The Society is composed of eleven divisions, covering subjects from the basic sciences of physics and chemistry through soils in relation to crop production, environmental quality, ecosystem sustainability, waste management and recycling, bioremediation, and wise land use.

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Water Environment Federation

The Water Environment Federation is a nonprofit, educational organization composed of member and affiliated associations throughout the world. Since 1928, the Federation has represented water quality specialists including engineers, scientists, government officials, industrial and municipal treatment plant operators, chemists, students, academic and equipment manufacturers, and distributors.

Qualified reviewers were recruited from the Federation's Hazardous Wastes Committee and from the general membership. It has been determined that the document is technically sound and publication is endorsed.

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1 INTRODUCTION

This monograph covering the *design, applications, and implementation* of Bioremediation is one of a series of seven on innovative site and waste remediation technologies. This series was preceded by eight volumes published in 1994 and 1995 covering the description, evaluation, and limitations of the processes. The entire project is the culmination of a multiorganization effort involving more than 100 experts. It provides the experienced, practicing professional guidance on the innovative processes considered ready for full-scale application. Other monographs in this design and application series and the companion series address chemical treatment; liquid extraction: soil washing, soil flushing, and solvent chemical extraction; stabilization/solidification; thermal desorption; thermal destruction; and vapor extraction and air sparging.

1.1 Bioremediation

Bioremediation exploits the ability of certain microorganisms — heterotrophic bacteria and fungi — to degrade hazardous organic materials to innocuous materials such as carbon dioxide, methane, water, inorganic salts, and biomass. Microorganisms may derive the carbon and energy required for growth through biodegradation of organic contaminants, or transform complex, synthetic chemicals through fortuitous cometabolism.

The processes discussed in this monograph fall into two categories: *natural bioremediation* and *enhanced bioremediation*. Natural bioremediation, sometimes referred to as intrinsic bioremediation, depends on indigenous microflora to degrade contaminants using only nutrients and electron acceptors available in situ. However, biodegradation rates will be less than optimal if the microbes' nutritional and physiological requirements are not met. Enhanced bioremediation technologies increase biodegradation rates by supplying those nutrients, electron acceptors, or other factors that are rate limiting.

Enhanced bioremediation can be used to degrade contaminants in situ or ex-situ. In situ and ex-situ processes may be used to treat contaminated liquids, solids, or air. Some examples of in situ processes include land treatment, bioventing, liquid delivery, and air sparging. Ex-situ technologies include slurry reactors, land treatment, composting, soil-piles, and biofilters.

1.2 Development of the Monograph

1.2.1 Background

Acting upon its commitment to develop innovative treatment technologies for the remediation of hazardous waste sites and contaminated soils and groundwater, the U.S. Environmental Protection Agency (US EPA) established the Technology Innovation Office (TIO) in the Office of Solid Waste and Emergency Response in March 1990. The mission assigned TIO was to foster greater use of innovative technologies.

In October of that same year, TIO, in conjunction with the National Advisory Council on Environmental Policy and Technology (NACEPT), convened a workshop for representatives of consulting engineering firms, professional societies, research organizations, and state agencies involved in remediation. The workshop focused on defining the barriers that were impeding the application of innovative technologies in site remediation projects. One of the major impediments identified was the lack of reliable data on the performance, design parameters, and costs of innovative processes.

The need for reliable information led TIO to approach the American Academy of Environmental Engineers®. The Academy is a long-standing, multidisciplinary environmental engineering professional society with wide-ranging affiliations with the remediation and waste treatment professional communities. By June 1991, an agreement in principle (later formalized as a Cooperative Agreement) was reached providing for the Academy to manage a project to develop monographs describing the state of available innovative remediation technologies. Financial support was provided by the EPA, U.S. Department of Defense (DoD), U.S. Department of Energy (DOE), and the Academy. The goal of both TIO and the Academy was to develop monographs providing reliable data that would be broadly recognized and accepted by the professional community, thereby eliminating or at least minimizing this impediment to the use of innovative technologies.

The Academy's strategy for achieving the goal was founded on a multiorganization effort, WASTECH® (pronounced Waste Tech), which joined in partnership the Air and Waste Management Association, the American Institute of Chemical Engineers, the American Society of Civil Engineers, the American Society of Mechanical Engineers, the Hazardous Waste Action Coalition, the Society for Industrial Microbiology, the Soils Science Society of America, and the Water Environment Federation, together with the Academy, US EPA, DoD, and DOE. A Steering Committee composed of highly respected representatives of these organizations having expertise in remediation technology formulated the specific project objectives and process for developing the monographs (see page iv for a listing of Steering Committee members).

By the end of 1991, the Steering Committee had organized the Project. Preparation of the initial monographs began in earnest in January 1992, and the original eight monographs were published during the period of November 1993 through April 1995. In Spring of 1995, based upon the receptivity of the industry and others of the original monographs, it was determined that a companion set, emphasizing the design and applications of the technologies, should be prepared as well. Task Groups were identified during the latter months of 1995 and work commenced on this second series.

1.2.2 Process

For each of the series, the Steering Committee decided upon the technologies, or technological areas, to be covered by each monograph, the monograph's general scope, and the process for their development and appointed a task group composed of experts to write a manuscript for each monograph. The task groups were appointed with a view to balancing the interests of the group principally concerned with the application of innovative site and waste remediation technologies — industry, consulting engineers, research, academe, and government.

The Steering Committee called upon the task groups to examine and analyze all pertinent information available within the Project's financial and time constraints. This included, but was not limited to, the comprehensive data on remediation technologies compiled by EPA, the store of information possessed by the task groups' members, that of other experts willing to voluntarily contribute their knowledge, and information supplied by process vendors.

To develop broad, consensus-based monographs, the Steering Committee prescribed a twofold peer review of the first drafts. One review was conducted by the Steering Committee itself, employing panels consisting of two

members of the Committee supplemented by other experts (see *Reviewers*, page iii, for the panel that reviewed this monograph). Simultaneous with the Steering Committee's review, each of the professional and technical organizations represented in the Project reviewed those monographs addressing technologies in which it had substantial interest and competence.

Comments resulting from both reviews were considered by the task group, appropriate adjustments were made, and a second draft published. The second draft was accepted by the Steering Committee and participating organizations. The statements of the organizations that formally reviewed this monograph are presented under *Reviewing Organizations* on page v.

1.3 Purpose

The purpose of this monograph is to further the use of innovative bioremediation site remediation technologies. Innovative technologies are not commonly applied and their use is encouraged where they can provide better, more cost-effective performance than conventional methods. To this end, the monograph documents the current state of bioremediation technology.

1.4 Objectives

The monograph's principal objective is to furnish guidance for experienced, practicing professionals and users' project managers charged with site remediation responsibility. The monograph and its companion monograph are intended to be supportive, not prescriptive. It is intended to aid experienced professionals in applying their judgment in deciding whether and how to apply the technologies addressed under the particular circumstances confronted.

In addition, the monograph is intended to inform regulatory agency personnel and the public about the conditions under which the processes it addresses are potential applicable.

1.5 Scope

The monograph addresses innovative bioremediation technologies that have been sufficiently developed so that they can be used in full-scale applications. It addresses all aspects of the technologies for which sufficient data were available to the Bioremediation Task Group to review the technologies and discuss their design and applications. Actual case studies were reviewed and included, as appropriate.

The monograph's primary focus is site remediation and waste treatment. To the extent the information provided can also be applied elsewhere, it will provide the profession and users this additional benefit.

Application of site remediation and waste treatment technology is site-specific and involves consideration of a number of matters besides alternative technologies. Among them are the following that are addressed only to the extent that they are essential to understand the applications and limitations of the technologies described:

- site investigations and assessments;
- planning, management, and procurement;
- regulatory requirements; and
- community acceptance of the technology.

1.6 Limitations

The information presented in this monograph has been prepared in accordance with generally recognized engineering principles and practices and is for general information only. This information should not be used without first securing competent advice with respect to its suitability for any general or specific application.

Readers are cautioned that the information presented is that which was generally available during the period when the monograph was prepared. Development of innovative site remediation and waste treatment technologies is ongoing. Accordingly, postpublication information may amplify, alter, or render obsolete the information about the processes addressed.

This monograph is not intended to be and should not be construed as a standard of any of the organizations associated with the WASTECH® Project; nor does reference in this publication to any specific method, product, process, or service constitute or imply an endorsement, recommendation, or warranty thereof.

1.7 Organization

This monograph and others in the series are organized under a outline intended to facilitate cross reference among them and comparison of the technologies they address.

Chapter 2, Application Concepts, summarizes the process, its scientific basis, and key requirements necessary for bioremediation to be used for site renovation. Chapter 3 discusses measures of bioremediation performance and their use. Chapter 4 provides detailed information essential for the design and operation of bioremediation technologies appropriate for treating contaminated soils — Bioventing, Land Treatment, and Soil Cells. The emerging technology of phytoremediation is also discussed. Chapter 5 similarly addresses bioremediation technologies appropriate for the treatment of contaminated groundwater — the Raymond Process (enhanced bioremediation of aquifers), Intrinsic Remediation, Above-Ground Reactors, Biosparging, and emerging technology of Permeable Migration Barriers. Chapter 6 provides detailed information for designers and operators on technologies used for Vapor Treatment Systems. Chapter 7 addresses integrated technologies such as Bioslurping.

The information provided for each of the technologies addressed in Chapters 4 to 7 covers the topics intended for this series of monographs, i.e., principles of operation, design principles, process diagrams, pre- and posttreatment requirements, instrumentation and controls, sample calculations, safety considerations, cost data, design validation procedures, permitting requirements, design checklists, start-up procedures, operation practices, and monitoring.

Chapter 8 presents a series of case histories of specially-selected projects which have been prepared to document actual experience in using most of the technologies addressed in this monograph.

2 APPLICATION CONCEPTS

2.1 Scientific Principles

2.1.1 General Considerations

Bioremediation systems use biological processes to transform and/or destroy contaminants in soil, vapor, and groundwater. Such treatment systems modify existing environments to encourage the growth and reproduction of natural or exogenous microorganisms. To grow and reproduce, these microorganisms require a source of energy (i.e., electron donor) and a means of extracting this energy from the electron donor via an appropriate electron acceptor as shown in Equation 2.1 for heterotrophic organisms:

Microbes + Electron Donor (Energy & Carbon Source) + Nutrients + Electron Acceptor >> More Microbes + Oxidized (aerobic) or Reduced (anaerobic) End Products (2.1)

Biological systems generally treat contaminated media by using waste contaminants of concern as the electron donor and supply microorganisms with the required electron acceptors and nutrients. The anaerobic dechlorination of chlorinated solvents is the exception. Here the chlorinated solvents serve as the electron acceptor under highly reducing conditions. Generally, the limiting factor in full-scale engineered, biological treatment systems is the rate of transfer of the electron acceptor to the reaction site. Electron acceptors are those chemicals that can be used by biological systems to extract energy from electron donors for cell growth and replication. The main electron acceptors of interest include oxygen, nitrate, sulfate, iron, manganese, carbon dioxide, and organic carbon. If oxygen is present it will be utilized preferentially over the other electron acceptors because it provides a

maximum energy yield to the microorganism, resulting in the maximum possible amount of cell production and organism growth per unit amount of electron donor used. In addition to yielding higher energy releases than other terminal electron acceptors, oxygen (1) allows a wide variety of chemicals to be degraded, (2) generally yields a more rapid rate of contaminant degradation, and (3) results in oxidized endproducts that can be safely released into the environment. Oxygen-based biological systems are also the preferred engineered systems due to their inherent stability and process performance.

Once oxygen is depleted at a site, facultative and anaerobic microorganisms use other electron acceptors. Micoorganisms use acceptors in sequence based on the relative energy yield of each — nitrate, manganese, iron, sulfate, carbon dioxide, and finally, organic carbon. A detailed discussion of biochemical topics relevant to the bioremediation process is provided in the companion monograph entitled *Innovative Site Remediation Technology — Bioremediation* (Ward et al. 1995). The approximate relative energy release from each of these electron acceptors is listed in Table 2.1.

Table 2.1
Approximate Relative Energy Yield from Various Terminal Electron Acceptors

Electron Aaceptor	Relative Energy Yield
Oxygen	50
Nitrate	45
Manganese	10
Iron	10
Sulfate	2
Carbon Dioxide	1
Organic Carbon	1

Biological treatment processes at contaminated sites are generally directed toward the aerobic conversion of organic contaminants of concern to carbon dioxide and water (*mineralization*) or the oxidation of complex parent compounds to smaller, more oxidized constituents (*transformation*). Depending upon the starting substrate, biological intermediates may or may not persist under prevailing site conditions. For example, because

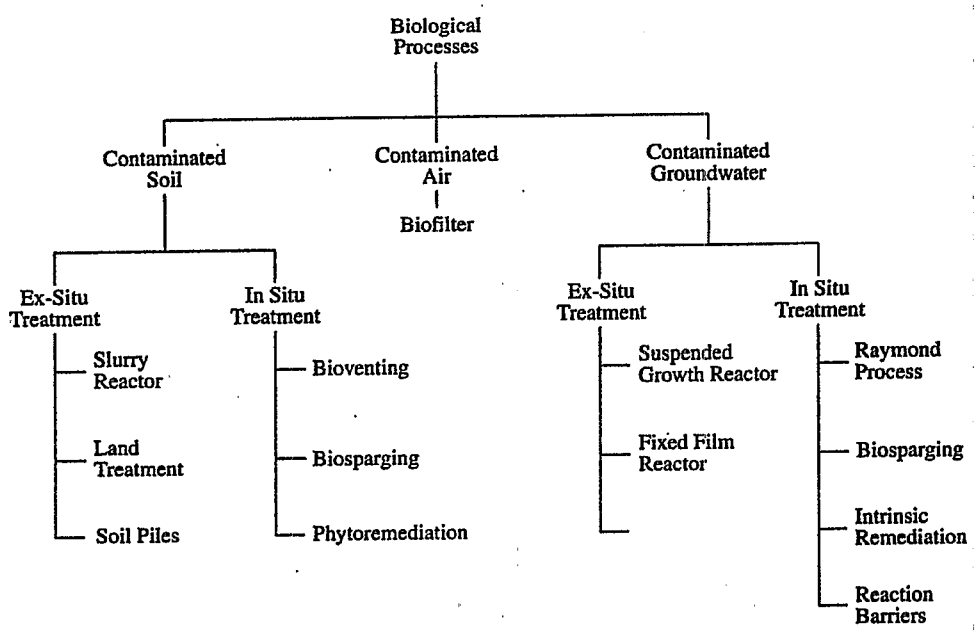
components of gasoline consist of straight- and branched-chain and aromatic hydrocarbons, few, if any, intermediate products can be expected to persist, and bioremediation, if feasible, will result in complete contaminant mineralization. On the other hand, biological transformation of highly oxidized chlorinated solvents, which primarily occurs under anaerobic, highly-reduced conditions, results in the production of a series of less-chlorinated intermediate products, some of which have been observed to accumulate at contaminated sites when these solvents are used as an electron acceptor. As indicated later in this monograph, data on the nature and relative distribution of these biological intermediate products may be used to confirm that biodegradation is taking place and to quantify reaction rates under actual field conditions.

A variety of engineered biological systems for soil, soil gas, and groundwater treatment have been developed and are summarized in Figure 2.1. Organization of these processes according to contaminated media is convenient, but does not reflect the integrated nature of many of these remediation techniques or their ability to treat multiple media. For example, phytoremediation is an innovative biological technology that has been applied for remediation of both contaminated soil and groundwater. Recent biosparging applications have integrated contaminant removal from groundwater via air stripping and assimilation of the volatile organic material in the vadose zone through stimulation of aerobic microbial respiration (i.e., bioventing technology). Potential applications of these varied biological treatment technologies in integrated approaches for site remediation are discussed in Chapter 7, and several case studies highlighting integrated remedial approaches are presented in Chapter 8.

If applicable to a given site, biological systems have advantages over other types of treatment technologies because they:

- can result in the transformation or complete destruction of contaminants of concern under ambient pressure and temperature conditions to non-hazardous end products;
- are highly cost-effective due to low-temperature and pressure reaction conditions;
- generally require minimal chemical addition to maintain optimal operating conditions, and generate no chemical sludges;
- produce no solid residues if conducted in situ; and
- can be designed to treat contaminated solids, slurries, water, and gases (in biological reactors).

Figure 2.1
Biological Processes Applicable to Contaminated Soil, Soil Gas, and Groundwater



However, because they are biological in nature, the applicability of such systems is limited to those sites where:

- contaminants of concern can serve as a source of energy and carbon for cell growth [specialized applications to chlorinated solvents and some polycyclic aromatic hydrocarbons (PAHs) have been demonstrated utilizing co-metabolic reactions as discussed later in this monograph]; and
- toxicants or chemicals that can inhibit microbial activity, including high concentrations of some organic compounds, and particularly moderate-to-high concentrations of heavy metals, are not present.

In spite of the limitations just listed, biological processes are applicable to a broad spectrum of organic chemicals of environmental concern. Table 2.2 presents some common contaminants of concern that have been shown to be susceptible to biodegradation. However, high concentrations (≥1% by weight) of otherwise biodegradable compounds may not be amenable to biodegradation due to toxicity and/or inhibition that may develop at high

contaminant levels. When free product is present, some inhibition can be expected; therefore, product recovery is highly recommended, especially prior to in situ treatment, to enhance bioremediation performance.

Table 2.2
Biodegradable, RCRA-Regulated Compounds*

Compound Type	Aerobic	Anaerobic	Fermen-tation	Co-Oxidation
Straight-Chain Alkanes	X	X	X	X
Branched Alkanes	X	X	X	X
Saturated Alkyl Halides	X	X		X
Unsaturated Alkyl Halides		X		
Esters, Glycols, Epoxides	X	X	X	
Alcohols, Aldehydes, Ketones	X	X		
Carboxylic Acids, Amides, Esters	X	X		
Nitriles, Amines, Pthalate Esters	X	X		
Nitrosamines		X		
Cyclic Alkanes	X		X	X
Nonhalogentated Aromatics	X	X		
Halogenated Aromatics	X	X		X
Simple Aromatic Nitro Compounds	X			
Aromatic Nitro Compounds with Other Functional Groups	X	X		X
Phenols	X	X	X	X
Fused-Ring Hydroxy Compounds	X			
Nitrophenols		X		
Halophenols	X			
Phenols - Dihydrides, Polyhydrides	X			X
Two-, Three-, Four-, & Five-Ringed Fused Polycyclic Aromatic Hydrocarbons	X			X
Biphenyls, Chlorinated Biphenyls	X			
Organophosphates	X	X		
Pesticides and Herbicides	X	X		

*Biodegradable does not indicate complete mineralization nor does it imply the rate or extent of degradation. It indicates the potential for loss of parent compound under the conditions listed.

Source: US EPA 1985b

2.1.2 Microbiology and Biochemistry

A detailed discussion of microbiological and biochemical topics relevant to the bioremediation process is provided in *Innovative Site Remediation Technology — Bioremediation* (Ward et al. 1995). A summary of this material is provided below.

Heterotrophic bacteria and fungi are the primary agents of decomposition of natural organic matter in the biosphere. Some of these microorganisms have the capability to use complex natural organic compounds, such as hydrocarbons, phenols, cresols, acetone, and cellulosic materials, as sources of carbon and energy.

Some highly-substituted as well as some naturally-occurring compounds (i.e., PAHs with four or more rings) might not be suitable growth substrates. However, they may be degraded as the result of co-metabolism. These fortuitous reactions stem from the lack of substrate specificity of some microbial enzymes. A variety of reactions, including oxidation, hydrolysis, reductive dehalogenation, and nitro-groups reduction, generate enzymes which are able to catalyze co-metabolic processes.

If the indigenous microbial community does not have the capability to degrade specific synthetic chemicals of concern at a particular site, inoculation with strains known to be capable of degrading the contaminant may be helpful. This approach has proven successful in laboratory applications, however, few field trials have been adequately documented to show the benefit of exogenous microbial amendment, particularly in in situ applications. Pentachlorophenol (PCP) has been treated in soil bioreactors by adding active biomass that has been grown on other substrates (Ward et al. 1995).

It is critical that bioremediation systems be designed with a full understanding of the biological processes upon which they rely. Understanding metabolic pathways allows for evaluation of the extent of biodegradation, potential for intermediate metabolite accumulation, and nutrient and electron acceptor requirements that must be fulfilled for successful bioremediation system performance.

2.1.3 Microbial and Environmental Factors Limiting Bioremediation

A number of microbial and related environmental factors significantly affect the efficiency of bioremediation of contaminated media, including the following:

- *Microbial Populations.* An acclimated indigenous population of microorganisms capable of degrading the compounds of interest must exist at the site if bioremediation is to be successful. If an active population of indigenous microorganisms does not exist at a site, inhibitory and/or toxic conditions should be suspected, and alternatives to bioremediation should be considered since delivery and control over microbial amendments is difficult at best;
- *Oxygen.* As indicated above, oxygen is the preferred electron acceptor and is necessary for aerobic biodegradation of organic contaminants. Residual oxygen concentrations >1.0 mg/L in the aqueous phase and >2 to 4% (by volume) in the gas phase should be maintained to ensure that oxygen is not limiting overall microbial reaction rate;
- *Soil Water.* This parameter is important in soil-based systems as the microorganisms rely on the soil water as a habitat for growth and survival. The soil water also provides a medium for transfer of contaminants from the product or solid phases and affects the overall bioavailability of the contaminants to the microorganisms. Soil water should be from 25 to 85% of field capacity (the water content of soil after it freely drains by gravity) to sustain microbial activity. Optimal soil water content is generally 75% of field capacity and higher;
- *pH.* pH, a measure of the hydrogen ion concentration, should range from 5.5 to 8.5 for optimal biological treatment performance. Soil pH is often difficult to modify, and thus can be used as a primary indicator of the feasibility of soil bioremediation when examining site assessment data;
- *Nutrients.* Nutrients can be classified into major, minor, and trace element groupings. The common major nutrients for bioremediation include nitrogen and phosphorus, and the minor nutrients include sodium, potassium, calcium, magnesium, iron, chloride, and sulfur. The major nutrients are required at order-of-magnitude higher levels than the minor and trace nutrients and subsequently are the nutrients managed in bioremediation. A typical C:N:P ratio of 100:10:1 on a weight basis is often used to ensure that adequate levels of N and P exist for unhindered bioremediation. These values are approximately half of that found in cell material (generally estimated to be $C_5H_7O_2N$, where the C:N:P is 50:10:1) based on the assumption that half of the carbon in the contaminant is used to produce cell

material and the balance is used for energy production by the cells. One additional note is important: for many in situ soil remediation systems, nutrient addition has not been shown to improve bioactivity and is generally considered unnecessary because of nutrient cycling within these systems.

- *Temperature.* Biological systems can operate over a wide range of temperatures — from 5 to 60°C. Three temperature ranges have been identified based on the growth of distinct groups of microorganisms:
  - Psychrophilic — <15°C, (59°F)
  - Mesophilic — 15 to 45°C (59 to 113°F), and
  - Thermophilic — >45°C (113°F).

  In general, most contaminated site temperatures are in the mesophilic range and should be adequate to support active microbial growth. If systems are exposed to temperatures below 10°C (50°F) for extended periods during winter months, their performance should be expected to deteriorate until temperatures rise. A rule of thumb regarding temperature effects on microbial activity suggests that reaction rates will increase or decrease by a factor of 2 for each 10°C (50°F) rise or fall in temperature, respectively. In addition, soil- and groundwater-based treatment systems in northern climates have not shown a significant lag period in system performance when temperatures rise, indicating that summertime performance should rapidly resume as soil/groundwater temperatures rise to within the mesophilic range; and

- *Toxicants in the Waste.* Because of the biological nature of bioremediation systems, any material that disrupts the biochemical processes taking place within the microorganisms employed in the treatment system will cause a disruption and eventual failure of that system. A variety of organic and inorganic toxicants can adversely affect the biological treatment system. The microbial consortium within the biological treatment system can acclimate to some of these materials, and by design (i.e., by blending contaminated soil with adjacent uncontaminated soil in a soil pile or land farm system), toxicant concentrations can be reduced below inhibitory levels to allow for their degradation over time. Because of the site-specific nature of toxicity, a field-scale toxicity assessment should be considered during feasibility studies of bioremediation technology.

2.1.4 Waste Characteristics Limiting Bioremediation

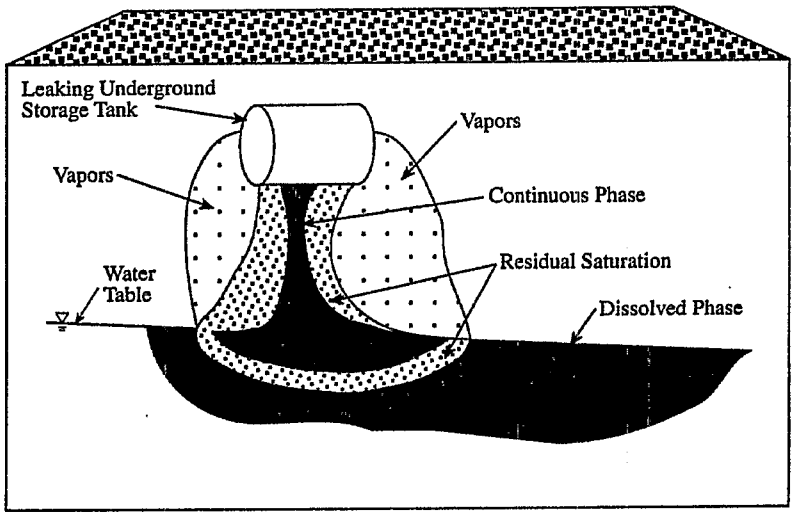
The pattern of contamination at most sites is complex and highly heterogeneous. A release of petroleum product (a nonaqueous phase liquid [NAPL]) from a underground storage tank (UST) (Figure 2.2) is a good example of a complex release. As released contaminants move through the vadose zone, a portion of the NAPL remains there, trapped by capillary forces. A plume of vapors forms in the soil gas within the vadose zone surrounding the free product. This NAPL is less dense than water (a light NAPL or LNAPL) and may flow by gravity to the capillary fringe above the water table where it spreads laterally. Groundwater coming into contact with the LNAPL will dissolve the LNAPL's more water-soluble components, and carry them downgradient with the groundwater flow. In these situations, the site contains three distinct regions of contamination:

- *Contaminated Vapor* located within the unsaturated zone surrounding the free product;
- *Free Product* serving as a source of long-term contamination to the vadose zone gas, and to the groundwater (this region may exist as recoverable product or as residual saturation held within and sorbed to the vadose and saturated zone soils); and
- *Dissolved Plume* containing water-soluble contaminants emanating from the LNAPL phase either from direct contact with product or via leachate moving through residual saturation within the vadose zone.

To evaluate the applicability of bioremediation systems, characterization of a contaminated site should include collection of information on:

- *NAPL Phase Distribution and Mobility.* The distribution of both the liquid and gas phases, and the sorption potential of NAPL constituents affect their fate and transport within the site environment. Soil gas surveys are typically used to provide information regarding the nature and extent of the vapor plume associated with a NAPL release. Soil core and groundwater sampling provide information regarding the nature and distribution of NAPL and dissolved constituent composition throughout the site. Particular attention should be paid to free product within monitoring wells and evidence of free product in soil core samples because this indicates the need for product recovery prior to final remedial design. Mobility information is generated from air permeability tests (Section 4.2) and groundwater slug tests (Section 5.2); and

Figure 2.2
Regions of Contamination in a Typical Release from an UST



Source: Wilson et al. 1989

- *NAPL and Constituent Degradability and Toxicity.* These characteristics determine the potential for use of biological or physical degradation methods to destroy a contaminant and the potential toxicity of the contaminant to the bioremediation system, and/or to the environment near the release. The indication of toxicity and the potential degradation rate of contaminants under field conditions can be determined from initial soil gas surveys that are designed to quantify both soil gas hydrocarbon concentrations and microbial activity as evidenced from Equation 2.1, (i.e., oxidized endproducts in the form of CO_2 and utilization of the electron acceptor in the form of O_2). Procedures for these soil gas respiration measurements are discussed in detail in Section 4.2.

2.1.5 Site and Soil Characteristics Limiting Bioremediation

General characterization information needed for bioremediation system selection and design includes data regarding the type and extent of contamination, soil subsurface conditions at the site, and climatic and hydrogeologic conditions existing at the location where bioremediation may take place.

This information is necessary to make a pre-determination of the potential competitiveness and effectiveness of bioremediation technologies. This information is obtained from the following sources:

- *Type and Extent of Contamination.* These data come from waste information and site assessment activities — soil gas data indicate the nature and distribution of volatile contaminants throughout the site and soil core, and groundwater data indicate the extent of contamination related to the solid/NAPL and dissolved phases, respectively;
- *Subsurfance Soil Characteristics.* These data come from soil survey information and the site assessment; and
- *Climatic and Hydrogeological Site Conditions.* These data are gathered during site assessment.

In addition, the biodegradability of contaminants under site conditions may need to be assessed prior to implementation of a bioremediation system to ensure that bioremediation will be successful. Contaminant degradability and toxicity assessment procedures are discussed in Section 3.2, and in Chapters 4 through 8 for each of the biological remediation processes covered in this monograph.

An assessment should be made of soil and site conditions that may limit successful implementation of bioremediation at a given site. Soil and site conditions have a significant bearing on process delivery and recovery systems and, in turn, the cost of in situ technologies. For example, low-permeability soils at the site limit delivery and recovery of required reactants for in situ technologies. In these cases, ex-situ technologies may be more cost-effective and more technically feasible based on required closure criteria. In addition, if a site must be remediated quickly, ex-situ technologies may be better suited due to the relatively long time frame required for most in situ treatment methods.

Finally, regulatory constraints regarding the disposition of waste and reactant streams (i.e., air, water, or soil streams) proposed to be recirculated or injected at a site may significantly impact the technical feasibility and cost-effectiveness of a given remedy.

2.1.5.1 Site Characterization Considerations

Site characterization, particularly for in situ systems, must evaluate the macro-scale properties of the site and soil that impact the mobility and distribution of contaminants at field-scale. These properties also impact the

movement of fluid/reactant into and out of the soil and, therefore, affect the feasibility and efficacy of in situ remedial activities at a site. Significant site properties affecting bioremediation system design and performance include:

- *Fluid Mobility* — physical barriers, site surface structures, soil characteristics (porosity and tortuosity), etc., affect air and liquid phase permeability;
- *Subsurface Heterogeneity* — differences in soil structure and texture impact fluid flow and distribution of both contaminants and reactants throughout a site (e.g., lenses, fractures, etc., that lead to complex and unpredictable preferential flow patterns);
- *Product Distribution and Potential Mass Transfer Limitations* — mass transfer out of pockets of NAPL-saturated soils and/or mounding on low-permeability soil lenses that represent large reservoirs of contaminant may limit contaminant removal efficiency and overall rates of site remediation;
- *Depth to Groundwater* — the extent of an unsaturated zone affects the distribution of residual contaminant at a site and the potential for unsaturated zone source control and remediation;
- *Distribution of Components Among Phases* — contaminant distribution among soil, water, NAPL, and vapor phases determines the potential effectiveness of various phase-specific technologies at a site;
- *Moisture Balance* — net precipitation and run-on/run-off at a site must be considered due to microbial population requirements for adequate soil moisture for survival (25 to 85% field capacity). It also must be considered when evaluating bioventing and soil vapor extraction (SVE) at a site (≥5% by weight soil moistureconstrains vapor movement); and
- *Site Physical Characteristics* — existing structures, impervious surfaces, drains, etc., amplify the desirability of in situ treatment techniques.

2.1.5.2 Soil Characterization Considerations

Soil characterization for in situ systems must evaluate the micro-scale properties of the soil that impact the (1) mobility and distribution of contaminants, and (2) the microbial activity of the soil at the field-scale. These properties control the soil particle-scale movement and distribution of contaminants and reactants and, once again, significantly impact the feasibility

and efficacy of remedial action at a site. Significant soil properties affecting bioremediation system design and performance include:

- *Moisture Content* — affects the volume of the water compartment within a contaminated soil available for contaminant solubilization and thus a compound's bioavailability and the volume of soil pore space available for air movement. Moisture content is given as: weight of water/dry weight of soil;
- *Bulk Density* — the dry weight of soil per soil volume expressed as: dry soil weight/soil volume (g/cm^3);
- *Porosity (Total and Air Filled)* — fraction of the soil environment not containing solid soil particles. Total porosity represents the total fraction of soil containing soil air and soil water and is given as: 1 - (bulk density)/(particle density) where particle density generally ranges from 2.5 to 2.65. Air-filled porosity represents the fraction of the soil containing only soil air (i.e., that fraction available for vapor migration and oxygen transfer) and is given as: total porosity - (decimal moisture content)(bulk density);
- *Permeability* — affects the bulk flow of fluid through a soil. This property is highly correlated to the soil particle-size distribution, or soil texture;
- *Organic Carbon Content* — affects the distribution of nonpolar organic compounds to soil surfaces as well as the general microbial activity of soils. Higher soil organic carbon content values generally produce greater sorption of contaminants to the soil, resulting in lowered potential mobility of contaminants. In addition, soil microbial activity generally increases with an increase in soil organic carbon content, although increased soil organic carbon can increase contaminant binding to the soil matrix and may limit its bioavailability; and
- *Mineral Content* — this property generally affects contaminant distribution in low organic carbon soils ($\leq 1\%$ by weight organic carbon). This property also reflects the content of trace nutrients required for active microbial metabolism. Mineral content can be described as the type and weight % of clay minerals, i.e., wt% illite, kaolinite, smectite, etc., and mg/kg, meq/100 g or mg/L extractable ions, i.e., P, K, NO_3^-, Cu, etc.

2.2 In Situ Versus Ex-Situ Bioremediation Technology Characteristics

For the purposes of this monograph, the following definitions for in situ and ex-situ systems are used:

- *In Situ Systems* — soil and/or groundwater systems in which remediation and contaminant removal/destruction is conducted in-place without the removal of soil and/or water. Exogenous agents may be added to these systems, but contaminated material remains in the location in which it was found during the site assessment process. In situ treatment systems include in-place groundwater treatment systems using indigenous organisms and unsaturated zone treatment using bioventing, biosparging, and phytoremediation.
- *Ex-Situ Systems* — soil, air, and/or groundwater systems in which contaminant removal/destruction is conducted following the removal of soil, air, and/or groundwater from the location it was found during the site assessment process. Ex-situ treatment systems are generally preceded by excavation of contaminated soil for source reduction, and include contaminated soil treatment in slurry reactors; land treatment in prepared-bed systems, biomounds, and soil piles; contaminated vapor treatment using biofilters; and groundwater remediation in aboveground suspended-growth or fixed-film bioreactors.

In situ groundwater bioremediation systems have been used most commonly, and successfully, for the treatment of gasoline and other fuel releases. Such systems involve:

- the extraction of contaminated groundwater;
- treatment of the water aboveground to remove dissolved contaminants;
- mixing the treated water with required nutrients and electron acceptors; and
- reinjection of the amended water via injection wells or infiltration galleries.

These systems are labeled as Raymond Process systems and are described in detail in Section 5.2.

In situ treatment of hydrocarbon-contaminated soils using bioventing technology has been even more successful; this process is discussed in detail in Section 4.2.

In situ bioremediation systems of all configurations have the following advantages:

- contaminants sorbed to aquifer and vadose zone material as well as those in a dissolved plume can be treated;
- unsaturated zone contaminants can be treated effectively using infiltration galleries or bioventing technology;
- mineralization of the contaminants produces only oxidized endproducts and more cell mass;
- the time required to remediate subsurface contamination can be reduced significantly over pump-and-treat or vapor extraction approaches due to the limited solubility/vapor pressure of many contaminants of concern;
- the areal zone of treatment of saturated zone systems may be larger than other remedial options because the treatment moves with the plume; and
- costs of biological treatment are generally lower than other options, and with in situ systems, no excavation costs are incurred.

However, a number of disadvantages accompany using in situ biological treatment processes for contaminated soil and groundwater. These include:

- compounds not amenable to biological degradation are unaffected by this process;
- toxicity within the site limits the applicability and performance of biological systems. A lack of toxicity at the site is essential for in situ processes because toxicity is difficult to impossible to modify in situ;
- injection-well clogging in saturated zone systems can be a problem due to the abundant growth of microbial mass immediately adjacent to the injection point of electron acceptors and nutrients (remedies to this limitation are discussed in Sections 5.2 and 5.5);
- heavy doses of nutrients can adversely impact groundwater quality. This is a particular concern for nitrate since it can adversely affect health at concentrations of 10 mg/L or greater. In addition,

phosphate application can result in calcium phospate precipitation and chemical injection-well clogging in some soils;

- implementation of in situ technologies in low permeability soil and aquifer systems is problematic due to the difficulty of transporting the required reactants to the contamination site; and
- remediation times are generally increased compared to ex-situ systems due to mass transfer limitations.

In situ biological systems used for unsaturated zone treatment (i.e., bioventing systems) offer some of the same advantages of in situ biological saturated zone processes, including mineralization of degraded contaminants; accelerated remediation, particularly for semivolatile and non-volatile, biodegradable contaminants; and cost-effectiveness, since soil excavation is not required. These systems also overcome a number of the limitations of saturated zone treatment systems in that no injection well clogging or permeability limitations generally occur because they are applied within the vadose zone. As with all biological systems, unsaturated zone systems are limited to treatment of biodegradable contaminants and can be affected by toxicants throughout a site.

Ex-situ systems are attractive alternatives for soil remediation when site excavation costs can be minimized (i.e., where shallow contamination of a large areal extent exists or where site constraints require immediate excavation and removal of contaminated soil). Ex-situ systems would not generally be selected if they trigger RCRA Land Ban regulations. Ex-situ systems have advantages over in situ systems as they allow:

- enhanced control of reactant delivery and contaminant/product recovery by providing an opportunity to construct soil reactors that minimize flow pathways and have provisions for leachate recovery, etc.;
- modification of site soil and nutrient characteristics through addition of nutrients and/or bulking agents during reactor or pile construction to improve nutrient status and air permeability;
- enhanced control of migration pathways when modified to include a "tent" for volatiles or a "tub" for leachables; and
- management of the site to optimize remediation by:
    - aeration management using bulking agents with forced-air injection and extraction;

- moisture management by providing optimal moisture at 50 to 85% field capacity;
- nutrient management by providing optimal nutrient concentrations and intimate, effective mixing during pile or reactor construction; and
- soil texture management for optimal soil texture (i.e., loam), by blending contaminated soil with desirable uncontaminated soil.

With optimized treatment, generally less sampling and analysis will be required to provide documentation necessary to verify remediation system performance for ex-situ systems as compared to in situ systems. Long-term monitoring commitments will also be minimized when using ex-situ systems.

2.3 Limitations from Site, Soil, and Waste Characteristics

Bioremediation systems are generally applicable to contaminated soils with NAPL concentrations less than 10% (by weight) oil and to contaminated groundwater with total petroleum hydrocarbon concentrations up to 1,000 mg/L. Consequently, free product removal is generally essential for the successful implementation of bioremediation at contaminated sites.

In situ bioremediation systems for subsurface soil and groundwater treatment are limited by the following:

- *Range of Applicability* — soil types (fertile soils of medium texture) and constituents must be amenable to biodegradation;
- *Delivery/Recovery of Nutrients and Electron Acceptors* — reactants must be moved to the site of contamination in order for biological reactions to take place. Reactant transfer limitations due to low-permeability soils, fractures, and heterogeneities can severely limit the efficacy of bioremediation as well as other remediation technologies; and
- *Lack of Definitive Field Demonstration* — definitive studies at the field scale with controls and mass balance data are not generally available. This is particularly true for demonstrations where exogenous microbial amendments have been applied. Field-scale demonstration data are becoming more widely available for some

technologies, e.g., results are available from more than 100 U.S. Air Force bioventing field sites. However, independent field validation of technologies remains a limiting factor in the rapid adoption of some of the bioremediation technologies described in this monograph.

2.4 Remedial Technology Screening and Technology Selection

A number of publications provide guidance on the screening and selection of physical, chemical, and biological technologies for the remediation of various contaminants under site-specific conditions. A sampling of these documents includes:

- US EPA. 1989. *Corrective action: technologies and applications*. Seminar Publication. EPA/625/4-89/020. Center for Environmental Research Information, US EPA, Cincinnati, OH.
- US EPA. 1994. *Remediation technologies screening matrix and reference guide*. Second Edition. EPA/542/B-94/013. DoD Environmental Technology Transfer Committee, Washington, DC.
- US EPA. 1995. *How to evaluate alternative cleanup technologies for underground storage tank sites. A guide for corrective action plan reviewers.* EPA 510-B-95-007. Office of Solid Waste and Emergency Response, 5403W, Washington, DC.

The intent of these documents is to provide the regulatory community and practitioners with guidelines for the evaluation and application of given technologies for remediation of specific contaminants under site-specific constraints. Figure 2.3 is an example screening matrix from Remediation Technologies Screening Matrix and Reference Guide (US EPA 1994; AAEE 1995) showing the applicability of select physical, chemical, thermal, and biological technologies for the remediation of a range of chemical constituents. The recommendations in these documents should be reviewed and considered when carrying out a preliminary assessment of the applicability of technologies for a given site.

Figure 2.3
Remediation Technology Screening Matrix

NOTE: Specific site and contaminant characteristics may limit the applicability and effectiveness of any of the technologies and treatments listed below. This matrix is optimistic in nature and should always be used in conjunction with the *referenced text sections*, which contain additional information that can be useful in identifying potentially applicable technologies.

	Development Status	Availability	Residuals Produced	Treatment Train (excludes off-gas treatment)	Contaminants Treated: VOCs	SVOCs	Fuels	Inorganic	Explosives	System Reliability/ Maintainability	Cleanup Time	Overall Cost	O&M or Capital Intensive
SOIL, SEDIMENT, AND SLUDGE													
3.1 In Situ Biological Treatment													
4.1 Biodegradation	Full	■	None	No	■	■	■	△	■	△	△	◕	O&M
4.2 Bioventing	Full	■	None	No	■	■	■	△	I	■	◕	■	Neither
4.3 White Rot Fungus	Pilot	△	None	No	△	△	△	△	■	△	△	●	O&M
3.2 In Situ Physical/Chemical Treatment													
4.4 Pneumatic Fracturing (enhancement)	Pilot	△	None	Yes	●	●	●	◕	◕	■	NA	■	Neither
4.5 Soil Flushing	Pilot	■	Liquid	No	■	◒	◒	■	△	◒	△	I	O&M
4.6 Soil Vapor Extraction (In Situ)	Full	■	Liquid	No	■	●	■	△	△	■	●	■	O&M
4.7 Solidification/Stabilization	Full	■	Solid	No	△	◕	△	■	△	■	■	■	CAP
3.3 In Situ Thermal Treatment													
4.8 Thermally Enhanced SVE	Full	●	Liquid	No	●	■	●	△	△	●	■	◒	Both
4.9 Vitrification	Pilot	△	Liquid	No	●	●	●	■	△	△	■	△	Both
3.4 Ex Situ Biological Treatment (assuming excavation)													
4.10 Composting	Full	■	None	No	■	●	■	△	■	■	◕	■	Neither
4.11 Controlled Solid Phase Bio. Treatment	Full	■	None	No	■	◒	■	△	■	■	◕	■	Neither
4.12 Landfarming	Full	■	None	No	■	◒	■	△	◒	■			
4.13 Slurry Phase Bio. Treatment	Full	◒	None	No	■	◒	■	△	■				
3.5 Ex Situ Physical/Chemical Treatment (assuming excavation)													
4.14 Chemical Reduction/Oxidation	Full	■											
4.15 Dehalogenation (BCD)													
4.16 Dehalogenation (Ch													

I Inadequate Information
NA Not Applicable

■ Better
◒ Average
△ Worse

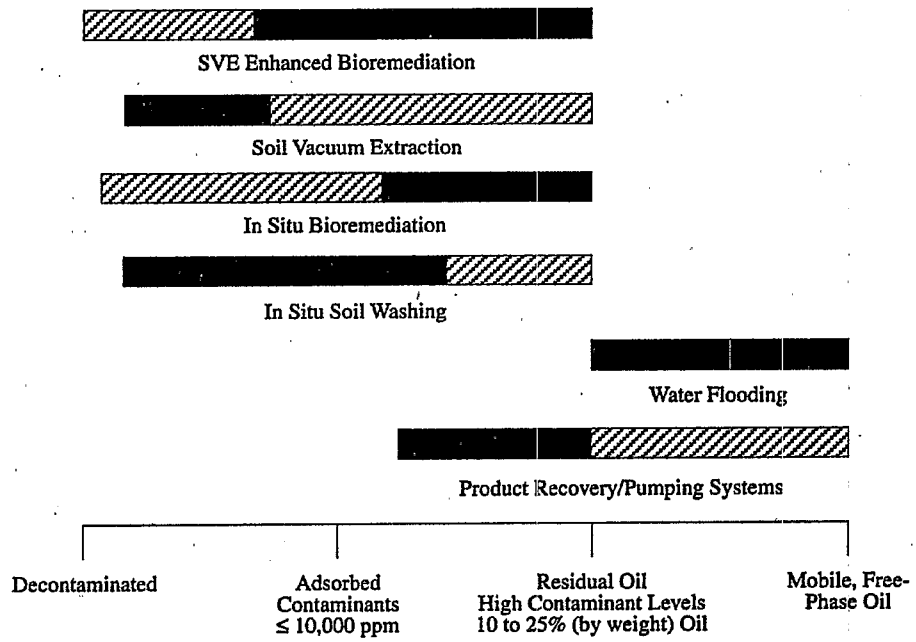
Source: US EPA 1994; AAEE 1995

Initially, a range of physical, chemical, thermal, and biological technologies should be considered for a site, along with the ability of such technologies to become part of a treatment train that can provide optimal site remediation — from existing contamination levels to decontaminated, closure conditions. This approach is illustrated in Figure 2.4 where the technical feasibility and cost-effectiveness of select techniques are depicted as a function of site contamination levels. This figure emphasizes the typicalneed for the application of a treatment train approach for site remediation regardless of the final treatment technology actually used. The treatment train approach can be summarized as the implementation of:

- free product recovery to the maximum extent practicable as determined by the responsible regulatory agency;
- reduction of NAPL-phase concentrations via physical recovery methods (i.e., flushing or solvent/vapor extraction) or ex-situ treatment methods (i.e., mixing with uncontaminated soil in a land treatment scenario) to optimize contaminant recovery per treatment dollar expended; and
- implementation of bioremediation technologies, either ex-situ (soil piles or aboveground reactors) or in situ (intrinsic remediation) for *de minimus* level treatment of residual contamination.

With this general approach and "designed-in" treatment system flexibility, an optimal solution for contaminant removal and site remediation using biological treatment systems is possible. The discussion that follows in Chapters 4 through 7 and the detailed case studies presented in Chapter 8 provide ample evidence of this.

Figure 2.4
Effective Range of Select In Situ Remediation Techniques



Technically Feasible
Most Cost-Effective

3

PERFORMANCE EVALUATION

Important elements in bioremediation technology include the microorganisms that metabolize the target organic compound(s), a reduction in mass and oxidation state of terminal electron acceptors (TEAs), and the biological consumption of mineral nutrients that are essential for growth of the microorganisms. It is logical, then, that bioremediation performance evaluation should generally focus on the following four parameters:

- a decrease in concentration of organic compounds transformed as a result of microbial activity and an increase in the concentration of transformation byproducts;
- a decrease in concentration of terminal electron acceptor(s);
- microbiological indicators; and
- a decrease in concentration of mineral nutrients.

Monitoring data for two or more site-specific indicator parameters of biological activity are often needed to conclusively demonstrate biodegradation. The case for demonstrating biodegradation is strengthened when data for multiple indicator parameters are integrated to provide a consistent analysis of biological processes taking place at a contaminated site. Abiotic processes also affect the transport and fate of these parameters in subsurface systems. It is often difficult to differentiate the role of biodegradation in complex subsurface or heterogeneous systems when both biotic and abiotic processes occur simultaneously. Despite the difficulties, it is useful to estimate the relative role of biodegradation in reducing contaminant concentrations since it will help evaluate whether the costs associated with enhanced biodegradation (i.e., mineral nutrients, electron acceptor, groundwater circulation, etc.) are justified.

Laboratory-, bench-, and pilot-scale studies and modeling, in conjunction with field data, can be used to help evaluate the role of biological processes on the fate of the contaminant. However, some uncertainty will remain regarding contaminant disappearance that can be attributed to biodegradation.

The costs of bioremediation performance evaluation can vary significantly depending on the type of contaminants of concern at a site, the specific bioremediation technology being evaluated, the size and complexity of the site, and the level of detail needed to satisfy technical and regulatory requirements for process verification. Correspondingly, the number of samples collected, the number of parameters measured, and whether or not laboratory-, bench-, or pilot-scale studies and modeling efforts will be conducted will vary from site to site given the above requirements. In many cases, especially for in situ bioremediation systems, performance evaluation is not a routine procedure. Section 5.3 discusses these measurements and biological process monitoring issues in the context of intrinsic remediation.

A discussion of the four bioremediation performance indicator parameters (microbiological parameters, organic contaminants and microbial transformation byproducts, terminal electron acceptor(s), and mineral nutrients) is presented below.

3.1 Monitoring Parameters and Methods

3.1.1 Microbiological Parameters

Often, microbial enumeration or activity monitoring parameters are not required by environmental regulators. Rather, these parameters have been used as supporting evidence to indicate either the potential for bioremediation or whether bioremediation is occurring. Statistically significant increases in microbial parameters are required to serve as an indicator of bioremediation; however, variability in these parameters is common in heterogeneous environmental systems which complicates data interpretation.

Microbial enumeration in soil and groundwater is a commonly-used microbiological indicator parameter. Subsurface investigations have revealed that the majority of microorganisms found in the subsurface are associated with the solid phase rather than with the aquifer liquid (Harvey, Smith, and George 1984). This is partially attributed to the fact that microbes have the ability to secrete an exopolysacharride material that allows surface attachment (van Loosdrecht, Lyklema, and Zehnder 1990), and improves their chances of survival in porous media.

Methods for microbial enumeration include direct microscopic and cultural techniques. Direct microscopic counting methods include the use of

classical buried slides, fluorescence microscopy, fluorochrome dyes, and transmission- and scanning-electron microscopy (Schmidt and Paul 1982). Two examples of direct-count methods using fluorescence staining are acridine orange (Hobbie, Daley, and Jasper 1977) and fluorescein diacetate (Schnurer and Rosswall 1982) methods. The acridine orange direct-count method involves applying acridine orange to a water sample or a soil sample extract, filtering the sample through a 0.2-μm filter, and mounting the filter on a microscope slide for direct counting. Cultural methods involve techniques such as the most probable number (Alexander 1982) and pour plate and plate counting (Wollum 1982). The underlying principles are straightforward: (1) disperse a sample, (2) distribute an aliquot to an appropriate medium, (3) incubate it under suitable conditions, and (4) count the developed colonies. Cultural methods assume that the sample is uniformly dispersed, the medium is specific for the organism(s) of interest, and no interaction occurs among microorganisms growing on the medium. Microbial enumeration and activity measurements using plate counts, most probable number, and direct counts have been correlated with petroleum hydrocarbon degradation in soil as an indicator of biological process function (Song and Bartha 1990).

Specific degraders have also been used to evaluate whether enhanced biological processes have occurred (Lehmicke et al. 1979; McGinnis et al. 1988). For example, microbes that degrade pentachlorophenol (PCP) and creosote compounds can be selectively isolated and an increase in their relative number usually indicates enhanced PCP or creosote biodegradation. For some substrates, counts of specific degraders may be important since their presence may not be apparent from an overall count of microorganisms using direct or total heterotroph counting methods.

An increase in the number of microorganisms in contaminated soil samples provides supporting information that biodegradation is occurring. As microorganisms metabolize organic compounds, they obtain energy, grow, and increase in number. In areas of a groundwater plume where sufficient oxygen is present to support microbial respiration, the number of aerobic microorganisms present in the soil and aquifer material increases over background concentrations. As the oxygen concentrations diminish, the concentration of aerobic microorganisms also decreases and facultative and anaerobic microbial populations increase sequentially, as illustrated in Figure 3.1. Adaptation studies have also been used where soils collected from contaminated and uncontaminated areas are spiked with a contaminant analog. Biodegradation of the contaminant analog in the contaminated soil but not in the uncontaminated soil indicate that microbes exist at the site, and

have acclimated to the contaminated environment. Theoretical stoichiometric relationships (i.e., specific yield) exist between carbon consumed and biosynthesis. However, obtaining accurate microbial enumeration or contaminant concentration data in heterogeneous systems to develop a meaningful correlation of this type is difficult.

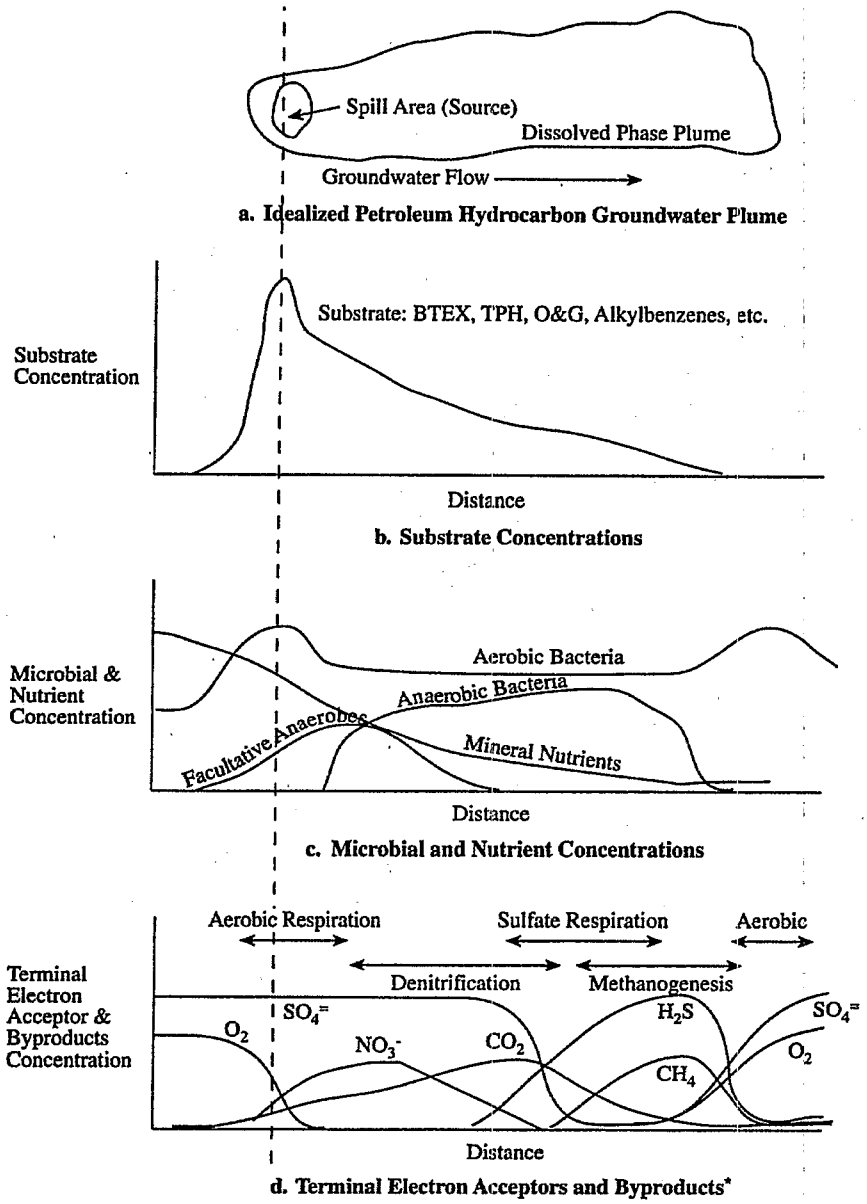
Biochemical reactions are catalyzed by microbial enzymes. Therefore, the presence and activity of enzymes can be monitored as indicators of biological activity. Many enzymes active in soil environments have been studied, but standard assays have been thoroughly evaluated for only a subset of these reactions. Some of the available enzyme assays include urease, phosphatase, phosphomonoesterase, phophodiesterase, inorganic pyrophosphatase, arylsulfatase, rhodanese, dehydrogenase, and glucosidase (Tabatabai 1982). The dehydrogenase test is a qualitative method to determine the presence of aerobic bacteria in an aquifer in quantities capable of biodegrading fuel hydrocarbons. A positive result indicates that a sufficient number of microorganisms capable of aerobic metabolism and/or denitrification are present. However, a negative result gives no indication of the relative abundance of anaerobic microorganisms (Wiedemeier et al. 1996). Daniel et al. (1992) reported a field method utilizing dehydrogenase activity (DHA) and established a correlation between DHA and the rate of gasoline vapor biodegradation. High DHA was also associated with high CO_2 production and O_2 consumption.

Adenosine triphosphate, an integral part of microbial energy metabolism (Wilson et al. 1986); florescent antibodies; fatty acid methyl esters; and polymerase chain reaction potential used with mRNA also indicate biological activity. However, these parameters have not been widely used in site remediation due to technical, analytical, and economic constraints and remain essentially research tools.

3.1.2 Substrate and Transformation Byproducts

Ideally, the contaminant(s) of concern in a bioremediation process serve(s) as the substrate for microbial metabolism within the treatment system. A primary substrate is degraded and used by the microbes to provide carbon for biomass and energy for growth. A secondary substrate does not benefit the microorganisms; instead, its degradation is a fortuitous occurrence during microbial degradation of another, nontarget compound. This type of biodegradation is referred to as *co-metabolism* (Semprini et al. 1992).

Figure 3.1
Indicator Parameters in an Idealized Petroleum Hydrocarbon Groundwater Plume for Bioremediation Performance Evaluation



*CO_2 serves as terminal electron acceptor during methangenesis; Mn (IV) and Fe (III) reduction of the aquifer solids occur prior to denitrification (Lovley and Phillips 1988) but have not been depicted in this figure.

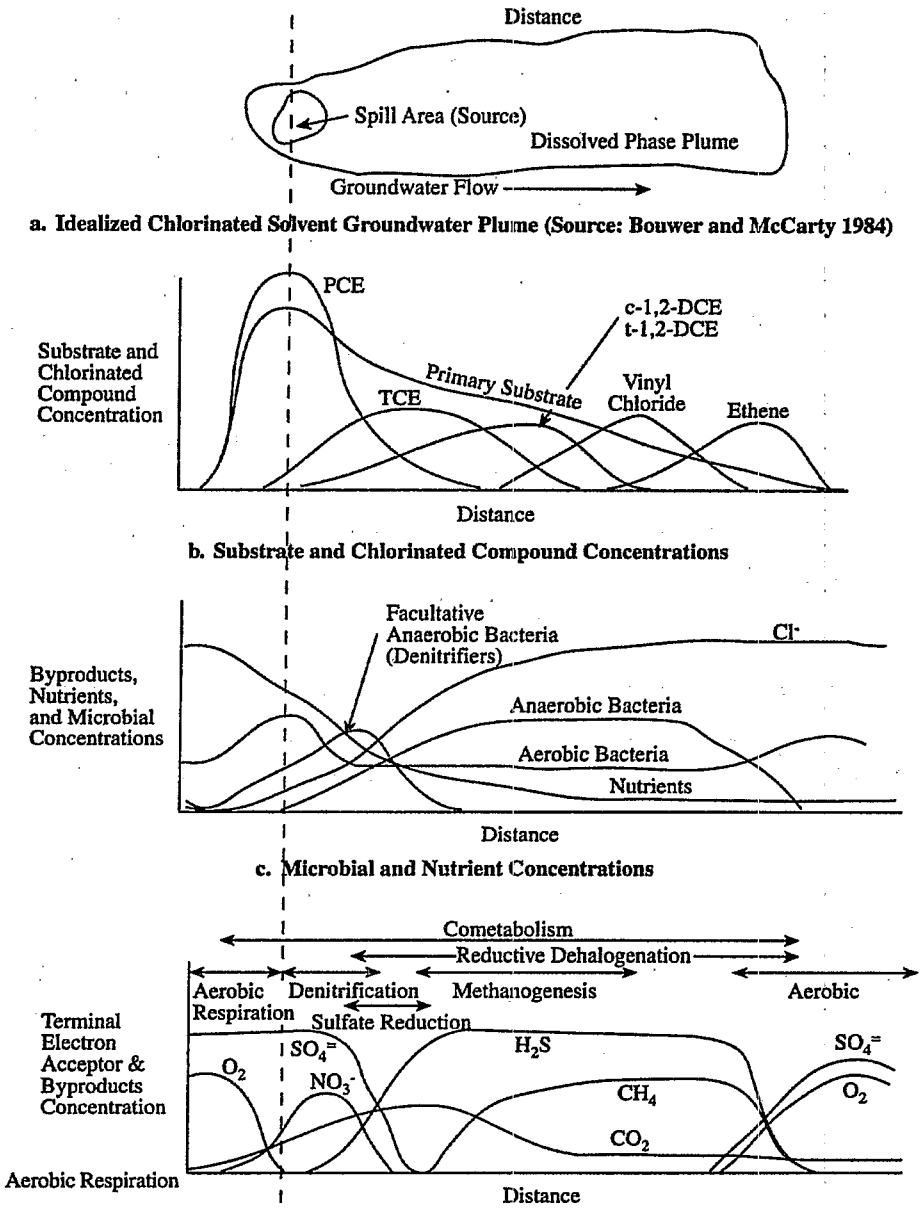
The objective of bioremediation, as is generally true for all remediation technologies, is to decrease contaminant concentrations to some remedial goal. Thus, the measurement of the contaminant before, during, and after active remediation is critical in performance evaluation to determine if the remedial goal has been met.

Contaminant concentration measurements can also be used to plan modifications or enhancements to the bioremediation system, or to estimate remediation time frames. Measurement of substrate concentration in the matrix of interest (for example, the loss of BTEX in Figure 3.1) provides information regarding the level of contamination and progress of treatment, but a decrease in substrate concentration does not unequivocally indicate contaminant loss due to biodegradation. Definite substrate-related evidence of biodegradation includes appearance of a metabolite or endproduct known to occur only through biotic degradation processes for that substrate. For example, *trans*-dichloroethylene oxide (and Epoxide) production generally serves as an unequivocal indicator of TCE cometabolism under anaerobic conditions (Madsen 1991). Another example involves the biologically-mediated reductive dechlorination of PCE and the sequential production and transformation of byproducts illustrated in Figure 3.2. Groundwater sampling results which indicate the occurrence and sequence of these chlorinated compounds provide supporting data concerning the active role of biological processes in the transformation of PCE.

In laboratory studies, the contaminant of interest can be labeled with a stable isotope and the production of metabolic products monitored (Madsen 1991). The concentrations of the intermediate or endproducts can be measured and related to the disappearance of the substrate, especially if the stoichiometry of the reaction is known. Other evidence for biodegradation includes the production of $^{14}CO_2$ by mineralization of a radiolabeled compound or an increase in CO_2 that cannot be attributed to other processes. For all practical purposes, performance evaluation methods involving radiolabeled compounds must be conducted in the laboratory. Data from the production of CO_2 by mineralization might not be reliable in some cases, however, due to formation of carbonates by reaction of the CO_2 with the contaminated soil (Norris 1993c).

Techniques for sampling soil, soil gas, and groundwater are well established (Barcelona et al. 1985; Boulding 1995). Techniques for sampling requirements specific to a particular technology are discussed in the appropriate section of this monograph; however, some general issues related to sampling are discussed here.

Figure 3.2
Indicator Parameters in an Idealized Chlorinated Solvent Groundwater Plume for Bioremediation Performance Evaluation



*CO_2 serves as terminal electron acceptor during methangenesis; Mn (IV) and Fe (III) reduction of the aquifer solids occur prior to denitrification (Lovley and Phillips 1988) but have not been depicted in this figure.

The contaminant can be present in the dissolved, sorbed, or gaseous phase or as a nonaqueous-phase liquid (NAPL). Mass transfer of the contaminant can occur among any of these phases. Thus, the contaminant does not exist in isolation in just one phase. Interpretation of the concentration data must account for this interphase mass transfer. Other issues regarding contaminant sampling include proper handling and preservation of the samples to prevent further biodegradation or loss through these interphase transfer processes.

Analytical methods for measurement of contaminants vary widely depending upon the type of contaminant, the matrix, and the concentration at which it is being measured. Standard procedures have been developed for numerous situations (US EPA 1986c, 1986d; Greenberg, Clesceri, and Eaton 1992) and include analyses using high-performance liquid chromatography, gas chromatography, gas chromatography/mass spectography, immunoassay, spectrophotometric and colorimetric techniques, and via gravimetric techniques and other chemical means.

The use of substrate, intermediate product, or endproduct concentration data depends on the specific project goals. Verification of attainment of a remedial goal might require a rigorous statistical procedure (US EPA 1989b, 1992a) using an appropriate number of samples. Future performance of a bioremediation technology, such as duration of treatment, is generally predicted by plotting substrate concentration data versus time. If a kinetic model for the remediation process is known or assumed, kinetic parameters (e.g., half saturation constant or maximum specific growth rate) can be identified, and future substrate concentrations predicted. The intermediate or endproduct concentration data may be plotted, and if the stoichiometric relationship between substrate and product is known, substrate behavior can be estimated. The intermediate or endproducts are also subject to transport and fate processes, and their concentration data might be affected by these processes.

3.1.3 Terminal Electron Acceptor

The general utilization of naturally-occurring terminal electron acceptors by microorganisms is from high energy-yielding compounds to low energy-yielding compounds in the following sequence: $O_2 > NO_3^- > SO_4^{-2} > CO_2$ (Vogel, Criddle, and McCarty 1987). Correspondingly, the disappearance of the TEAs in a groundwater plume attributable to biodegradation would adhere to this general order, refer to Figure 3.2(d).

Fe^{3+} and Mn^{4+}, primarily associated with aquifer material or soils, are also important TEAs for microbial activity in aquifers (Lyngkilde and Christensen 1992; Heron, Tjell, and Christensen 1994). Only a fraction of the Fe^{3+} and Mn^{4+} present in the aquifer material or soils is reducible under field conditions. A wet extraction technique has been used to measure the reducible fraction (Heron, Christensen, and Tjell 1992) but the procedure is much less developed than those used to quantify the other TEAs (in groundwater) identified above.

Biochemical redox reactions require an electron donor, which is usually carbon that becomes oxidized, and a terminal electron acceptor which then becomes reduced. Halogens (I, Br, Cl, F) are inherently electronegative and when the degree of halogenation increases on an organic compound, the organic compound becomes more oxidized. Under reduced conditions, halogenated compounds may also behave as TEAs which is referred to as *reductive dehalogenation* (Suflita et al. 1982). Upon accepting an electron, a halogen is replaced with a hydrogen. For example, the following compounds represent the order in a successive reductive dechlorination reaction: PCE, TCE, DCE, vinyl chloride, ethane. Based on the reduction potentials, carbon tetrachloride, PCE, chloroform, TCA, and TCE are energetically more favorable TEAs than nitrate. As the redox potential decreases, i.e., becomes more reduced, a greater range of halogenated compounds can act as electron acceptors and the reduction of these compounds under environmental conditions is likely.

Oxygen is the most thermodynamically favorable TEA for aerobic biodegradation in soil and groundwater. One of the byproducts from this biochemical redox reaction is CO_2 which can also be used as a TEA under certain conditions. Reduced concentrations of dissolved oxygen (DO) in groundwater or reduced oxygen concentrations in soil gas, and conversely elevated concentrations of dissolved CO_2 in the groundwater or elevated gaseous CO_2 levels in the soil gas, are generally good indications that aerobic biological processes are occurring. DO can be measured in groundwater with either a DO probe or by using the modified Winkler method (APHA 1989). Concentrations of O_2, CO_2, and CH_4 in soil gas can be measured in the field with a portable gas detector.

Oxygen is the most common electron acceptor used to enhance bioremediation system performance with NO_3^- used to a much lesser extent. In aerobic biodegradation, oxygen is consumed. Due to the low solubility of oxygen, and the limited rate of oxygen mass transfer from the air into the soil pore water and groundwater, DO is almost always the rate-limiting constituent in subsurface aerobic biodegradation. For example, in a field experiment where

benzene, toluene, and xylenes (BTX) were injected into a sandy aquifer, an irregular persistence of BTX occurred in a near-zero DO environment (Barker, Patrick, and Major 1987). The rate of biodegradation and thus, contaminant persistence, was reported to be controlled by the transport of oxygen into this BTX-contaminated groundwater. At another site, the low level of DO in creosote-contaminated groundwater was also identified as the probable factor limiting biodegradation (Lee and Ward 1984).

After DO has been depleted in groundwater, NO_3^- begins to be utilized as a terminal electron acceptor in a process referred to as *denitrification*. The byproduct from this reaction is N_2. Biodegradation of aromatic hydrocarbons utilizing NO_3^- as the TEA has been demonstrated (Hutchins et al. 1991; Hutchins 1992; Hutchins et al. 1995). During anaerobic biodegradation, Fe^{3+} can also be used as an electron acceptor (Lovley and Phillips 1988). This process produces Fe^{2+} which can be used as an indicator of anaerobic biodegradation. After DO, NO_3^-, and bioavailable Fe^{3+} are no longer present in the microbiologically-active treatment area, SO_4^{2-} is used as an electron acceptor. Under sulfate-reducing conditions, sulfide is produced as a byproduct, normally in the form of H_2S. Subsequent to sulfate-reduction, CO_2 is used as the TEA under methanogenic conditions yielding CH_4 as a byproduct. In the natural progression of TEA utilization, depletion of the TEA (O_2, NO_3^-, Fe^{3+}, Mn^{4+}, SO_4^{2-}, CO_2) and production of byproducts (N_2, Fe^{2+}, Mn^{2+}, H_2S, CH_4) can be used as indicators of biological activity as indicated in Figures 3.1d and 3.2d. This monitoring approach is discussed in detail in Section 5.3 on intrinsic remediation technology. This redox sequence is consistent with thermodynamic principles and has been closely matched by a leachate plume emanating from a landfill (Lyngkilde and Christensen 1992). Due to site-specific conditions controlling the presence, fate, and transport of the contaminants and TEAs present, this sequence may not always be observed. An overview of TEA processes is provided by Wiedemeier et al. (1994, 1996). Some of the limitations of monitoring these parameters to evaluate bioremediation system performance are discussed in Section 3.2.3.

Dissolved hydrogen (H_2) is a parameter which provides information regarding the redox potential and the dominant terminal electron acceptor process (TEAP) in anoxic groundwater. The predominant TEAP has been correlated with H_2 concentration: CO_2-reducing (methanogenesis) 7-10 nM H_2; sulfate-reducing 1-1.5 nM H_2; Fe(III)-reducing 0.2 nM H_2; and nitrate- or Mn(IV)-reducing < 0.05 nM H_2 (Lovley, Chapelle, and Woodward 1994). The basis for this correlation lies in the specific microbial H_2 utilization rate associated with each TEAP and the subsequent H_2 concentration in

groundwater. This correlation applies only to groundwater where DO is absent. If DO is present, it is assumed that O_2 reduction is the predominant TEAP. Overall, dissolved H_2 can be used to identify zones of the predominant TEAP in a groundwater plume. The methods and techniques in which H_2 is measured in groundwater are currently under development.

3.1.4 Nutrients

The nutritional needs of microbes include macronutrients (N, P, K, S, Mg, Ca, Fe) and micronutrients (growth factors such as vitamins, amino acids, and trace metals)(Alexander 1994). Carbon and the major macronutrients generally occur in a C:N:P ratio of approximately 50:15:3 in bacterial biomass on a dry-weight basis (Lim 1989). To approximate this ratio for the nutritional needs of the cell, a C:N:P ratio of 100:10:1 is generally used in bioremediation, based on the assumption that half of the carbon will be lost through evolution of CO_2 from energy-producing reactions. The contaminant provides a large supply of carbon, and thus to maintain a nutritional balance, macronutrients may need to be supplied (Alexander 1994). Generally, the micronutrients and growth factors are not limiting (Alexander 1994; Cookson 1995).

Nutrient concentrations in the soil or groundwater can be measured to evaluate bioremediation performance or to identify a limiting nutrient so the bioremediation process can be modified or enhanced. Measurement of the macronutrients in the soil or groundwater can indicate whether they are being used, as shown in Figures 3.1 and 3.2. Nutrient concentrations are usually measured prior to and during a bioremediation project to determine the need for supplemental nutrients. If the bioremediation system does not respond to addition of the macronutrients, measurement of trace elements may be necessary. In such cases, there may be a limiting nutrient other than N or P. A relative response to nutrient addition will demonstrate that biological activity is occurring (Madsen 1991). Measurement of the nutrients in a bioremediation system is also critical so that a proper dose of supplemental nutrients can be calculated to avoid osmotically shocking the microbes (Cookson 1995).

Agricultural research and experience has led to extensive knowledge of the fate and transformation of nutrients in soil, so that, in conjunction with the experience gained in the environmental field, sampling techniques for soil and groundwater are relatively well established (Page, Miller, and Keeney 1982; Boulding 1995). Particular concerns about sample size, location, number, sample preparation, etc. are discussed thoroughly in Page, Miller, and Keeney (1982). Analytical techniques for the macronutrients in

soil and groundwater are also well documented (USGS 1977; US EPA 1984c; Page, Miller, and Keeney 1982; Greenberg, Clesceri, and Eaton 1992).

3.2 Limitations to Performance Monitoring Methods

3.2.1 Microbiological Parameters

Direct-count methods using staining techniques generally do not distinguish between viable and nonviable microbes. There are similar limitations with soil enzyme analyses (i.e., it is difficult to distinguish between enzymes found in viable microbes and enzyme residues from nonviable microorganisms). Large differences in microbial enumeration are reported among results of plate counts using cultural methods and total counts using direct-count methods (Ghiorse and Balkwill 1990; Roszak and Colwell 1987). Roszak and Colwell (1987) provide an excellent discussion of these discrepancies, and tabulate numerous methods for differentiating between living and dead bacterial cells.

There are several limitations of enumerating soil microorganisms using cultural methods. For example, the sample may not be uniformly dispersed and thus the aliquot applied to the plate or the most probable number tube may not be representative. The medium used may favor the growth of a relatively small group of microorganisms present in the soil, thus only a fraction of the total microbial community might be quantified. Some microorganisms may produce antibiotics that inhibit the growth of other competing microbes.

Soil and aquifer material are discontinuous and the chemical, physical, and biological properties may vary significantly with space and time. Correspondingly, microbial numbers and activity may vary over a relatively small spatial scale. At hazardous waste sites, the number of microflora in the soil and groundwater may range from 10^2 to 10^9 cells/g soil and 10^2 to 10^6 cells/mL, respectively. Due to the significant variability of these parameters, one or more orders of magnitude difference is generally necessary to provide evidence of increased biological activity. However, microbial enumeration alone is typically insufficient to demonstrate bioactivity potential. These determinations are best used as supportive data in conjunction with substrate and TEA results.

Groundwater and core material in the vicinity of a monitoring or injection well may contain microbial populations representative of the well environment and not of the aquifer. Near-well aquifer material may be oxygenated from the air in the headspace in the well. This may support aerobic microbes in a relatively narrow region around the well. Injected water may contain microbes that are filtered out by the porous media, increasing the microbial density immediately adjacent to the well. The additional collector surface area of particles (i.e., the filtered biomass) increases the collector efficiency (Darby and Lawler 1990). Injected water may be of a different quality than the groundwater, and this may significantly alter microbial transport and change the microbial content in the vicinity of the well.

Attachment and detachment of microorganisms to solid surfaces can be attributed to many processes. These processes are affected by parameters associated with the solid surface, the microorganism, and the aqueous solution. Microbial transport in groundwater is affected by a wide range of parameters associated with the water including:

- Ca^{2+} and Mg^{2+} content (Marshall et al. 1971);
- pH (Scholl et al. 1990; Scholl and Harvey 1992);
- nutritional status, ionic strength (Marshall et al. 1971; Scholl et al. 1990; Alexander et al. 1991; Gannon et al. 1991);
- temperature (Fletcher 1977; McCaulou 1993);
- groundwater velocity (Marlow et al. 1990; Logan, Hilbert, and Arnold 1993; Gannon, Manilal, and Alexander 1991); and
- concentration of contaminants (van Loosdrecht et al. 1987a, 1987b).

In addition, the cell size (Logan, Hilbert, and Arnold 1993; Gannon et al. 1991), concentration (van Loosdrecht, Lyklema, and Zehnder 1990), and motility (Fletcher 1977; McCaulou 1993) affect microbial transport through porous media. Due to the numerous parameters affecting microbial transport, microbial enumeration data must be carefully interpreted.

3.2.2 Substrate

Measurement of the substrate concentration in the contaminated matrix can indicate a decrease in the contaminant concentration. However, the concentration of a substrate might decrease, not only by biodegradation, but also by attenuation through other fate and transport processes such as sorption, volatilization, dilution, diffusion, dispersion, and abiotic transformation reactions. Site activities such as water or air injection can significantly

affect the concentration of contaminants near the injection points. Each of these processes can be quantified and their effects on contaminant concentration can be predicted. For example, a compound with properties similar to the contaminant, yet not biodegradable, can be used as a tracer when examining the relative effects of dilution, dispersion, sorption, and biodegradation on the compound of interest. For fuel hydrocarbon plumes in groundwater, trimethylbenzene and tetramethylbenzene have been used as tracers, (Wiedemeier et al. 1995), but the fate of these compounds as valid tracers is still under evaluation. Section 5.3 provides further discussion of the use of tracer compounds to evaluate intrinsic remediation processes. Quantifying the effects of these other transport and fate processes requires additional time, labor, and expenditures, that should be balanced with the need for this information.

Abiotic degradation processes might also be responsible for apparent decreases in contaminant mass. The effect of abiotic processes can be examined by the use of abiotic or poisoned control systems (using radiation, sodium azide, or mercuric chloride), although this is restricted to laboratory studies and is difficult or impossible to accomplish in a pilot- or full-scale system. Comparison of the abiotic control to the biotic system will indicate the loss due strictly to biological process.

The correct sampling location, depth, or sampling interval for representative contaminant measurements can be difficult to determine. For example, sampling a well screened over an interval containing both high- and low-conductivity regions will preferentially collect groundwater from the high-conductivity region, obscuring the concentration of groundwater in the low-conductivity region. The inherent uncertainties in accurately estimating the nature and extent of contamination in groundwater and soil due to spatial heterogeneity of contaminant distribution can be mitigated by using an appropriate sampling plan. For example, a statistical analysis of initial soil data can provide an estimate of the uncertainty of the measurement and provide a basis for determining the number of samples to be taken that is sufficient to account for these uncertainties (USEPA 1989, 1992). A careful examination of the geological, hydrogeological, and geochemical conditions can also help in planning the sample locations or in explaining the variability in the results. Errors can result from sample sieving and mixing procedures that discard non-soil components such as rocks, especially if significant contamination exists in this discarded portion of the sample (Barth et al. 1989).

Oil and grease (O&G) or total petroleum hydrocarbon (TPH) measurements have been used to monitor biodegradation performance, and are sometimes required by state or federal regulation. However, due to limitations in the analytical methods, measurement of O&G or TPH can result in erroneous or uncertain conclusions relating to biodegradation (Riser-Roberts 1992; Rhodes et al. 1996). Measurements of individual compounds within the O&G or TPH or using a more sophisticated analysis for O&G or TPH may be more expensive but may provide additional and better data with which to evaluate the fate and transport of the target (regulated) compounds. This can be important since O&G and TPH are a broad measure of hydrocarbons comprising many different compounds in varying proportions which biodegrade and are transported at different rates.

Appearance of an intermediate or endproduct from degradation of the contaminant provides evidence of biodegradation, although the intermediate or endproduct might also be generated through an abiotic process. For example, 1,1-dichloroethane results from biological transformation of 1,1,1-trichloroethane (Vogel, Criddle, and McCarty 1987), and in an uncommon instance, can result from abiotic reduction of 1,1,1-trichloroethane by Fe(II) porphyrins (Klecka and Gonsior 1984). However, 1,1-dichloroethene is commonly observed as an abiotic transformation product of1,1,1-trichloroethane.

Interpreting the appearance of intermediate products might not be straightforward. Within the perchloroethylene biodegradation sequence shown in Figure 3.2, each biotransformation has its own rate (for example vinyl chloride has a slower degradation rate and will tend to persist in the groundwater), and the transport of each compound is also affected by a different degree of sorption. Thus, the distribution in groundwater is complicated by the interaction of each of these factors. Recognition and kinetic interpretation of substrate biodegradation can be further complicated if the waste source initially contained one or more of these compounds.

Performance evaluation of biodegradation by examining the distribution of contaminants in groundwater must be tempered by the recognition that different classes of compounds have different rates of degradation. For example, halogenated solvents will have different biodegradation rates than aromatic compounds. The type of substituent (e.g., Cl, Br, Fl) will affect the biodegradation rate, as will the position of the substituent (for example *ortho-*, *meta-*, or *para-*). Within a class of compounds, such as the polycyclic aromatic hydrocarbons (PAHs), the molecular weight will affect the biodegradation rate, with the heavier compounds generally having slower biodegradation rates.

3.2.3 Kinetic Expressions

Concentration data are generally assumed to fit first-order kinetics; however, this may not always be appropriate. Although many biodegradation studies have indicated that first-order kinetics are observed in the laboratory, biodegradation in the field may follow other kinetics rate laws (Cookson 1995). While the first-order kinetic assumption is convenient due to its mathematical simplicity and ease in establishing a half-life value, this assumption can be incorrect (Alexander 1994), and a more sophisticated model might be more appropriate under a given set of site-specific conditions. Construction of a kinetic model requires sufficient data collected over a long enough duration so that rapid initial degradation occasionally encountered does not bias the model.

In an extensive biotreatability study with numerous soils, the degradation of PAHs was determined to reach a plateau, below which further degradation did not occur. In this case, the use of first-order kinetics would have incorrectly predicted success in reaching the remedial goal and the remediation time frame would have been greatly underestimated (Morgan et al. 1992). Due to the significant concentration changes which are generally required to achieve cleanup goals, the order of the degradation rate reaction may change. For example, while biodegradation may initially adhere to pseudo first-order degradation rate kinetics, at low concentration, degradation rate kinetics may transition to a zero-order rate reaction. Additionally, other site-specific conditions may also affect the rate or order of reaction, i.e., temperature, nutrients, terminal electron acceptor, etc. Under these conditions, the initial kinetic model may not accurately estimate the time-frame required to achieve the desired/required clean-up concentration. Overall, judicious use of kinetic data is important when extrapolating data over periods where chemical, physical, and biological changes may affect the degradation rate law. An example is provided Figure 4.14 in Section 4.3.9.3, Field Data Analysis, in which the calculated half-life is erroneously short when only the initial portion of the data is examined.

3.2.3 Terminal Electron Acceptor

Decreasing concentrations of terminal electron acceptors (TEAs)(O_2, NO_3^-, SO_4^{2-}, CO_2) and increasing concentrations of byproducts of biochemical reactions (CO_2, N_2, Fe^{2+}, Mn^{2+}, H_2S, CH_4) suggests that these compounds are serving as TEAs and that biodegradation is occurring during site remediation. CO_2 is a byproduct from aerobic respiration where O_2 is used as a TEA, and CO_2 serves as a TEA under methanogenic conditions where it is reduced to CH_4.

The ideal stoichiometric relationship between carbon and oxygen in theoretical biochemical reactions provides one approach that can be used to correlate electron acceptor uptake with the amount of substrate being removed. However, it cannot be assumed that all of the TEA delivered to the subsurface is consumed biologically. Additionally, a mass balance approach is problematic in the field for both the electron acceptor and the substrate. If an electron acceptor mass balance can be achieved, uptake can be used as an indirect measurement of the mass of substrate removed from the site.

Abiotic DO sinks exist in the subsurface. Specifically, when oxygen is introduced into a subsurface environment under reduced conditions, the oxygen can be consumed abiotically when it reacts with reduced sediment. This reduction capacity of natural aquifer solids may contribute significantly to the overall oxygen demand and should be considered when equating oxygen utilization to target compound destruction (Barcelona and Holm 1991; Korom, McFarland, and Sims 1996). Dissolved oxygen is also consumed in noncontaminated soil and aquifer material where naturally-occurring organic matter, rather than the organic contaminant of concern, is undergoing decomposition.

Another possible error in the correlation between the oxygen delivered and biological consumption is the loss of oxygen from the system. Hydrogen peroxide decomposition, catalyzed by enzymatic and nonenzymatic reactions in aquifer systems, is extremely rapid and efficient. Rapid decomposition of hydrogen peroxide in conjunction with limited DO solubility can result in the formation of oxygen gas bubbles in the subsurface. Accumulation and liberation of the oxygen gas from the saturated zone into the unsaturated zone may result in loss of oxygen without its transfer to the contaminated aquifer (Huling, Bledsoe, and White 1990). Neither abiotic consumption nor gaseous losses are significant when nitrate is used as the TEA. To a lesser extent, the nitrogen component of nitrate may be used for cell biosynthesis, but this is assumed to be negligible.

Fuels are composed of hundreds of organic compounds degradable to varying degrees. When environmental conditions are favorable for biodegradation, numerous compounds may be preferentially degraded over compounds of regulatory interest. On a mass basis, the stoichiometry of BTEX degradation is roughly 3.1:1 Oxygen:BTEX and 1.1:1 Nitrate:BTEX (Hutchins et al. 1991). However, when oxygen or nitrate is consumed in a subsurface biological system, BTEX components of the NAPL are not necessarily degraded in the process. A preferential correlation between the target compounds and the electron acceptor consumed cannot be assumed in a complex waste system.

Difficulties can arise when monitoring Fe^{2+} as an indicator of the biological reduction of Fe^{3+} as a TEA. Iron can exist in many solid states either as a precipitate or in crystalline form. Fe^{3+} may be present in large quantities in the solid phase in soil and groundwater, but quantifying the bioavailable fraction of this Fe^{3+} is problematic. Despite the difficulties with quantifying the amount of Fe^{3+} that is reduced, the presence of Fe^{2+} in the groundwater is an indication of biodegradation using Fe^{3+} as an electron acceptor. Methods involving measurements of the total oxidation capacity of aquifer material quantifying all TEAs (O_2, NO_3^-, Fe^{3+}, Mn^{4+}, SO_4^{2-}, TOC) have been used to evaluate the available soluble and insoluble solid-phase forms of TEAs (Heron, Tjell, and Christensen 1994).

Subsurface heterogeneities dictate complex flow paths that are generally beyond current practice to quantify. Unfortunately, TEAs injected into the subsurface will also follow these circuitous routes. Mechanisms that tend to reduce the concentration of TEAs between two monitoring points (i.e., dispersion and diffusion) in conjunction with hydraulic heterogeneities make it difficult to maintain a mass balance and to quantify the TEA uptake. Overall, TEA uptake may yield useful information regarding biological reactions in the subsurface; however, abiotic TEA sinks must be considered when correlating TEA loss and biodegradation.

3.2.4 Nutrients

Many of the limitations to sampling and analysis for contaminants also apply to nutrients. These include media heterogeneities and problems in selection of the proper sampling location. Groundwater or soil solution chemistry can have a profound effect on the measurement or availability of nutrients. Sorption or ion exchange of the nutrients will be governed by other chemical species. Analysis for, and modeling of, different chemical species within the matrix may be necessary to determine the behavior of a given nutrient complex in the soil or groundwater. For example, analysis and modeling may be necessary to determine whether a particular form of phosphorus will be sorbed and become immobile if it is added to a contaminated aquifer system.

Laboratory studies often indicate that nutrient addition stimulates biodegradation. This information is frequently used in conjunction with field measurements of nutrient concentrations to plan nutrient additions to the bioremediation systems. Unfortunately, in the field, the planned nutrient addition may have a different impact due to difficulties in nutrient distribution or other limiting factors (Cookson 1995). Consequently, nutrient data

must often be used in conjunction with more comprehensive site information to adequately monitor and control nutrient application at a full-scale remediation site.

3.3 Additional Performance Monitoring Considerations

3.3.1 Integrated Site Information

Horizontal or vertical cross-sections of a site, in conjunction with microbiological, contaminant, TEA, and mineral nutrient data, can be used collectively to infer biological activity occurring throughout a site. At a site where an aviation fuel spill occurred, groundwater samples were collected along the longitudinal and transverse axes of the plume and analyzed for DO, CH_4, and alkylbenzene concentrations (Wilson and Bledsoe 1986). In background areas where no alkylbenzenes were found, the DO concentration was greatest and as the concentration of alkylbenzenes increased along the periphery of the plume on either axis, DO concentration decreased. Within the core of the plume where the concentration of alkylbenzenes was high, the DO concentration decreased rapidly to zero, and the concentration of CH_4 increased, indicating the anaerobic biodegradation of aviation gasoline fuel components. The use of TEA and substrate data together to demonstrate the role of biodegradation at a site is discussed further in Section 5.3.

3.3.2 Laboratory Studies

Due to the limitations of collecting, assimilating, and interpreting field data, laboratory studies are often instrumental in providing supportive evidence of the role of biological processes in the fate of contaminants at field sites. Laboratory studies are performed under carefully controlled conditions where a mass balance of the target substrate, possibly a radiolabeled compound, can be performed using site core material. Laboratory assays can provide definite evidence for microbial metabolism through the use of abiotic controls, and mass balances are possible by performing degradation experiments in sealed vessels (Madsen 1991). In addition to using the appropriate controls to differentiate abiotic processes (dilution, sorption, volatilization, dispersion) from biotic processes, sterile controls can be used to differentiate biotic and abiotic contaminant transformations. Sterile controls

can be achieved via several methods (mercuric chloride, sodium azide, irradiation, propylene oxide, antibiotics, etc.). Some sterilization methods may be more effective than others and may also influence the chemical and physical nature of the soil such as soil, surface area, cation exchange capacity, and extractable Mn, Al, and Fe (Wolf et al. 1989). Biodegradation rate constants can also be determined in laboratory studies. However, these laboratory-generated rates are generally greater than those observed in the field. The difference is partially due to optimal environmental and maximum mass transfer conditions that occur in laboratory reactors as compared with those that are observed under full-scale conditions in the field. Additionally, contaminants spiked into soil can respond differently to fate processes than contaminants which have been in the soil for a long period of time. Contaminants in soil and aquifer material are subject to an aging process in which a fraction of the contaminant introduced into the soil will diffuse into and be sorbed within soil micropores. These contaminants are more resistant to mobilization, volatilization, chemical transformation, or biodegradation (Pignatello 1986; Steinberg et al. 1987; Pignatello et al. 1990). Aged compounds have also been demonstrated to be less bioavailable to microorganisms and plants (Scribner et al. 1992; Alexander 1995; Hatzinger and Alexander 1995). There are factors that may affect contaminant availability relative to these mass transfer processes. Pulverization of soil can increase the rate and extent of volatilization (Steinberg et al. 1987) and mixing of soil contaminated with aged compounds using uncontaminated soil and addition of compost may stimulate degradation of the aged residues (Felsot and Dzantor 1997).

3.3.3 Modeling

Several fate and transport models have been developed for unsaturated and saturated subsurface conditions that mathematically simulate contaminant advection, dispersion, sorption, and biodegradation. These models can be used to aid in bioremediation performance evaluation by integrating numerous chemical, physical, and biological reactions simultaneously. Such models are only as accurate as the input data.

Models used to simulate fate and transport in the saturated zone include BIO1D (Srinivasan and Mercer 1987, 1988), Bioplume II (Rifai et al. 1989), BIOSCREEN (Groundwater Services, Inc. 1996), and BioTRANS (ES&T, Inc. 1994). The Regulatory and Treatment Zone (RITZ) model can be used for the unsaturated zone (Nofziger, Williams, and Short 1988).

BIO1D is a finite difference numerical groundwater flow and solute transport model that incorporates modified Monod kinetics to simulate the degradation of fuel hydrocarbons. The model can simulate the fate of one substrate and one terminal electron acceptor at a time. BIO1D has been used by Dow Chemical to support intrinsic remediation for contaminant containment at a Superfund site (Klecka et al. 1990) and at a manufacturing facility (Davis, Klier, and Carpenter 1994).

Bioplume II is based on the well-documented two-dimensional finite difference numerical method developed by Konikow and Bredehoeft (1978). The model computes the concentration changes with time due to advection, dispersion, mixing, and biodegradation (Rifai et al. 1989). Bioplume II solves a transport equation twice, once for hydrocarbon and once for oxygen, at every time-step. An instantaneous reaction is assumed to occur between the hydrocarbon and oxygen. The model can simulate natural biodegradation, retardation, advection, and enhanced in situ biodegradation scenarios. For the enhanced biodegradation scenario, injection wells can be simulated that introduce supplemental oxygen into the aquifer to enhance in situ bioremediation. Additionally, the model includes a reaeration constant that can simulate gaseous oxygen diffusion from the unsaturated zone into the groundwater.

BIOSCREEN has been developed as a tool for simulating natural attenuation of dissolved hydrocarbons at petroleum release sites. It involves solute transport with biodegradation as a first-order decay process or as an instantaneous reaction as is assumed in Bioplume II.

BioTRANS is a vertically-averaged model that includes advection, dispersion, sorption, volatilization, and biodegradation for the prediction of the transport of up to five species in fractured or porous aquifer systems. Oxygen transport and multispecies oxygen-limited decay can be predicted using this model as can dissolution from residual or free NAPL.

The RITZ model was developed to examine the fate and transport of contaminants in the unsaturated zone, primarily oily waste compounds in land treatment units (Nofziger, Williams, and Short 1988). Simulated processes include sorption, leaching (advection), biodegradation, and volatilization. A soil transport and fate (STF) database (Sims, Sims, and Hansen 1991) was developed to be used in conjunction with RITZ. The database provides quantitative and qualitative information concerning the behavior of organic compounds and a limited number of inorganic compounds in soil environments. Numerous soil chemical parameters are provided that describe chemical processes including degradation, transformation, partitioning (water, air, soil, and oil), toxicity, and the propensity of a compound to bioaccumulate.

RITZ, the STF database, and Bioplume II software and users manuals can be obtained at no charge from the Center for Subsurface Modeling Support (CSMoS) at the US EPA Robert S. Kerr Environmental Research Center in Ada, Oklahoma.

3.3.4 Quality Assurance/Quality Control

A Quality Assurance/Quality Control (QA/QC) plan should contain the practices to be used in the project to ensure the accuracy, precision, completeness, representativeness, and comparability of project data as described in *Test Methods for Evaluating Solid Waste, SW 846* (US EPA 1986c, 1986d) and the *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans* (US EPA 1980). A general outline for such a QA plan is presented in Table 3.1. In addition, engineering practices to ensure data quality and QC should include:

- ongoing review of health and safety practices;
- review of sampling, chain of custody, and analysis procedures;
- routine calibration and verification of fate and transport models;
- ongoing training of new field personnel; and
- routine maintenance and calibration of all field monitoring and sampling equipment.

QA/QC guidance is generally broad which is intended to cover a wide range of issues which affect data quality. Monitoring parameters requiring quantification to adequately evaluate performance of the technologies presented in this monograph are diverse. For example, representative samples for groundwater, aquifer solids, soil, soil vapors, soil pore water, air, surface water, slurries, etc., are collected and analyzed for a wide variety of parameters. Other pertinent parameters affecting QA/QC include the data quality objectives, desired confidence, regulatory monitoring requirements, sampling, analytical methods, etc. Therefore, application of the relevant QA/QC guidelines is necessary to identify the appropriate steps and practices to ensure QA/QC on a site-specific basis. The criteria, parameters, and requirements vary among sites and remedial technologies and, therefore, cannot be adequately addressed in this monograph. The following documents provide general guidelines on which QA/QC and quality assurance project plans can be based.

- *Test Methods for Evaluating Solid Waste,* Vol. 1A 3rd ed. SW 846 (US EPA 1986c)

- *Test Methods for Evaluating Solid Waste*, Vol. 1B 3rd ed. SW 846 (US EPA 1986d)
- *EPA Requirements for Quality Assurance Project Plans,* QA/R-5 (Draft, October 1997)
- *Guidance on Quality Assurance Project Plans*, QA/G-5 (Draft, September 1997)
- *Guidance for the Data Quality Objectives Process,* QA/G-4 (EPA/600/R-96/055, September 1995)
- *Data Quality Objectives Decision Errors Feasibility Trials (DEFT)*, Software V. 4.0, (EPA/600/R-96/056, September 1994)
- *Guidance for the Preparation of Operating Procedures for Quality-Related Operations* (EPA/600/R-96/027, November 1995)
- *Guidance for the Data Quality Assessment Process: Practical Methods for Data Analysis,* (EPA/600/R-96/084, July 1996)
- *Data Quality Objectives Process for Superfund: Interim Final Guidance*, (EPA 540-R-93-071, September 1993)
- Taylor, J.K. 1987. *Quality Assurance of Chemical Measurements*, (Lewis Publishers Inc., Chelsea, MI)

The US EPA Quality Assurance Division (QAD) prepares and publishes documents which provide technical guidelines regarding QA/QC issues. Several of the documents identified above may be obtained from QAD based on their availability.

Table 3.1
Outline for Comprehensive Quality Assurance Project Plan

1.0 Data Generators
2.0 Data Review/Approver
3.0 QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability
4.0 Precision and Accuracy
  4.1 Audit and Check Samples
  4.2 Objectives for an Analyte in Sample Matrix
5.0 Completeness
6.0 Representativeness
7.0 Comparability
8.0 Sampling Procedures
  8.1 Soil Core Sampling
  8.2 Groundwater Sampling
  8.3 Soil Gas Sampling
9.0 Sample Documentation, Handling, and Custody
10.0 Calibration Procedures and Frequency
11.0 Analytical Methods
  11.1 Metal Analysis
  11.2 Organic Analysis
  11.3 Anion Analysis
  11.4 pH and EC
  11.5 Analytical Balances
  11.6 Drying Ovens and Refrigerators
12.0 Data Reduction, Validation, and Reporting
13.0 Internal Quality Control Checks and Frequency
  13.1 Laboratory Certification
  13.2 Laboratory Operations QC
    Duplicates and Spikes
    Blanks
    Laboratory Control Sample
    Instrument Set-up
    Calibration
  13.3 Detection Limits and Quantification Limits
  13.4 Performance and System Audits
  13.5 Preventive Maintenance
  13.6 Routine Procedures to Assess Data Precision, Accuracy, and Completeness
  13.7 Corrective Action
    Determination of the Cause of the Problem
    Determination of a Corrective Action to Eliminate the Problem
    Assigning and Accepting Responsibility to Implement the Corrective Action
14.0 Quality Assurance Reports
15.0 Cited References

4 SOIL TREATMENT SYSTEMS

4.1 Introduction

Site, soil, and waste constituent characteristics that are important in the evaluation and design of soil treatment system technologies are summarized in Table 4.1. Technologies applied in situ (i.e., bioventing and phytoremediation) are affected by site conditions (e.g., groundwater table fluctuations, heterogeneous layered soil lenses) that negatively impact the uniform distribution and transport of reactants throughout the contaminated site. Ex-situ soil treatment technologies (i.e., land treatment, soil cells, and slurry reactors) are not sensitive to these restrictions because their implementation allows the modification of limiting soil characteristics through textural modifications, homogenization, etc. All technologies are impacted by soil conditions that affect microbial activity (i.e., water content, soil pH, nutrient limitations), although ex-situ systems can be designed to manage these soil properties relatively easily. Finally, all technologies are influenced by waste constituent characteristics that affect a contaminant's toxicity, biodegradability, and bioavailability. Again, ex-situ techniques can overcome at least the toxicity and biodegradability limitations through modification of the soil and waste environment via tilling, mixing with uncontaminated soils to reduce contaminant levels below inhibitory concentrations, addition of carbon sources to stimulate co-metabolic degradation, etc.

The following sections detail each of the soil treatment technologies listed in Table 4.1 and provide additional discussion of technology applications and limitations appropriate for soil remediation at field scale.

Table 4.1
Impact of Various Site, Soil, and Waste Constituent Characteristics on Soil Treatment Technology Performance*

		BV	LT	SC	SR	PR
Site	Climatic conditions	N	I-	I	N	I-
	GW table fluctuations	I-	N	N	N	N
	Surface structures	I+	N	N	N	I-
	Layered formation	V	N	N	N	I
	Product existence.distribution	V	I	I	N	V
Soil	Fine grained	I	N	N	N	I-
	High-water content	V-	I	I	N	I-
	Low-water content	I-	I	I	N	I
	Nutrients	N	I	I	I	I
	pH	N	I	I	I	V
Waste Constituent	Volatility	I-	I-	I	I	I-
	Biodegradability	V	V	V	V	I
	Bioavailability	V	V	V	V	I
	Water solubility	I-	I-	I-	I	I-
	Toxicity	V-	V-	V-	V-	V-

*BV = Bioventing
LT = Land Treatment
SC = Soil Cells
SR = Slurry Reactors
PR = Phytoremediation
GW = Groundwater
N = Not important related to the performance of the technology
I = Important related to the performance of the technology
V = Very important related to the performance of the technology
+ = Characteristic positively impacts the performance or selection of the technology
- = Characteristic negatively impacts the performance or selection of the technology

4.2 Bioventing

4.2.1 Principles of Operation

4.2.1.1 Process Definition

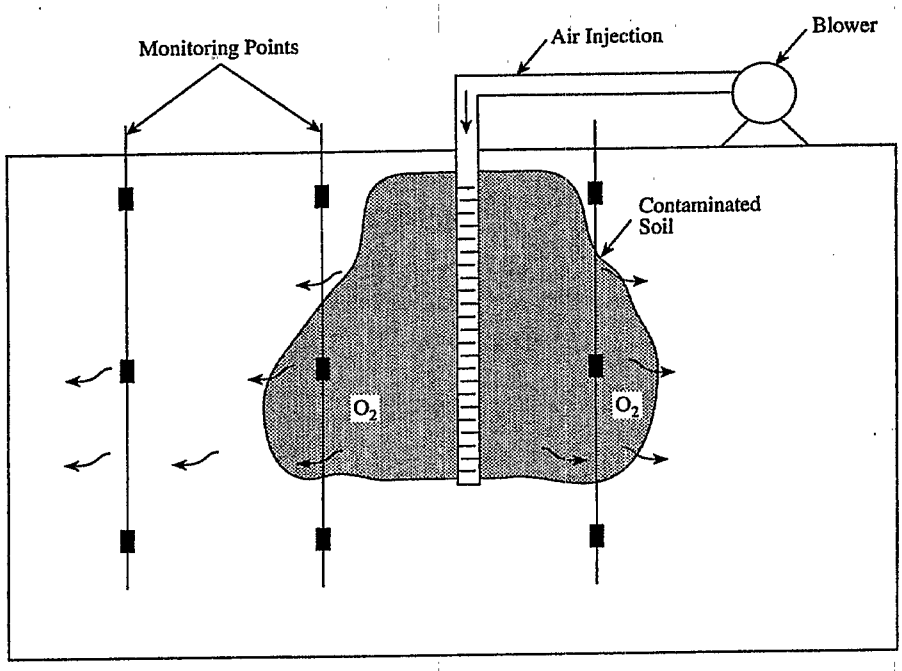
Bioventing is an in situ process to enhance biodegradation of hydrocarbons by providing oxygen, generally in the form of air, to aerobic soil microorganisms. Bioventing is normally accomplished using mechanical blower systems to inject air into unsaturated soils. Figure 4.1 illustrates a typical air injection bioventing system. In shallow sandy soils, bioventing is often a natural process as oxygen is exchanged through barometric pressure shifts and simple diffusion. Passive air injection systems using changes in barometric pressure to exchange air through vent wells are also being investigated (Foor et al. 1995). Aboveground soil cells have also been configured for bioventing by placing perforated horizontal pipes through the cell. Soil cells are discussed in detail in Section 4.4.

Bioventing is mechanically similar to soil vapor extraction (SVE); however, the objective of bioventing is significantly different. SVE systems are designed and operated at high air flow rates to maximize the volatilization of low-molecular weight hydrocarbons. In SVE, some biodegradation occurs as oxygen-rich soil gas moves through the contaminated soil. For more information on SVE, consult *Vapor Extraction and Air Sparging*, Holbrook et al. (1998). In contrast, bioventing uses low air flow rates to provide only enough oxygen to maintain aerobic biodegradation with minimum vapor migration. Sorbed hydrocarbons are degraded in place and vapor-phase hydrocarbons are degraded as they slowly move through biologically-active soil. The conversion of hydrocarbon vapors to carbon dioxide has been documented in a carefully monitored site at Hill Air Force Base, Utah (Sayles et al. 1992).

4.2.1.2 Bioventing Application

Although bioventing is a relatively new technology, it is now being applied internationally at thousands of petroleum-contaminated sites. The Air Force Center for Environmental Excellence (AFCEE) recently completed a comprehensive bioventing pilot test initiative at 145 petroleum-contaminated sites nationwide. The test was unique in that a standard test protocol was followed on every site to provide comparable data among sites (Hinchee et al. 1992). Based on this comprehensive study, the following observations were made with respect to the general applicability of bioventing (success

Figure 4.1
Air Injection Bioventing System



Source: AFCEE 1995

was defined as respiration rates statistically greater than background, uncontaminated soil rates).

- Of the 145 sites tested, air injection and oxygen distribution were unsuccessful at only two sites. Both of these sites had fine-grained soils with high moisture content. Over 20% of the successful test sites had soils consisting of greater than 50% silt and clay by weight. High soil moisture was a greater deterrent to bioventing success than fine-grained soils. Sites with very dry soils (<4% moisture) had limited bioactivity and at one site, biodegradation rates were too slow for commercial application. The addition of moisture to the soil at the Hill AFB site (Dupont, Doucette, and Hinchee 1991), and at a site in the California desert (Zwick et al. 1995) increased respiration rates.

- Air injection was the primary method of oxygen supply. Vapor extraction was used at five gasoline-contaminated sites as a precaution to prevent uncontrolled vapor migration. After high concentrations of vapors were removed from these sites, the systems were converted to air injection for long-term bioventing.
- Favorable rates of biodegradation were measured in a wide variety of climates including the interior of Alaska and the deserts of southern California.
- Bioventing was successful for a variety of petroleum products including JP-4 jet fuel, diesel, gasoline, waste oils, hydraulic fluids, and Stoddard solvent.

In situ respiration rates, air permeability, and oxygen influence were determined for each site and a multi-variable statistical analysis was completed on data from over 120 sites to determine what factors had the greatest impact on the aerobic biodegradation rates (Leeson et al. 1995). The study concluded that:

- no single factor that was measured (nitrogen, phosphorous, moisture, or pH) had a strong correlation to increased rates of aerobic respiration;
- sites with higher levels of soil gas hydrocarbons produced slightly higher rates of aerobic respiration;
- some correlation exists between higher natural nitrogen levels and aerobic respiration; however, this correlation was too weak to suggest that nitrogen addition will always have a beneficial effect; and
- some correlation exists between higher soil moisture and higher aerobic respiration rates, although the benefits of moisture addition would be greatest for arid sites with initial moisture levels under 25% of field capacity. Too much moisture will reduce air-filled porosity and inhibit air (oxygen) transfer.

In summary, bioventing has almost universal application as an enhancement to the natural biodegradation of petroleum hydrocarbons in the vadose zone. If air can be moved through the soil, native microorganisms are generally available to carry out the biodegradation process. High soil moisture levels can prevent air movement and create conditions that are unsuitable for bioventing. Based on AFCEE testing, no single factor has a dominant impact on the rate of in situ biodegradation. In general, biodegradation rates have decreased over time at each Air Force test site, indicating that as the

process proceeds, less biodegradable hydrocarbons make up a greater fraction of the total remaining hydrocarbons. The decreasing bioavailability of hydrocarbons may be an important factor in determining long-term rates of biodegradation and overall remediation times. Post-bioventing soil sampling indicates that more water-soluble and bioavailable compounds, such as alkylbenzenes, are preferentially biodegraded using bioventing treatment. Due to site-specific variables such as air permeability of the soil, radius of oxygen influence, and biodegradation rates, pilot testing is recommended prior to finalizing any full-scale bioventing design.

4.2.1.3 Determining Site-Specific Applicability

A relatively simple field study is required to determine if bioventing is appropriate for any given site. Minimum site characterization requirements include:

- a review of existing soil contamination data, groundwater elevations, and source of contamination;
- soil sampling (if necessary) to complete a simple three-dimensional model of contaminant distribution;
- a soil gas survey using existing monitoring wells or temporary soil gas probes to measure initial oxygen, carbon dioxide, and volatile hydrocarbon concentrations in several contaminated locations and at least one uncontaminated "background" location. Depleted oxygen levels generally correspond to areas of significant hydrocarbon contamination and indicate that natural soil microorganisms are present and degrading hydrocarbons, producing oxygen-limited conditions within the contaminated soil;
- additional soil characterization for contaminants present; average moisture content; grain-size analysis; and total Kjeldahl nitrogen (TKN) have also been recommended for each site to establish baseline conditions and properly interpret pilot test results (Leeson and Hinchee 1995); and
- microcosm studies and bacteria plate counts are not required at most sites when aerobic respiration can be confirmed through oxygen utilization testing. Microcosm studies using site soils can be performed if the biodegradability of a specific chemical is in question.

Pilot testing is recommended at all candidate sites to determine the ability of a bioventing system to uniformly distribute oxygen throughout the site

and to establish the initial rates of biodegradation using in situ respiration tests. Rates of in situ respiration are determined by injecting air into contaminated soil and then monitoring the soil gas for the biological uptake of oxygen over time. The Air Force has published a standard pilot testing protocol (Hinchee et al. 1992) that recommends three primary on-site tests: (1) an in situ respiration test, (2) an air permeability test, and (3) a long-term oxygen influence test to establish the radius of treatment for each air injection well. The first two tests can generally be completed in two to three days while the radius of oxygen influence is more accurately determined after the air injection blower has been operating for at least one week. For larger sites, pilot test data can be used in vadose zone flow models to optimize placement of multiple wells. Bioventing pilot testing requires a modest investment in test equipment, and for sites with shallow soil contamination, the entire test sequence can often be completed with temporary soil gas probes and a single air injection vent well. On small sites, the pilot test vent well and blower are often converted into the full-scale treatment system following successful initial pilot testing.

4.2.2 Process Design Principles

4.2.2.1 Primary Design Criteria

The primary objective of bioventing design is to establish and maintain a subsurface oxygen supply that is equal to or greater than the biological oxygen demand of hydrocarbon-degrading microorganisms. For sites contaminated with volatile hydrocarbons, an equally important design concern is minimizing air injection to prevent undesirable or dangerous vapor migration. Design modifications to make bioventing safer for volatile organics are presented in Section 4.2.4.1.

There are three primary design features associated with standard air injection bioventing systems:

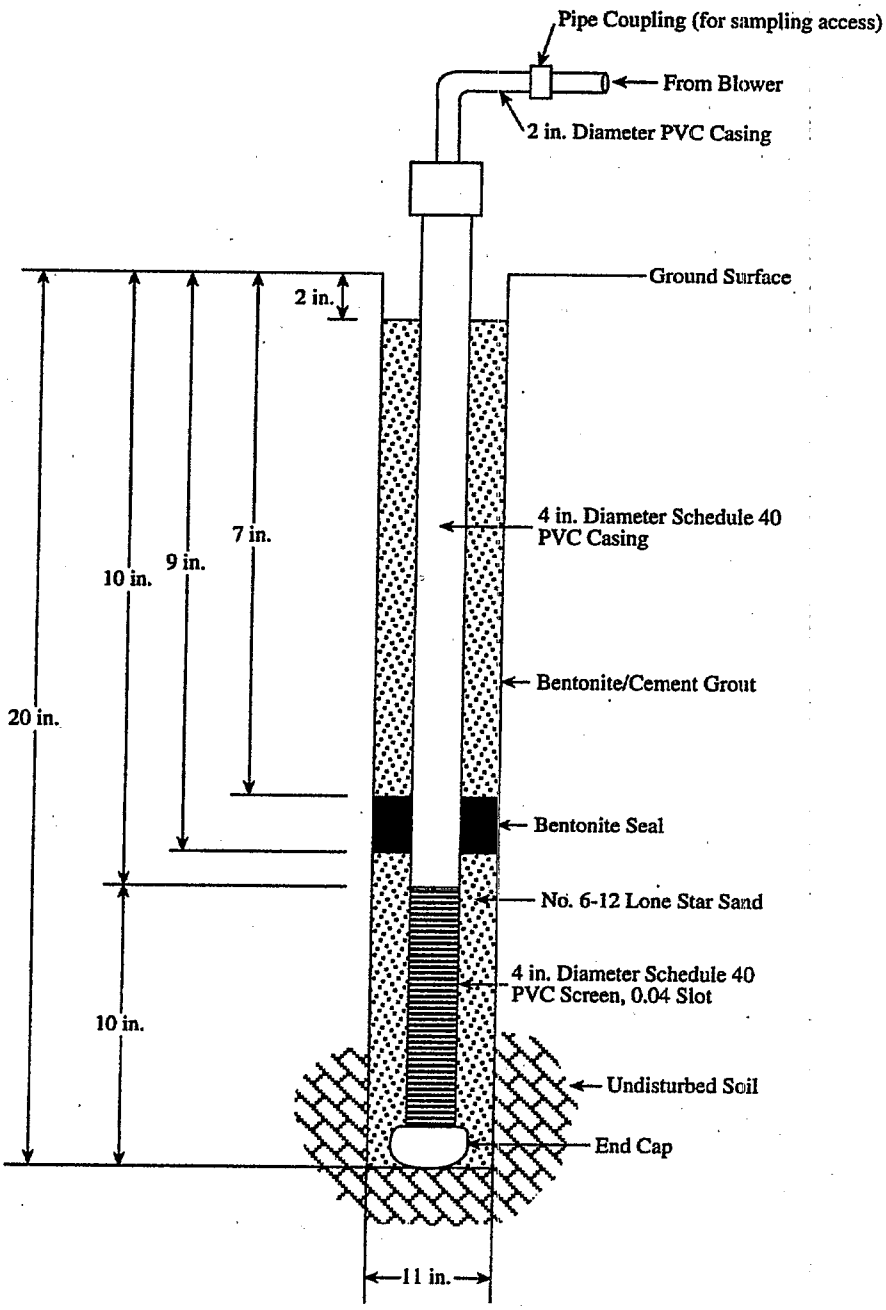
- the vent well(s) must be designed to efficiently deliver air throughout the entire contaminated soil volume;
- the blower must be sized to deliver the required air flow over a range of soil entry pressures that will change as seasonal soil moisture or groundwater elevations vary; and
- the site must be properly monitored using soil vapor monitoring points located strategically inside and outside of the contaminated soil volume.

Site characterization and pilot testing as discussed in Section 4.2.1.3 are crucial to establish these design criteria. The following paragraphs describe each of these design features in greater detail.

Vent Well Design. Bioventing vent wells (VWs) are typically constructed with 5- or 10-cm (2- or 4-in.) diameter polyvinyl chloride (PVC) well material with the screened interval above the water table and corresponding to the soil contamination interval. Stainless steel screens are rarely installed, but may be necessary in fuel-saturated soils that will require several years of bioventing. In the presence of free product, PVC screens have been know to soften, causing the slots to close. Five-cm (2-in.) diameter VWs are appropriate for more permeable sandy soils and 10-cm (4-in.) diameter wells are preferred for less permeable soils to minimize air entry pressures. Figure 4.2 illustrates a typical air injection VW design. One key feature of VW design is the bentonite seal and cement grout that is used to prevent injected air from short-circuiting to the surface. In low permeability soils, a minimum of 1.5 m (5 ft) of bentonite and grout are recommended. In sandy soils, 0.6 to 1 m (2 to 3 ft) may be acceptable. Screen slot sizes of 0.05 to 0.10 cm (0.02 to 0.04 in.) are generally used in bioventing applications with screen intervals being 10 to 15 feet to provide optimal control of gas movement in the subsurface. Because the VW is to provide a uniform supply of oxygen to the contaminated soil, it is generally located in the center of the contaminated soil volume. When multiple wells are required, the wells should be spaced so that the radius of oxygen influence (RI) from each well overlaps. A spacing of 1.5 times the RI provides a conservative design. The total volume of influence is best determined by a one-week air injection pilot test, but can also be estimated based on oxygen demand, soil air permeability, and flow rate. Section 4.2.9 provides additional details on estimating the radius of influence.

Blower Selection. The blower is selected based on the desired flow rate and total delivery pressure of the air manifold and vent well. Flow rates are determined through pilot testing and are a function of the site-specific oxygen demand and the geometry of the soil volume to be aerated. Dupont, Doucette, and Hinchee (1991) suggested that as little as 0.1 to 0.5 pore volume exchanges per day are normally sufficient to provide the oxygen required to sustain aerobic biodegradation. Most bioventing air delivery systems are overdesigned, which can lead to rapid displacement of volatile organics and, in arid climates, acceleration of soil drying. Air injection pressure is equally important in selecting the proper blower. Pilot testing is the only reliable method for determining air injection pressure that is measured at the wellhead during the standard air permeability test. One day of air injection is recommended as soil entry pressures often decrease during the test.

Figure 4.2
Typical Vent Well
(not to scale)



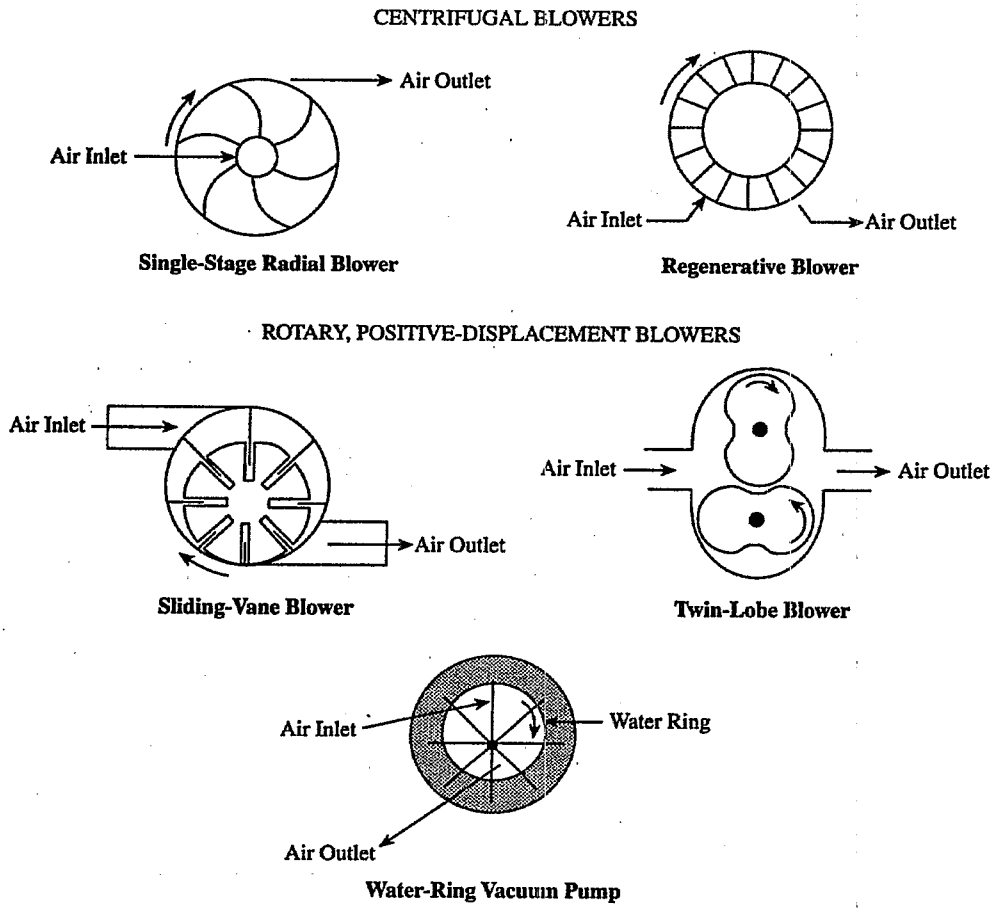
Source: Hinchee et.al. 1992

Once a desired flow rate and operating pressure are determined, standard blower performance curves are used to select the blower that best matches flow and pressure requirements. There are two primary types of blowers used for bioventing applications: centrifugal blowers and positive-displacement blowers (Figure 4.3). Centrifugal blowers produce higher flow rates and lower pressures and are suited for sandy soils. Small centrifugal blowers are preferred for bioventing because they are less expensive and relatively maintenance-free. Positive-displacement blowers can produce much higher pressures and are used when pilot testing indicates that soil entry pressures will exceed 0.2 atm (3 psig). Of the 145 sites tested by the Air Force, only 10% required positive displacement blowers.

Soil Vapor Monitoring Points. Soil vapor monitoring points (VMPs) are extremely important in determining the potential effectiveness of bioventing and in long-term monitoring of bioventing progress. When properly located, these points can be used for measuring the soil gas pressure response at varying distances from the air injection vent well, the uniformity of oxygen distribution, and the rate of oxygen utilization in respiration tests. For shallow sandy sites (<3 m to 7.5 m) (<10 to 25 ft), soil gas probes identical to those used in soil gas surveys are often driven into the soil to save time and money. In more cohesive soils, the metal drive rod can be removed and replaced with a 1.3-cm (0.5 in.) PVC well point for a more permanent installation. On deeper sites or on sites with difficult-to-penetrate soils, standard drilling using hollow-stem augers provides the best installation of permanent monitoring points. Several monitoring points are generally installed at varying depths at each location. Figure 4.4 illustrates a typical multidepth monitoring point design. The following criteria determine the number and location of VMPs in both pilot- and full-scale applications.

- For air permeability pilot testing, VMPs should be located at three different, equally-spaced distances from the air injection vent well. VMP spacing can be increased to over 6 m (20 ft) in permeable soils, but a 3-m (10-ft) spacing is common in less permeable silts and clays.
- At least three VMPs on each site should be located in the contaminated soil to estimate average in situ respiration rates.
- At least two monitoring depths are recommended for sites with a 2- to 3-m (6- to 10-ft) interval of contaminated soil. For sites with larger contaminated intervals, monitoring points should be located every 3 m (10 ft) if economically feasible. VMPs should also be located in every contaminated soil layer that is expected to exhibit a different air permeability than surrounding layers.

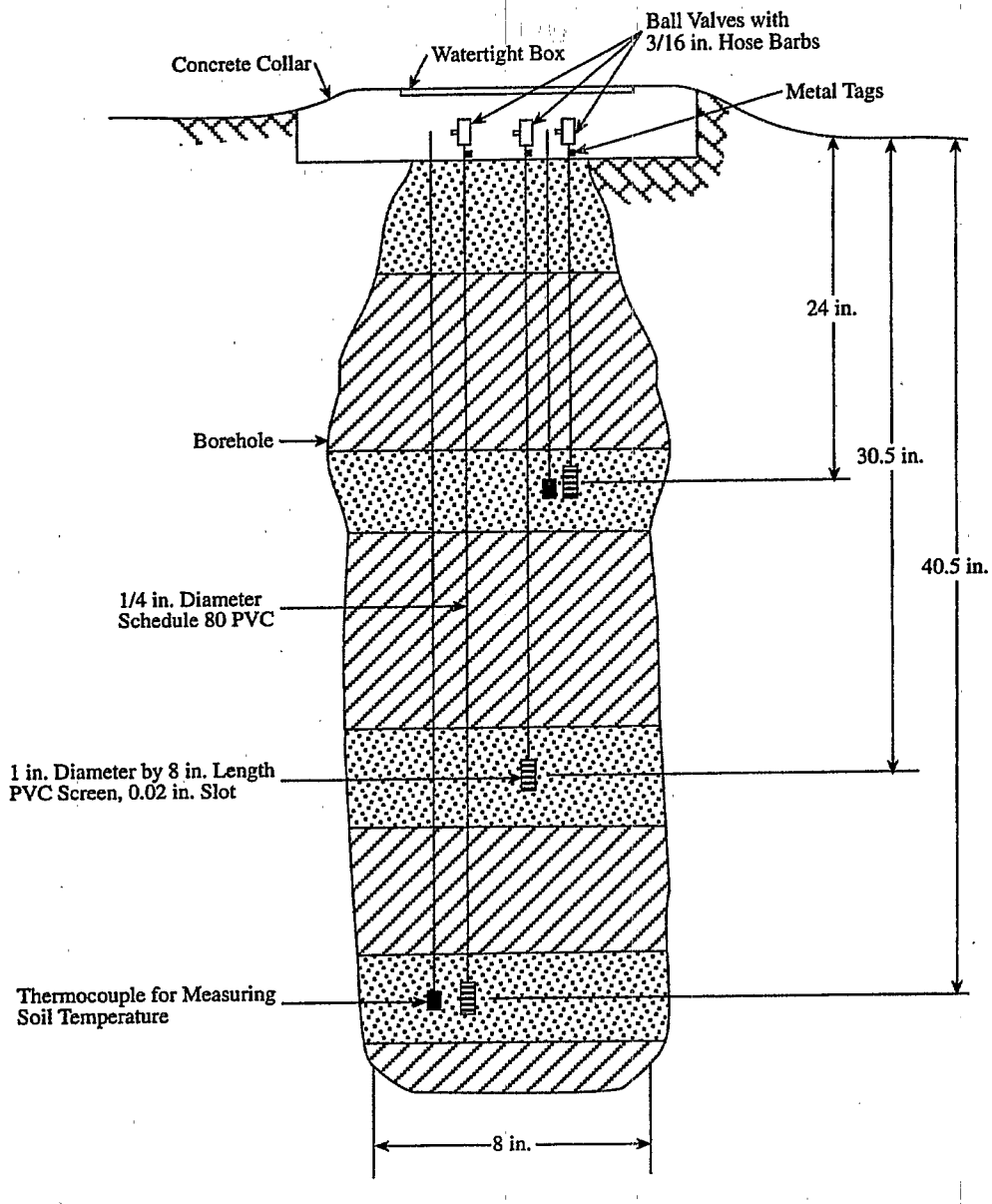
Figure 4.3
Bioventing Blowers



Source: Leeson and Hinchee 1995

- At least one background multidepth VMP should be installed at least 30 m (100 ft) from the contaminated area to monitor ambient soil oxygen and carbon dioxide levels and to perform background respiration tests.
- For full-scale installations, there should be approximately one VMP for each air injection vent well. VMPs should be strategically located across the site to monitor the uniformity of oxygen distribution at all contaminated depths.

Figure 4.4
Typical Vapor Monitoring Point
(not to scale)



No. 6-12 Lone Star Sand
Bentonite

Source: Hinchee et al. 1992

4.2.2.2 Additional Design Considerations

Additional design considerations include vapor migration control, seasonal groundwater variation, persistently high water tables, contamination beneath buildings, and layered formations. Each of these considerations is discussed below.

Controlling Vapor Migration. Although a properly-designed air injection bioventing system will minimize vapor migration, there are situations where air injection should not be considered. At sites that have soils contaminated with gasoline or other volatile organics near buildings or underground utility corridors, soil vapor extraction should be used to reduce the soil vapor concentrations. Soil vapor extraction is also recommended for small sites where vapors can migrate onto adjoining properties. Section 4.2.4.1 describes how the bioventing process can be modified to maximize biodegradation of the more volatile hydrocarbons.

Seasonal Groundwater Variations. Rising and falling groundwater elevations will impact bioventing effectiveness if contaminated soil is located in the capillary fringe or below the water table. Bioventing will be most effective during the dry season when the maximum volume of soil can be exposed to air flow. During the wet season, bioventing will be limited to unsaturated soils and in some locations, bioventing should be terminated since air is not moving through contaminated soil. To account for variable groundwater elevations, vent well screens should be installed at the depth corresponding to the lowest seasonal groundwater elevation. The deepest VMPs on the site should be installed approximately 0.3 m (1 ft) above the seasonal low groundwater elevation.

Persistent High Water Table. For sites with 2 m (6 ft) or less to groundwater, horizontal vent wells offer distinct advantages over vertical wells. Because horizontal wells provide a much greater screen area per vertical length than standard vertical screens, they can deliver more air over a larger area at a lower pressure. This reduces the chance of short-circuiting, particularly when the horizontal well is constructed with an overlying layer of bentonite to encourage horizontal flow. Horizontal wells are often more effective in delivering air to larger volumes of shallow soil. Another design modification that can increase the volume of soil exposed to bioventing is the use of air injection pressure to pneumatically dewater a portion of the capillary fringe (Hall, Downey, and Reed 1995; Reisinger et al. 1995). This approach seems to work best in soils with lower permeability where the injected air exerts a higher pressure on the capillary fringe.

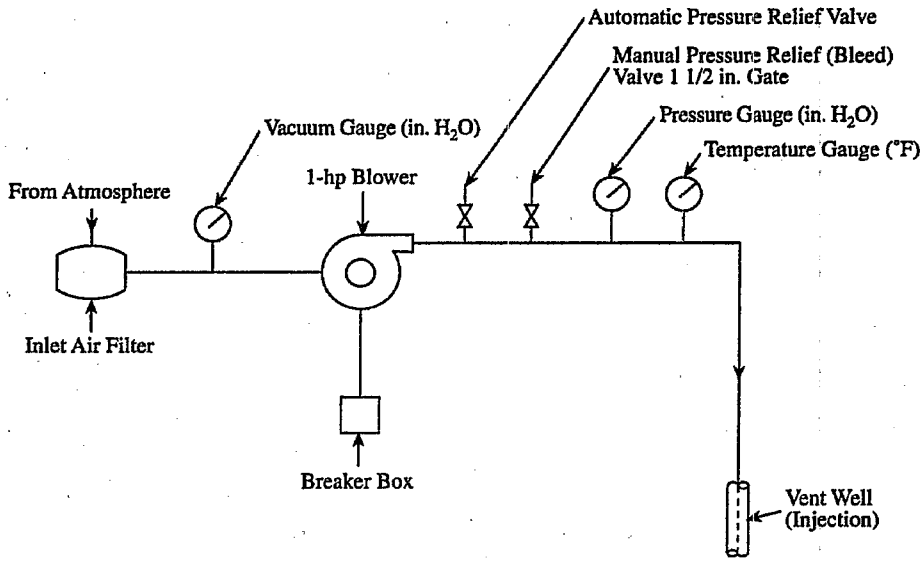
Contamination Beneath Buildings. One distinct advantage of SVE and bioventing over other soil remediation technologies is that contaminated soils beneath buildings and other valuable structures can be treated with minimal disturbance. SVE is the technology of choice for volatile hydrocarbons beneath occupied buildings to ensure vapor control. Bioventing provides a very cost-effective alternative for less volatile hydrocarbons. Pilot testing is critical on these sites to establish the radius of oxygen influence for each vertical well. In permeable soils and for smaller buildings, vertical air injection wells constructed around the perimeter of the structure will often provide oxygen to the entire soil volume beneath the structure. For larger structures, horizontal vent wells may be the only feasible air delivery system.

Bioventing in Layered Formations. Layered formations with significant changes in air permeability pose unique challenges for the bioventing design engineer. Frequently, if layers are less than 1 to 1.5 m (3 to 5 ft) thick, air will preferentially flow through higher permeability layers but sufficient oxygen may diffuse into adjoining silt and clay layers. This phenomenon can actually extend the radius of oxygen influence in soils that are predominantly silt and clay (Phelps, Stanin, and Downey 1995). On sites with much thicker layering, separate vent wells are often constructed in each major soil unit. Separate blowers are generally required to deliver air at different pressures to separate vent wells. Again, pilot testing and careful VMP placement is required to verify that a vent well design can deliver oxygen to each of the contaminated soil layers.

4.2.3 Process Configuration

Bioventing systems are mechanically simple and generally consist of a motor and blower with accessory air filter, pressure relief valve, manual air bleed valve, and flow and pressure measuring devices. To prevent damage to the blower, the pressure relief valve is set to open before the maximum operating pressure of the blower is reached. This feature is particularly important on sites where variable groundwater and soil moisture levels can significantly increase the soil entry pressure. A manual bleed valve is often used on sites with highly permeable soils to prevent excess air from being injected into the subsurface. The motor, blower, control valves and gauges are normally installed inside a small, weatherproof enclosure that is ventilated to prevent motor overheating. A standard process and implementation diagram for air injection is provided as Figure 4.5.

Figure 4.5
Process and Instrumentation Diagram for Air Injection Bioventing



Source: Hinchee et al. 1992

4.2.4 Process Modifications

The standard air injection bioventing system can be modified to address unique site conditions such as dangers from uncontrolled vapor migration, overly-dry or nutrient-poor soils, and low-permeability or low-temperature soils. The following discussion focuses on process modifications that can extend the application of bioventing to these difficult conditions.

4.2.4.1 Controlling Vapor Migration

As discussed in Section 4.2.2.2, sites with gasoline and other highly volatile contaminants require special design and process modifications to ensure that dangerous vapor migration does not occur. The following process modifications can safely control vapor migration at these sites.

Pulsed Air Injection. The use of pulsed air injection can provide the required mass of oxygen while limiting excess air which can spread volatile contamination. This method is well suited for sites with deep volatile contamination in the soil and where air injection will not create a vapor accumulation problem in surface or subsurface structures. Once the oxygen

utilization of soil bacteria has been established, the pulse cycle can be set to ensure that oxygen never falls below 5% in the contaminated soil volume. At one gasoline-contaminated site, the pulse cycle resulted in one, 8-hour air injection for every four days of operation (Downey et al. 1995).

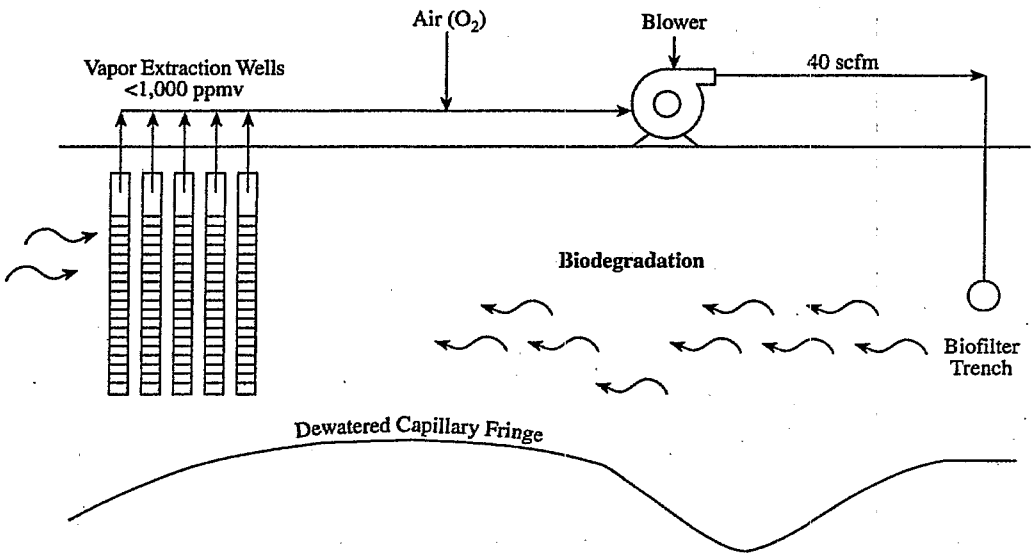
Low-Rate SVE. SVE has often been used to remove potentially explosive hydrocarbon vapors and radon concentrated near building basements and underground utilities. By installing vent wells away from buildings and extracting soil vapor from these wells, the flow of vapors can be induced away from the structure. When low SVE rates are used, oxygenated soil gas from surrounding clean soils is drawn through the contaminated soils, producing the same bioventing effect as air injection. Often vapor discharge can be minimized so that expensive off-gas treatment is not required.

Vapor Recirculation. On sites where even low-rate SVE will require expensive offgas treatment, vapors can be both controlled and treated by reinjecting the vapors into soils away from structures and allowing soil bacteria to degrade the vapors in an expanded soil bioreactor (Downey et al. 1995). Figure 4.6 provides an example of a vapor recirculation design and process modification that has been successfully used on gasoline-contaminated sites. Successful vapor recirculation will depend on maintaining low flow rates and adequate open area to install the vapor recirculation wells. Vapor recirculation wells should not be installed close to property boundaries or open underground utilities such as storm drains. Air permits can generally be avoided if flux monitoring over the vapor injection area indicates that little or no hydrocarbons are being released to the atmosphere, although some states may require a permit to reinject the vapors. VMPs should be installed surrounding the vapor reinjection well to monitor the conversion of hydrocarbon vapor to carbon dioxide.

Short-Term, High-Rate SVE. Sites with high concentrations of volatile organics (>40,000 ppm_v) are most cost-effectively treated using a high rate of SVE over the first few months of treatment. Although sites differ in the quantity of volatile contamination, over 90% of the volatiles are normally removed from the soil during the first three to four months of high-rate SVE. At one test site, an internal combustion engine (ICE) equipped for SVE was used for three months to remove over 2,700 kg (6,000 lb) of gasoline vapor. Based on respiration testing at this site, that same 2,700 kg (6,000 lb) would have required three years to biodegrade in situ (Downey et al. 1995). In addition to eliminating a vapor migration hazard at this site, approximately $40,000 in long-term bioventing operation and maintenance costs were saved compared to the $15,000 required to operate the ICE for three months. After the high levels of hydrocarbon vapor are removed from the soil, the

SVE system can be reconfigured for air injection bioventing using the same wells, piping, and blower to remove the less volatile hydrocarbons. A similar combination of SVE and bioventing was successfully used at a large JP-4 jet fuel site at Hill AFB, Utah (Dupont, Doucette, and Hinchee 1991).

Figure 4.6
Vapor Recirculation for Bioventing



Source: Downey et al. 1995. Used with permission.

4.2.4.2 Overcoming Adverse Soil Conditions

Site conditions such as overly-dry or nutrient-poor soils, low-permeability soils, and low-temperature soils can be obstacles to effective bioventing. Process modifications such as those discussed below can be employed to overcome these adverse soil conditions.

Moisture Addition. In soils with an average moisture of less than 25% of field capacity, the addition of moisture has been shown to increase in situ respiration rates. In a controlled experiment at Hill AFB (see case study in Chapter 8 of this monograph) approximately 3,700 m^3 (1 million gal) of water were added to a large JP-4 contaminated site. Following this water

addition, neutron probes indicated that the average site soil moisture was increased from 25 to 60% of field capacity. Respiration tests performed at 14 VMPs indicated a doubling of the mean oxygen uptake rate following moisture addition. At another site in southern California, drip irrigation was used to increase the average soil moisture from 4 to 10% (by weight) to a depth of approximately 15 m (50 ft). The result was nearly an order-of-magnitude increase in oxygen utilization rates in the impacted soil (Zwick 1995). Both of these sites had relatively permeable soils that allowed surface infiltration of moisture. Published accounts of moisture addition in less permeable soils are not available.

Nutrient Addition. Although laboratory bioventing studies have generally shown that nitrogen and phosphorous addition will increase biodegradation rates (Hinchee and Arthur 1990), field attempts to enhance biodegradation with nutrients have not produced encouraging results. Pilot testing at both Hill AFB, Utah (Dupont, Doucette, and Hinchee 1991), and Tyndall AFB, Florida (Miller and Hinchee 1990), provided no evidence that a controlled nutrient addition had any positive effect on respiration rates, although at both sites, soil sampling indicated that the added nutrients had been well distributed in the contaminated soils. Natural TKN levels as low as 20 mg/kg and phosphorous levels as low as 3 mg/kg have been sufficient to sustain biological respiration at several bioventing test sites. In summary, nutrient availability has not yet been shown to be the limiting factor in documented pilot testing. Oxygen, and possibly, the bioavailability of the hydrocarbons, are more often limiting the rates of in situ biodegradation.

Pure Oxygen Injection. The injection of pure oxygen gas has been suggested as one method of increasing the oxygen supply in low-permeability soils where only small flow rates can be injected into the soil column. Final field test results from F.E. Warren AFB, Cheyenne, Wyoming, indicate that soil gas oxygen concentrations can be increased under the influence of pure oxygen injection, without any apparent affect on respiration rates (Utah Water Research Laboratory 1995). A monitoring point that had not achieved ambient soil oxygen concentrations under air injection was found to have 50% by volume oxygen under pure oxygen injection, with approximately equivalent oxygen mass flow rates. Pure oxygen injection did not significantly affect temperature-corrected respiration rates compared to ambient air rates for a majority of soil gas monitoring points. Of the pure oxygen influenced rates that were significantly different, the rates were approximately equally divided between those that increased and those that decreased, when compared to rates under ambient air injection conditions.

Soil Temperature Enhancement. Previous bioventing research has shown that the vanít Hoff-Árrhenius equation provides a good estimate of temperature effects on soil microbial activity (Miller and Hinchee 1990). This relationship predicts a doubling of microbial activity for every 10°C increase in soil temperature. In deeper soils, seasonal soil temperature changes are of minor concern. However, in colder climates the soil temperature of shallow soils often drops below freezing and biological activity nearly stops until summer temperatures warm the soil. Under these extreme conditions, soil warming techniques have been demonstrated to increase annual average biodegradation rates at Eielson AFB in Fairbanks, Alaska (Sayles et al. 1995). Even relatively low cost warming techniques, such as heat tape installed 1 m (3 ft) below the ground surface, produced biodegradation rates two to three times greater than unheated soil plots. The Eielson study concluded that using heat tape to warm the soil could reduce the treatment time from nine to three years and would slightly reduce the total treatment costs. Blower systems also produce heated air that, when injected into the soil for long periods of time, can maintain warmer soil temperatures during winter months. At an AFCEE bioventing site in Michigan, an average soil temperature of 12°C (54°F) was maintained throughout the winter, and snow falling on the bioventing test area was thawed to melt in a 12-m (40-ft) radius where injected air had heated the soil (Leeson et al. 1995).

4.2.5 Pretreatment Processes

With the exception of moisture addition as described in Section 4.2.4.2, there are no soil pretreatment steps normally associated with bioventing. Pneumatic and hydraulic fracturing have been attempted to enhance the airflow in clay formations. These processes will often increase airflow through existing fractures, but the value of fracturing for bioventing is unknown.

4.2.6 Posttreatment Processes

Because bioventing is normally an in situ remediation process, soils are left in place following treatment, and posttreatment of soils is unnecessary. When SVE is used to stimulate bioventing, the offgas from the SVE system will often require treatment. A variety of technologies are available for offgas treatment including activated carbon, thermal oxidation, catalytic oxidation, flares, internal combustion engines, and biofilters (see Section 6.2).

4.2.7 Process Instrumentation and Control

Typical instrumentation for air injection bioventing is shown in Figure 4.5. In addition to blower performance, subsurface soil gas movement and oxygen use during in situ respiration testing require monitoring. The following paragraphs describe both the aboveground and in situ monitoring associated with a typical bioventing process.

4.2.7.1 Flow Measurement

Adjustments in air injection flow rate to each well are required to provide adequate oxygen to the contaminated soil volume and to minimize the migration of volatiles. Several types of devices are available to measure air flow. For larger systems with pipe diameters of 10 cm (4 in.) or more, pitot tubes or orifice plates and differential pressure gauges are used to determine flow velocity; these devices require regular adjustments and more operator attention. For 5- to 10-cm (2- to 4-in.) diameter pipes, hand-held thermal anemometers are preferred over other flow measurement devices. The tip of the anemometer is inserted into the center of the airstream through an open port in the pipe, and the meter provides a digital readout of air velocity. Due to explosive hazards, thermal anemometers are not recommended for SVE applications. For small blower systems, an in-line rotameter can be used to measure flow. However, rotameters can create significant head loss at higher flow rates.

4.2.7.2 Pressure Measurement

Two pressure gauges are used in simple bioventing systems (see Figure 4.5). The first gauge is located between the inlet air filter and the blower to monitor the condition of the air filter and the inlet vacuum on the blower. The second gauge is located immediately downstream of the blower to measure the total injection pressure of the system. Standard metal diaphragm pressure gauges are generally used; however, on rotary-vane and positive-displacement blower systems, oil-filled gauges are more resistant to vibration damage. During air permeability pilot testing, hand-held pressure gauges are used to measure changes in soil gas pressure at each VMP as air is injected at the VW.

4.2.7.3 Soil Gas and Soil Emission Flux Monitoring

Oxygen and Carbon Dioxide Monitoring. A high-quality, hand-held oxygen and carbon dioxide analyzer is the most important piece of equipment used to monitor the bioventing process. This gas analyzer is used both

to monitor the uniformity of oxygen supply in the soil gas and to measure the biological uptake of oxygen during respiration testing. The analyzer must be capable of measuring 0 to 20.8% oxygen and should be capable of measuring 0 to 15% carbon dioxide. A small, 1/10 horsepower vacuum pump is generally used to remove soil gas from each VMP while a sidestream of the extracted gas is analyzed for oxygen and carbon dioxide. A complete description of these procedures is provided in the *Air Force Bioventing Protocol* (Hinchee et al. 1992).

Hydrocarbon Soil Vapor Monitoring. A hand-held hydrocarbon vapor analyzer is required to monitor initial and changing soil gas concentrations. The analyzer should have a wide calibration range as soil gas hydrocarbon levels from 100 to 100,000 ppm_v may be encountered depending on contaminant type. For vapor concentrations in excess of 10,000 ppm_v, most gas analyzers require a dilution fitting. Either a platinum-catalyst or flame-ionization detector is recommended for bioventing applications.

Soil Emissions Flux Monitoring. For some sites, local regulatory agencies may require soil emission flux monitoring to ensure that injected air does not displace significant amounts of hydrocarbon vapors to the atmosphere. In conjunction with emission flux monitoring, hydrocarbon vapor monitoring is required to determine the mass of hydrocarbons displaced per unit area of the site. A simple flux monitoring procedure developed for land treatment units can be easily adapted for use on bioventing sites (Kienbusch 1986; Dupont 1988). It is important to complete two flux tests using three to five representative sampling locations selected from throughout the site to capture the expected subsurface heterogeneity that might exist. The first test is completed before the air injection system is turned on to determine the natural flux of hydrocarbons to the soil surface. The second test should be conducted with the blower running and during the same day and same time of day as the "system off" test to minimize temperature and barometric pressure differences. A comparison of flux rates measured at each sampling location before and during air injection indicates the impact of air injection on contaminant emission flux rates occurring throughout the site. Flux monitoring completed at five sites and varying air injection depths and fuel types resulted in an average displacement of only 130 grams (0.3 lb) of hydrocarbon vapor to the atmosphere each day with an average area of 700 m^2 (837.2 yd^2) (AFCEE 1994). Rates of in situ biodegradation were typically 100 times greater than the rates of volatilization at these sites.

4.2.7.4 Temperature Monitoring

Temperature monitoring is optional for bioventing processes, but may provide valuable information on seasonal soil temperature changes and the potential impact of temperature on in situ biodegradation rates. To monitor temperature, thermocouples can be placed in the sand pack surrounding the VMP screened interval (see Figure 4.4). Type K thermocouples are typically used and a hand-held digital thermometer is used to collect temperature readings from each thermocouple. A temperature gauge can also be installed near the blower outlet to monitor the injected air temperature and determine if the blower is overheating due to excessive exit pressure or poor ventilation.

4.2.8 Process and Instrumentation Diagram

Figure 4.5 provides a complete process and instrumentation diagram for a standard bioventing system.

4.2.9 Sample Calculations

4.2.9.1 Biodegradation Rates

The rate of oxygen utilization measured during field testing (Section 4.2.1.3) must be converted into a biodegradation rate that can be used to: (1) compare bioventing efficiency to other technologies, and (2) estimate the duration required to achieve the target level of hydrocarbon removal. Figure 4.7 illustrates data from a typical respiration test. Respiration tests should be conducted using all VMPs that are located in contaminated soils and have low (<5%) initial oxygen levels.

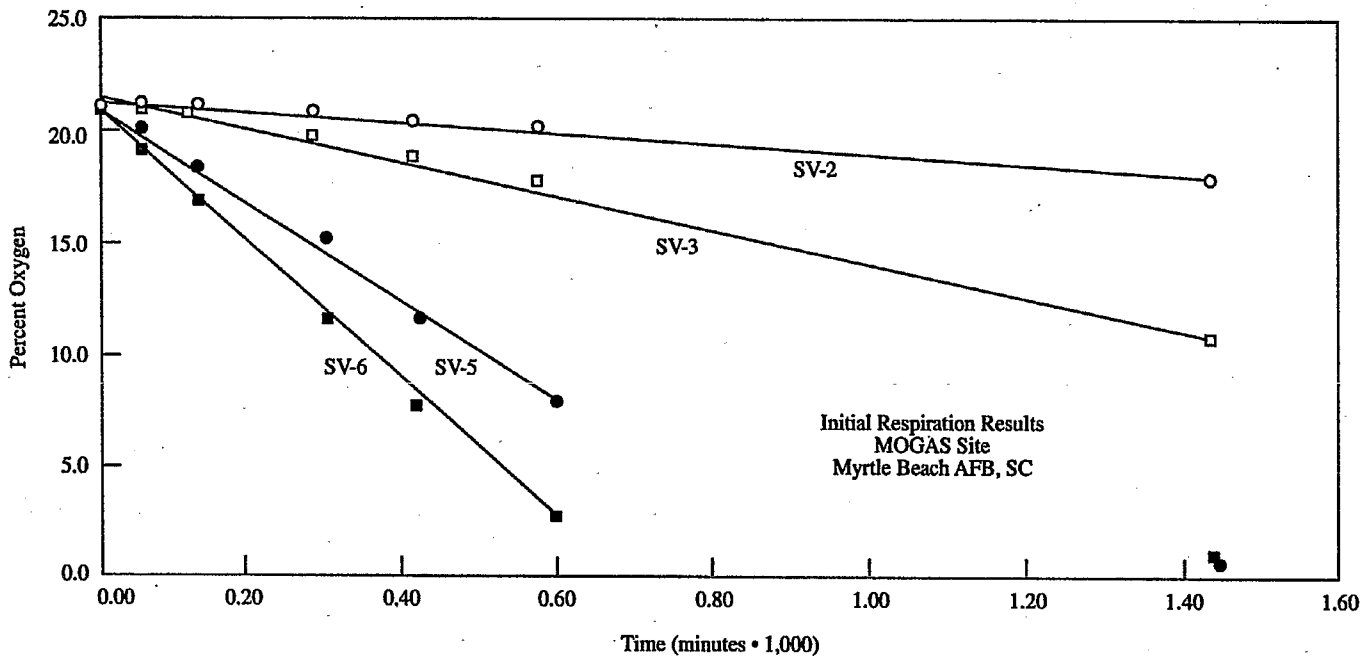
The rate of oxygen utilization (K_o) is estimated using a best-fit line through the first four to eight respiration data points. Using a conservative stoichiometric ratio of 3.5 grams of oxygen for every gram of hydrocarbon mineralized to carbon dioxide, the rate of hydrocarbon biodegradation can be estimated with Equation 4.1 (Leeson and Hinchee 1995):

$$K_b = \frac{K_o \theta_g \rho_{O_2} C}{100 \rho_k} \tag{4.1}$$

where:

K_b = biodegradation rate (mg/kg-day);
K_o = oxygen utilization rate (%/day);
θ_g = gas-filled pore space (cm^3 gas/cm^3 soil);

Figure 4.7
Typical Oxygen Utilization Data



Oxygen Utilization Rates
SV-2 ko = 0.022%/minute
SV-3 ko = 0.030%/minute
SV-5 ko = 0.0057%/minute
SV-6 ko = 0.0066%/minute

ρ_{O_2} = density of oxygen (1,330 mg/L at 20°C);
C = mass ratio of hydrocarbons to oxygen required for mineralization (0.29); and
ρ_k = soil bulk density (g/cm³).

Biodegradation rates will vary across each site; higher rates often occur in the center of the contaminated soil volume. Typical biodegradation rates range from 2 to 10 mg/kg-day, although rates in excess of 20 mg/kg-day have been observed at some locations (Leeson et al. 1995). Perhaps the most difficult parameter in this equation to estimate is the gas-filled porosity of the soil (θ_g) which is a function of total porosity, soil bulk density, and moisture content. This parameter is best determined by using literature values for various soil types to estimate total porosity (θ_t), bulk density (ρ_k), and soil mineral density (ρ_T) and analyzing soil samples for percent moisture (M). The gas-filled pore space can then be estimated using Equation 4.2:

$$\theta_g = \theta_t - \rho_k M = 1 - \frac{\rho_k}{\rho_T} - \rho_k M = 1 - \rho_k\left(\frac{1}{\rho_T} - M\right) \qquad (4.2)$$

4.2.9.2 Air Injection Flow Rate and Radius of Oxygen Influence

The second calculation required for proper bioventing design and operation defines the theoretical relationship between the air injection rate at each VW and the expected radius of oxygen influence that will result from varying flow rates. Understanding this relationship is particularly important for multiple VW designs, where each additional VW and associated piping and controls increase system costs. Most bioventing designs based on short-term pilot testing underestimate the actual radius of oxygen influence. The radius of oxygen influence can best be determined by allowing the pilot system to inject air for at least 7 days before determining the outward limit of oxygen transfer. At shallow sites, hand-driven soil gas probes are very useful for providing a profile of oxygen at various distances from the VW. At sites with deeper contamination, the cost of drilling and installing additional VMPs may be prohibitive, and a calculated radius of influence will be required for proper full-scale VW spacing. Equation 4.3 provides a useful relationship between air injection rate and theoretical radius of influence (Leeson and Hinchee 1995):

$$R_I = \sqrt{\frac{Q\Delta_{O_2}}{\pi h K_o \theta_g}} \qquad (4.3)$$

where:

R_I = radius of oxygen influence (m);

Q = air injection rate (m^3/day);

Δ_{O_2} = the acceptable oxygen depletion from the VW to the perimeter of influence (assume that a minimum oxygen content of 5% is needed so Δ_{O_2} = 20.8% - 5% = 16 %); and

h = aerated thickness (m).

A well spacing of 1.5 times the radius of influence is recommended for a conservative design.

4.2.10 Safety Requirements

4.2.10.1 Safeguarding Electrical Systems

Electrical power for bioventing systems should be installed by a licensed electrician who is knowledgeable of local electrical codes for exterior wiring. Whenever possible, the bioventing blower and electrical connections should be located outside of potentially explosive atmospheres. This normally includes gasoline dispensing areas around retail service stations. If the blower must be located in a Class I explosive zone, an explosion-proof motor, blower, and electrical supply will be required. If SVE is used to enhance bioventing, explosion-proof blowers, motors, and wiring are generally required, and offgas treatment equipment will require additional safety precautions.

4.2.10.2 Preventing Subsurface Vapor Migration

Section 4.2.4.1 discusses several process modifications that can reduce or eliminate the potential for unsafe vapor migration. Perhaps the greatest danger related to bioventing is the possible migration of explosive vapors into a confined space. Whenever volatile organics, such as gasoline, are involved, safety and vapor control are essential.

4.2.10.3 Monitoring of Buildings and Underground Utilities

To ensure that vapors are not accumulating in buildings or underground utilities such as storm sewers, hydrocarbon monitoring equipment that provides a lower-explosive-limit (LEL) warning should be used. Baseline vapor levels should be measured before the bioventing system is turned on to determine the actual contribution of any bioventing-induced vapor migration. Then, buildings and utilities should be monitored daily for the first week of

bioventing operation. Low air injection rates greatly reduce the potential for vapor accumulation.

4.2.11 Specifications Development

4.2.11.1 Vent Wells and Vapor Monitoring Points

Specifications for VWs and monitoring points will generally follow state-specific standards for monitoring well installation. General specifications are provided in Figures 4.2 and 4.4.

4.2.11.2 Piping and Control Valves

Air injection piping can be constructed of PVC or galvanized steel depending on the application. Schedule-80 PVC is generally preferred for shallow burial applications and for connections to individual VWs. Galvanized piping and valves are used for all connections entering and exiting the blower and for all aboveground piping. American Society for Testing and Materials (ASTM) Standards A53 and D1785 provide general specifications for low-pressure piping and valves associated with bioventing.

4.2.11.3 Motors and Blowers

Motors and blowers should conform to American Society of Mechanical Engineers (ASME) Standard PTC-9 and the National Electric Code. For operation in potentially-explosive atmospheres, NEC Sections 500-505 also apply.

4.2.12 Cost Data

Based on pilot- and full-scale applications of this technology on over 140 sites, the total cost of in situ bioventing using air injection has ranged from \$13 to \$80/m^3 of soil remediated (AFCEE 1994). On sites with over 7,500 m^3 of contaminated soil, costs of less than \$13/m^3 have been achieved. On small sites with less than 400 m^3 of soil, costs in excess of \$80/m^3 are common because of the fixed costs involved in project planning, permitting, drilling a vent well, installing a bioventing blower system, and site monitoring. However, even on small sites, bioventing can offer a significant advantage over more disruptive excavation options. Table 4.2 provides typical costs for planning, designing, installing, and operating a full-scale bioventing project for a large site (10,000 to 20,000 m^3). Costs also include final soil sampling and site closure activities.

Table 4.2
Typical Full-Scale Bioventing Costs[a] for Air Injection Systems

	Cost Element	Unit Cost ($)	No. of Units	Cost ($)
Pretreatment Costs	Prepare Work Plan [b]	2,000	Lump Sum	2,000
	Install VWs and VMPs [c]	25.00	450 LF	11,250
	Conduct Pilot Testing	10,000	Lump Sum	10,000
	Data Analysis/Full-Scale Design	4,000	Lump Sum	4,000
Treatment Costs	Install Blower System (7 HP)	9,000	Lump Sum	9,000
	Conduct Annual Respiration Testing	7,500	4 Years	30,000
	Complete 2-Year Soil Sampling	10,000	Lump Sum	10,000
	Annual O&M/Reporting Expenses	5,000	4 Years	20,000
	Annual Power Cost	2,400	4 Years	9,600
Posttreatment Costs	Complete 4-Year Soil Sampling	12,000	Lump Sum	12,000
	Prepare Site Closure Report	1,000	Lump Sum	4,000
	Properly Abandon VWs and VMPs	4,400	Lump Sum	4,400
Total Project Cost		**$11.00**	**11,500 m^3**	**$126,250**

(a) Typical costs for large bioventing sites with >10,000 m^3 of contaminated soil.
(b) Higher costs would be expected at sites with RCRA permitting requirements.
(c) Installation based on open-field construction. Cost would be greater if constructed in a concrete or asphalt-covered area.

4.2.13 Design Validation

As with any engineering design, bioventing design assumptions and calculations should be subject to peer review. Less detail is required if the design contractor is also responsible for system installation. In some states, design drawings must be sealed by a qualified professional engineer. However, in most states these relatively simple designs are included in remedial action plans and approved as a part of the remediation plan without a comprehensive design review by regulatory officials. In this case, design firms must ensure that adequate internal reviews are completed prior to

construction of the system. The Air Force has produced a comprehensive design guide for bioventing systems (Leeson and Hinchee 1995).

4.2.14 Permitting Requirements

Based on bioventing installations in 35 states and in all ten US EPA regions, this technology has been widely implemented with relatively few permitting requirements. In some states, the construction of VWs and VMPs requires a standard well permit. However, in most states, the use of wells for air injection and soil vapor monitoring is exempt from the permits normally required for groundwater monitoring wells. Most states do not require air permits for bioventing, but several require soil surface emission flux monitoring during system startup to establish that soil vapors are not being displaced to the atmosphere. In some states, disposal of drill cuttings that may contain Resource Conservation and Recovery Act- (RCRA) listed wastes is often an expensive and time-consuming byproduct of bioventing field work. In some states, injection of materials into the subsurface requires a permit. This could include recirculated vapors or nutrients to enhance the system. Finally, in some states, a building permit may be required if bioventing equipment is being set up inside a building or enclosure.

4.2.15 Design Checklist

Table 4.3 is a basic checklist for bioventing design that should be applicable for a wide range of site conditions.

4.2.16 Implementation

4.2.16.1 Selecting a Drilling Contractor

A qualified drilling contractor is essential for successful installation of bioventing systems. In addition to having experience in environmental drilling, soil sampling procedures, and OSHA 40-hour safety certification, the driller must understand that VW and VMP construction requires attention to detail and the instruction of the supervising geologist or engineer. A competent driller will be able to provide a list of references that should be contacted.

4.2.16.2 Installing a Bioventing System

On small sites, a single contractor will often design *and* build the system. On larger sites, it may be more economical for the prime contractor to subcontract blower installation, trenching, and pipe fitting tasks, and retain only

Table 4.3
Bioventing Design Checklist

Site Characterization	Type of hydrocarbon
	Soil moisture content
	Contaminated soil volume
	Soil gas volatile organics
	Initial oxygen and carbon dioxide
Site Features	Nearest power source
	Building/confined spaces locations
	Underground utilities
	Concrete/asphalt surfaces
Pilot Testing Results	Air permeability
	Radius of oxygen influence
	Oxygen utilization rates
	Vapor migration/surface emission flux testing
Vent Well Design	Screened intervals
	Well spacing
	Unique requirements (vapor control, high water table, layered soils)
Blower Design	Injection versus extraction
	Required flow rates
	Blower type and size
	Special requirements (explosion proof, noise abatement)
	Off-gas treatment requirements
Vapor Monitoring Points	Depth and spacing
	Background VMP location

construction management responsibilities. The following sequence is generally followed for installing a full-scale bioventing system:

- visit site, obtain digging permits, and locate blower position near electrical supply;
- mobilize driller and install VWs and VMPs;

- erect blower enclosure and install blower inside enclosure;
- complete electrical hookups using a licensed electrician, ensure proper blower rotation;
- complete shallow trenches from blower to VWs;
- connect piping manifold and pressure test before backfilling;
- backfill, and as necessary, repair asphalt or concrete; and
- complete start-up procedures described in the next section.

4.2.17 Start-up and System Optimization Procedures

Start-up and optimization of a full-scale bioventing system is normally completed over one to two weeks, although a technician will not be required at the site each day of the start-up period. The following paragraphs summarize the key procedures that are followed in the startup of any bioventing system.

4.2.17.1 Initial Soil Gas Chemistry

Oxygen, carbon dioxide, and hydrocarbon vapor concentrations should be measured in every VMP. These data are required to determine the impact of air injection on oxygen transport and hydrocarbon vapor migration.

4.2.17.2 Blower Check

With the air bleed valve wide open (see Figure 4.5) to minimize back pressure, the blower is started to ensure that the air filter and piping are unobstructed. The bleed valve is slowly closed with the predetermined design flow into the vent wells is obtained.

4.2.17.3 Vent Well Integrity Check

With the blower running, each VW and connecting piping should be checked for leaks. In low-permeability soils, the benonite seals around the VWs will sometimes fail, causing short-circuiting of air to the surface. Such short-circuiting can sometimes be prevented by gradually increasing the air pressure and flow to the wells (e.g., by gradually closing the bleed valve over a 24-hr period) rather than applying the full pressure of the blower immediately. Once the seal is broken, it is very difficult to repair, and a new well may be required.

4.2.17.4 Safety Checks for Vapor Migration

If vapor migration is a concern, nearby buildings and underground utilities should be checked frequently in the first hours of air injection. These procedures are described in Section 4.2.10. If unsafe vapor migration is detected, the air injection flow rate should be immediately reduced and buildings and confined spaces carefully monitored until no vapor migration is detected.

4.2.17.5 Oxygen Influence Check

During the first 48 hours of system operation, all valves that control air flow to individual wells should be wide open. After the first 48 hours, soil gas oxygen levels should be measured at each VMP. If all VMPs contain in excess of 5% oxygen after 48 hours, flow balance among wells may not be required. If one or more of the VMPs contains less than 5% oxygen, airflow can be balanced by reducing the flow to VWs in well-oxygenated soils and forcing more of the flow into VWs that influence soils with low oxygen. This process may take several days of flow adjustments before a balance is achieved. The goal is at least a 5% oxygen level in all VMPs under steady-state flow conditions.

4.2.17.6 Surface Emission Flux Monitoring

On sites where regulatory agencies require surface emission flux testing, this testing should be completed before the system is turned on and again after the first week of air injection (see Section 4.2.7.3). Unless required by regulatory agencies, tests during the first day of bioventing should be avoided because the flux to the surface on this day will be maximized and will not provide an accurate estimate of long-term daily emissions from the site.

4.2.18 Performance Evaluation

4.2.18.1 Blower Operation Monitoring

Bioventing systems are mechanically simple and should require minimum maintenance. Once each week, the blower system should be checked to ensure that desired operating pressures are maintained and that the air filter is not clogged with dirt. In dusty areas, the air filter may need to be changed once every three to four months. Changes in soil moisture may result in increased or decreased flow to the VWs. Flow and pressure entering a well can be easily adjusted with the bleed valve.

4.2.18.2 Oxygen Influence Monitoring

During the initial months of bioventing operation, the oxygen levels at each VMP should be checked once a month to ensure that the level is at least 5% at all locations. If oxygen levels are consistently above 15% at all locations, the air injection rate can be decreased to further reduce any volatile migration potential at the site.

4.2.18.3 Respiration Tests

In situ respiration testing is recommended at six-month intervals. This will (1) provide a more accurate estimate of annual biodegradation rates, (2) allow for summer and winter soil temperature effects to be averaged, and (3) allow for adjustments and balancing of flows as necessary.

4.2.18.4 Quality Assurance/Quality Control

Quality assurance and quality control (QA/QC) is extremely important when monitoring bioventing. Soil gas analyzers must be calibrated prior to each monitoring event using laboratory-grade standards. Proper calibration of the oxygen sensor is critical during respiration testing where oxygen changes of 1%/day or less are common. Flow measuring devices and pressure relief valves also require calibration to ensure proper operation of the air injection blower. Soil and soil gas sampling must be completed in accordance with written and approved field sampling plans to ensure consistency of results.

4.2.18.5 Determining When the Site Is Clean

As bioventing progresses at a site, a smaller mass of hydrocarbon is available for biodegradation. This lack of carbon source will result in lower rates of oxygen utilization during in situ respiration testing and eventually to respiration rates that approach those of background soils. This phenomenon has been observed at a Burlington Northern Railroad site over 4 years of bioventing operation (Ratz, Guest, and Downey 1994) and at Hill AFB (Dupont, Doucette, and Hinchee 1991). If strict TPH standards apply to a site, the bioventing system should operate until background respiration rates are achieved. At that point, confirmatory soil sampling can be completed with some assurance that the average TPH concentration is less than 100 mg/kg. Under more realistic risk-based clean-up standards, BTEX concentrations will often determine the level of risk reduction required at the site. In this case, soil gas samples should be collected at the end of every year of bioventing to determine bioventing progress. Soil gas samples should be

collected after the system has been off for at least 30 days to allow residual BTEX in the soils to reequilibrate with soil gas. If soil gas BTEX concentrations are near background levels, a final soil sampling can be planned to support a risk-based site closure.

4.3 Land Treatment

4.3.1 Principles of Operation

Background information on the principles of land treatment technology is included in a previous monograph, *Innovative Site Remediation Technology — Bioremediation* (Ward et al. 1995) and therefore is not repeated here. The sections of that monograph that explicitly describe land treatment technology include:

- Section 2.5.1.1 — overview of land treatment processes;
- Section 2.5.2.2 — description of ex-situ land treatment;
- Section 3.5.1.1.1 — in situ land treatment description, objectives, types of waste, design and operating factors, site preparation and equipment, performance, advantages/disadvantages;
- Sections 3.5.1.3 and 3.5.2.2.5 — costs;
- Section 3.5.2.2.2 — ex-situ land treatment description; and
- Section 6.2 — limitations.

Additional information on the principles of land treatment can be obtained from the following excellent sources: Loehr et al. (1979); US EPA (1983); Loehr and Malina (1986); US EPA (1986b); US EPA (1986e); Sims, Sims, and Matthews (1989); and Pope and Matthews (1993).

4.3.1.1 Potential Limitations

There are numerous variables that may limit land treatment performance. These may be site factors, soil parameters, or waste constituents. In addition, the required target clean-up concentration may be a limitation if the specified concentration cannot be achieved within an acceptable time frame.

Site Factors. A shallow or seasonally-high water table, high rainfall conditions, and poorly-drained soil or sites with poor drainage may result in poor soil aeration that severely limits aerobic biodegradation. Relatively

cold climates may limit the amount of time during the year when significant treatment occurs. Soil cells (Section 4.4), which conserve heat better than land treatment units (LTUs), or a covered, thermally-controlled LTU may be more appropriate under extreme cold-climate conditions. Excessive rainfall in conjunction with a shallow water table and highly-permeable soil may leach contaminants resulting in groundwater contamination. Under these conditions, a liner and leachate collection system would be appropriate. Collectively, these site factors may limit LTU performance. Site selection factors are also discussed in Section 4.3.2.6.

Soil Parameters. Soils with pHs either too low (<5) or too high (>8) are not conductive to microbial activity and may limit biodegradation. The extremes of pH may result in increased solubility and bioavailability of heavy meals or organic acids and bases which may be toxic to microbial activity. Soils high in salinity are also not conducive to microbial activity. Soils which are treated with various amendments, e.g., adding fly ash to stabilize them during emergency actions may experience significant increases in it that may also reduce microbial activity. Biological treatment of these stabilized materials may not be possible due to pH limitations.

Fine-textured soils with a high clay content are problematic for bioremediation treatment as they usually exhibit poor drainage and poor soil aeration. In addition to limiting the biodegradation in water content, causing tilling equipment to function poorly or become stuck in poor-drained, fine-textured soils when only minor changes in water content.

Waste Constituents. Compounds that are slightly soluble and tightly bound to the soil are generally not as bioavailable. Specifically, these compounds can be described as hydrophobic with high molecular weight, complex structure, and high octanol-water (K_{ow}) or organic carbon (K_{oc}) partition coefficients. These compounds include the four- to six-ringed PAHs, dioxins, polychlorinated biphenyls (PCBs), and many pesticides. Soils with a high organic carbon content exhibit greater sorption of hydrophobic compounds onto the solid phase, which limits their bioavailability. Therefore, soils with high organic carbon content and contaminated with hydrophobic compounds are likely to be difficult to treat biologically. *Co-oxidation* is a term that describes the gratuitous transformation of nontarget compounds when microbial enzymes are produced to metabolize other growth substrates. Co-oxidation is one mechanism responsible for the biodegradation of complex compounds, such as the four- to six-ring PAHs (Keck et al. 1989). Piwoni and Keeley (1990) provide an excellent review of the basic concepts of contaminant sorption at hazardous waste sites.

Some chemical compounds in sufficient concentration will inhibit microbial activity. For example, pentachlorophenol (PCP), creosote, and heavy metals (As, Cr, Cu) have been used to prevent the decay of wood products because the chemical compounds are toxic to wood-degrading micro- and macroorganisms commonly found in the soil. Low soil concentrations of these residues, relative to the initial concentrations used to preserve wood products, may limit biodegradation due to their toxicity. Numerous soil parameters collectively affect the bioavailability of these chemical species. Therefore, the concentration at which microbial activity becomes limited varies from soil to soil. A treatability study can provide the site-specific, cost-effective means to determine whether toxicity is inhibiting microbial activity.

Preferential substrate utilization is the condition where several organic compounds are present in soil and the target compound is not biodegraded due to the presence of more easily degradable organic compounds. For example, PCP is a poor carbon and energy source for microbes, and when other carbon sources are present in the soil, the non-target carbon is preferentially consumed. Under this condition, little PCP would be mineralized until the preferred substrate concentrations decreased. Other wastes co-disposed with the target compound (i.e., petroleum hydrocarbons, etc.) or naturally occurring carbon may serve as the preferential substrate.

Target Clean-up Concentrations. The feasibility of land treatment performance is partially dependent on the clean-up concentration for the indicator parameter(s). For example, the required clean-up concentration may be very low and may not be achieved within an acceptable time frame. A review of clean-up goals at 10 wood preserving waste Superfund sites where clean-up concentrations have been specified, showed the concentration range for total carcinogenic PAHs (TCPAHs) and PCP was 0.005-700.0 mg/Kg and 1.0-37.0 mg/Kg, respectively. Assuming the required clean-up concentration was at the low end of this concentration range, the feasibility of land treatment to achieve the desired concentration is low. The greater the initial concentration and lower the required clean-up concentration, the more difficult it is to achieve the desired goal. Bioavailability and preferential substrate limitation contribute to the inability to achieve desired clean-up goals. Therefore, in addition to site, soil, and chemical factors described above, a performance limitation also exists.

4.3.1.2 Treatability Studies

Land treatment technology has been described as a proven full-scale technology for both in situ and ex-situ applications (Ward et al. 1995). However, this does not imply that the technology is foolproof. As indicated above, the success of land treatment largely depends on several site-specific parameters including the type of target compound, initial and target concentrations, time allowed for cleanup, and biological inhibiting factors (pH, salinity, bioavailability, heavy metals, etc.). Therefore, treatability studies that precede field-scale implementation can provide valuable site-specific information regarding the feasibility and limitations of the technology. Ultimate limitations of bioremediation at a specific site are usually related to: (1) time required for cleanup, (2) level of cleanup attainable, and (3) cost of cleanup using bioremediation (Sims, Sims, and Matthews 1989). Recognizing the limitations of land treatment, the field-scale implementation of land treatment without conducting appropriate treatability studies may result in a significant cost expenditure without satisfactory field performance.

Numerous protocols, guidance documents, and discussions have been published regarding treatability studies for laboratory-, bench-, and pilot-scale systems (US EPA 1986e; US EPA 1988b; Nakles and Smith 1989; US EPA 1990b; Morgan et al. 1990; Hosler 1990; Shelton 1990; Dupont 1990; Morgan et al. 1992; Samson, Greer, and Hawari 1992; US EPA 1993a; Rogers, Tedaldi, and Kavanaugh 1993; University of Cincinnati 1993; Korfiatis and Christodoulatos 1993). Other publications present the results of laboratory-scale and bench-scale treatability studies (Sims et al. 1986a; McGinnis et al. 1988; Sims et al. 1988; Loehr 1989). Prior to implementation of full-scale land treatment operations, laboratory-, bench-, and pilot-scale treatability studies should be used to evaluate the feasibility of using the technology to achieve specified clean-up goals. Based on the results of each treatability study, data can be obtained to determine whether sufficient treatment occurs within an acceptable time frame. Subsequently, additional investigations can be initiated with a different set objectives to evaluate feasibility.

Treatability studies are used to provide site-specific information concerning the potential application of land treatment at field-scale by cost–effectively evaluating the fate and behavior of contaminants and the rate and extent of remediation under simulated field conditions. Treatability studies are usually conducted at laboratory-scale in microcosms involving flasks, at bench-scale involving box or pan reactors, or at pilot-scale in the field involving one or more small-scale treatment plots. Table 4.4 presents a general comparison of the different scales at which treatability studies are conducted.

Table 4.4
General Comparison of Laboratory, Bench, and Pilot-Scale Treatability Studies

Scale	Type of Data Generated	Critical Parameters	No. Replicates	Study Size	Volume of Soil	Time Required	Cost $
Laboratory	Qualitative	Several	Single/ Duplicate	Flask/Pan	Small	Weeks-Months	5,000-50,000
Bench	Quantitative	Few	Duplicate/ Triplicate	Pan/Box	Medium	Weeks-Months	25,000-100,000
Pilot	Quantitative	Few	Duplicate/ Triplicate	FieldPlot	Large	Weeks-Months	50,000-200,000

Source: US EPA 1990b

Laboratory-Scale. Laboratory treatability studies are generally used to establish proof of concept (i.e., that a specific compound or group of compounds can degrade under a given set of operating conditions). In some cases, there may be a concern that the soil contains inhibitory or toxic concentrations of chemical compounds. For example, wood-preserving, waste-contaminated soil may contain heavy metals (Cr, Cu, As), creosote, or PCP at concentrations that inhibit biological processes. The associated toxicity effects may limit or completely prevent the degradation of the soil contaminants, such as PAHs, PCPs, oil and grease, and TPH. A treatability study designed to examine the rate and extent of degradation of any of these indicator compounds will provide information regarding whether toxicity is a limitation.

Depending on the treatability study objectives, the design can be relatively simple or sophisticated. If it is only necessary to determine whether an indicator compound degrades, the study can be simple and inexpensive. However, to evaluate biodegradation, immobilization (partitioning and humification), leaching, detoxification, production of hazardous decomposition products, volatilization, etc., sampling, analysis, data collection, and interpretation increase in complexity and costs. In this scenario, a sophisticated mass-balance approach is necessary to accurately quantify the fate of the compounds via the various pathways identified as important to monitor. Excellent reviews of the mass-balance approach are given in other publications (Sims, Sims, and Matthews 1989; Sims 1990; Sims et al. 1995a). In a treatability study involving radiolabelled compounds, the mineralized

radiolabel (e.g., $^{14}CO_2$) is captured and used to quantify compound loss in the form of a biodegradation rate. However, the radiolabel may also be biologically incorporated into the biomass or become humified and associated with the solid-phase material. Both of these processes represent a loss of the radiolabelled compound from the system. Therefore, the biodegradation rate as expressed by the mineralization rate may be significantly lower than the rate of radiolabel removed due to the combined effects of mineralization, biomass incorporation, and humification. Combustion of the solid phase following Soxhlet extraction provides an indication of the microbially incorporated/residue-bound component of contaminant loss observed during the study. Finally, biologically-poisoned controls (poisoned with mercuric chloride, sodium azide, etc.) are essential for distinguishing biologically-mediated transformations from abiotic reactions which take place during the treatability study in these control reactors. Contaminant loss in biologically active reactors, corrected for loss in the poisoned control reactors indicates, the true biological component of contaminant transformation in the test systems.

Laboratory studies are generally not appropriate for generating design or cost data (US EPA 1989a). However, an additional objective of laboratory studies is to screen various parameters, such as contaminant concentration or amendments (manure, acid/base, nutrients, etc.). The soil sample is generally small, and single or duplicate sample analysis is adequate. Depending on the sophistication of indicator parameters to be analyzed (e.g., TPH or oil and grease) and the time frame of the study, the costs can be relatively minimal.

Bench-Scale. One of the objectives of a bench-scale treatability study is to quantify the rate and extent of degradation. These data can be used to evaluate whether the required endpoints can be achieved. Assuming the initial concentration in the soil is high, the required target clean-up concentrations are low, and the compound degrades slowly, the bench-scale study may take several months to a year to complete. The cost will primarily depend on the number of samples, type of analyses, duration of the study, and labor necessary to maintain the reactors.

Pilot-Scale. Pilot-scale testing is conducted to generate quantitative performance, cost, and design information once bench- and/or laboratory-scale studies indicate promising results for a given soil/waste site situation. Similar to a bench-scale study, a pilot-scale treatability study can quantify the rate and extent of degradation, which can be used to determine whether the required endpoints can be achieved within a specified time frame. Additionally, pilot-scale studies provide valuable information regarding the field-scale effects of site-specific conditions, such as weather (rain,

variations in temperature, wind, etc.), tilling/mixing, or leaching, which cannot be accurately simulated at the laboratory- or bench-scale.

Treatability studies usually represent optimum conditions with respect to mixing, contact of soil materials with waste constituents and microorganisms, and homogeneous conditions throughout the microcosm (Sims 1990). However, at the field-scale, heterogeneous distribution of contaminants, poor soil mixing, and poor mass transfer can limit remediation. Therefore, it is reasonable that optimum performance will occur at the laboratory-scale, and less than optimum performance at the bench- and pilot-scales. Pilot-scale performance provides the best approximation of the performance that will occur at field-scale.

The pilot-scale treatability study has limitations since it is generally conducted over a short time frame and may not fully represent actual conditions. For example, weather conditions which occur during the study may not be representative of long term field-scale conditions. Therefore, treatment performance during exceptionally wet or dry, or cold or hot seasons may be different. It is desirable to use contaminated soil that is representative of the soil to be treated; however, this is not easily accomplished. Further, worst- or best-case soil conditions may be used during the pilot study which may yield inaccurate estimates of field-scale conditions. Use of well-mixed soil in treatability studies at any scale is desirable to minimize this variability. However, this may also enhance mass transfer conditions which cannot be achieved at field-scale. Overall, it should be recognized that some departures from the actual and simulated conditions will exist. Nevertheless, treatability studies can identify both the limitations and the potential for successful treatment which is ultimately used to: (1) evaluate the feasibility of land treatment relative to other technologies; (2) support the decision to select or reject the technology; and (3) aid in the design of a field-scale unit.

4.3.2 Process Design Principles

There are two general approaches to land treatment that have been used to successfully degrade large quantities of contaminated material: ex-situ and in situ. Ex-situ involves the treatment of waste, sludges, or contaminated soil in a prepared bed. The food processing, wastewater, and petroleum industries have used this technology for years to treat wastes to environmentally acceptable endpoints. The 1984 Hazardous Solid Wastes Amendments (HSWA) to RCRA initiated many changes to the regulatory framework applicable to the use of land-based technologies for disposal of hazardous waste. The land disposal restrictions of the Superfund Amendments and Reauthorization Act of 1986 (SARA) placed stringent performance

requirements on land treatment operations, essentially eliminating land treatment as a waste management option for industries that routinely generate hazardous wastes. These impacted industries include those generating petroleum (40 CFR 261.32, K048 to K052) and wood-preserving (K001) wastes. However, land treatment of waste residues and contaminated soil from petroleum, wood-preserving, and manufactured gas plants continues to occur at sites where cleanup of past waste management activities is required. This discussion of LTUs focuses on the ex-situ and in situ treatment of contaminated soils and sludges at uncontrolled hazardous waste sites.

LTUs can be designed and operated to degrade, immobilize, and detoxify waste constituents in surface soils. Correspondingly, migration of chemical constituents from LTUs can be prevented, making "open-design" LTUs adequate. Depending on the specific criteria required by regulatory agencies, designs may range from simple tilling of soil in place to sophisticated lined, leachate collection systems designed to satisfy land-ban regulations. Several design parameters are discussed in the following sections.

4.3.2.1 Size

Several factors may contribute to the size of the LTU including: (1) the volume of soil requiring treatment; (2) the availability of land; and (3) the length of time allowed for treatment. The volume of contaminated soil should be based on an estimate of the "loose" soil rather than the compacted, undisturbed volume of soil. The volume of loose soil can be 30% greater than the undisturbed volume. The accuracy of estimating the volume of soil to be treated is strongly correlated with the degree of certainty of the aerial and vertical extent of contamination. A rigorous subsurface investigation will generally yield a reasonable estimate of the volume of contaminated soil. However, a good design will account for any uncertainty regarding soil volume and LTU size. Ideally, contaminated soil is excavated and stockpiled to yield an accurate estimate of the soil volume.

The availability of land for LTU construction may ultimately determine its size. For example, in an industrialized area, the amount of land available may be constrained by the surrounding development.

The length of time allowed for treatment also affects the size of the LTU. In cases where time is limited, the rate of treatment (i.e., the time it takes to reach an acceptable concentration) and the volume of soil per lift (a lift is the layer of soil applied to the LTU) affect LTU size. The rate of treatment is dependent on several variables, including initial concentration of the target compound, treatment endpoint, weather, and soil variability (i.e., chemical,

physical, and biological characteristics). "Hot spots" may exist in soil where the concentration is much greater than the average concentration, requiring additional time to reach the target end-point concentration. Additionally, elevated concentrations may inhibit the microbial community that degrades the target compound, and longer treatment time may be necessary. Extreme weather conditions may also affect treatment time. Soil type may vary within a relatively short distance and the rate of degradation may vary accordingly (e.g., contaminated clay soil may be more difficult to till and dewater than sandy loam soil). The depth of the soil lift applied to the LTU affects the rate of soil application, i.e., the mass of soil applied per unit area. Ultimately, this affects the size of the LTU needed for a given mass of contaminated soil.

Various design criteria representing site-specific and regulatory factors ultimately control the size of an LTU. These design criteria are affected by parameters that need to be identified and evaluated on a site-specific basis. As indicated above, a design should include contingencies to allow for uncertainties regarding the volume of soil.

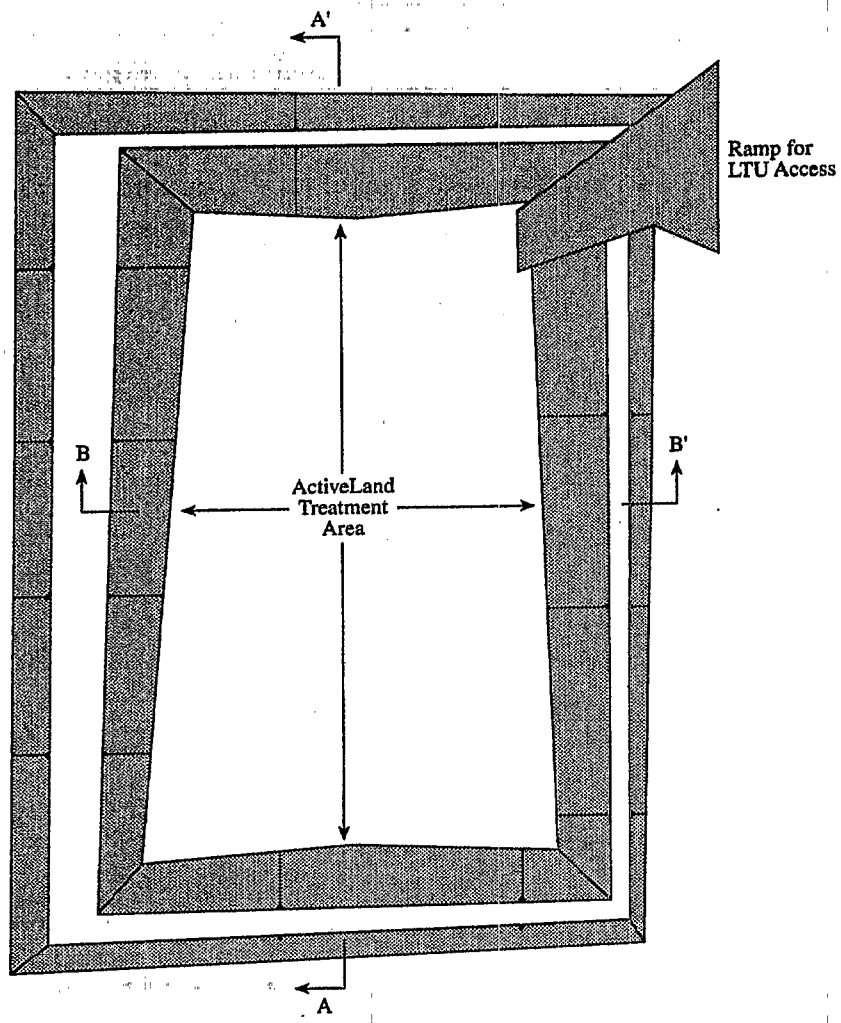
4.3.2.2 Berms

Berms are designed to prevent run-on and runoff of water (refer to Figures 4.8 and 4.9). Run-on to the LTU is limited to: (1) keep the LTU from becoming too wet, which limits oxygen transfer; and (2) prevent the generation of contaminated surface water and leachate that may require treatment and disposal. Run-on design criteria generally involve a specific regulatory requirement such as containment of the 25-year, 24-hour storm event with a minimum freeboard. Runoff control is necessary to prevent washout of soluble waste constituents and contaminated soil from the LTU which may consequently be deposited in nearby water bodies or on uncontaminated soil. Preventing the runoff and associated loss of waste constituents will also minimize the potential for unnecessary exposure pathways. The berms should be:

- keyed into the liner/leachate collection system;
- based on the total height of contaminated soil to be treated; and
- keyed into the final cover of the LTU.

A ramp for vehicular access should also be incorporated into the berm design.

Figure 4.8
Plan View of Land Treatment Unit

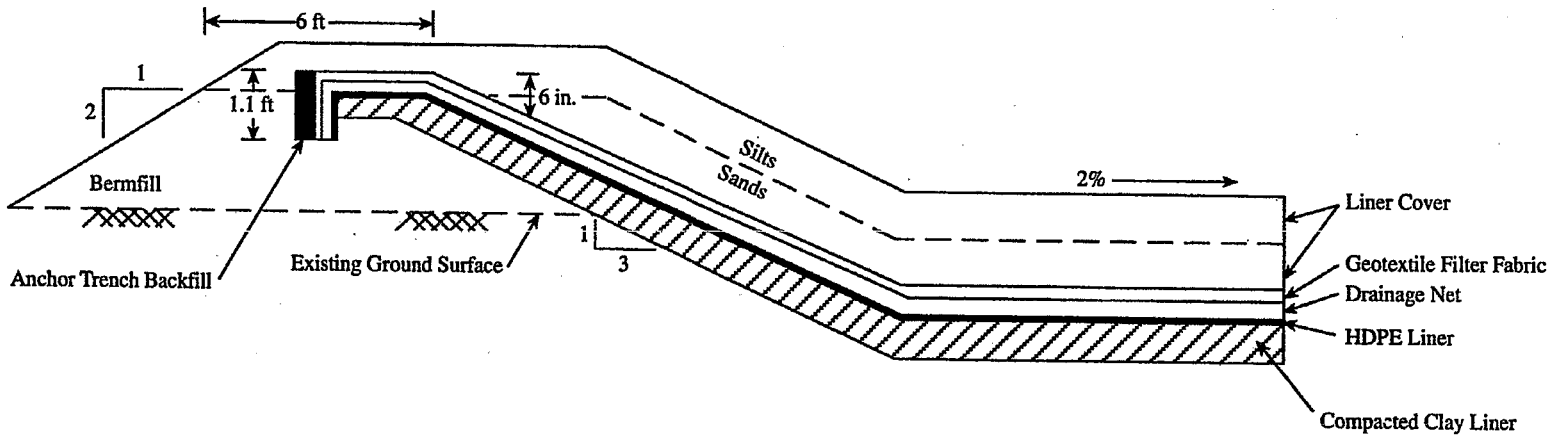


Source: Woodward-Clyde Consultants 1991

4.3.2.3 Liner System

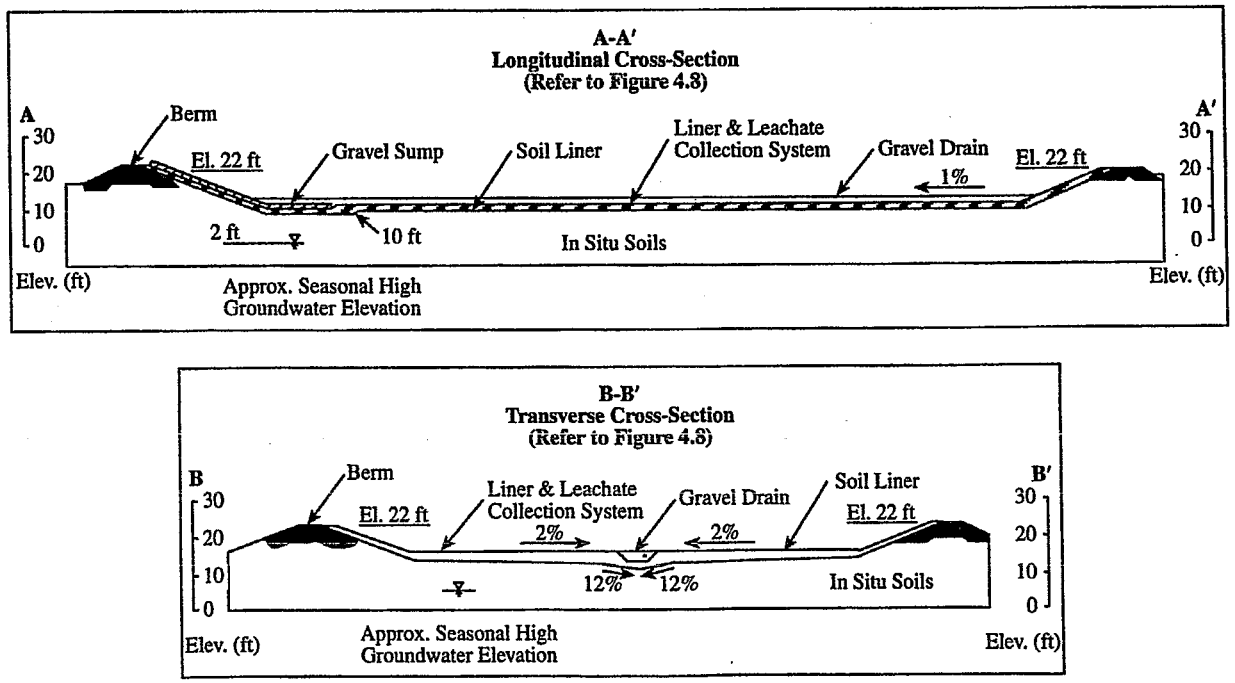
The purpose of the liner system (Figures 4.10 and 4.11) is to prevent leachate from migrating below the LTU and to provide a collection point for leachate recovery. The liner system design will vary depending on performance and design criteria. The liner system described below is a double liner-leachate collection system, which represents conservative design requirements.

Figure 4.9
Cross-Section of a Land Treatment Unit Berm
(not to scale)



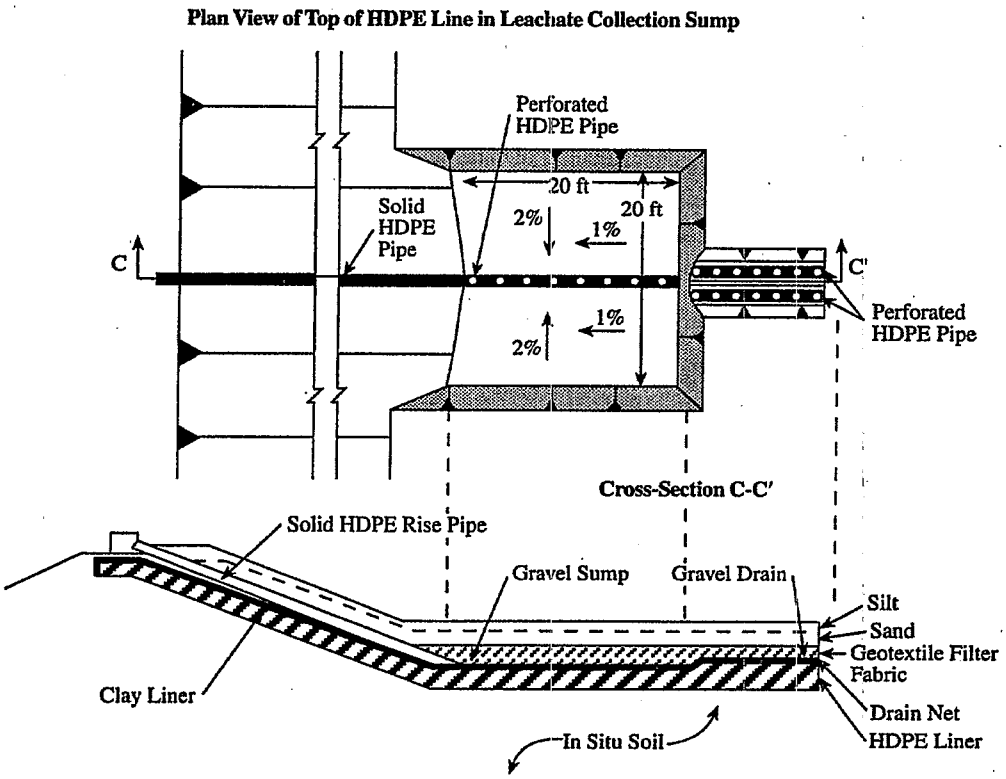
Source: Woodward-Clyde Consultants 1991

Figure 4.10
Longitudinal and Transverse Cross-Section of a Land Treatment Unit
(not to scale)



Source: Woodward-Clyde Consultants 1991

Figure 4.11
Geomembrane/Soil Liner System for Leachate Collection
(not to scale)



Source: Woodward-Clyde Consultants 1991

The bottom layer of the liner system consists of 30 to 60 cm (1 to 2 ft) of compacted, low-permeability (10^{-7} cm/s) clay material. Permeability, sieve size, and moisture content requirements for the clay material are usually necessary. The clay liner is graded (2%) towards the gravel drain located along the central axis of the LTU (Figures 4.9 and 4.10, B-B' cross-section) and also graded (1%) to a collection sump located at one end of the LTU. A flexible membrane liner is placed on top of the compacted clay liner. A variety of materials may be used for this liner, but usually, high-density polyethylene (HDPE) is selected due to its durability and compatibility with leachate. Leak testing is recommended to ensure that the membrane liner is properly installed. Many other liner designs exist and the reader is referred to US EPA 1988d for such information.

4.3.2.4 Leachate Collection, Removal, and Storage

The leachate collection system drains, captures, and removes any leachate generated in the LTU. Removal of leachate prevents the buildup of hydrostatic head on the liner and minimizes leakage potential. The leachate collection system consists of a drainage layer that lies on top of the HDPE liner to convey the flow of leachate to the central collection system. A geotextile filter fabric is placed over the drainage net to capture migrating particles that can clog the drainage net and leachate collection system. Site-specific water filtration criteria and appropriate testing are the basis for filter fabric selection. Drainage pipe consisting of slotted HDPE pipe 10 to 15 cm (4 to 6 inches) in diameter and wrapped in filter fabric is placed along the longitudinal axis of the LTU in the drainage trough (Figure 4.11) and covered with gravel and again with filter fabric. Nonangular gravel is used to prevent puncture of the synthetic liner material. A gravel sump is constructed at the low end of the leachate collection system for central leachate collection (Figure 4.11). A riser pipe extends from the bottom of the collection sump to the exterior of the LTU from which leachate can be removed and analyzed. The system shown in Figures 4.8 and 4.11 should be considered a general guideline; there are different versions of this design that will successfully contain leachate within the boundary of the LTU.

4.3.2.5 Treatment Zone

Prior to application of contaminated soil, a layer of uncontaminated, coarse-textured material (e.g., sand) is placed on top of the geotextile filter fabric and a layer of fine-textured (e.g., silt, sandy-silt) material is placed on top of the sand (Figure 4.9). This material protects the liner and leachate collection system when heavy equipment is driven onto the LTU to till or apply soil or water. The fine-textured material is placed over the coarse material to allow drainage into the leachate collection system and to prevent the vertical migration of fines that may clog the leachate collection system or contaminate the leachate.

The treatment zone is the surface layer of soil (i.e., lift of soil) applied to the operating surface of the LTU (i.e., on the fine-textured soil) that is managed by tilling (discing, mixing, etc.), moisture control, nutrient amendment, and monitoring. The depth of the treatment zone is generally 15 to 30 cm (6 to 12 in.) and is based on the depth of soil that can be effectively tilled and treated. A distinction is made between the active treatment zone, the uppermost lift in the LTU where active soil management occurs, and the lower treatment zone, the lifts of contaminated soil previously applied to the LTU and treated. It has been demonstrated that treatment continues to occur in

the buried lifts after successive layers of soil are applied to the LTU (Sims et al. 1995a; Huling et al. 1995a). In LTUs where sludges and contaminated soil are applied and tilled into the native soil, the treatment zone has been identified as the upper 1.2 to 1.4 m (4 to 4.5 ft) of soil underlying the 15 to 30 cm (0.5 to 1 ft) zone of incorporation (i.e., active treatment zone) (US EPA 1984a, 1986b, 1986e). In this scenario, the active treatment zone is considered the zone of incorporation, or the depth of tilling.

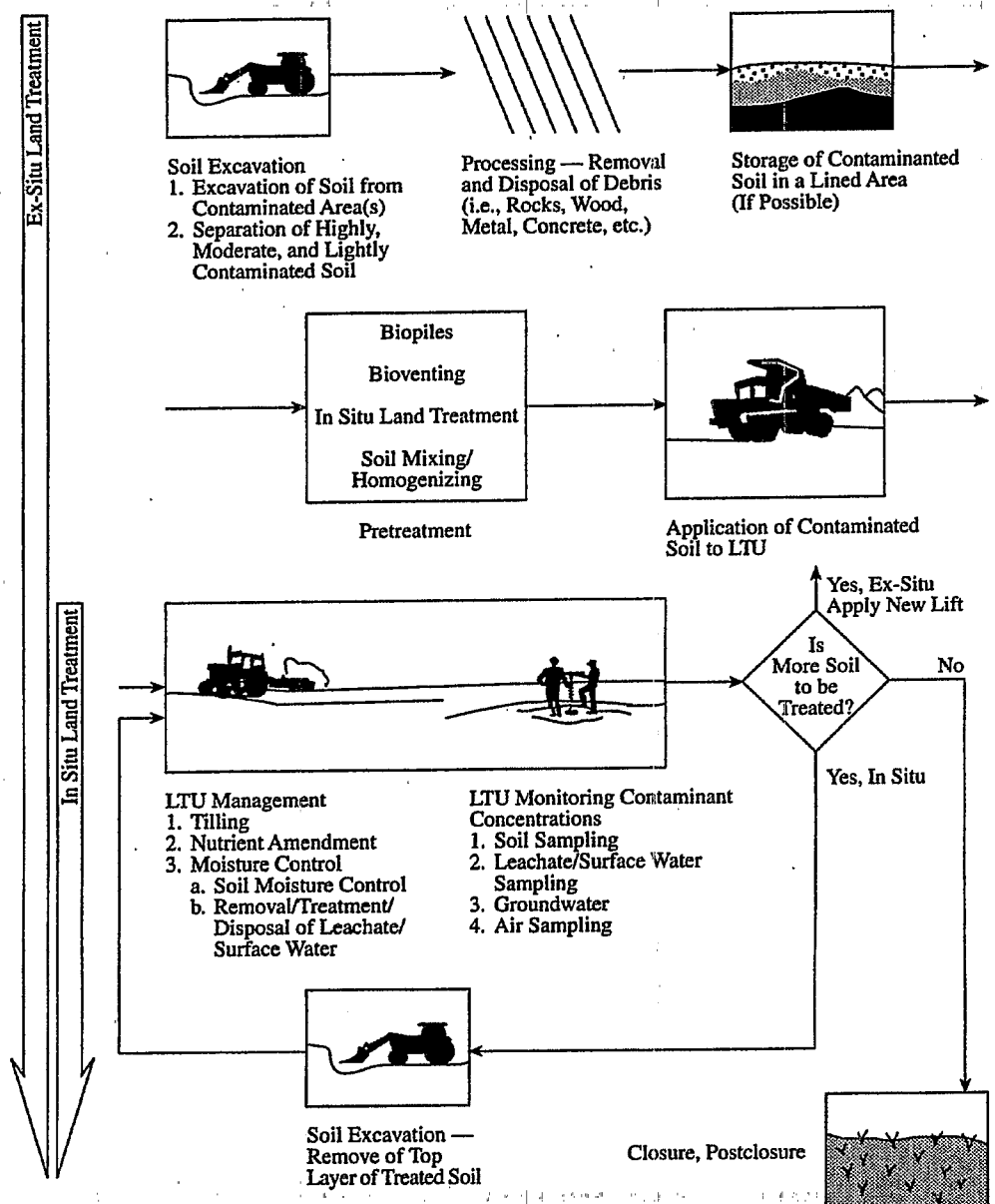
4.3.2.6 Location

To minimize transport costs and exposure pathways, the LTU should be located close to the source of contaminated materials. In addition to designing the berms to meet storm duration and intensity requirements, the LTU should not be constructed in flood-prone areas. A common performance requirement for LTUs is to demonstrate that groundwater contamination does not occur from land treatment operations. This demonstration would be difficult if the LTU were constructed in an area where the groundwater was contaminated with the same compounds as the soil to be treated. Therefore, construction of the LTU in an area where the groundwater is not contaminated minimizes the complexity of interpreting groundwater monitoring data. The LTU should be constructed in an area where the seasonal high groundwater table location is at least 1.5 m (5 ft) below the bottom of the LTU. Fuller (1986) discusses a process of screening and evaluating a wide range of fundamental site selection criteria.

4.3.3 Process-Flow Diagram

The general steps involved in ex-situ and in situ land treatment are presented in Figure 4.12. Ex-situ land treatment involves soil excavation, processing, excess soil storage, pretreatment, soil application to the LTU, soil management to enhance biodegradation, monitoring the rate and extent of degradation, and closure and postclosure of the LTU. In situ land treatment does not involve the initial excavation, storage, pretreatment, or application to the LTU. It may involve some of the processing however, because debris may be present at the site that is not amenable to treatment or that may interfere with treatment operations. Several decisions regarding in situ land treatment are predetermined, e.g., location of the LTU, liner design, and pretreatment considerations. Details regarding the difference in these approaches are presented in Section 4.3.4.1.

Figure 4.12
Process-Flow Diagram of Ex-Situ and In Situ Land Treatment



4.3.4 Process Modification

4.3.4.1 Ex-Situ Versus In Situ

When there are several locations where contaminated soil exists at a given site and the depth of soil requiring treatment is too deep for in situ treatment, it may be necessary to excavate the soil and treat it in a common LTU. Where the contaminated soil is relatively shallow or where it has been determined that only the surface layer of soil requires treatment, an in situ design is an option.

The depth of treatment which can be accomplished using in situ land treatment systems is complex and site specific. It depends primarily on the extent to which oxygen (O_2) can be transported into the soil (via diffusion and advection) and the adequacy of that flow to satisfy the rate of biological oxygen demand. There are numerous parameters that affect the rate of O_2 transport and utilization and such parameters can vary greatly with location, depth, and time.

A potential modification of the in situ process is to treat one level of soil, excavate the treated soil, and treat the next level of soil in a similar manner. It is reasonable to assume that the depth of excavation and soil removal would be determined by the depth of tilling. Therefore, the depth of treatment for an in situ LTU may essentially be determined by the depth of tilling. Refer also to Section 4.3.16.5 for additional information regarding tilling.

4.3.4.2 Lined Versus Unlined LTU

The stringent performance requirements of SARA require that ex-situ land treatment units have liners and leachate collection systems. The details of liner and leachate collection system design are discussed in Sections 4.3.2.3 and 4.3.2.4. If leachate migration is a concern, in situ land treatment, which has no liner, is not possible.

4.3.4.3 Covered Versus Uncovered LTU

Site-specific environmental variables, such as the type of wastes to be treated, exposure pathways, and weather conditions may exist whereby a cover for an LTU is necessary and is cost-effective. Wastes with noxious gases or volatile emissions can pose an odor problem or result in an unacceptable exposure pathway. Land treatment activities can also release fugitive dust emissions that may pose unacceptable risks to workers or nearby residents. These conditions may also warrant the use of a cover over the LTU.

Heavy or frequent rainfall, in conjunction with clay soils, can result in poor soil drainage. This condition is undesirable since saturated soils limit soil aeration and aerobic biodegradation. Additionally, the effectiveness of tilling wet, clayey soils is severely limited. A cover that prevents rain from reaching the LTU will enable soil management activities such as tilling and nutrient amendment to help maintain soil conditions conducive to optimal biodegradation. Although the covered LTU may be protected from excessive rainfall, a moisture amendment system must be incorporated into the land treatment operations to maintain adequate soil moisture. Finally, in regions where the average annual temperature is very low and the treatment season limited, a covered LTU with heat can extend the treatment period and accelerate site cleanup.

4.3.4.4 Soil Versus Sludge Application

Generally, sludge is applied with a truck-mounted tank equipped with a spreader system allowing the sludge to be uniformly applied on the soil and then tilled into surface soil. Soil treatment generally involves the application of contaminated soil to an LTU in lifts with a dump truck or front-end loader. The piles of soil are spread using a tractor-mounted box blade prior to being tilled into surface soil (refer to Section 4.3.16.1).

4.3.5 Pretreatment Processes

Assuming the contaminated soil is excavated, stockpiled, and awaiting application to an LTU, the soil can be pretreated to degrade contaminants or it can be conditioned for optimal treatment in the LTU. If possible, stockpiling the contaminated soil in a lined area will prevent contaminants from leaching. Placement of the soil in an area that is already contaminated will minimize the impact of leaching contaminants.

4.3.5.1 Excavation and Removal of Debris

Contaminated soil usually contains a wide variety of debris including rocks, roots, trees, and miscellaneous metal and wood items. Waste pits used to dispose of sludges and other contaminated waste products were also commonly used for the disposal of many other materials that were used at the site, including concrete debris, pipes, old vehicles, treated lumber (ties and poles), etc. Excavated waste material should be screened for such debris that may interfere with treatment processes. For example, Champion International at Libby, Montana, used a portable trommel plant (i.e., de-rocking equipment commonly used in road construction) to remove rocks from the

excavated soil prior to land treatment. Removing the rocks significantly reduced the volume of contaminated soil to be treated (Sims et al. 1995).

4.3.5.2 Soil Homogenization

One form of pretreatment involves homogenizing the contaminated soil. Simply mixing the soil in the stockpiled area tends to more evenly distribute the contaminants in the soil. Highly-variable contaminant concentrations occur when the soil is excavated from the contaminated area(s) without homogenization. Mixing the hot spots into surrounding soil with lower concentrations results in more uniform concentrations and treatment in the LTU. A reduction in concentration variability also aids in data interpretation.

4.3.5.3 Soil Treatment

Biopiles, bioventing, land treatment, composting, etc., can be used to treat the soil prior to its application to the LTU. The O_2 content may be low or non-existent in stockpiled soil. Increasing the soil O_2 concentration may enhance biodegradation and decrease contaminant concentrations and the treatment time in the LTU. In addition, pH adjustment, nutrient amendment, moisture control, and soil mixing can be used to pre-treat or precondition contaminated soil.

4.3.6 Posttreatment Processes

There are several options for the closure of an LTU or a site with contaminated soils, all of which involve the careful management of the site during the closure and post-closure periods (Loehr et al. 1990). The most appropriate steps for closure and post closure must be selected on a site-specific basis. Assuming the contaminated soil is a hazardous waste, there may be regulatory requirements under RCRA (i.e., 40 CFR 264.280) for the disposition of the site after contaminated soils have been remediated.

4.3.6.1 Closure

Ex-situ LTU closure occurs when all the contaminated soil has been treated to an acceptable level. In situ closure occurs when treatment of a specific depth of contaminated soil has been achieved. Closure activities generally involve: (1) collection and analysis of soil, soil pore liquid, groundwater, and air samples to confirm that contaminants have been contained in the LTU, and (2) construction of a cover (i.e., cap or vegetative cover), to provide long-term containment and possibly continued degradation of contaminants.

Vegetative Covers, Caps, Monitoring. The selected closure options (Table 4.5) should account for the mobility, toxicity, and migration potential of the contaminants remaining in the soil (US EPA 1987; Loehr et al. 1990). Factors to be considered when evaluating closure options include (but are not limited to) the following:

- concentration of contaminants left in place;
- mobility and persistence of the contaminants;
- environmental and soil conditions (i.e., high precipitation, low evaporation, soils of high permeability and/or low sorptive capacity, high runoff potential);
- contaminant characteristics (i.e., volatility, solubility, concentrations, degree of hazard presented by the residual constituents);
- results of mathematical models used to predict long-term mobility;
- proximity of groundwater relative to the contaminated soil;
- potential for direct contact including drinking groundwater or inhaling fugitive dust emissions and volatile gases; and
- potential for further degradation to occur in place.

Table 4.5
Options for Land Treatment Unit Closure

- Removal of the contaminated soil and subsequent disposal as a hazardous waste
- Placement of an impermeable cap over the sites such as a synthetic liner or low permeable material (e.g.,clay).
- Installation of a vegetative cover, groundwater monitoring, run-on and runoff control.
- Continued management of the contaminated soils.
- Combination of two or more of the above

Source: Loehr et al. 1990

Each option will affect conditions in the soil at the site over time (Loehr et al. 1990). For example, excavation may increase the oxygen content, aerobic biodegradation, and volatilization at lower depths. Constructing an

impermeable cap will reduce infiltration, maximize runoff, minimize leaching of contaminants, reduce the oxygen content and aerobic biodegradation rate, and alter the redox conditions that may affect the mobility of some metals. Establishing a vegetative cover may slightly decrease the diffusion of oxygen into the LTU or volatiles from the LTU and may increase the rate of infiltration. These conditions, in conjunction with the migration potential, should be evaluated on a site-specific basis when considering the construction of a cover at an LTU. A combination of various cover options may be necessary to accommodate design requirements.

Performance of an LTU cover should be evaluated based on its ability to:

- prevent migration of contaminants from the LTU and minimize direct contact;
- minimize maintenance;
- promote drainage from the LTU;
- minimize erosion;
- accommodate settling and subsidence without compromising the integrity of the cover; and
- have a permeability less than the bottom liner, if one exists.

US EPA (1985b) provides a detailed discussion of final cover criteria, materials, soil testing and additives, design, gas control, hydraulic barrier layers, drainage layers, vegetative covers, surface water management construction, and construction quality assurance and quality control (QA/QC).

A summary of the main features and advantages and disadvantages of the different closure options has been presented elsewhere (US EPA 1987). These include the following:

1. *Excavation* — generally not recommended unless there is a high potential for migration from the LTU in conjunction with potential for direct exposure to toxic compounds. Excavation reduces the risk at the location of the LTU, but excavation, transportation, and disposal costs are significant; future liability exists; exposure and release potential is significant during excavation; and the potential for subsequent release and exposure exists.
2. *Vegetative Cover* — highly recommended. The advantages include prevention of water and windborne erosion, minimization of the transport of soil waste materials (fugitive dust/soil emissions), control of infiltration, continued treatment of contaminants in the LTU, minimization of exposure to workers and the

public during excavation and transportation, and pleasing aesthetic qualities. Disadvantages of vegetative covers include continued maintenance, potential phytotoxicity of the contaminants in the soil, and potential biomagnification, particularly for metals. Establishment of a vegetative cover on an LTU involves selection of species adapted for the site, seed bed preparation, seeding/planting, and cover maintenance. Additional discussion of the use of a vegetative cover can be found in Section 4.5 (Phytoremediation) of this monograph.

3. *Capping* — generally not recommended. The advantages of capping include prevention of surface water infiltration, erosion control, isolation and containment of the soil/waste mixture, and minimization of exposure to workers and the public during excavation and transportation. However, capping reduces the oxygen transfer rate into the LTU that may decrease aerobic biodegradation. Decreasing the oxygen content also leads to a decrease in the oxidation potential that may increase the mobility of some metals. The cap must be graded to manage surface water infiltration and runoff and should be revegetated to provide a stabilized surface. Caps require long-term maintenance and care.

4. *Continued Management (In-Place Treatment)* — used to contain the source of contamination by immobilization or to reduce the source through degradation (US EPA 1984b). These techniques include naturally-occurring processes within the soil to accomplish treatment, supplemented with amendments or management and operational practices to accomplish the desired degree of treatment. The advantage is that many of the techniques are easily implemented and inexpensive (e.g., photo-degradation, biodegradation, volatilization, etc.). Other treatment techniques for immobilization involve sorption, ion exchange, and precipitation. The disadvantage is that there is still potential for migration and direct contact with the waste residues since soils are left in place without a cover. This approach may be useful where the remaining soil contaminant concentrations and the associated risks are not significant. In the long term, additional measures may be necessary to minimize the potential for migration and exposure pathways.

Based on the low migration potential of PAH compounds, freon extractables, and metals in the soil at several hazardous waste land treatment units as determined from laboratory studies and modeling, it was concluded

that it was unnecessary to cap the sites at closure (Loehr et al. 1990). It was also concluded that the leave-alone option or the option to continue active site management was protective of human health at the sites. In situ land treatment of petroleum wastes achieved concentrations at the Baldwin Waste Oil Superfund Site (Robstown, Texas) which were protective of human health and the environment. The closure technique involved a leave-alone option and native vegetation has been re-established (naturally) in the land treatment area.

Soil pore liquid monitoring may be necessary for a specified period to detect contaminants leaching from the treatment zone. However, if a leaching problem exists, it is likely to be detected during the active period of the LTU. Assuming soil pore liquid or leachate analysis indicates the presence of contaminants above an acceptable level, closure activities should evaluate why the release from the LTU occurred. Steps necessary to minimize the continued release of contaminants from the LTU should then be taken. If soil pore liquid or leachate does not contain contaminants at concentrations of concern, a reduced frequency of monitoring is justified.

4.3.6.2 Post Closure

If it is demonstrated during closure that acceptable performance has occurred, post closure begins. The post-closure period is primarily characterized by continued monitoring with reduced frequency. In LTUs constructed with a liner and leachate collection system, water infiltrating into the LTU will continue to be captured, and its removal will be necessary to prevent the LTU from becoming saturated. Assuming that the leachate in a lined leachate collection system does not contain contaminants at concentrations of concern, there is no longer a need to capture, collect, or analyze the leachate. One option may be to puncture the bottom liner to prevent leachate collection. Where minimal risks exist, this minimizes the costs of maintaining and monitoring the LTU system, otherwise, continued removal of the leachate is necessary to avoid the saturation of the LTU.

The cover system, consisting of either a cap or vegetative cover, will require routine maintenance. Periodic reliming and fertilization of nitrogen-, phosphorus-, or potassium-deficient soils may be necessary to maintain optimum yearly growth on seeded plots (US EPA 1985b). Periodic mowing and the judicious use of herbicides will help control undesirable weeds or brush species. A cap will also require a vegetative cover to stabilize the surface and minimize erosion. Although a vegetative cover requires frequent maintenance, it actually prevents more costly maintenance that would result from

erosion of the surface soil of the cap (US EPA 1985b). Caps sometimes require resurfacing/regrading during the post-closure period.

4.3.7 Process Instrumentation and Control

Pumps, blowers, valves, filters, pressure gauges, breaker boxes, etc. are not an integral component of LTU operations. Therefore, process instrumentation and control is generally unnecessary.

4.3.8 Process and Instrumentation Diagrams

Pumps, blowers, valves, filters, pressure gauges, breaker boxes, etc. are not an integral component of LTU operations. Therefore, process and instrumentation diagrams are unnecessary. Figure 4.12 illustrates the main steps associated with ex-situ and in situ land treatment.

4.3.9 Sample Calculations

4.3.9.1 Volume Estimates

The estimate of the in situ volume of soil to be treated based on planimetry methods must be corrected for the change of the density of the soil from its in situ state, or the bank volume, to its ex-situ state, or the loose volume. For example, the density of the in situ soil may be 1926 kg/m^3 (120 lb/ft^3) while the density of the ex-situ soil in the LTU is 1524 kg/m^3 (95 lb/ft^3). Since the mass of soil is the same but its density less, the volume must increase. Assuming the moisture content does not change, the percent increase is calculated as shown in Equation 4.4.

$$\text{Volume increase} = \frac{(1926 - 1524)}{1926}(100) = 21\% \qquad (4.4)$$

Also, adjustments in volume must account for soil compaction in the LTU as additional lifts of soil are placed on top of treated lifts.

4.3.9.2 Treatability Study Data Analysis

Laboratory-, bench-, pilot-, and field-scale soil concentration data can be used to estimate the degradation rate and to predict the time frame to reach target concentrations. Assuming first-order degradation rate kinetics, soil concentration data can be described based on Equation 4.5.

$$dC / dt = -kC \qquad (4.5)$$

where:

k = the first-order degradation rate constant, T^{-1}; and
C = the concentration of contaminant in soil (mg/kg).

The integrated and linearized form of this equation can be used to estimate the degradation rate and the half-life of the contaminant in soil.

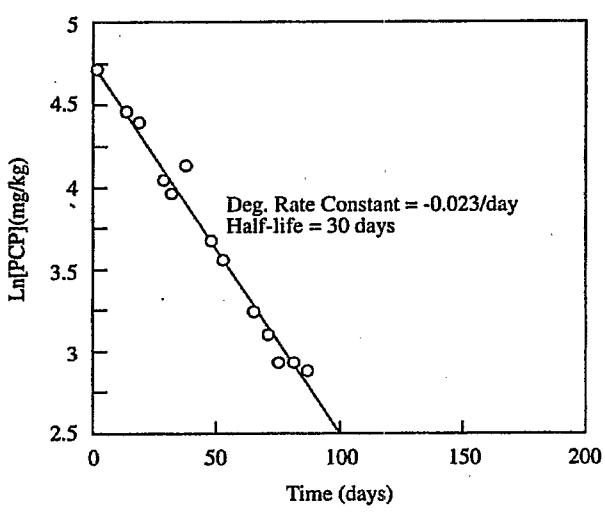
$$\ln C = \ln C_0[-k(t)] \tag{4.6}$$

where:

$\ln C_o$, $\ln C$ = the natural logarithm of the concentration of the contaminant at time 0 and time t, respectively.

Data from a treatability study have been plotted as a function of time in Figure 4.13, and the degradation rate constant (k), coefficient of determination (r^2) and half-life ($t_{1/2}$) of the compound have been calculated. In laboratory studies, concentration data usually conform well to the first-order degradation kinetic rate model due to uniform concentrations, mixing, and optimum mass transfer. The half-life represents the time it takes the concentration to degrade to half of the initial concentration. This is easily calculated by dividing ln (0.5) by the degradation rate constant. Equation 4.6 can be solved for time (t), to estimate the time it will take to reach this 50% concentration, given an initial concentration (C_o).

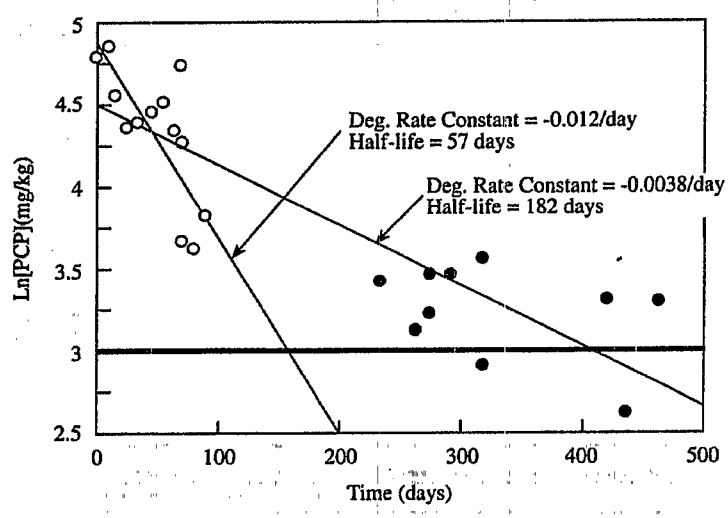
Figure 4.13
Linearization of Laboratory Pentachlorophenol Soil Concentrations to Estimate the Degradation Rate and Predict the Cleanup Time Frame



4.3.9.3 Field Data Analysis

Pilot- or field-scale data are less ideal than laboratory- and bench-scale data due to heterogeneous soil concentrations and mass transfer and mixing limitations. Therefore, conformity to degradation rate models is generally less likely. Figure 4.14 illustrates the linearization of field-scale pentachlorophenol soil concentration data using Equation 4.6. Greater variability is observed in the contaminant concentrations at field-scale relative to the data obtained in the laboratory-scale treatability study. Spring through summer LTU data (0 - 100 days) and spring through winter LTU data (0 - 300 days) have been plotted in Figure 4.14. These data illustrate that degradation rate kinetics for the spring-summer time frame is not inaccurate if extrapolated through the winter. The temperature decreases during the winter as does the microbiological activity and degradation rate kinetics. Correspondingly, the estimated first-order degradation rate constant decreased and the half-life increased when the spring through winter data are used. Judicious use of kinetic data is important when extrapolating kinetic data over periods where chemical, physical, and biological changes may affect the degradation rate or where such changes may exist in different lifts of soil applied to the LTU.

Figure 4.14
Linearization of Field Pentachlorophenol Soil Concentrations to Estimate the Degradation Rate and Predict the Cleanup Time Frame



○ Spring and Summer Data
● Spring thru Winter Data
▬ Soil Clean-up Concentration

4.3.10 Safety Requirements

Field activities that could expose personnel to contaminants at a land treatment site include excavating, transporting, and stockpiling contaminated soil; separating debris from excavated soil; placing contaminated soil in the LTU; tilling the soil; sampling soil, leachate, and groundwater; and installing monitoring wells. Appropriate steps and controls need to be developed on a site-specific basis to minimize exposure pathways during these activities. Designation of hot (exclusion), warm (contaminant reduction), cold (support), and decontamination zones around the LTU and the rest of the site is useful to indicate the specific level of protection that is required for each zone. One of the most likely exposure routes at LTUs is inhalation of fugitive dust emissions. Dust can be suppressed by watering the soil or by constructing windbreaks. A health and safety plan for the site should be developed that addresses all of these issues.

4.3.11 Specifications Development

A wide range of technical specifications must be developed depending on the type of LTU constructed, site-specific design criteria, and availability and cost of materials. Technical specifications for an in situ LTU are the simplest, but are more complex for an ex-situ LTU where a lined unit with leachate collection system is required. The technical specifications that will be required in most cases include (but are not limited to) the following: availability of utilities (electricity and water), borrow excavation and transportation, classification and/or textural analysis of berm material, etc. In the case of ex-situ LTUs, additional technical specifications are required, including clearing, water control, excavation, permeability, moisture content, and soil mateirals (clay, sand, silt, and gravel), (refer to Figures 4.8 through 4.11). In addition, technical specifications must be developed for construction of the liner, including surface clearing and preparation, compaction, flexible membrane liner (type, thickness, density, installation, sealing/seaming, leak detection and repair, and QA/QC), geotextile filter fabric, drainage net, leachate collection system (diameter, slot size, material), construction of liner and leachate collection system, anchoring the liner system, etc. Slope stability analyses should be performed on the berms constructed at the LTU to prevent failure. Technical specifications must also be prepared for the LTU cover (i.e., cap and/or vegetative cover). These may include the grade of cap, clay material classification/textural analyses specification, compaction and field permeability testing, seed type, seed rate, preparation of seed bed, QA/QC, etc.

4.3.12 Cost Data

Due to the numerous factors affecting design, construction, operation, maintenance, and monitoring of LTUs, cost data are difficult to extrapolate among sites. It is also difficult to develop costs per volume of soil treated for several reasons: (1) numerous site-specific variables affect cost; (2) costs vary as more soil is applied (i.e., the average cost per yd^3 decreases due to the initial capital costs averaged into the calculation); (3) most ex-situ LTUs are still active; and (4) closure and post-closure costs have not been incurred or estimated for these active sites. Despite these limitations, information has been compiled from different sources to estimate the type and range of expenses expected to be incurred in applying land treatment at contaminated sites. Construction costs are provided for two lined, leachate collection land treatment systems. These costs are provided as a function of area, rather than volume of soil treated since the cost only includes construction of the unit.

- Champion International Superfund Site, Libby, Montana (Cosgriff 1996):
  - lined, leachate collection system; and
  - actual construction and engineering costs, $400,000 for two 0.4-ha (1-acre) LTUs; or $50/m^2$ ($41.40/yd^2$).
- Broderic Superfund Site, Denver, Colorado (Simpkin 1996):
  - lined, leachate collection system; and
  - estimated construction costs; or $22 to $32/m^2$ ($18-$26/yd^2$).

Activities that clearly affect the overall land treatment cost but are not included in the estimated construction cost of the LTUs at Libby, Montana include remedial investigation, feasibility study, treatability study, remedial design, remedial action, oversight, sampling and analysis, data management, moving/applying contaminated soil, water (surface, leachate) management, and regulatory interaction. Equipment and supplies to carry out these activities also affect the overall land treatment cost and are also not included in the cost estimates presented above.

The estimated costs for in situ treatment activities at the Baldwin Waste Oil Superfund site (Robstown, Texas) include construction of berms, removal and disposal of debris (piping, concrete, wood), tilling, sampling and analysis, data management, and moisture and mineral nutrient amendment. The costs for this site are summarized as follows:

- in situ land treatment of upper 15 cm (6 in.) of soil, 0.4 ha (1 acre);

- oil contaminated by a mixture of waste petroleum products at a recycling site;
- no liner/leachate collection system, berms were constructed to prevent run-on/runoff;
- tilling, mineral nutrient amendment, and soil sampling for oil and grease, and TPH; and
- total costs of $50,000; or $12.50/m^2 ($10.35/yd^2).

The 1985 cost for revegetating a hypothetical site was estimated by US EPA (1985b) to be $3,110/ha ($1,260/acre). This estimate includes hydroseeding application of lime, fertilizer, and seed.

4.3.13 Design Validation

All design calculations and assumptions should be peer reviewed and checked by qualified individuals. In some states, design drawings must be sealed by a licensed professional engineer. Many of the drawings are relatively simple, but generally require approval by state and federal regulatory agencies.

4.3.14 Permitting Requirements

Site-specific conditions relating to environmental regulations may require a land treatment permit. The most logical starting point to determine if a permit is required is to evaluate whether the waste to be treated is classified as hazardous or nonhazardous under RCRA. Assuming the waste to be treated is classified as hazardous (listed or characteristic), RCRA permit requirements and regulations would apply to the LTU. Assuming Superfund regulations are applicable to the site, the RCRA land disposal restrictions may also apply, and a no-migration demonstration may be necessary to waive the land disposal restrictions. The no-migration petition application involves a demonstration that hazardous waste constituents are prevented from migrating from the LTU into the surrounding air, groundwater, and soil. State environmental regulations may also provide additional technical guidelines and requirements for an LTU.

Assuming the waste to be treated is not classified as hazardous, a nonhazardous LTU permit may be required by some states. However, a no-migration variance from the land disposal restrictions would not be required and it is likely that the rigorous design and operational criteria required by such a no-migration requirement would also be unnecessary.

4.3.15 Design Checklist

Table 4.6 provides the basic checklist for LTU design.

Table 4.6
LTU Design Checklist

Soil/Waste Parameters	Site Parameters	Regulatory Parameters
Volume of contaminated material	25-year, 24-hr. storm event	Hazardous waste permit
Degradation rate constant	Nearest utilities	No-migration waiver
Initial concentrations	Water source	Monitoring requirements
Lab, bench, pilot testing results	Average annual rainfall	Clean-up concentrations
Depth of lift	Climate information (temp., snow, wind, etc.)	
Ex-situ versus in situ	Proximity of residents	
Final cover (cap, vegetative cover)	Exposure pathways	
Type of waste (soil, sludge, etc.)	Depth to groundwater	
Pretreatment requirements	Groundwater contamination	
Nutritional status of soil	Storage capacity for leachate/runoff	
Covered versus uncovered		
Soil textural analysis		

4.3.16 Implementation

4.3.16.1 Soil Application, Depth, and Oxygen Considerations

Soil is applied by transporting the contaminated soil, usually in a dump truck or front-end loader, from the source location(s) to the LTU. Piles of soil in the LTU are evenly spread, usually with a tractor mounted box-blade. The LTU surface is graded, generally within a 0.5 to 1% slope toward one end of the unit so that surface runoff accumulates in one convenient location for efficient removal. The grade should not be too steep to avoid excessive erosion. The lift depth is generally limited to 15 to 30 cm (6 to 12 in.) but should be determined on a site-specific basis. If the soil lift is too deep, significant biological O_2 utilization, in conjunction with ineffective tilling, may result in inadequate O_2 concentrations in the soil, especially toward the

bottom of the lift. Some specialized tilling equipment can mix the soil deeper than 15 to 30 cm (6 to 12 in.) and may provide adequate O_2 transfer. If the soil depth is too shallow, the rate of soil application and its treatment in the LTU is not optimized, thus increasing treatment time and cost.

Recently, continued degradation of target compounds (PCP and PAHs) in soil has been demonstrated in soil lifts that were buried by more recently applied lifts (Sims et al. 1995a; Huling et al. 1995a). Additionally, reduced O_2 concentrations in soil microcosms indicated that degradation of PCP and PAHs was not limited at 2, 5, or 10% soil gas O_2 concentrations relative to atmospheric O_2 levels (Hurst et al. 1996; 1997). This study used soil from the same LTU where it was observed that degradation occurred in buried lifts. These observations raise an important issue regarding the depth of a lift and whether it is necessary to wait for the surface layer of soil to reach the target concentration before applying a second lift. One approach to lift depth determination may be to estimate the critical O_2 concentration that should be maintained in the soil based on the rate of O_2 treatment by diffusion and advection, relative to the O_2 uptake (biological O_2 demand). The critical O_2 concentration for optimal treatment of petroleum wastes may be greater than for wood-preserving wastes due to the higher rate of biological O_2 demand associated with petroleum wastes.

During in situ land treatment, contaminated surface soil remains in place, and treatment occurs as the uppermost soil layer is managed to enhance biodegradation. In situ land treatment can also be implemented by excavating the surface soil and managing underlying contaminated soils to enhance degradation.

4.3.16.2 pH Control

Optimum biodegradation in soil occurs in the pH range of 6 to 8. The pH of soil affects microbial activity, availability of nutrients, plant growth, immobilization of metals, rate of abiotic transformation of organic waste constituents, and soil structure (Pope and Matthews 1993). Ammonia nitrogen is the form of nitrogen most bioavailable. At high pH (> 8.5), ammonia predominates and may escape into the atmosphere in significant quantities (Loehr et al. 1979). Some soils with high pH (>7.5) are deficient in micronutrients such as iron and zinc (Brady 1990), resulting in calcium phosphate precipitation that may reduce the bioavailability of phosphate. At low pH (<5) the solubilities of iron and aluminum increase, making them available to react with soluble phosphate to form a precipitate that is also no longer bioavailable. The solubility of phosphorus, an important nutrient in biological systems, is maximized at a pH of 6.5 (Sims, Sims, and Matthews 1989).

The cation exchange capacity (CEC) for most soils increases with increasing pH, and at pH 6 and below, the CEC is generally constant (Brady 1990). The pH either directly or indirectly affects several mechanisms of metal retention by soils. As soil pH increases, the adsorption of all cations (e.g., Pb, Ni, Zn, Cu, etc.) increases and that of the oxyanions (e.g., As, Se, hexavalent chromium) decreases (McLean and Bledsoe 1992). Soil pH outside the optimum range may result in an increase in: (1) the bioavailability and toxicity of metals to soil microorganisms and (2) the potential for metal migration. Pentachlorophenol (PCP) is an organic acid ($pK_a = 4.7$) yielding two forms of the compound: one that is protonated or un-ionized at low pH, and one that is ionized (PCP^-) at higher pH (i.e., 99% ionized at pH 6.7). The solubility of ionized PCP^- is approximately 10 times greater than the solubility of the un-ionized form. With increasing pH, the bioavailability and potential toxicity of PCP increases.

Geographic areas with low rainfall and high evaporation tend to have alkaline soils because cations (Ca^{2+}, Mg^{2+}, K^+) predominate and the formation of hydroxide is favored, resulting in high pH (US EPA 1983). In areas of high rainfall, mining areas where oxidation of iron pyrite and other sulfides occurs, or where conifer forests drop acidic pine needles, the soil may become acidic. Management of soils with either low or high pH may be quite difficult and may require chemical amendment to adjust the pH within the LTU to the optimal range for maintaining biological activity. Soil samples should be collected to evaluate whether the soil pH is in the optimal range. Soil pH is an easy and rapid measurement and there are several techniques available (Brady 1990). US EPA (1983) discusses several methods to adjust the soil pH into the appropriate range. The addition of lime (CaO) has been used to increase the soil pH by reducing the hydrogen ion activity. Other chemicals used to raise soil pH include calcium hydroxide [($Ca(OH)_2$)], calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), and calcium silicate slags. Application of lime will raise the soil pH, but its effects are not instantaneous and sometimes take months. Assuming contaminated soil is stockpiled prior to treatment, liming low pH soil would be an effective pretreatment practice. Sources of lime, application techniques, requirements, and sample calculations for required dosages are reported elsewhere in the literature (Brady 1990; US EPA 1983). Soil pH is generally lowered by adding various sulfur compounds, such as ferrous or aluminum sulfate, elemental sulfur, or sulfuric acid (US EPA 1983).

4.3.16.3 Nutrient Amendment

Contaminated soil may lack mineral nutrients required for indigenous microbial populations to degrade contaminants to an acceptable level. Soil may initially contain a sufficient amount of nutrients but processes, such as nutrient leaching, immobilization/utilization, complexation (precipitation, adsorption, ligands, etc.), volatilization, and other losses may deplete nutrients. In this case, amending the soil with mineral nutrients may be necessary to sustain appropriate levels of microbial activity. Also, wastes may lack the required micronutrients for microbial growth and biodegradation, but the soil will likely contain sufficient supplies (Huddleston, Blackman, and Wolf 1986). The macronutrients, C, N, and P, must be present in sufficient amounts to ensure that microbial growth is not limited. Recommended C:N:P ratios range from 120:10:1 (Sims, Sims, and Matthews 1989) to 300:10:1 (Pope and Matthews 1993). A C:N ratio <25 leads to mineralization while a ratio >38 leads to depletion of mineralized N, which would limit biodegradation (Huddleston, Blackman, and Wolf 1986).

Nutrients may be applied to the soil in either a solid or liquid form. Forms of N used as fertilizers include ammonium (NH_4^+), nitrate (NO_3^-), and organic-nitrogen. While NH_4^+ and NO_3^- are both available to plants and microorganisms, NH_4^+ is much less mobile than NO_3^- which may be readily leached from the soil and present a health hazard (US EPA 1983). Organic forms of nitrogen become bioavailable as they are mineralized (i.e., through hydrolysis to NH_4^+ and by oxidation to NO_3^-). The forms of commercially-available nitrogen applied to soil include ammonium nitrate (NH_4NO_3), ammonium chloride (NH_4Cl), diammonium hydrogen phosphate [$(NH_4)_2HPO_4$], and organic-nitrogen.

Decomposition of organic wastes and inorganic fertilizers provides a variety of organic and soluble forms of P including orthophosphate, condensed phosphate, tripolyphosphate, adsorbed phosphate, and crystallized phosphate (US EPA 1983). Hydrolysis and mineralization convert these forms to a soluble phosphate form that is available to plants and microorganisms. There are several forms of P that have been applied to soil as fertilizers, including diammonium hydrogen phosphate, orthophosphate, and tripolyphosphate.

The solid form of nutrients, or agricultural fertilizer, is available as pellets or powders. Under field conditions it is generally easier to apply pelletized fertilizer than powdered fertilizer. Water-soluble fertilizer, or simply the solid form dissolved in water, may also be used and can be applied in conjunction with moisture control activities. Soluble mineral nutrients in the appropriate chemical form, or solid mineral nutrients dissolved in soil pore

water, are immediately bioavailable. Animal (chicken, cattle, etc.) manure is generally high in organic nitrogen content and has also been successfully used as a source of nutrients. Manure may be less desirable than agricultural fertilizers, however, as it contains a high carbon content, that when mineralized by microorganisms, may deplete the available nitrogen.

4.3.16.4 Water Management

Soil Moisture Control. Following a wetting event (e.g., rainfall, irrigation, or surface runoff), there will be a relatively rapid downward movement of some of the water due to gravity flow. After 2 to 3 days, the downward movement becomes negligible, and most of the water remaining is present in micropores. The moisture content at that time is referred to as field capacity (Brady 1990) or water-holding capacity. Measurement of the soil moisture content is a gravimetric procedure and is expressed as the weight of the water normalized to the dry weight of the soil.

Huddleston, Blackman, and Wolfe (1986) indicate that a wide range of soil water-holding capacity (25 to 85%) has little affect on biodegradation in soil. Pope and Matthews (1993) recommend 70 to 80% field capacity, and Sims, Sims, and Matthews (1989) recommend 25 to 85% water-holding capacity. A 14, 12, and 59% decrease in the half-lives of anthracene, phenanthrene, and fluoranthene, respectively, were observed when the soil moisture content was increased from 20-40% to 60-80% (Sims 1986), indicating that increasing soil moisture to recommended optimal levels clearly has a positive effect in some soils. However, no significant effect was observed on PCP or phenanthrene mineralization at 40% field capacity relative to 80% field capacity in laboratory treatability studies (Sims et al. 1995a).

Optimum moisture content is soil-specific. This is partially due to the ambiguity of measuring water-holding capacity, but, primarily, because the soil at each site has different chemical, physical, and biological characteristics that collectively determine the optimal soil moisture content for biodegradation. Too little soil water will reduce the contact area where solubilization and biodegradation can occur, and will dehydrate microbes. Both limit biodegradation. Too much soil water may result in contaminant leaching and anaerobic conditions in soil by completely filling soil pores with water. A site-specific moisture content treatability study may be necessary to determine the optimum soil moisture content. Soil moisture is usually applied via sprinkler systems where a supply of pressurized water is available. In remote locations, water may be pumped from nearby water bodies or trucked in and surface applied.

Surface Water. Surface drainage can be managed by diversion structures such as berms, ditches, or surface contouring to remove excess water before the soil becomes saturated. Surface water drainage control in an LTU is important in high rainfall areas due to the problems associated with prolonged soil saturation (poor soil aeration, increased leaching, etc.). Direct precipitation onto the LTU can be useful if it occurs at a time when the soil moisture content is low, but becomes problematic when soil moisture is high. Water that infiltrates into the soil, in excess of the field capacity, can be captured and removed, assuming a liner and leachate collection system exists below the treatment zone. Surface water can be removed by pumping it into a storage vessel. In some cases, surface water may have to be stored and analyzed to determine whether treatment is required before disposal. One option to minimize treatment costs is to use the stored water for soil moisture control.

Leachate. In LTUs that are constructed with liners and leachate collection systems, leachate is captured and drained to a collection sump. Leachate removal reduces the hydrostatic head on the liner system and the potential for liner leakage. Additionally, high leachate levels may saturate lower lifts (i.e., buried lifts) producing undesirable anaerobic conditions within the lower levels of the LTU. A small-diameter pipe can be inserted into the riser pipe (Figure 4.11) to pump leachate from the collection sump. An automatic high- and low-level indicator can be used in the sump to control pumping of leachate to a storage tank. Similar to the surface water collected from the LTU, leachate analysis may be required to determine whether treatment is required before its disposal. To avoid treatment costs, leachate can be stored and used to maintain the appropriate soil moisture content in the LTU during dry periods.

4.3.16.5 Tilling

Soil mixing, or tilling, has several purposes: (1) to enhance O_2 diffusion into the soil; (2) to mix the waste with the soil to achieve greater contact among waste/soil/microbes that improves mass transfer; and (3) to mix the microbes from previously treated soil into the new soil to decrease acclimation time. One additional purpose of tilling is to homogenize the soil and distribute contaminants more evenly throughout the zone of incorporation. With tilling, hot spots become dispersed and the concentration of soil contaminants tends toward a uniform, average value within the LTU, simplifying soil monitoring, sample analyses, and data interpretation become less complex. Although tilling enhances O_2 diffusion into soil, maintaining a maxi-

mum O_2 concentration in soil is not always necessary. For example, as indicated above, it was observed that the degradation of PCP and PAHs at 2, 5, and 10% O_2 concentrations in soil was not limited relative to an atmospheric 21% O_2 concentration (Hurst et al. 1996; 1997).

Equipment. A tractor-mounted rotary tiller is commonly used in agriculture and is commercially available. The rotary tiller creates a thorough soil-waste mixture and aerates the soil in one pass. Other techniques include discing and moldboard plowing. Discing is also common, but accomplishes less mixing than rotary tilling and may require two or more passes. One disadvantage of discing is that during dry periods when the soil can become hardened, the discs do not penetrate the soil and adequate soil mixing is not achieved. Specialized equipment, such as tractors with low bearing pressure for use in wet soils, are also readily obtainable (US EPA 1983). In addition, flotation tires for farm equipment, such as spreaders and tank wagons, and equipment for hauling and spreading solid wastes are commercially available for use in LTU applications.

Frequency. Tilling frequency may be limited when the soil is too wet or when the LTU is in a remote location and access is limited. Generally, tilling should occur at least once per week to once per month, but the frequency should be determined on a site-specific basis. Too little tilling may not provide optimal O_2 content in the soil and may prevent adequate mass transfer and mixing of acclimated microbes into freshly applied soil. An inadequate frequency of tilling may increase treatment time. Excessive tilling can destroy soil structure, reduce soil porosity, prevent soil aeration, and increase soil compaction — all of which are undesirable.

4.3.16.6 Soil Additives

Various soil additives have been applied to contaminated soil to enhance degradation including manure, carbon substrate, surfactants, and exogenous microbial mixtures. Manure contains nutrients, microbial populations, and organic matter that may improve the quality of the soil for biodegradation. A decrease in the half-lives of 15 PAH compounds was observed when the pH was adjusted and manure was added to a contaminated soil (Sims 1986). However, no effect was observed in the degradation of benzo[a]pyrene relative to a control when cow manure was added to a clay loam soil (Coover and Sims 1987). Use of other additives, including surfactants, microbes and simple carbon substrates, such as molasses and glucose are not well documented in the literature.

4.3.17 Start-up Procedures

In the case of ex-situ land treatment, start-up procedures consist of placement of the contaminated soil into the LTU. An initial round of soil samples should be collected and analyzed to determine the initial concentrations, moisture content, and nutritional status (i.e., C:N:P ratio) of the soil. In the case of in situ land treatment, after site preparation has been completed (i.e., berm construction, removal of debris, etc.), startup consists of tilling the upper layer of soil followed by an initial round of soil sampling.

4.3.18 Performance Evaluation

4.3.18.1 Operation Monitoring

A monitoring program is important at any LTU for performance evaluation and operational feedback. Monitoring will occur during the active life of an LTU and during closure and post-closure. The monitoring program usually includes the soil, surface water, leachate, groundwater, and air media.

Operational and Compliance Soil Samples. Soil samples are collected from an LTU for two distinct purposes: (1)operational and (2) compliance monitoring. Both of these types of samples should be collected from throughout the LTU in a random fashion. Operational samples are collected periodically and analyzed for indicator parameters to monitor the rate and extent of contaminant degradation. This information is used to ascertain whether clean-up concentrations have been achieved, or to estimate the time in which clean-up concentrations may be achieved. To reduce cost and save time, it is not necessary to have operational soil samples analyzed by an EPA-certified laboratory. However, a good correlation among laboratory results is useful to support appropriate and sound operational decisions.

Operational samples should be collected after a new lift is applied in ex-situ cases or when a new lift is exposed in in situ cases. Samples are collected and analyzed for TOC, TKN, and total phosphorus to assess nutrient requirements. Assuming pretreatment operations of the stockpiled contaminated soil exist, soil sampling to assess nutrient requirements may already have been conducted. Operational samples may also be collected on a weekly basis for soil moisture measurements to determine whether water should be applied to the LTU. Soil contaminant concentration data can be used as a diagnostic to assess initial concentrations, hot spots, treatment achieved, whether clean-up goals have been reached, or the time to reach clean-up goals. For example, if it is determined that one area of the LTU contains elevated contaminant concentrations which may inhibit microbial

activity, soil mixing could be performed to dampen concentrations and assure more uniform treatment.

Compliance samples are collected after the results of operational samples indicate that the required concentrations have been achieved. The purpose of these samples is to validate the operational sampling data and to demonstrate cleanup. Assuming that the LTU is regulated under a federal statute, these samples must be analyzed by an EPA-certified laboratory.

In an in situ LTU, soil samples may be used to evaluate whether chemical species are migrating downward from the LTU. In an ex-situ LTU with a liner and leachate collection system, monitoring the concentration of contaminants in the leachate will provide more rapid feedback on contaminant migration than samples collected from soils below the liner.

Discrete Versus Composite Soil Samples. Soil monitoring can be done using either discrete or composite samples. Discrete samples are collected as individual samples and are not mixed with other samples. Discrete sampling provides information on the variability of parameter values within the LTU. These data can be used to delineate the range of concentrations found in an LTU. One advantage of this sampling approach is that hot spots in the LTU are more easily identified.

Alternatively, composite sampling involves collecting several samples from within the LTU and mixing samples into a common sample. A subsample of the composited sample is then collected and analyzed. The compositing process reduces the variability in parameter concentrations, and the concentration data tend to be closer to the mean concentration of the LTU but do not show the full range of concentrations actually present. Advantages of compositing are that a greater area of the LTU is represented in the sample and fewer samples are generally required to yield results within an acceptable confidence interval of the mean. Generally, the average value of a parameter in the LTU is more useful in terms of operational management than the range of values shown from discrete sampling. The half-lives of PCP, pyrene, and total carcinogenic PAHs estimated from the analysis of composite and discrete samples collected from the same lift in the LTU, differed only by 15%, 19%, and 31%, respectively (Huling et al. 1995).

Soil Sampling Devices. In most cases, hand-operated soil sampling equipment is suitable for LTUs since the depth of a lift being treated is only approximately 15 to 30 cm (6 to 12 in.). Assuming deeper soil core samples are desired, techniques involving multipurpose or auger drill rigs may be required (US EPA 1986b). Hand-operated drilling and sampling devices include screw-type augers, barrel augers, post-hole augers, Dutch-type

augers, sand augers, mud augers (US EPA 1986b) and tube-type samplers (US EPA 1983). These techniques involve driving, digging, or augering down to a certain depth and recovering the soil sample directly from the auger or from the core barrel.

Number of Samples. The number of samples collected depends upon sample variability and may be as few as three if variability is low (US EPA 1983). Sample variability should be established for the LTU by obtaining and analyzing five replicate samples. If the variance is low (i.e., 5 to 10% of the mean), fewer samples will suffice. If the variance is high (i.e., > 25% of the mean), more than five samples may be needed (US EPA 1983). It is important to note that sample variability will be a function of: (1) the contaminated soil applied to the LTU (ex-situ) or the contaminated soil in place (in situ), (2) soil mixing/tilling, and (3) whether discrete or composite samples are being collected. Estimating the mean concentration within an acceptable margin of the variability of the mean may require a different number of samples with each lift. One practical approach may involve more soil mixing to reduce sample variability. The LTU sampling strategy used at one Superfund site (Huling et al. 1995a) involved the following:

1) divide a 0.4-ha (1-acre) LTU into four evenly-divided quadrants;
2) collect an equal amount of soil over the same depth interval from four random locations within each quadrant;
3) composite the soil samples from each quadrant in a stainless-steel bowl; and
4) analyze the four separate composited samples.

Leachate Samples. Leachate monitoring can include a wide range of activities depending on the type of LTU. The simplest form of leachate monitoring involves pumping leachate from the sump of the leachate collection system through the riser pipe into a sample vessel (Figure 4.11). Leachate is analyzed to evaluate the performance of the LTU (i.e., to determine whether contaminants are leaching). For LTUs without a leachate collection system, monitoring the leachate or soil-pore water is discussed below.

Soil-Pore Liquid Samples. For ex-situ LTUs without a liner or leachate collection system and for in situ systems, it may be necessary to sample soil-pore liquid below a certain depth to evaluate whether specific indicator compounds are migrating out of the LTU. The presence of soil-pore liquid can be measured with tensiometers. While tensiometers do not actually collect soil-pore liquid samples, they can be used to determine whether there

is sufficient soil-pore liquid present for collection via one of the methods described below.

Soil-pore liquid samples can be collected using several techniques including porous cup lysimeters, cellulose acetate hollow-fiber samplers, membrane filter samplers, and pan lysimeters (US EPA 1986b). Suction samplers or lysimeters collect soil-pore liquid samples under negative pressure. There are three types of suction lysimeters: ceramic, hollow-fiber, and membrane filter. The ceramic-type sampler is the most common and involves placing a vacuum on a porous cup that is in intimate contact with the soil. Soil-pore liquid is pulled, under vacuum, into the porous cup and retained for collection and analysis.

A pan lysimeter is suited for sampling soil-pore liquid from macropore or fracture-flow regimes. A trench or pit is dug in or adjacent to the LTU. Water draining freely in the macropores collects in the soil just above the pan and drips into the pan, which funnels the sample to a collection vessel. US EPA (1986b) discusses the advantages, disadvantages, and criteria for using these various soil-pore liquid sampling techniques.

Groundwater Sampling. Before LTU operations commence, groundwater sampling is necessary to determine if the groundwater is contaminated. Assuming the groundwater is contaminated, trend analysis of contaminant concentrations will be necessary to evaluate whether LTU operations are impacting groundwater quality. In the case where a liner and leachate collection system are constructed, leachate analysis will provide a preliminary indicator of whether contaminants are leaching from the LTU treatment zone.

Air Sampling. Ambient air monitoring may be necessary or required to detect and quantify emissions from the LTU. Air monitoring is used to determine if ambient concentrations present an adverse health effect to potentially-exposed receptors. Sample parameters are selected based on the compounds present in the waste material and their potential health effects, and may include both particulate and gaseous contaminants. Air samples should be collected on all sides of the LTU and used in conjunction with meteorological data to determine whether the samples collected represent upwind or downwind air quality. Alternatively, surface emission measurements can be used in conjunction with air dispersion modeling to assess the impact of LTU operations on downwind receptors. Dupont and Reineman (1986), Dupont (1986b, 1987, 1988), and Kienbusch (1986) provide details regarding measurement of volatilization rates from LTUs for air impact assessment.

4.3.18.2 Quality Assurance/Quality Control

Quality Assurance/Quality Control (QA/QC) is essential in LTU operations. The QA objectives, the procedures to be followed to accomplish the objectives and the methods for controlling quality, must be clearly identified. The primary focus of QA/QC in LTU operations is generally on ensuring the representative and accurate determination of soil contaminant concentrations. Quality control procedures involving the appropriate matrix spikes, duplicates, blanks, and procedural blanks are necessary to assure soil, soil-pore liquid, groundwater, and air concentration measurements are accurate. QA/QC is also important during construction of the compacted clay liner, placement of the HDPE liner, and construction of the leachate collection system. An appropriate QA/QC plan should be developed specifically for these construction activities. Refer to US EPA (1980) for guidance regarding the content and preparation of QA project plans.

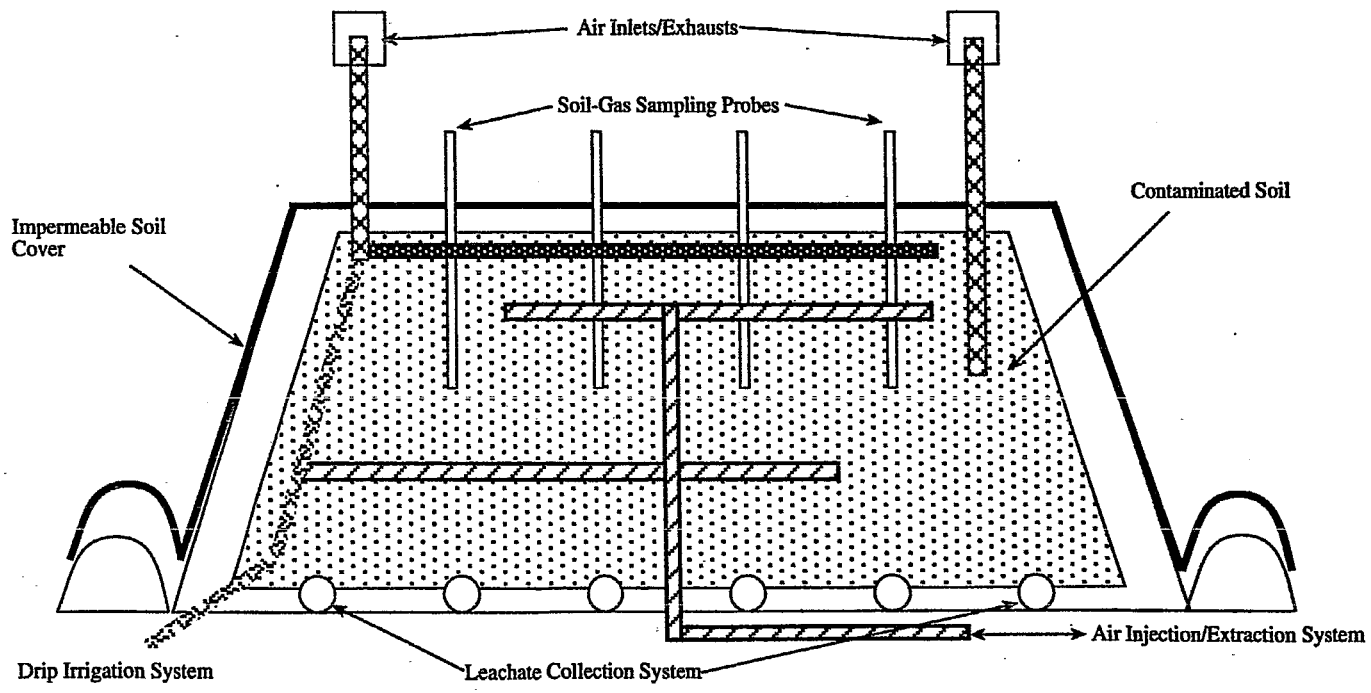
4.4 Soil Cells

4.4.1 Principles of Operation

Soil cells can be viewed as an ex-situ form of bioventing. In this process, soil or sediment is excavated, homogenized if necessary, amended with nutrients, and placed in a constructed cell equipped so that air can be circulated though the soils to provide oxygen. Compared to bioventing, this process incurs the added costs associated with excavation, soil handling, and construction of the soil cell as well as requiring approximately 0.2 ha (0.5 acres) for each 765 m^3 (1,000 yd^3) of soil being treated. On the other hand, soil cells allow for greater control over the treatment process (e.g., homogenization, blending of nutrients, control of moisture levels, and textural modifications possible to produce greater soil porosity) and higher degradation rates than in situ treatment. Operations and monitoring for soil cells are similar to bioventing.

Figure 4.15 shows the basic components of a soil cell — bottom liner, leachate collection system, nutrient-amended soil, aeration manifold, blower, cover, and soil gas sampling points. Once constructed, the system should contain the necessary indigenous bacteria, nutrients, and moisture. Only an electron acceptor is required, and that is provided by either a continuous or intermittent supply of air.

Figure 4.15
Schematic of a Typical Soil Cell Treatment System Using a Vacuum to Aerate the Piled Soil, Drip Irrigation for Soil-Water Management, and an Impervious Cover to Minimize Volatile Contaminant Release



Soil cells have been used primarily to treat petroleum hydrocarbon-contaminated soils, but are applicable to treatment of any soils where aerobic biodegradation compounds will result in acceptable treated soil quality. The lighter commercial petroleum hydrocarbon blends are easily treated, although the relatively high proportion of volatile compounds found in, for example, gasoline and jet fuel, can result in the need for offgas treatment. Moderately heavier molecular weight fuels, such as diesel and #2 fuel oil, are also easily treated and result in modest requirements for offgas treatment. Heavier hydrocarbon blends require longer times to degrade and might be difficult to treat to site-specific or state-mandated clean-up levels. Treatment of aerobically biodegradable chlorinated compounds, such as dichlorobenzene, may generate HCl in the offgas and may require caustic scrubbing prior to discharge as well as special materials for system construction.

Soil cells are most applicable to sandy soils and least applicable to soils with a high clay content. As with other bioremediation processes, tighter soils limit air flow velocities and thus restrict the rate of delivery of electron acceptors and nutrients. Further, handling of soil with a high clay content is more difficult. To improve biocell performance, clayey soils can be shredded if not too moist, and mixed with gypsum to adsorb moisture and with bulking agents, such as bark chips, or gravel to improve porosity and reduce compactibility. Addition of bulking agents increases the volume of material to be treated; therefore, the size of the cell must be increased proportionately. Further, the properties of the soil will be modified and the soil may no longer be suitable for backfill in areas where future construction is anticipated.

Soil cells, where applicable, provide an alternative to disposal at off-site landfills when disposal is permitted. The regulatory requirements and costs for off-site disposal vary considerably from state to state. The total costs include transportation, tipping fees, and replacement of the excavated soils. Another consideration is that biotreatment destroys the contaminants rather than transferring them to another location where some level of risk for future liability remains.

In the last few years, thermal desorption units have become quite cost competitive, especially for treatment of soils contaminated with lighter commercial fuels. Both on-site and fixed-location thermal treatment units are now quite common and can treat soils for as low as $30 per ton (Hater et al. 1994). A third competitive technology for on-site soil cells are permanent soil cell or land treatment systems (see Section 4.3). These permanent locations will accept soils for a fixed fee, treat the soils, and then sell the soil to an industrial or municipal landfill for daily cover.

4.4.2 Process Design Principles

Soil cell designs do not follow strict standard protocols but consist of relatively common components that are combined to fit site-specific needs. For instance, the dimensions of the cell must take into account available space, type of soil, and construction equipment availability. To optimize soil cell performance, the design must provide adequate nutrients, electron acceptors, air circulation, drainage and leachate control, temperature control, moisture levels (50 to 80% field capacity), pH (near neutral), offgas treatment, and performance monitoring.

Leachate collection (if any) and runoff control are provided by grading the base of the soil cell to allow runoff to collect at one end of the cell. Some designs include a sump in the form of a trench at the low end of the cell. The liner then extends through the trench and water can be pumped back to the cell or treated and discharged. Cells built on existing asphalt or concrete surfaces require other methods of collecting leachate.

Bottom liners are required where there is potential to contaminate the underlying soil or where leachate control is necessary. Liners are made from synthetic impermeable fabrics and geomembranes such as visquine with a minimum thickness of 10 mil if reinforced. Bottom liners need to extend past the edges of the soil cell and are typically extended over the top of berms that circle the soil cell. Berms can be constructed from clean site soil, bales of hay, or other readily-available material. Berms are usually 0.15 to 0.3 m (0.5 to 1 ft) high and 0.3 to 0.6 m (1 to 2 ft) wide.

The dimensions of the cell must conform to the available space, with allowances for operating room for the construction equipment. The height of the cell and slope of the sides determine the areal requirements for a given volume of soil. Typically, soil cells are 2 to 3 m (6 to 9 ft) high, although significantly taller cells have been built. The compactability of the soil is a primary consideration in setting the maximum height. If compaction is too great at the bottom of the cell, air flow will be inhibited.

The type of soil and equipment used to load the cell need to be considered when determining the cell length and width. If compaction is a potential problem, the use of front end loaders with extended booms can spread soil over cells with a width of 6 to 7 m (20 to 22 ft) without entering the cell. Finally, cell dimension requirements and space availability may dictate the use of two or more cells.

Some contractors prefer to place a geogrille or a high-permeability filter fabric over the top of the bottom liner before placing the porous material. The geogrille protects the bottom liner (requiring less liner thickness) and

allows any leachate to flow toward the sump. A porous material (gravel or sand) is placed on the liner and may contain drainage pipes to direct leachate to the leachate collection system. The porous layer allows leachate to drain free of the soils and allows air to flow through the soils at the bottom of the cell. A geofabric, basically a soil filter, is placed on top of the porous material to prevent soil from settling into the porous material and blocking leachate drainage and/or air flow.

The soils to be treated are homogenized, shredded, and amended with nutrients as discussed in Section 4.4.5 before placing in the cell. In most instances, commercially-available, high-nitrogen, low-phosphorus fertilizers can be used. Nutrient addition may not be required. However, nutrients are inexpensive and it may be less costly, particularly for small cells, to add nutrients based on the mass loading of the contaminant and existing nutrient levels (obtained from soil analysis for total phosphorus, TKN, ammonium ion, and nitrate/nitrite) than experimentally determining the nutrient requirements. Moisture is also frequently provided to reach optimum soil moisture levels of 50 to 80% field capacity through the addition of aqueous solutions of nutrients.

In nearly all cases, soil cells are operated using indigenous microorganisms. The addition of commercial or isolated bacteria is typically of little benefit because they do not generally survive for more than several days in the constructed pile. Exceptions, as discussed in Section 4.4.4, are the addition of manure for composting and the use of fungi. Some practitioners have professed a more enthusiastic view with regard to commercial sources of bacteria (Forsyth, Tsao, and Bleam 1995), but reported results often do not validate claims of performance improvements following application of microbial amendments.

Amended soils are placed on the geofabric in 0.6- to 1-m (2- to 3-ft) lifts. At each lift, slotted PVC pipes are placed across the soil perpendicular to the long axis of the cell. Solid pipe extends from the edges of the pile approximately 1 meter to reduce the potential for short circuiting through the sides of the cell. Typically, the slotted pipes run parallel to the shorter axis of the cell to minimize pressure drops along the length of the slotted section and so that air flow is more uniform across the cell. One end of each length of PVC pipe is fitted with a control valve and sampling port and connected to a manifold that is in turn connected to a blower. The other end of the length of pipe is typically capped. The cap should be removable so that the pipe length could also be used as a passive air inlet. Horizontal spacing between the PVC pipes is typically 1.5 to 3 m (5 to 10 ft).

An impermeable cover (reinforced tarp) is placed over the top of the cell and secured with ropes, sand bags, used tires, etc. The cover controls dust and air emissions and prevents rainfall from saturating the soil. The liner should extend over the berms, but it must be loose enough to permit air flow or must fit over ducts that will allow air into the space between the cell and the cover.

Sampling ports are spaced throughout the cell. The sampling ports consist of soil gas sampling points or hollow pipes. They allow air samples to be collected from within the soil pores and thus permit analysis for volatile compounds, oxygen, and carbon dioxide as discussed in Section 4.4.18.2. Sampling ports should be placed between each line of slotted PVC pipe and at several locations within the soil including each side and in the middle of the cell.

A critical aspect of the design is the blower size and operating schedule. The total amount of oxygen, and thus air, that needs to be provided to the cell can be estimated from the mass of the contaminants as discussed in Section 4.4.9. In most cases, air can be provided at rates far exceeding the rate at which the bacteria can use oxygen for biodegradation. However, operating at higher flow rates than dictated by degradation rates increases the percentage of volatile components that will need to be treated in the offgas and may contribute to depleting moisture below acceptable levels. Oversizing the blower and operating at excessive flow rates also increases capital and energy costs.

The maximum oxygen utilization rate is approximately five times the maximum rates achievable during bioventing and is likely to be in the range of 20 to 100 mg/kg of soil per day for many petroleum hydrocarbon blends. Laboratory treatability (respirometry) tests can be used to approximate achievable rates. A better estimate of optimum oxygen utilization rates can be achieved by modifying the in situ respiration tests (Hinchee and Ong 1992; Wurdemann et al. 1994) developed for bioventing (Section 4.2.). Oxygen and carbon dioxide concentrations should be monitored once at several locations throughout the cell during the first few days of air circulation and over a two-day period with air flow interrupted to determine the rate of injection/extraction of air needed to meet the oxygen demand. This process should be periodically repeated because degradation rates change as a result of acclimation and because contaminant composition changes due to differential degradation of contaminants over time. For soils with appreciable VOC content, the rate of VOC removal should also be determined so that adequate offgas treatment can be provided.

Respiration data can also be used to estimate the treatment time taking into consideration the rate of VOC removal, starting concentrations, and remediation targets. Typically, zero- or first-order kinetics are assumed, but they can be quantitatively determined from the respiration rate data collected as discussed in Section 4.2. This estimation must take into account the preferential degradation of the individual compounds present in the soil. For hydrocarbon blends, the heavier compounds may persist significantly longer than would be predicted using oxygen uptake data and assuming a single, first-order biodegradation rate.

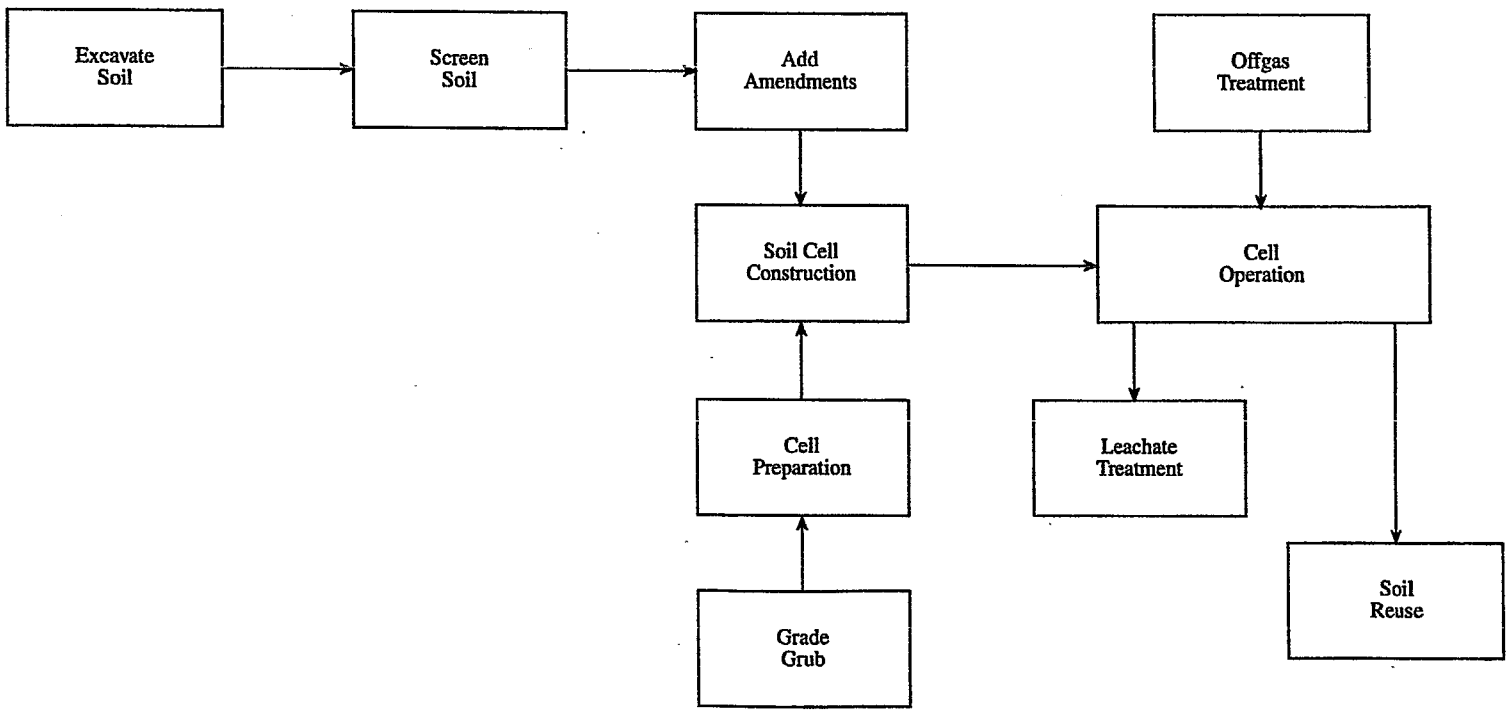
Laboratory treatability and contaminant degradability tests are not always useful, but can be cost-effective, especially where a large volume of soil is to be treated and/or confidence in the treatment method is relatively low for the particular soils and contaminants. Microbial enumerations (plate counts) can be used to determine if an active microbial community exists when there is reason to suspect that conditions unfavorable to microbial growth may exist or additional assurance of biological process performance success is desired. These tests serve primarily to identify conditions where microorganisms are not proliferating. Microcosm studies can be conducted to estimate degradation rates and extent of degradation. Unfortunately, the studies may take as long to conduct as would full-scale treatment and are not always good indicators of degradation rates that would occur at full-scale. Many practitioners have used water-soil slurry microcosms to evaluate degradability because significantly shorter times are required to conduct the tests; however, the rate data from these slurry studies have little relevance to unsaturated soil cells and are of limited value to full-scale system design.

The selection of the offgas treatment system will depend upon the specific compounds present, the air flow velocity, and the concentrations of the individual components. As discussed in Sections 4.4.6 and 4.4.18.1, the operating procedures, including air velocities and offgas recirculation, depend to some extent upon the offgas treatment system selected.

4.4.3 Process-Flow Diagrams

Figure 4.16 is a typical flow sheet for the soil cell process. It includes excavation, soil conditioning, nutrient amendment, cell construction, soil loading, offgas treatment, and leachate collection with recirculation and/or discharge.

Figure 4.16
Soil Cell Flow Diagram



4.4.4 Process Modification

Soil cell modifications include alternative methods of introducing the electron acceptor and/or nutrients, permanent cells, subsurface systems, percolation systems, anaerobic systems, fungi-based systems, and composting.

4.4.4.1 Alternative Electron and Nutrient Addition Methods

Air Injection. For soils with low levels of VOCs and/or where regulations permit, air can be injected into the cell instead of being extracted. The type of design is applicable, for example, for heavy molecular weight hydrocarbon blends. This design does not allow for control of offgas and does not generate a point source that would need to be treated. Consequently, it is not possible to collect an air sample representative of the whole cell or sections of the cell, other than soil gas probe samples located within the cell, unless provisions are made to extract air for short periods to obtain representative samples. In cold climates, the injected air can be heated (Steward and Laford 1995) to maintain soil temperatures within satisfactory limits in order to avoid reduction in degradation rates that will occur at lower temperatures (Goloeke and Diaz 1989; Bourquin 1989). During periods where the night-time temperatures drop below freezing, air injection can be controlled by a timer or by a thermostat so that air is injected only during the warmest part of the day.

Passive Air Systems. If the cell is constructed with a highly-porous medium and the dimensions are relatively small (e.g., all soil is within 0.5 m (1.5 ft) of the cell surface), sufficient diffusion of air may occur passively and active air supply may not be necessary. Several small systems have been constructed using bulking and/or foaming agents blended with nutrients and, in some cases, surfactants or microorganisms to increase soil porosity.

Use of Slow Release Oxygen Compounds. Field tests have been conducted with both calcium peroxide and magnesium peroxide. Upon contact with moist soils, these compounds will release oxygen over a period of a few months to a year. Their use eliminates the need for injection or extraction of air thereby simplifying construction and operation (no piping or mechanical system is required and no point discharge is created). Once constructed, the cell requires no attention other than periodic monitoring to ensure adequate soil moisture levels and to determine the progress of soil treatment. These sources of oxygen are relatively expensive on a per-pound basis; to be cost-effective, the mass of contaminant to be treated must be relatively small

and the savings achieved by eliminating an air system and operating and maintenance labor must offset the cost of the oxygen source.

4.4.4.2 Permanent Cells

Cells can be built into the side of hills or otherwise incorporated into the landscape. Permanent cell construction is very similar to that of standard cells, except that when soil remediation is complete, the hardware is removed, and the soil remains in place. Depending upon the construction of the cell and the future use of the area, the liner may be removed and the top of the cell seeded.

4.4.4.3 Subsurface Systems

Where space is at a premium, soil cells can be built in a lined excavation, either the excavation from which the treated soils were removed or a new excavation. These cells are built along the same principles as a standard bioremediation soil cell, except they are located beneath the surface and left in place after treatment is complete.

The first known subsurface system was constructed at a service station in Riverside, California in 1985 and was the basis of U.S. Patent 4,849,360. This cell was built by adding 10 to 15 cm (4 to 6 in.) of gravel to the bottom of a lined pit in which was placed a slotted PVC manifold. One end of the manifold was connected to an inlet pipe that extended above the surface. The other end was connected to a PVC pipe that extended to the top of the service station building and was fitted with a windblown turbine to provide a slight negative pressure. Soil amended with nutrients and moisture was added in 2-ft lifts. Ten to 15 cm (4 to 6 in.) of gravel was placed along with another PVC manifold between each soil layer. The top of the cell was completed at ground level with an impervious cover, 10 to 15 cm (4 to 6 in.) of gravel, and asphalt. The only surface indication of the cell were four manhole covers that served as sampling locations. Other below-grade cells have been constructed using vertical, slotted-PVC pipes to extract air. This modification simplifies construction.

4.4.4.4 Percolation Systems

Any of the above modified methods or the standard design can be modified to include the percolation of water amended with nutrients and/or electron acceptors if relatively-permeable soil matrices are to be treated. Drip irrigation systems or other suitable tubing is placed on the top of or within the soils and are connected to an amended water source. Water is added

periodically and allowed to flow down through the soil cell. If too much water is added, portions of the cell will become anaerobic unless the water is amended with sufficient oxygen. If too little water is added, only a portion of the soils will be affected by the water addition.

4.4.4.5 Aerobic Composting

The applicability of soil cells can be extended to treat less easily-degradable compounds by including compost components: bulking agent (e.g., hay), organic food source (e.g., horse feed), and manure (e.g., cow, horse, chicken) (Norris et al. 1996). The microorganisms growing in the manure use the organic food source to grow new cells and fortuitously release enzymes that can break down difficult-to-degrade compounds such as explosives (e.g., TNT, RDX, HMX) (Williams, Ziegenfuss, and Sisk 1992) and chlorophenol (Semple and Fermor 1995). The degradation of the organic food source generates heat and can raise the compost temperature sufficiently (to 40 to 60°C) to activate thermophilic microorganisms at the expense of the mesophilic microorganisms. When animal waste is used as an amendment, temperatures of approximately 70°C must be retained for 3 days in order to ensure pathogen destruction and prevent the spread of disease. EPA guidance on pathogen control in composting systems should be followed.

Under thermophilic conditions, degradation rates are faster and may result in a greater degree of mineralization, whereas at lower temperatures production of toxic byproducts such as aminodinitrotoluenes and diaminonitrotoluenes from TNT may occur. Because of the large amount of heat that can be produced, aeration is critical to prevent temperatures detrimental to the thermophilic microorganisms. Systems similar to a standard soil cell, windrow systems that are turned daily but lack active aeration, and mechanical reactor systems have all been used. Most of the published work in this area has resulted from projects sponsored by the US DoD (Griest et al. 1991; Wilson 1992; Major, Ballag, and Ames 1994). A good discussion of the engineering practices associated with composting is found in *Bioremediation Engineering: Design and Application* (Cookson 1995).

4.4.4.6 Anaerobic Composting

Compared to aerobic composting systems, anaerobic composting produces about 20% as much biomass, requires less energy input during operation because oxygen is not provided to the treatment system, uses approximately 10 times higher loading factors, and produces a smaller volume of residue. On the other hand, anaerobic systems are less stable and require

additional controls; offgas treatment may be required for odor control; the acclimation period may be longer unless a source of bacteria is added to the compost; and the microorganisms may be more susceptible to toxicants, thus requiring adapted microorganisms. Anaerobic systems are compatible with sustainable-growth objectives because methane is produced and can be used for an energy source (at a value equivalent to 10 to 20% of composting costs) and the solid residue is a good soil additive. Anaerobic compost systems are now being used in Europe to treat pulp wastes, chlorophenols, and munitions such as TNT. They also can be used for reductive dechlorination of chlorinated solvents.

4.4.4.7 Fungi-Based Systems

Another approach to addressing compounds that are difficult to degrade is the use of various types of fungi, primarily species related to white rot fungus (Norris and Harvey 1994). The soil to be treated is mixed with: (1) cultures of fungi that have been tested using the site soil to determine the effectiveness of the fungal culture; and (2) a bulking agent such as hay, sawdust, or rice hulls. The enzymes produced by the fungi are capable of degrading a wide range of compounds including PCBs, PAHs, pesticides, and explosives. Limited field demonstrations and a few commercial applications have met with some limited success.

4.4.5 Pretreatment Processes

Pretreatment for soil treatment cells includes site and soil preparation and nutrient addition as required by site-specific conditions. The area where the cell is to be constructed may require grubbing and grading. The contaminated soils may have to be screened to remove large objects such as rocks, timber, limbs, etc. If the soils are too wet, they may require draining or spreading to remove excess moisture.

Soils with a high clay content are especially problematic. The possible pretreatments include:

- shredding to reduce particle size;
- adding bulking agents such as wood chips or gravel to improve aeration;
- adding Pozzolanic materials for stability; and
- adding gypsum and sand to reduce moisture content and plasticity tendencies.

However, the total volume of additives should not increase the soil volume by more than 5 to 10% or the cost of the amendments plus costs for treating a larger volume may negate the cost-effectiveness of the pretreatment.

Typically, soils to be treated are blended with nutrients. The amount of nutrients required can be determined in laboratory tests or estimated using a C:N:P ratio varying from 100:10:1 to 350:10:1 based on the stoichiometry of these elements within cells and taking into account that: (1) nutrients can be recycled, and (2) some of the contaminant will be mineralized rather than utilized for cell growth. In some cases, easily-degraded organic material is added to stimulate growth.

Nutrients can be added to the soil blend prior to homogenization or shredding in the stockpile, or in the treatment cell. One labor-intensive method is to add the nutrient blend to the top of a small pile of soil and work the soil with a bulldozer or front-end loader. A second method is to spray the soil with a nutrient solution whose concentration is based on both the nutrient requirements and the need or tolerance for additional moisture. The nutrient solution can be sprayed on soils when they are being stockpiled or it can be added to the cell. For large cells, a water truck can be used to periodically spray the soil as the cell is being constructed. Periodic determination of the soil moisture content is necessary so that timely adjustments to the spraying schedule can be made.

4.4.6 Posttreatment Processes

Posttreatment may be required for gases or leachate generated during treatment. The selection of an offgas treatment system will depend upon the specific compounds present, the air flow rate, and the concentrations of the individual components. Typically, unless the air flow rate is gradually increased over the first several weeks of operations, the concentration of VOCs in the offgas will decrease rapidly after a few weeks of operation. The load on the offgas treatment system can be reduced by recirculating a portion of the offgas during the initial period of operation and/or by initially operating at a low air flow rate. Where the concentrations of VOCs in the offgas are relatively low, a biofilter (see Chapter 6) may be a cost-effective offgas treatment system and could be constructed similarly to a soil cell. Where the air flow velocity and VOC concentrations are both relatively small but still require treatment, activated carbon is probably the most cost-effective offgas treatment system. For offgases with high VOC concentrations, a catalytic converter or combustion unit may be preferable, especially during the initial operating period.

In a few cases, it will be necessary to treat leachate from the cell. The leachate may require filtration to remove fines and can generally be treated using activated carbon unless heavy metals exceeding discharge limits are present.

Treated soils can be returned to the excavation, spread on the ground, or used as fill material. If bulking agents are used, they must be separated from the treated soil prior to use in locations where soil stability will be an issue.

4.4.7 Process Instrumentation and Control

Biocells are fairly simple systems to operate and thus require less instrumentation and controls than most other remediation systems. The active components are the blower and, in some cases, an offgas treatment system. Unless the cell is being routinely inspected (e.g., every few days), it is advisable to provide sensing equipment and telemetry so that operating personnel can be alerted to a blower shutdown. The blower should be interconnected with an offgas treatment system using combustion units or catalytic converters so that the blower will shut off if the treatment unit fails.

Some states require that the discharge from the offgas treatment system be continuously monitored so that the entire system can be shut down if air discharge limits are not being met. In these cases, automatic sampling systems and programmable logic controllers should be used. Once this level of sophistication is incorporated into the system, a remote access system should be used so that monitoring can be conducted from the operator's office.

Monitoring can be extended to measuring air samples ahead of the offgas treatment system and at several or all gas extraction lines if required. In addition to measuring VOC concentrations, oxygen and carbon dioxide can be measured on a continuous or periodic basis using meters with recorders or, preferably, linked to a computer for permanent record generation.

4.4.8 Process and Instrumentation Diagrams

Process and instrumentation diagrams should illustrate the following:

- dimensions of the cell(s) including height, length, width, slopes, and berms as well as liners and permeable bases;
- electrical system and controls; and
- blower system and offgas treatment system.

Details should include location and type of pressure gauges, valves, sampling ports, meters, and controller sensors.

4.4.9 Sample Calculations

During the technology evaluation stages, it is relatively easy to calculate the total mass of contaminants present and thus the stoichiometric requirements for electron acceptors and nutrients. In calculating the total mass of contaminants, it is necessary to understand the variability inherent in soil samples and the compounds being measured. For example:

- results of TPH analysis of sample splits using the same analytical method vary widely among laboratories. Plus, TPH measures *all* nonvolatile compounds containing carbon-hydrogen bonds;
- BTEX analysis reports only those four monoaromatic hydrocarbons and thus does not identify many of the compounds that exert an electron acceptor demand; and
- a full GC/MS analysis does not identify many compounds that add to electron acceptor consumption.

Therefore, soil samples should be well homogenized and representative of the complete range and distribution of contaminant concentrations contained within the cell.

As previously indicated, it is common to estimate oxygen demand as equal to three times the mass of total biodegradable hydrocarbons, and nutrient requirements according to the C:N:P ratio of 100:10:1 to 350:10:1.

The time required to supply the needed oxygen is calculated from the design air flow rate, the oxygen demand, and an estimate of the percent of the oxygen utilized (consumed in the cell).

The mass of contaminant in the soil is calculated as follows:

$$M = V_s \rho_T C_{avg} / 10^6 \tag{4.7}$$

where:

M = contaminated mass (kg)
V_s = soil volume (m^3);
ρ_T = soil bulk density ($\cong$ 1,350 kg/m^3); and
C_{avg} = average contaminant soil concentration (mg/kg).

The oxygen requirement for biodegradation is estimated as three times the contaminant mass:

$$V_a = \frac{3M}{\rho_{air}(FO_2)} \tag{4.8}$$

where:

V_a = the volume of air (m^3);
ρ_{air} = the air density (12 kg/m^3); and
FO_2 = fraction of O_2 in air (0.21).

Assuming zero-order kinetics, the average concentration of the contaminant can be divided by the measured biodegradation rate (K_o), to estimate a time required for soil remediation as:

$$T = \frac{C_{avg}}{K_o} \tag{4.9}$$

where:

T = the estimated treatment time (days); and
K_o = the measured biodegradation rate.

If K_o is not known, calculations should be done with a range of biodegradation rates to estimate worst- and best-case scenarios for soil pile treatment time. The normal range of biodegradation rates reported in the literature is 20 to 100 mg contaminant/kg of soil/day.

The volume of air required, V_a, is then divided by the estimated treatment time, T, to yield an estimated design air flow rate.

4.4.10 Safety Requirements

Safety considerations include preparation and review of a site-specific health and safety plan (HSP) which prescribes safe practices for excavation and handling of soil, electrical systems (including provisions for ground fault protection), and handling of contaminated soils and gases. The offgas from some soil cells may exceed the lower explosive limit (LEL) for the particular gas mixture. Consequently, all gas handling and treatment system components should be intrinsically safe; catalytic converters need to be designed to draw dilution air if the effluent exceeds the LEL. LEL and VOC meters should be used during construction and operation of the cell to identify leaks or gases that exceed levels specified in the HSP.

4.4.11 Specification Development

System specifications must prescribe the essential design features discussed in the preceding section. Table 4.7 summarizes the range of design parameters commonly encountered.

Table 4.7
Physical and Operational Characteristics of Typical Soil Cell Systems

Parameter	Typical Range of Values
Compound Type	Biodegradable
Soil Concentration	Below Inhibitory/Toxic Levels
	(<10 wt% TPH)
Operating Mode	Maximum Retention Time and Aerobic Conditions
Air Flow Rates	4.6 to 23 actual L/s (2 to 10 acfm) Continuous
	230 to 920 actual L/s (100 to 400 acfm) Intermittent
Operating Vacuum	25 to 50 cm (10 to 20 in.) H_2O
Optimal Soil Moisture	75% Field Capacity
Nutrient Requirement	C:N:P 100:10:1[a]
Soil Gas O_2 Levels	>2 vol%
Pile Configuration	Height: 1.5 to 2.5 m (5 to 8 ft)
	Width: 9 to 20 m (30 to 65 ft)
	Length: 30 to 50 m (100 to 165 ft)
Average Volume/Pile	200 to 1,500 m^3 (260 to 1,600 yd^3)
Air Piping Diameter	10 to 15 cm (4 to 6 in.)
Monitoring Well Diameter	2.5 to 5 cm (1 to 2 in.)

[a]This ratio represents a maximum theoretical requirement that may or may not be needed at a given site.

Bottom liners should provide sufficient strength and tear resistance to withstand the construction process without failure. The condition of the base beneath the liner and the properties of the porous material placed on the liner will dictate the liner minimum thickness and material type.

Covers must be sufficiently strong to withstand the strongest winds that might be encountered in the treatment area and the limited loadings that may occur when sampling soil gas and, less frequently, soils.

Typically, 100-mm (4-in.) diameter Schedule 80 PVC pipe is used for the air extraction pipes placed within the cell. Depending upon the air flow rate and the longest distance to the blower, either 100-mm (4-in.) or 150-mm (6-in.) diameter PVC pipe is used for the headers.

Regenerative blowers are commonly used for soil cells. Blower selection is based on volumetric air flow rates because pressure drops are usually insignificant. Blowers must be intrinsically safe.

Water traps should be placed between the soil cell and the blower to prevent damage to the blower. The water traps should also be capable of removing fines that may become airborne. Trapped water will have to be disposed or added to the leachate sump.

4.4.12 Cost Data

Costs are highly dependent on cell size. To treat under 1,000 m^3 (1,300 yd^3) of contaminated soil, costs will be approximately \$100/m^3 (\$76/yd^3). For soil volumes in excess of 10,000 m^3, costs should approach \$25 to \$30/m^3 (\$19 to \$23/yd^3). Offgas treatment for soils with greater than 100 mg/kg of VOCs can add 25 to 50% to the cost. Even higher costs will result if halogenated VOCs must be treated. The skill and experience of the contractor will also affect the costs; inefficient soil handling techniques can add \$5 to \$10/m^3 (\$4 to \$8/yd^3). Table 4.8 summarizes the costs for treatment of 5,000 m^3 of #2 fuel oil-contaminated soil with offgas treatment solely for control of nuisance vapors.

4.4.13 Design Validation

The dimensions of the designed cell should be compared to the volume of soil to be treated and the available space to ensure that all of the soils requiring treatment can be accommodated. Sometimes this may be difficult because the final volume of soils to be excavated will be determined by bottom and side wall sampling during the excavation. In these cases, the design must be flexible and allow for variations in the height or the footprint of the cell.

Designs and estimated treatment times should be compared to case histories to identify any oversights. Oxygen requirements and anticipated degradation rates should be confirmed with available information including either laboratory or field respirometry test results.

Blower capacity and offgas treatment system capacity should be compared. The offgas treatment system's ability to treat offgas components at the expected flow rate should be confirmed by the manufacturer and compared to past experience and design recommendations.

Because soil cells are ex-situ systems, some validation tasks cannot be conducted until startup as discussed in Section 4.4.17.

Table 4.8
Typical Soil Cell Process Costs[a,b,c]

Cost Element	Unit Costs ($)	No. of Units	Costs ($)
ENGINEERING			
Prepare Work Plan	2,000	1	2,000
Laboratory Tests	1,000	1	1,000
Design	5,000	1	5,000
Subtotal, Engineering			**8,000**
TREATMENT COSTS			
Soil Excavation and Handling	4/m^3	3,000	12,000
PAD Preparation	10,000	1	10,000
Materials	20,000	1	20,000
Construction	10/m	3,000	30,000
Operation & Maintenance	12,000	1	12,000
Analytical	5,000	1	5,000
Management	4,000	1	4,000
Subtotal, Treatment Costs			**93,000**
CLOSURE			
Final Soil Sampling	3,000	1	3,000
Final Report	4,000	1	4,000
Site Restoration	12,000	1	12,000
Subtotal, Closure			**19,000**
GRAND TOTAL			**120,000**

[a]Assumes 5,000 m^3 and 6 months operation. Contaminant is 2,000 - 5,000 mg/kg #2 fuel oil. Air emissions treated with activated carbon to control odors.
[b]State-mandated program with minimal requirements for work plans, etc.
[c]Assumes site investigation completed.

4.4.14 Permitting Requirements

As with all other technologies, permit requirements vary from state to state. The major permitting concern is the air discharge permit. In some states, these air permit requirements are fairly lenient while in others, they are strict and complex. A discussion on air permit requirements is provided in the corresponding section on bioventing, Section 4.2.14. In some cases, water discharge permits may also be required.

All construction and electrical permits will have to be obtained from the appropriate local regulating body.

4.4.15 Design Checklist

Prior to implementation of the design, the items listed in Table 4.9 should be reviewed.

4.4.16 Implementation

An important aspect of soil cell implementation is the management of soil during construction. Stockpile locations, as well as soil pretreatment areas, need to be located so that soil handling and types of equipment used are minimized. Equipment selection, both type and size, is important to the efficiency of the process. Where rain may be heavy during construction, provisions need to be made to cover the soils within the excavation, stockpiles, and uncompleted cell areas.

The liner must be installed so that the porous material can be put in place without damaging the liner. Depending upon the equipment used and the dimensions of the cell, it may be necessary to roll the liner out as the addition of the porous material proceeds.

Homogenization, shredding, blending, and amending of soils should be performed close enough to either the excavation area or the constructed cell so that transport of soil in front-end loaders or other equipment is minimized. If a screen/shredder is used, amendments can be added at the same time, and if transport over long distances is necessary, the pretreated soil can be added directly to a dump truck.

Prior to soil placement in the cell, representative soil samples should be collected to provide a statistically significant (five to eight samples) determination of baseline concentration(s) of the contaminants.

Placement of the soils on the cell must be accomplished such that minimal compaction occurs and damage to the geofabric is avoided. Front-end loaders, conveyor belts, and low compaction equipment have all been used for soil placement. Consideration has to be given to the sequence of adding soil and installing PVC pipelines. While all pipes do not have to be precisely placed, it is important to avoid creating voids and to ensure that each pipe is laid on a slope so that water will not be trapped in the soil pipe section between the slotted PVC pipe and the manifold. For most soils, it is advisable to wrap the slotted PVC pipe sections with a geofabric to prevent fines from clogging the pores or filling the pipes.

Table 4.9
Soil Cell Design Checklist

Soil Characterization	Type and distribution of contaminants
	Soil type (particle size distribution)
	Soil moisture content (% field saturation)
	Total mass VOCs
	Volume/extent excavation
Site Information	Infrastructure near excavation
	Space for cell and cell construction
	Underground utilities
	Paved areas
	Normal site use/traffic patterns
Test Results	Laboratory
	Respiration
Design	Leachate recovery
	Off-gas treatment
	Blower capacity
	Electrical system
	Monitoring system
	Liners
	Piping, valves, controls
	Nutrient levels/source
	Remedial goals achievable
O&M Plan	Cover maintenance
	Leachate control
	Off-gas treatment
	Monitoring
	Soil moisture
Health and Safety	HSP complete/kept on-site
	Personnel trained
	Ground faults
	Electrical system inspection
	Security
	Emergency shutdown procedures
Miscellaneous	Permits
	O&M manual reviewed
	Monitoring schedule
	Treated soil placement
	Site restoration

The electrical supply and equipment pads should be in place prior to or during the early stages of construction so that the system can be started as soon as possible, thus minimizing the opportunities for anaerobic conditions to develop.

In addition to the blower and the offgas treatment system, all electrical equipment, meters, valves, gauges, controllers, and monitors should be tested as early as practical so that replacements, if needed, can be obtained quickly to minimize or avoid delays.

4.4.17 Start-up Procedures

All personnel involved with the project should review all operating, shutdown, and safety procedures before arriving at the site and again before turning on the system.

All of the meters, gauges, and electrical components; the blower; and the offgas system should be inspected and tested to the extent practical before turning on the blower. The blower should be started with all valves in their wide-open positions including the blower air relief valve so that there is a relatively low flow rate from the soil cell, allowing the offgas treatment system to be tested. Then, the blower relief valve is closed gradually until the design flow rate is achieved. Discharge from the offgas treatment system is continuously monitored to ensure compliance.

Air flow rate, pressures, and VOC concentrations are determined for the blower influent and effluent as well as for the offgas treatment system. Once it is clear that discharge requirements are being met, the air flows and pressures at the individual PVC lines are measured, and the system is balanced so that flows from each line are approximately equal unless the design calls for higher flows through some soils based on the level or type of contamination. After the cell has been operating for 24 hours, oxygen, carbon dioxide, and VOC levels are determined from each PVC line sampling port and from the soil gas probes. This sampling is repeated in another 48 hours. Based on the relative oxygen and carbon dioxide levels in the various parts of the soil cell, the flow rates from individual areas are modified to keep all parts of the cell aerobic.

4.4.18 Performance Evaluation

Performance evaluation is much the same as for bioventing. Routine measurements of the air samples for oxygen, carbon dioxide, and VOCs provide the basis for implementing changes in operating conditions.

Respiration rates are routinely measured as indicators of progress of treatment as discussed in Section 4.2.18.3.

4.4.18.1 Operation Practices

Operation is fairly simple, consisting primarily of adjustments to the air flow rate to achieve a balance between minimization of offgas treatment costs and achievement of the shortest practical treatment time. Management of soil moisture and temperature may also be important.

During operation, flow rates from individual sections of the cell may be modified based on differences in degradation rates and/or contaminant loadings. To avoid "dead spots", some PVC extraction lines can be turned off and/or switched from extraction to inlet lines. Other options include cycling the cell from off to on and cycling some air extraction lines to air inlet lines. Once VOC levels have decreased sufficiently, it may be advisable to switch the system to air injection and terminate offgas treatment. Another possibility is to recycle a portion of the extracted air to avoid offgas treatment or reduce the demand on the offgas treatment system. However, catalytic converters and combustion units will operate less efficiently after the VOC concentration drops below concentrations at which the energy from the oxidation of the VOCs is contributing significantly to preheating of the influent gas.

In some cases, it may be necessary to add more nutrients or moisture if the moisture level drops below about 30% field capacity. Preferably, nutrient requirements and soil moisture are managed during soil preparation and by control of operating conditions. If not, water must be added to the top of the cell and/or through the PVC extraction lines. If irrigation lines were not provided, the cover must be removed, and the top of the cell must be irrigated or sprayed with nutrient-amended water. However, addition of water increases the probability of generating leachate that may need to be recycled to the cell or treated and disposed.

In cold climates, it may be necessary to preheat air introduced into the cell. The requirement for heat can be minimized by covering the cell with several centimeters of hay. The hay will act as insulation and can also generate heat through decomposition. A dark-colored cover will also absorb heat during daylight hours. The energy requirements for heating the air can be minimized by injecting air (or introducing it under the cover) only during the warmest part of the day.

4.4.18.2 Operation Monitoring

Routine measurements are made for VOCs, oxygen, carbon dioxide, air flow rate, vacuum readings, and offgas treatment efficiency. These measurements consist of:

- vacuum readings at soil gas probes;
- air flow rates at the end of individual air extraction lines, the manifold, and the blower discharge;
- contaminant levels in air samples from soil gas probes, individual air extraction lines, blower influent, and offgas treatment effluent;
- carbon dioxide and oxygen concentrations in air samples from soil gas probes, individual extraction lines, and the manifold;
- moisture content in air samples collected from the manifold;
- air temperatures within the soil cell, blower inlet, and blower effluent;
- respiration tests (oxygen utilization rate determinations with the blowers off to assess the progress of contaminant degradation in the soil cell); and
- moisture, nutrients, and contaminant levels in soil samples.

Respiration tests are easily conducted and more cost-effective than analyzing numerous soil samples. The tests are performed by interrupting air flow and measuring oxygen and carbon dioxide concentrations in soil cell sampling points over time prior to air flow being re-established. The test results can be compared to the respirometry test results obtained prior to startup as an indication of the removal of degradable contaminants in the soil cell over time.

To the extent practical, measurements should be automated. Most VOC measurements can be made with portable photoionization or flame ionization organic vapor analyzers (see Section 4.2.18.3 for a discussion of respiration rate methods) with periodic laboratory or field gas chromatography verification of field instrument results.

Monitoring frequency is highest during startup and the first several days of operation and decreases over the first month of operation. In subsequent months, monthly or bimonthly measurements for all parameters are adequate unless regulatory requirements dictate otherwise.

The data, primarily the oxygen and carbon dioxide data, are used to calculate the extent and rate of degradation and to identify changes in operating conditions that will improve performance and/or reduce costs.

Carbon dioxide production and oxygen depletion data should be used to estimate contaminant degradation rates. These estimates should be compared with periodic soil sample analyses for contaminant levels, the total VOC removal in the offgas, and the initial contaminant concentrations.

4.4.18.3 Quality Assurance/Quality Control

Quality assurance and quality control practices include those common to other remediation technologies, i.e., the use of blanks, blind duplicates, and spiked samples for laboratory and field measurements and review of data for consistency to identify potential mislabeling and similar problems. Quality practices specific to soil cells are very similar to those for bioventing as discussed in Section 4.2.18.4.

4.5 Emerging Technology — Phytoremediation

Phytoremediation can be broadly defined as the direct or indirect use of green plants for in situ or ex-situ remediation of contaminated soil, groundwater, surface water, wastewater, or air. Phytoremediation is an emerging biologically-based technology that has generated interest due to its potential application as a feasible remediation technology that is economically favorable and environmentally acceptable relative to other more active and intrusive remedial technologies. However, commercialization of phytoremediation has been limited to date. This section provides a brief introduction to this emerging technology, an overview of the principles and processes of phytoremediation, and examples of phytoremediation research and application.

Phytoremediation is a diverse field for research and application efforts. Numerous definitions of phytoremediation have been used that focus on, or are limited to, the particular contaminant, matrix, process, or objective of interest to the researcher (Raskin et al. 1994; Gatliff 1994; Schnoor et al. 1995; Salt et al. 1995; Cunningham, Berti, and Huang 1995a; Cornish et al. 1995). The broad definition given above encompasses all of these aspects. Many terms have been used in association with the overall concept of

phytoremediation, generally with the prefix "phyto-" (Cunningham, Berti, and Huang 1995a). Some commonly used terms for different phytoremediation processes may overlap somewhat in meaning but are useful for understanding the basis of each phytoremediation process:

- *Phytoextraction* — The uptake of toxic metals and radionuclides from soil by plant roots, with accumulation of the contaminants in the aboveground portion of the plant that can be harvested and processed (Raskin et al. 1994; Kumar et al. 1995; Salt et al. 1995; Cunningham, Berti, and Huang 1995b).
- *Phytostabilization* — The use of plants to alter the soil environment or contaminant chemistry in order to decrease the transport of toxic metals by precipitating, absorbing, sequestering, or degrading the contaminant (Raskin et al. 1994; Cunningham, Berti, and Huang 1995a, 1995b).
- *Rhizofiltration* — The removal of heavy metals from water by absorption, precipitation, and concentration of the metals on plant roots (Dushenkov et al. 1995; Salt et al. 1995).
- *Rhizodegradation* — The enhancement by plants of microbial degradation of organic contaminants in the rhizosphere (the soil zone around the plant roots that has significantly greater microbial numbers and activity than the bulk soil) (Cunningham, Berti, and Huang 1995a); also called plant-assisted bioremediation (Salt et al. 1995) or plant-aided in situ biodegradation (Shimp et al. 1993).
- *Phytodegradation* — The conversion of organic contaminants into nontoxic materials through absorption, uptake, or degradation by the plant or plant-associated microflora (Cunningham, Berti, and Huang 1995b).
- *Phytovolatilization* — The uptake, transpiration, and volatilization of contaminants by a plant (USEPA 1996a).
- *Hydrologic Control* — The use of vegetation to remove or contain contaminated groundwater or vadose zone water or to prevent infiltration into or leaching of contaminated media.

These terms and their definitions indicate that phytoremediation is actually a group of processes controlled or affected by plants and applicable to different contaminated media and different types of contaminants. The overall technology of phytoremediation encompasses many processes and applications. The basic mechanisms, applicability under certain conditions,

efficacy, and many practical details of most of these processes and applications are still being investigated. There are limited field data for experimental phytoremediation systems, let alone for large-scale systems. A small subset of phytoremediation processes or applications, such as poplars as landfill covers to reduce infiltration and to metabolize nutrient-rich wastewater, have seen some large-scale use, but most phytoremediation processes or applications have not yet been used on a routine basis.

Vegetation has long played a role in environmental activities and the use of plants for environmental remediation is not limited to contaminated soil. Plants may be used in natural, engineered, or ex-situ systems to remediate groundwater, surface water, or wastewater. Vegetation, including both trees and plants, has been used to influence the movement of contaminated groundwater and vadose zone water. Plants have been used to reclaim mine tailings and land impacted by mining and smelter operations, stabilize and optimize soil systems for land application of wastes, and cover hazardous waste sites. Vegetation can be used in hazardous waste site investigations as an indication of the presence of soil contamination, or as a bioassay to assess the effectiveness of other remedial activities. The major forms of phytoremediation are summarized in Table 4.10.

4.5.1 Principles of Operation

Phytoremediation principles of operation depend on the contaminant matrix and the type of contamination. Several excellent review articles provide detailed discussions and examples of the various phytoremediation principles (Anderson, Guthrie, and Walton 1993; Shimp et al. 1993; Schnoor et al. 1995; Salt et al. 1995; Cunningham, Berti, and Huang 1995a, 1995b). Principles of phytoremediation operation for soil and water along with additional remediation-related uses of plants are presented below.

4.5.1.1 Soil

Phytoremediation of contaminated soil occurs through three general processes: (1) plant uptake of the contaminant (phytoextraction, phytodegradation, and phytovolatilization); (2) stimulation of microbial biodegradation in the soil by plant roots (rhizodegradation); and (3) modification of soil chemistry by the plant that causes immobilization or degradation of the contaminant (phytostabilization and phytodegradation). In addition, vegetation can alter the chemical, physical, or biological characteristics of the soil in ways that can affect processes controlling chemical transport and fate.

Table 4.10
Mechanisms and End Results of Phytoremediation Processes

Term/Process	Primary Mechanisms	End Result	Target Contaminant	Depth	Comments
Phytoextraction	Plant uptake	Contaminants harvested above-ground	Metals, radionuclides	Plant root zone	Consumption by animals is a concern; low biomass limits effectiveness
Phytostabilization	Root uptake, alteration of soil chemistry	Contaminants immobilized in soil or in roots	Metals, radionuclides	Plant root zone; perhaps slightly deeper effect	Translocation of contaminant to aboveground portion is undesirable
Phytodegradation	Plant or microbial degradation	Contaminants mineralized or degraded	Organics	Plant root zone; perhaps slightly deeper effect	Some overlap with rhizodegradation
Rhizodegradation	Microbial degradation	Contaminants mineralized	Organics	Plant root zone; perhaps slightly deeper effect	Magnitude of effect still unclear
Rhizofiltration	Root absorption, precipitation	Contaminants immobilized or degraded	Metals, nutrients, organics	Plant root zone in solution	Currently used for organics, with constructed wetlands
Hydrologic Control	Water uptake by plants	Groundwater or soil water containment or control	Dissolved contaminants	Tree or plant root zone	Commercial use has started
Phytovolatilization	Plant uptake	Contaminants transported through plants and released to the atmosphere	Volatile metals, organics	Plant root zone; perhaps slightly deeper effect	Transfer of contaminants to the air phase without treatment a concern here

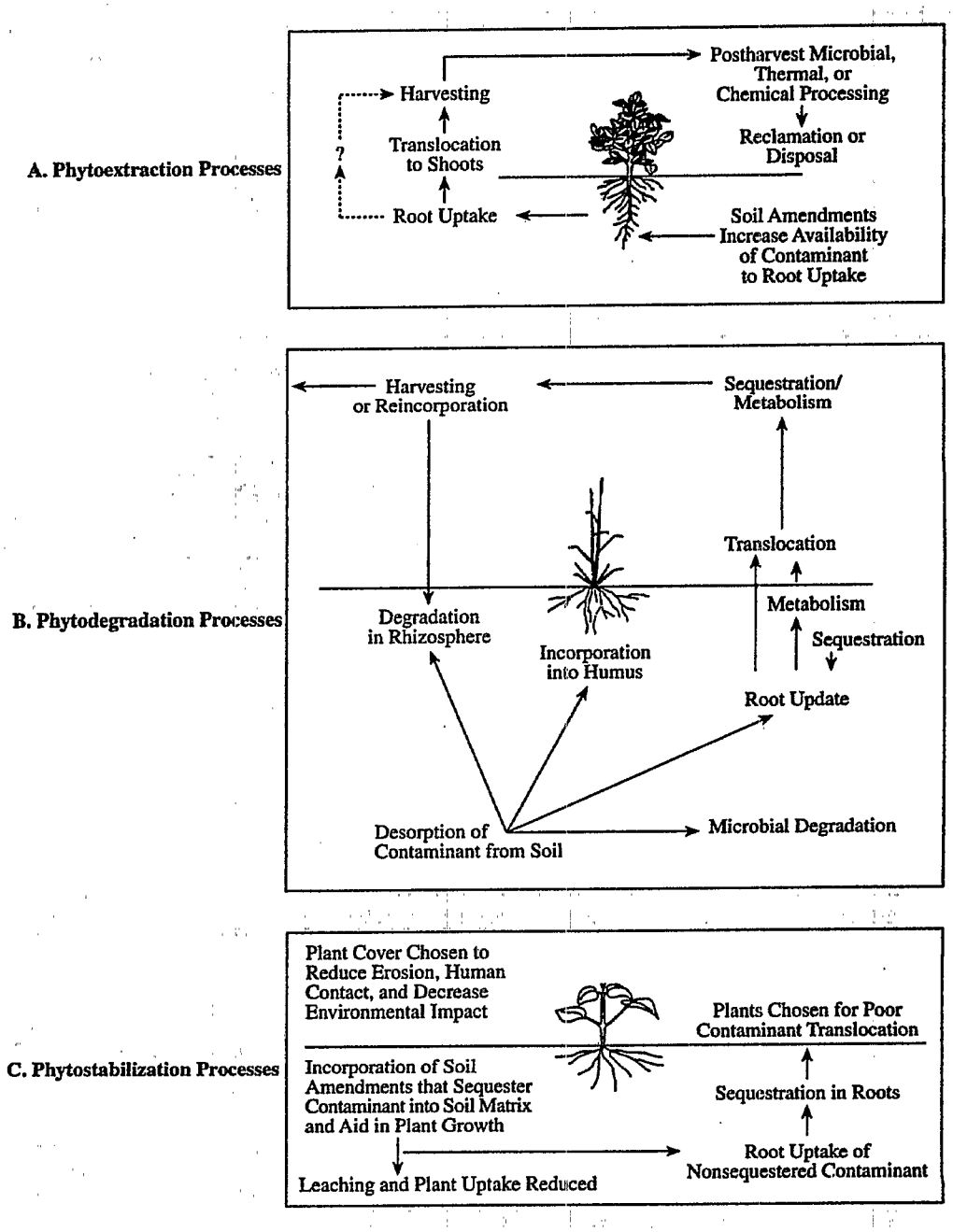
Plant Uptake. Organic and inorganic contaminants are taken up into the plant from the soil. Inorganic nutrients and organic contaminants are then either stored or metabolized within the plant through phytodegradation. In phytoextraction, metals or radionuclides are removed from the soil and accumulated in the aboveground portion of the plant. This part of the vegetation is harvested and disposed or processed for metal reclamation. Reviews and discussions of phytoextraction are provided by Chaney (1983); Cunningham, Berti, and Huang (1995b); Salt et al. (1995); and Cornish et al. (1995). The processes involved in phytoextraction are illustrated in Figure 4.17.

All plants accumulate metals necessary for growth, such as Fe, Mn, Zn, Cu, Mg, Mo, and possibly Ni. Some plants accumulate metals that are not necessary for growth, such as Cd, Cr, Pb, Co, Ag, Se, and Hg (Salt et al. 1995). *Metallophytes* are plants that can grow only in metal-rich soils (Baker, Brooks, and Reeves 1988).

Metallophyte plants have long been sought as an indicator of ore in mineral prospecting (Kumar et al. 1995). Herbarium specimens have been analyzed for metal content, and as far back as 1924 high levels of lead (1300 μg/g) were detected in a plant (*Armeria maritima* var. *halleri*) (Reeves and Brooks 1983). *Hyperaccumulators* are metallophytes that are capable of accumulating an exceptionally high level of a metal, reaching a specified concentration within the dried plant tissue, typically the leaf (Brooks et al. 1977; Baker 1995). The concentration criteria of hyperaccumulators for metals in leaf dry matter are 100 μg/g (0.01%) for Cd; 1,000 μg/g (0.1%) for Co, Cu, Pb, and Ni; and 10,000 μg/g (1.0%) for Mn and Zn (Reeves and Brooks 1983; Baker 1995). Hyperaccumulators have also been defined as those plants containing a toxic element at concentrations 100 times greater than that in other plants growing in the same soil (Cornish et al. 1995). Additional metals, metalloids, non-metals, and radionuclides that have been found in hyperaccumulators include Cr and Hg; Se and As; B; and ^{90}Sr, ^{137}Cs, ^{239}Pu, and ^{238,234}U respectively (Cornish et al. 1995; Kumar et al. 1995; Salt et al. 1995).

Examples of hyperaccumulators include *Thlaspi caerulescens* (alpine pennycress) for Ni and Zn (Brown et al. 1994), *Thlaspi rotundifolium* for Pb (Kumar et al. 1995), *Alyssum wulfenianum* for Ni (Reeves and Brooks 1983), and *Brassica juncea* (Indian mustard) for Pb, Cr, Cd, Ni, ^{90}Sr, B, and Se (Salt et al. 1995). *T. rotundifolium* grown in mine tailings and river gravels contaminated by lead-zinc mines contained up to 8,200 μg/g lead (0.82%) and 17,300 μg/g zinc (1.73%) in the dried leaves, the highest ever reported for any flowering plant (Reeves and Brooks 1983). The extent of hyperaccumulation is defined by the phytoextraction coefficient, which is a

Figure 4.17
Processes Involved in Phytoremediation of Contaminated Soil



Source: Cunningham, Berti, and Huang 1995b

quantitative measurement of the degree of concentration of the metal in the plant defined as the ratio: μg metal/g dry weight tissue to the μg metal/g dry weight soil. Phytoextraction coefficients determined experimentally for *B. juncea* were 58 (Cr^{6+}), 52 (Cd^{2+}), 31 (Ni^{2+}), 17 (Zn^{2+}), 7 (Cu^{2+}), 1.7 (Pb^{2+}), and 0.1 (Cr^{3+}) (Kumar et al. 1995).

Few plant species are hyperaccumulators. One tabulation of hyperaccumulators indicated more than 300 taxonomic groups (taxa) for Ni, 26 for Co, 24 for Cu, 18 for Zn, 8 for Mn, 5 for Pb, and 1 for Cd. The most significant plant families containing hyperaccumulators include the *Brassicaceae*, *Euphorbiaceae*, *Asteraceae*, *Lamiaceae*, and *Scrophulariaceae* (Baker 1995); plants within each family accumulate a variety of metals.

Indicator plants do not accumulate metals to the same extent as hyperaccumulators. Instead, they are plants whose metal concentrations, acquired through passive uptake, reflect the soil concentration (Baker 1995). *Silene vulgaris* (bladder campion) is an example of an indicator plant. Indicator plants do not effectively concentrate metals for phytoextraction but can tolerate high concentrations of metals and therefore can be used to stabilize soils at sites prone to erosion (Brown et al. 1994).

Phytoextraction is complex, but Salt et al. (1995) have provided some explanations of the mechanisms. For root uptake, the plant solubilizes bound metals in the soil by secreting metal-chelating molecules (phytosiderophores) or metal-chelating proteins related to metallothioneins or phytochelatins. Plants also solubilize bound metals by using specific plasma membrane-bound metal reductases or by acidifying the soil through proton release. Soluble metal ions are transported into the root cells via specific or generic transmembrane ion carriers or channels. In the translocation of metals from the roots to the shoots, the metal ions move from root cells through intracellular pathways across the Casparian strip into the xylem. Once in the xylem, they are transpired, assisted by metal-chelate complexes. Metals may also be transported in the phloem (Salt et al. 1995). Despite these translocation mechanisms, the roots generally contain higher metal concentrations than the shoots. An upper limit to the metal concentration within the root is known to occur. For example, root uptake of lead by plants grown in hydroponic solution reached a maximum concentration and did not increase further as the lead concentration of the solution increased (Kumar et al. 1995).

Plants resist heavy metals by limiting cellular uptake, detoxifying the heavy metals, or developing heavy-metal-resistant metabolisms. The most likely resistance mechanism is detoxification by chelation and accumulation

within the vacuoles by compartmentalization or precipitation (Salt et al. 1995). Metal exclusion is by reduction of metal uptake, restriction of root-to-shoot transport, and accumulation in roots and shoots (Baker 1995). It is not clear if a plant's tolerance to one metal will induce tolerance to another metal (Reeves and Brooks 1983). Other mechanisms may prevent adverse effects of metals on plants. Lead, which is generally toxic to plants, is usually not accumulated in plants, possibly due to precipitation of lead as sulfate at the plant roots (Reeves and Brooks 1983).

Plants can also take up radionuclides from soil. Corn, sunflower, and tall fescue took up ^{222}Rn and ^{226}Ra (Lewis and MacDonell 1990); ^{99}Tc was absorbed by barley (Sheppard and Evenden 1985); and ^{244}Cm and ^{238}Pu have additionally been identified as being accumulated in trees (Entry et al. 1997). Removal of ^{137}Cs and ^{90}Sr from contaminated soil near the Chernobyl nuclear reactor in Ukraine was accomplished using *B. juncea* (Adler 1996). Uranium and thorium have also been extracted from contaminated soil near uranium mines by harvesting high-yield plants (Koganov and Dawson 1995). Phytoremediation of radionuclides may be appropriate for ^{137}Cs and ^{90}Sr, as there is significant evidence of the accumulation of these radionuclides in vegetation (Entry et al. 1997). There is less evidence for the feasibility of phytoremediation of other radionuclides, and few field trials have been conducted compared to phytoremediation of metals or organics.

In addition to metals, metalloids, radionuclides, and nutrients, plants can take up organic compounds from solution. At least 70 organic chemicals representing many classes of compounds were taken up and accumulated by 88 species of plants and trees (Paterson et al. 1990), although the mechanisms and locations of uptake varied. The degree of uptake varies as a function of plant species and the properties of the chemical compound, such as polar vs. non-polar, solubility, and k_{ow}. Low solubility compounds are less available for transpiration and compounds with intermediate log k_{ow} are more likely to be translocated within the plant. Contaminants such as BTEX, TCE, and chlorinated benzenes can be taken up by vegetation and phytovolatilized. Plant uptake of some contaminants may be uncertain. For example, a study of soil spiked with PCP indicated that after 155 days in the presence of grass, 36% of the PCP was associated with the plant (21% in roots, 15% in shoots)(Qiu et al. 1994). Other studies, however, found minimal uptake of PCP by several plants (Bellin and O'Connor 1990) or insignificant uptake of PAHs by grasses or alfalfa (Schwab and Banks 1994).

Phytovolatilization and hydrologic control depend on the uptake of contaminated water by the plant. In root uptake, water that may contain organic chemicals is absorbed from the soil solution into the outer tissue of the root.

The chemical moves through the epidermis to and through the Casparian strip, and then through the endodermis, where it may be sorbed, bound, or metabolized. Generally, root uptake and bioconcentration within the root is inversely proportional to water solubility or directly proportional to octanol/water partition coefficient. Highly hydrophobic compounds tend to accumulate in roots. The chemicals or metabolites that do pass through the endodermis and reach the xylem are then transported in the transpiration stream or sap. These compounds may react with or partition into plant tissue, be degraded, or be released to the atmosphere through stomatal pores via phytovolatilization (Paterson et al. 1990; Shimp et al. 1993). Phytovolatilization of TCE has occurred in poplar trees; the TCE released by transpiration may break down quickly in sunlight (Adler 1996). Plants can also transpire and volatilize selenium, first converting it from the more toxic selenate form into the less toxic dimethylselenide gas (Adler 1996; Banuelos et al. 1997). Phytovolatilization of mercury has also been studied; the more toxic forms of mercury are converted to elemental mercury and released as a gas (Watanabe 1997).

A root concentration factor for non-ionized compounds taken up by plants with non-woody stems is defined as the concentration in roots divided by the concentration in the external solution. Concentration factors have been similarly defined for the transpiration stream and the stem. Correlation equations have been developed to relate the octanol/water partition coefficient to these concentration factors. The bioconcentration factor (defined on dry weight basis) is the ratio of the concentration in aboveground plant parts to the concentration in the soil (Paterson et al. 1990).

The primary phytoremediation processes for organic compounds that are taken up by plants are phytodegradation (metabolism within the plant) and phytovolatilization (release of the volatile compound or metabolized product) through the stomatal pores. Phytoextraction, or plant harvesting, of organic compounds is unlikely and has not generally been investigated. The harvesting of roots would be infeasible to remediate highly hydrophobic compounds, such as PCBs and DDT that are concentrated in the roots due to their log k_{ow} being too high to allow translocation within the plant.

Stimulation of Biodegradation. Plant roots may stimulate contaminant biodegradation by increasing the microbial populations and activity in the rhizosphere; the roots contribute exudates to the soil that serve as microbial substrates. These exudates include sugars, amino acids, organic acids, fatty acids, sterols, growth factors, nucleotides, flavanones, enzymes, and many other compounds (Shimp et al. 1993; Schnoor et al. 1995). Leachate from roots of specific plants contained compounds that stimulated the growth of

PCB-degrading bacteria (Fletcher, Donnelly, and Hegde 1995). The processes involved in rhizodegradation are shown in the phytodegradation portion of Figure 4.17. Rhizodegradation is applicable to organic contaminants that remain in the soil without being taken up by plants (including relatively strongly-sorbed or hydrophobic compounds), but can also apply to contaminants prior to plant uptake.

Alfalfa plants and associated microorganisms promoted biodegradation rather than volatilization of organic substances from groundwater (Davis et al. 1994). Some enhancement of rhizosphere biodegradation has been found using various grasses in soils contaminated with PAHs (Aprill and Sims 1990; Schwab and Banks 1994), in rhizosphere soil contaminated with the pesticides atrazine and metolachlor (Anderson and Coats 1995), and in TCE-contaminated soil (Anderson and Walton 1995). Radiolabelled PCP was used to examine mineralization in systems planted with crested wheatgrass (*Agropyron desertorum*). After 155 days, 22% of the PCP was mineralized in the planted system, but only 6% in unplanted controls. PCP mineralization rates in soil were 23.1 mg /kg in 20 weeks in the planted system, and 6.6 mg/kg soil in 20 weeks in the unplanted controls (Ferro, Sims, and Bugbee 1994). Mineralization of pyrene also occurred sooner in systems planted with crested wheatgrass than in unvegetated controls (Ferro et al. 1994).

Modification of Soil Environment. Phytostabilization is the use of metal-tolerant plants to reduce erosion of metal-contaminated soil or to reduce leaching of metals by converting them from a soluble to an insoluble oxidation state (Salt et al. 1995). For example, the leaching of metals from soil was reduced by greater than 98% using *B. juncea* (Raskin et al. 1994). Plant root exudates may change the soil pH, which can impact the dissociation of organic compounds or affect metal solubility and mobility. Phytostabilization also refers to the incorporation of organic compounds into the plant lignin (Cunningham, Berti, and Huang 1995b). Phytostabilization processes are summarized in Figure 4.17.

The term phytodegradation can also refer to the degradation of soil contaminants through the chemical action of enzymes released by a plant (Cunningham, Berti, and Huang 1995b). This form of phytodegradation is not dependent on microbial activity, and since plants can grow in the absence of soil microorganisms, it may possibly occur in sterile soils. The extent of this effect will depend on the transport of the enzymes to the contamination site. If the enzymes are not strongly sorbed, they may be transported through the soil so that degradation can occur in locations away from the actual plant root. However, by analogy to the rhizosphere effect, this effect

may be limited to near-root areas. Phytodegradation processes are also shown in Figure 4.17

Indirect Effects on Soil. The presence of a plant that does not directly degrade or remove a contaminant may still be advantageous for other remedial activities, assuming the plant can survive the contamination. Plants contribute organic matter that improves the tilth and water-holding capacity of the soil. The openings formed by plant roots can act as distribution channels into the subsurface for nutrients, water, or oxygen applied at the surface (Shimp et al. 1993). Thus, infiltration of nutrients, water, or oxygen may be aided by the presence of appropriate plants over a large area.

4.5.1.2 Water

Contaminant Immobilization or Removal. Plants may be used in natural systems (wetlands), engineered systems (constructed wetlands), or ex-situ systems (reactors) to remediate groundwater, surface water, or wastewater through degradation or accumulation and removal of the contaminants. Rhizofiltration is the use of plants to withdraw metals from aqueous solutions (Raskin et al. 1994; Dushenkov et al. 1995). Mechanisms that plants use to remove toxic metals or radionuclides such as Pb, Cd, Zn, Cr, Mn, U,and ^{90}Sr from solutions include the nonbiological process of surface sorption (due to chelation, ion exchange, and specific adsorption) and biological processes (intracellular uptake, vacuolar deposition, and translocation to the shoots, in addition to and root-mediated precipitation) (Salt et al. 1995). For example, lead was removed via tissue absorption and by root-mediated precipitation of insoluble lead phosphate (Raskin et al. 1994; Salt et al. 1995). A bioaccumulation coefficient is used to describe the extent of rhizofiltration and is defined as the ratio of the metal in the plant (μg/g dry weight) to the initial solution concentration of the metal (Salt et al. 1995).

Terrestrial or aquatic plants can be used in rhizofiltration of metals and radionuclides. Hydroponically-grown sunflower roots reduced water concentrations of Cr^{6+}, Mn, Cd, Ni, Cu, U, Pb, Zn, and ^{90}Sr (Salt et al. 1995). Roots of plants grown hydroponically concentrated Cr, Cr^{6+}, Cd, Ni, Zn, and Cu from wastewater, with lead having the highest bioaccumulation coefficient and zinc the lowest (Raskin et al. 1994). The aquatic plants, water hyacinth (*Eichhornia crassipes*), pennyworth (*Hydrocotyle umbellata*), duckweed (*Lemna minor*), and water velvet (*Azolla pinnata*) took up Pb, Cu, Cd, Fe, and Zn from solution (Salt et al. 1995).

A few field trials of phytoremediation for radionuclides have been conducted. Rhizofiltration of ^{137}Cs and phytoextraction of ^{90}Sr were tested using

a raft of sunflowers in a contaminated pond near the Chernobyl site. The immobilization of the ^{137}Cs in the roots and the translocation of the ^{90}Sr into the shoots indicated that these phytoremediation methods may be feasible for remediation of water contaminated by radionuclides (Adler 1996). Sunflowers were also used in a successful trial of remediation of uranium-contaminated water at a DOE uranium-processing plant in Ashtabula, Ohio, with further tests planned for uranium-contaminated water at the Oak Ridge National Laboratory (Adler 1996).

Wetland plants can be used in engineered or constructed beds to take up or degrade contaminants. Aquatic macrophytes were used to remove chromium in contaminated wastewater (Vajpayee et al. 1995). Accumulation of arsenic and zinc was also observed in the rhizosphere of wetland plants (Otte, Kearns, and Doyle 1995). Various aquatic macrophytes were evaluated for the removal of nitrogen and phosphorus (Reddy and De Busk 1985).

Water contaminated by organic compounds can also be treated using vegetation. The aquatic plant parrot feather possesses the enzyme that enhances degradation of wastewater containing TNT. Parrot feather decreased TNT from 128 ppm to 10 ppm in flooded mesocosms of soil (Schnoor et al. 1995). Enzymes derived from horseradish roots were used in ex-situ reactors to treat water contaminated with chlorinated phenolic compounds (Dec and Bollag 1994).

Hydrologic Control. Contaminated groundwater and vadose zone water movement can be contained and controlled using plants and trees. Vegetative caps can be used for landfills, sediments, sludges, or contaminated soils as a pollution prevention method. The uptake of water by vegetation can prevent infiltration of rainwater or vadose zone water into the contaminated media and can prevent leacheate formation. Vegetative caps can also be a remediation mechanism as well as a containment mechanism. The vegetation in the cap may remediate the contaminants through rhizodegradation, phytodegradation, or phytovolatilization. Hydrologic control can also be used as a treatment method in conjunction with phytovolatilization. For example, contaminated groundwater or leachate can be pumped and applied to plants or trees for irrigation (Gatliff 1994; Schnoor et al. 1995). Cottonwood and hybrid poplar trees were used at seven sites in the East and Midwest to extract and treat shallow groundwater contaminated with heavy metals, nutrients, or pesticides in conjunction with pump-and-treat systems. The trees apparently contributed to water table drawdown by pumping 190 to 1330 L/day (50 to 350 gal/day) per tree. Tree growth was greater and nitrogen uptake was faster the closer the root ball was planted to the shallow groundwater (Gatliff 1994). Although plant root growth may be restricted to

above the water table, the roots can still influence contaminants in the groundwater. Barley roots were confined to the oxidized zone of the soil, which occurred about 10 cm (4 in.) above the water table interface, but could still absorb Fe, Tc, U, and P that diffused upward from the capillary fringe (Sheppard and Evenden 1985).

4.5.1.3 Additional Applications

Plants can be used to reclaim degraded mining land and stabilize soil for land application of wastes. Uptake of contaminants by crop plants and the potential adverse effects on the food chain were of concern in managing land treatment sites and the motivation for research into uptake mechanisms (Chaney 1983).

Plants useful for the restoration of wetlands that provide wildlife habitat can also remediate contaminated water in the wetlands. A natural salt marsh contaminated with heating oil was restored using *Spartina alterniflora* (smooth cordgrass). The most abundant bacteria in the wetland were those that could metabolize naphthalene as a sole carbon source. The plant provided oxygen to its root zone, so the addition of these plants, along with fertilizers, could have stimulated aerobic biodegradation of the heating oil in the root zone (Bergen and Levandowsky 1994).

Plants can be used as bioassays to assess soil or groundwater contamination or the effectiveness of other remedial activities. Phytotoxicity testing was used to evaluate the degree of bioremediation of a contaminated soil (Baud-Grasset, Baud-Grasset, and Safferman 1993). Sandhu et al. (1991) used an on-site plant (*Tradescantia*) assay to test for levels of As, Cr, and Cu in soil; changes in the micronucleus of the plant correlated with the contaminant levels in the soil. Data from tree rings were used to determine the direction and velocity of a chloride plume in groundwater near a landfill (Vroblesky and Yanosky 1990) and to correlate with concentrations of nickel in a groundwater plume near a landfill and stainless steel plant (Yanosky and Vroblesky 1992).

Plants can be useful in hazardous waste site assessment as indicators of site conditions (i.e., the presence and/or concentrations of soil contaminants) since the visual appearance of the vegetation may reveal overall plant health and associated ecological stresses. Remote sensing and historical air photos can be used in a more elaborate site assessment of vegetation (Nicholson and Safaya 1993). However, correlating plant appearance or health with soil contaminant levels may be difficult or limited to areas of severe contamination or abrupt boundaries since subtle differences in vegetation health or appearance may be due to factors unrelated to the soil contamination.

4.5.1.4 Site, Soil, and Waste Characteristics

Characteristics of the site, soil, and waste that have to be considered when evaluating the applicability of phytoremediation include:

- site characteristics, such as climatic conditions (temperature, precipitation, and length of growing season), open space availability and exposure to sunlight, and disturbance from site activities;
- soil characteristics including chemical characteristics (pH, nutrient content, organic carbon, acidity, salinity, etc.) and physical characteristics (water content, air-filled porosity, hydraulic conductivity, structure, texture, bulk density, tilth, etc.); and
- waste characteristics, such as contaminant concentrations, physical form, contaminant types (amenable to phytoremediation), and contamination depth (not greater than the root zone).

Proper site and soil conditions are critical to plant growth. For example, water-logging resulted in shallow roots and poor growth of buffalograss (*Buchloe dactyloides*) and warm season prairie grasses in phytoremediation test plots established at an industrial site in soils contaminated with relatively low levels of PAHs and PCP (Qiu 1995a).

Some plants can tolerate high concentrations of organics and nutrients better than soil microorganisms (Schnoor et al. 1995). Toxicity screening of different organisms indicated that plants (as measured by seed germination tests) were less sensitive to heavy metal contamination than were bacteria (Miller et al. 1985). This suggests that if microbial degradation of PAHs or PCP fails due to metal toxicity, such as in cases where Cr, Cu, and As wood-preservative solutions are also present, phytodegradation due to secretion of plant-formed enzymes might succeed. Modification of the waste by amendments may be required to meet the requirements of growing plants. Contaminants potentially amenable to phytoremediation include toxic metals and radionuclides; pesticides (Anderson and Coats 1995); TNT, nutrients, and BTEX (Schnoor et al. 1995); the chlorinated solvent TCE (Anderson and Walton 1995); PAHs (Schwab and Banks 1994); PCP (Aprill and Sims 1990); and PCBs (Fletcher, Donnelly, and Hegde 1995). Phytoremediation of wastes with mixed contaminants has not generally been addressed in research; however, there is some evidence that plants can tolerate mixed organic and metal contamination (Schnoor et al. 1995).

4.5.1.5 Pilot Testing

To determine the applicability of the technology, pilot testing is performed to select the plants, determine their growth potential in the contaminated soil under the site conditions, and to assess contaminant removal or degradation. Preliminary screening of candidate plants can save time and money by determining contaminant concentrations that are phytotoxic or inhibitory to germination of the plant seeds. Prior to field testing, seeds can be placed into the contaminated soil in the laboratory to determine the level of contamination that is phytotoxic or inhibitory. One biotreatability study was designed to investigate the potential for grasses to enhance biodegradation in soil from a Superfund site contaminated with PCP, PAHs, dioxins, As, and Cr. Grass germination and establishment failed in this study due to elevated concentrations of PCP (SBP Technologies, Inc. 1994). In experiments investigating a vegetative cover for soil/waste mixtures, incomplete seed germination and grass kill were seen in germination studies with three native grasses in soil contaminated with petroleum wastes (Overcash et al. 1985). In contrast, laboratory germination studies using soil contaminated with PCP did not find any significant detrimental effects on seed germination, with buffalograss seed being tolerant to >300 mg/kg PCP (Qiu et al. 1994).

Greenhouse trials can provide further preliminary information on the growth patterns of the plants and can be used to screen candidate plants. Outdoor test plots should be used to determine the growth characteristics of the plant in the contaminated soil under actual site conditions. An estimate of the contaminant removal or degradation rate can be developed using measured concentrations in the plant or soil. For example, based on biomass measurements and metal concentration in the plant, a tested cultivar of *B. juncea* could theoretically remove 630 kg Pb/ha (562 lb Pb/acre) if the shoots were harvested (Kumar et al. 1995).

4.5.2 Process Design Principles

Because phytoremediation is an emerging technology, there is limited experience with field applications and the principles of design are not well established. However, there are several design considerations that are important in field implementation for soil remediation. The process design principles described here are primarily for soil remediation, although many also apply to other contaminated matrices.

4.5.2.1 Plant Selection

The selection of useful plants is based on the particular method or goal of the phytoremediation effort and on criteria such as the plant's ability to take up and translocate or degrade contaminants, its growth rate and biomass production, root characteristics, stress tolerance, and cultural demands. The cultivation of the plant should not be labor- or cost-intensive.

The optimum plant for rhizofiltration and phytostabilization will not translocate metals from the roots to the shoots because the aboveground portion of such plants has the potential for food chain accumulation of metals by animals or humans. In addition, the optimum plant for rhizofiltration will have rapidly-growing roots and the ability to remove heavy metals (Salt et al. 1995).

On the other hand, the optimum plant for phytoextraction would tolerate, translocate, and accumulate high concentrations of heavy metals in the harvestable, aboveground portion of the plant, in its shoots and leaves. The aboveground portion of the plant is the desired location of metals since this biomass will be collected and disposed or treated before food chain accumulation can occur. The ideal plant for phytoextraction also has a rapid growth rate and a large biomass (Salt et al. 1995). Although many currently identified metal hyperaccumulators do not meet these criteria, one favorable candidate is *B. juncea*, a high biomass plant that accumulates lead (Kumar et al. 1995). Screening of different plant species revealed that *B. juncea* had the best ability to transport lead to the shoots, with >1.8% lead in the shoots. It could also concentrate Cr^{6+}, Cd^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+} (Raskin et al. 1994). However, a large genetic variability was seen in the ability of *B. juncea* cultivars to accumulate Pb, with 0.04% to 3.5% in shoots and 7% to 19% in roots (Kumar et al. 1995).

Plants suitable for rhizodegradation of organic contaminants should produce appropriate compounds or enzymes and should not take up the contaminant of interest. The identification of specific plant-formed compounds that are known to stimulate cometabolism of a contaminant and the screening of plants for these compounds can increase the success rate of rhizodegradation (Fletcher, Donnelly, and Hegde 1995). The optimum plants for phytodegradation will produce enzymes or have metabolic pathways capable of degrading the contaminants. For successful hydraulic control or phytovolatilization, the plant must take up and transpire a sufficiently large amount of water. Metabolism within the plant should not result in more toxic intermediate products that would be released into the atmosphere.

Information on phytotoxicity of contaminants can be collected, such as was done with the PHYTOTOX database (Fletcher, Johnson, and McFarlane 1988), to determine the compatibility of a site contaminant and potential plant candidates. A survey of vegetation at a site may be useful to identify plants that can tolerate the stresses of site conditions. However, the presence of a plant may indicate only tolerance to the soil contaminants and not necessarily that it has any beneficial effect relative to site remediation. In a survey of vegetation at 15 hydrocarbon-contaminated sites, members of the Leguminosae family were most common and the best competitors at these sites. Their presence may have been due to lack of need for soil nitrogen that was consumed by microorganisms degrading the hydrocarbons (Gudin and Syratt 1975).

Root type, shape, and depth are important factors related to plant selection for site remediation. Fibrous root systems have numerous fine roots spread throughout the soil while tap root systems are dominated by a deep central root (Aprill and Sims 1990). The fibrous root system provides maximum contact with the soil and can extend to a 3-m (10-ft) depth in some grasses. However, root depth varies greatly among different types of plants. For example, trees may be useful for extraction of groundwater less than 9.1 m (30 ft) deep (Gatliff 1994).

Valuable information and experience, such as identification of particular species appropriate for varied climatic and soil conditions, was gained in the use of vegetation in connection with land application of hazardous waste and for hazardous waste site covers (Chaney 1983; US EPA 1983; McAneny et al. 1985). Some criteria for establishing a vegetative layer as part of a Subtitle C hazardous waste landfill cap may not be applicable to the vegetative or evapotranspirative caps used in phytoremediation. For example, avoiding deep tap root systems is desirable in the design of impermeable waste site covers to prevent penetration of an engineered cap underlying the vegetative cover. It might be desirable, however, to use such a deep root system in some phytoremediation projects that do not involve impermeable covers.

4.5.2.2 Cultural Practices

The proper cultural practices are crucial to establish and maintain healthy vegetation. Seeds used at a site should be obtained from the region of the site so that the plants are adapted to the climatic conditions characteristic of the site. Seed suppliers, agricultural extension agents, and horticultural associations can supply this information. The seeding timing, depth, and density are dependent on the plant species used, as are the planting and cultivation

methods. Some seeds may require special treatment prior to germination, such as some prairie grass seeds that require storage over winter. Proper moisture, fertilization, and protection from pests and diseases are also important during establishment and maintenance of the crop. The amount and timing of irrigation, fertilizer, and pesticides should be carefully considered. Due to the added stress of a contaminated soil environment, these factors may have to be carefully monitored if plant cultivation at a contaminated site is to be successful. Complete soil characterization is important not only for soil bioremediation, but is crucial for establishing and maintaining vegetation.

4.5.3 Process Modifications

To increase the bioavailability of metals to plants for phytoextraction, the soil can be amended with metal chelates, a moderately acidic soil water pH can be maintained, and reducing organic acids can be added to alter the redox status of the soil (Salt et al. 1995).

4.5.4 Cost Data

Information on phytoremediation costs is not yet readily available due to limited field applications and commercial experience in most areas. Some speculative estimates or predictions have been made that vary widely depending on the specific phytoremediation process used. Annual cropping system costs of $200 to $10,000/ha ($80 to $4,050/acre) would represent costs of $0.02 to $1.00/m^3 ($0.015 to $0.76/yd^3) for phytoremediation assuming a 1-m (3-ft) depth of roots (Cunningham, Berti, and Huang 1995b). Costs for groundwater control and treatment using trees were estimated to be less than for pump-and-treat methods in a 6-m (20-ft) deep aquifer (Gatliff 1994). Predictions of the total treatment cost for phytoremediation of metal-contaminated soils were $16.50 to $55/metric ton ($15 to $50/ton) compared to $110 to $220/metric ton ($100 to $200/ton) for other treatment methods (Raskin et al. 1994). A cost estimate to remediate 0.4 ha of 50-cm (1 acre of 20-in.) thick sandy loam using phytoextraction was $60,000 to $100,000 versus a minimum $400,000 for just excavation and storage of this soil (Salt et al. 1995). Cornish et al. (1995) have prepared comparative cost estimates for phytoremediation and soil washing for a hypothetical case of a 50-cm (20-in.) thick layer of Cd-, Zn-, and ^{137}Cs-contaminated sediments from a 0.5-ha (1.2-acre) chemical waste disposal pond (Table 4.11). Although the cost estimates are speculative, they do indicate the potential savings of phytoremediation over other site remediation technologies.

Table 4.11
Cost Estimate for Phytoremediation vs. Soil Washing of Sediments in a Hypothetical Chemical Waste Disposal Pond

Activity	Cost Estimate $		Summary of Activity Components
	Phytoremediation[a]	Soil Washing	
Site preparation	63,000	61,000	Surveying, staking, and light clearing of area, access construction, excavation, installation of water supplies, and construction of fences and other structures.
Production/processing	395,000	1,336,000	Operation and maintenance of treatment system for the duration of the project, including heavy equipment rental and services.
Waste management/ disposal	35,000	175,000	Consolidation of waste materials and haulage of same to eventual storage facility, as well as necessary testing prior to disposal. Costs for long-term storage have not been calculated due to uncertainties regarding the ultimate disposition of some wastes.
Project closeout	18,000	62,000	Demobilization of heavy equipment, removal of constructed facilities, and site restoration
Environmental, safety, & health (ES&H), engineering design (ED), and project management overhead (PMO)	153,000	490,000	Calculated as 30% of above costs
Overall estimated cost	664,000	2,124,000	Subtotal plus ES&H, ED, and PMO costs
Costs per tonne[b] of sediment	200	600	Based on treating 2,500 m^3 of sediment @ 1,420 kg/m^3

a. Costs shown for phytoremediation assume a production period of 20 years.
b. Denotes units of metric tons (1,000 kg per tonne)

Source: Cornish et al. 1995

Costs associated with phytoremediation include work plan and report preparation, treatability and pilot testing, soil preparation, seeds, planting, irrigation, fertilization, plant and soil sampling and analysis, and plant disposal costs.

4.5.5 Design Validation

Full-scale application of all forms of phytoremediation has not yet been accomplished. Since it is an emerging technology, most work in phytoremediation has been at the research level in the laboratory or small-scale field plots. Research experience with remediation of metals is discussed in the previous sections. It is possible that more research has been conducted for phytoremediation of metals than for organic compounds, but field trials for metals phytoremediation remain limited and large-scale implementation is not yet achievable, especially for soil as opposed to water. Significant research has been conducted in some areas of phytoremediation for organic compounds, such as for TCE in groundwater. Some laboratory studies have been conducted with contaminated soil from Superfund sites and field experiments have been conducted at numerous sites contaminated with organics.

In a laboratory and greenhouse study, soil contaminated with PCP and PAHs was obtained from a Superfund wood-preserving waste site to examine the effect of the contaminants on the germination and growth of prairie and other grasses and to assess the potential for rhizodegradation. This study indicated that rhizodegradation of PCP was likely only at relatively low PCP concentrations. However, it is believed that this is strongly influenced by site-specific factors. Under other site conditions, rhizodegradation could occur at lower or higher PCP concentrations. An experimental plot was established at another wood-preserving waste Superfund site to evaluate whether PCP degradation could be enhanced in a LTU by rhizodegradation. Adverse temperature and precipitation conditions at this site greatly increased the difficulty of establishing a healthy vegetative crop (Pivetz, unpublished data).

A laboratory study conducted with PAH- and PCB-contaminated soil from an industrial site indicated a statistically significant increase (α=0.05) in benzo(a)pyrene [B(a)P] biodegradation under a tall fescue crop as compared to an unvegetated control, although B(a)P mineralization was low — less than 0.3% of the B(a)P was incorporated into the plant (Qiu 1995b).

Hybrid poplars have been successfully used in full-scale applications to: (1) decrease nitrate from up to 100 mg/L in surficial groundwater to less

than 5 mg/L, (2) take up 10% to 20% of atrazine applied in a field, and (3) reduce infiltration at a landfill by capping it with 10,000 trees per hectare (4,050 trees per acre)(Schnoor et al. 1995).

4.5.6 Permitting Requirements

Requirements for implementation of phytoremediation include obtaining regulatory acceptance, which will likely require more effort than for proven remedial technologies. The potentially longer time frame for phytoremediation to be effective may influence regulatory decisions, in a manner similar to that for intrinsic remediation, which may also take longer than more active remedial technologies. Reports on a field trial of *T. caerulescens* indicated that it would take 13 to 14 years to remediate the heavy metal-contaminated site (Salt et al. 1995) using phytoremediation technology. Despite potentially longer time frames for remediation, phytoremediation has been studied or proposed for part of the remedial solution at several Superfund sites, including for TCE-contaminated groundwater and for TNT-contaminated soil and surface water.

4.5.7 Implementation

The potential negative impacts of phytoremediation should be fully evaluated before implementing this technology. The interactions of the plants and all contaminants at the site should be studied. For example, application of fertilizer to optimize plant growth may increase the mobility of some metals in the soil because many common nitrogen-containing fertilizers lower the soil pH. If the plant does not take up the metals, they may be leached to the groundwater. Unintended increased mobility of contaminants and increased exposure pathways can be limitations of phytoremediation.

If toxic contaminants are bioconcentrated in the plants, the ultimate fate of the plant must be considered to prevent chemical or toxin ingestion by animals or humans. Research on uptake and degradation of metals and organic compounds was initially fueled by concern that vegetation used in land treatment systems might be a potential hazard in this manner (US EPA 1983).

The selected plant may be inherently toxic to other plants (allelopathy), animals, or humans, and its presence at a site can have risks that are significantly greater than the risks posed by the contaminants. Substances extracted from *Datura innoxia* (thorn apple) can be beneficial for removal of metals in certain situations (Drake et al. 1996); however, this does not justify widespread planting of this attractive but very toxic plant at a site because the risk of a child fatally ingesting a leaf is much greater than the risk of the

child being harmed by ingesting large amounts of the contaminated soil. The deliberate introduction of noxious or invasive weeds, such as purple loosestrife, can have adverse economic, ecological, or aesthetic impacts outweighing any benefits to site remediation. The impacts of establishing any particular plant should be considered in the planning stage. Other considerations include the impact of plants and biomass on other technologies being used at the site and the potential for plants (such as trees) to be physical impediments to movement or operations at the site.

The presence of plants may decrease contaminant biodegradation if the plant organic matter is used as a carbon source instead of the contaminant. The presence of debris of the salt marsh plant *Spartina alterniflora* decreased the amount of degradation of oil in laboratory sediment columns, perhaps from competition for limited oxygen and nutrients by both indigenous oil-degrading microorganisms and by microorganisms degrading the plant organic matter (Molina, Araujo, and Bond 1995).

4.5.8 Performance Evaluation

Evaluation of phytoremediation performance depends on the type of phytoremediation process employed, but generally involves determination of the percent removal of a contaminant or attainment of a remedial goal in the contaminated matrix. The degree of phytoextraction is easy to assess because extraction and analysis techniques for metals in plants are straightforward (Brown et al. 1994). The concentration in the soil, plant leaves, and shoots can be measured, and the bioconcentration and accumulation factors can be calculated. If the biomass production rate is measured using standard agronomic techniques, the mass and rate of metal removal can be calculated.

Detection and measurement of organic compounds in plants can be more difficult than for metals and can be complicated by the presence of breakdown products. Measuring target compound concentrations in the soil is the easiest method for evaluating performance. However, humification (incorporation into humic material) of organic compounds or their breakdown products can complicate the interpretation of analytical results. Radiolabelled compounds have been used in research to quantify transport or mineralization of organic compounds. For example, the fate of ^{14}C-PCP and ^{14}C-atrazine in laboratory and outdoor experimental soil-plant units containing carrots, maize, and barley has been assessed (Scheunert, Qiao, and Korte 1986), and the potential effect of plant roots on biodegradation of ^{14}C-TCE has been examined (Anderson and Walton 1995). Walton and Anderson (1990) used ^{14}C-labeled TCE to determine that mineralization from rhizosphere soil was significantly greater than that of non-rhizosphere soils

contaminated with low levels of TCE from a site naturally vegetated with a grass, legume, composite herb, and Loblolly pine. However, use of radiolabelled compounds in field situations is virtually impossible.

The contaminant may not degrade uniformly throughout the soil since rhizodegradation is postulated to occur in a discrete zone around the plant root. Unless the plant roots are distributed uniformly throughout the soil, the selection of soil sampling locations or the interpretation of analytical results will have to take into account the location of the sample relative to the root. Microbial counts or respiration in these soil samples can also provide information on the degree of rhizodegradation. The problem of sample location would not arise in water treatment systems because influent and effluent concentrations representative of the larger system can be easily measured.

4.5.9 Research Needs for Further Technology Implementation

Interest in phytoremediation has increased greatly since the late 1980s. University, industry, and government research groups have been active in examining various aspects of phytoremediation, producing numerous research publications. Interest in phytoremediation has resulted in symposia related to this technology, focusing on organics (Anderson and Coats 1994) and metals (Interdisciplinary Plant Group 1995; DOE 1994). Some phytoremediation technologies have been applied commercially, and information on phytoremediation has reached the general public and business community through articles in newspapers and business magazines. This last aspect is important as it may lead to increased commercial and regulatory acceptance of this technology that would spur even more research efforts and lead to further field-scale applications.

The use of phytoremediation adds an additional layer of complexity to a remedial action since it introduces another biological system that has its own characteristics. A multidisciplinary approach is needed to plan and implement phytoremediation, potentially involving ecologists, botanists, horticulturists, turfgrass and wetland specialists, and agricultural experts in addition to hydrogeologists, engineers, microbiologists, and soil scientists. Specialists in each field have valuable knowledge and expertise: for example, forestry experts can identify appropriate tree species or hybrids, and provide cultural techniques for the trees; botanists can identify useful plant exudates, identify processes within the plant, and help with plant selection; and soil scientists and agronomists can provide details on soil characterization and plant cultural practices. Much of the information from these fields has not generally been applied in the past towards remediation of contaminated soil

or groundwater. This information needs to be distilled into a useful form and then integrated into a remediation-focused effort. Full use of resources such as farmers, agricultural extension services, and even local garden clubs and nurseries may provide additional information on potentially useful local plants or cultural practices for application to site remediation problems.

Research on the applicability of phytoremediation to wastes with several types of contaminants would greatly expand the potential use of this technology. An important research goal for phytoextraction is to identify fast-growing and high-biomass-producing plants that have the ability to take up toxic metals (Raskin et al. 1994; Kumar et al. 1995). Genetic modification may be necessary to develop such plants. Wackett and Allen (1995) indicate that research on specific plant-microbe interactions and their effect on biodegradation may be more productive than randomly screening combinations of plants, soils, and contaminants.

Extrapolation of lab results to field situations is problematic; therefore, pilot testing in the field under controlled site conditions will be critical. Evaluation of rhizodegradation performance may depend on the location of soil samples because the rhizosphere distribution changes with time and may not be uniform throughout a site. Sampling techniques and evaluation of rhizodegradation still need to be addressed.

The emerging technology of phytoremediation consists of the use of green plants for remediation of a wide variety of contaminants in soil, groundwater, surface water, wastewater, and air. The specific processes and design considerations can vary greatly depending on the contaminant type and matrix being treated. The selection and use of an appropriate plant is critical. The depth of soil remediation is likely to be limited by the depth of the plant roots. Practical implementation of phytoremediation will require more information on techniques, costs, and integration of phytoremediation with other remedial technologies. Phytoremediation is the subject of intensive research; however, routine field application and remediation success for contaminated soils has not yet been achieved.

5 GROUNDWATER TREATMENT SYSTEMS

5.1 Introduction

Site, soil, and waste constituent characteristics that are important in the evaluation and design of groundwater treatment system technologies are summarized in Table 5.1. Technologies applied in situ (i.e., enhanced bioremediation, intrinsic remediation, biosparging, and migration barriers) are affected by site conditions (e.g., groundwater table fluctuations, heterogeneous layered soil lenses) that negatively impact the effective distribution and transport of reactants throughout the contaminated site. Ex-situ, aboveground reactor technology is less sensitive to these restrictions because its implementation is unaffected by site conditions once contaminated groundwater is extracted from the aquifer. All technologies are impacted by aquifer conditions that affect microbial activity (i.e., soil pH and nutrient limitations), although the ex-situ system can be designed to modify these properties in a controlled reactor environment. All technologies are affected by waste constituent characteristics that affect a contaminant's toxicity, biodegradability, and bioavailability. Toxicity and biodegradability limitations can be controlled in an aboveground reactor through modification of extracted groundwater conditions via dilution, addition of carbon sources to stimulate co-metabolic degradation, etc. Both biosparging and aboveground reactors rely on contaminant mobility for aquifer treatment so a contaminant's solubility has a significant impact on the effectiveness of these methods.

The following sections describe each of the groundwater treatment techniques listed in Table 5.1, and discuss technology applications and limitations appropriate for groundwater remediation systems applied at the field-scale.

Table 5.1
Impact of Various Site, Soil, and Waste Constituent Characteristics on Groundwater Treatment Technology Performance*

		RP	IR	AGR	BS	MB
Site	Climatic conditions	N	N	N	N	N
	GW table fluctuations	I	I	I	I	I
	Surface structures	N	I	N	I	I
	Layered formation	V-	V	V	V-	V-
	Product existence/distribution	V	V	V	V	V
Soil	Fine grained	V-	I	I-	V-	V-
	High-water content	N	N	N	N	N
	Low-water content	N	N	N	N	N
	Nutrients	I-	I-	N	I	I
	pH	I-	I-	N	I	I
Waste Constituent	Volatility	N	I	I	V	N
	Biodegradability	V	V	V	V	I
	Bioavailabiltiy	V	V	V	V	V
	Water solubility	V	V	V	I	V
	Toxicity	V-	V-	V-	V-	V-

*RP = Raymond Process
IR = Intrinsic Remediation
AGR = Aboveground Reactors
BS = Biosparging
MB = Migration Barriers
GW = Groundwater
N = Not important related to the performance of the technology
I = Important related to the performance of the technology
V = Very important related to the performance of the technology
+ = Characteristic positively impacts the performance or selection of the technology
- = Characteristic negatively impacts the performance or selection of the technology

5.2 Raymond Process (Enhanced Bioremediation of Aquifers)

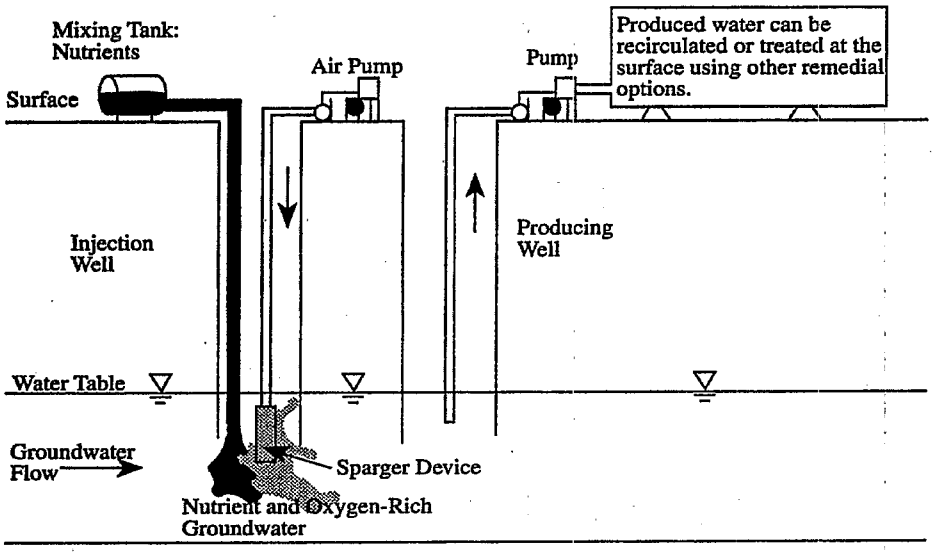
5.2.1 Principles of Operation

Although land farming and wastewater treatment have been commercialized for many years, the first process to become widely known as a bioremediation process was in situ treatment of aquifers. This process was first field

tested in 1972 by Richard L. Raymond of Sun Tech in conjunction with the American Petroleum Institute (Raymond, Jamison, and Hudson 1976; Raymond et al. 1978; Brown, Norris, and Raymond 1984). The process became commercial in the mid-1980s and consists of:

- extraction of groundwater;
- aboveground treatment of the extracted water;
- amendment of the water with an electron acceptor and, typically, nutrients; and
- reinjection of the water so that it will sweep through the contaminated soils and groundwater towards the groundwater recovery system as shown in Figure 5.1.

Figure 5.1
Well System for Liquid Delivery



Source: Ward et al. 1995

The process relies on the injection of electron acceptors and nutrients to stimulate microbial growth and enhance the rate of biodegradation of the organic contaminants. Depending upon the solubility of the contaminants,

the hydrogeology, and the system design, varying proportions of contaminant mass reduction will occur as a result of removal of contaminants in the recovered water.

The first systems used oxygen that was supplied by sparging air within the injection well(s) as the electron acceptor (Raymond 1974). Subsequently, other sources of electron acceptors including hydrogen peroxide (Raymond et al. 1986), nitrate (Hutchins et al. 1991), and sulfate (Beeman et al. 1993) were used as electron acceptors. The use of alternate electron acceptors for petroleum hydrocarbons (Reinhard 1994) and chlorinated solvents (Bouwer 1994) are discussed in the *Handbook of Bioremediation* (Norris et al. 1994).

In its current state of development, the Raymond Process is applicable to remediation of petroleum-based hydrocarbons (including commercial fuel blends), creosote, oxygenated solvents such as alcohols and ketones, some chlorinated compounds, and (to some extent) PAHs. It is also being field tested with some success for treatment of chlorinated solvents such as trichloroethylene and trichloroethane. Commercial treatment of pesticides, herbicides, PCBs, high molecular weight hydrocarbons, and most energetics is not likely to be available for some time.

Generally, the process is most suited to relatively permeable soils and is most easily applied to homogeneous aquifers. The aquifer hydraulic conductivity and saturated interval thickness determine the rate at which groundwater can be transported to deliver electron acceptors and nutrients. The minimum acceptable hydraulic conductivity depends upon the mass loading of the contaminants and the oxygen demand that must be met by the added electron acceptor. Sample calculations are provided in Section 5.2.9 of this monograph.

As discussed in Section 5.3, it is now recognized that many sites, especially those where the contamination is limited to petroleum hydrocarbons and/or other readily biodegradable compounds, do not represent an immediate risk to human health or the environment because natural attenuation processes will prevent migration to downgradient receptors. As a result, many regulatory agencies are accepting or even requiring a combination of risk evaluation and intrinsic remediation to be considered at UST sites. Thus, many sites that have been remediated using the Raymond Process would, today, be addressed by intrinsic remediation or a combination of the two technologies.

A comprehensive introduction to the Raymond Process can be found in the preceding monograph, *Innovative Site Remediation Technology*:

Bioremediation (Ward et al. 1995), in Chapter 2 of the *Handbook of Bioremediation* (Norris et al. 1994), in *A Guide for Railroad Industry Use of In Situ Bioremediation* (Brubaker et al. 1994), and in *In Situ Bioremediation: When Does It Work?* (Rittman et al. 1993).

5.2.2 Process Design Principles

As a result of the release of hydrocarbons to the subsurface, contamination will impact unsaturated soils. If sufficient quantity is released relative to the retention capacity of the unsaturated zone, free-phase hydrocarbons on the groundwater surface (light nonaqueous-phase liquids or LNAPLs), contaminated saturated zone soil, and contaminated groundwater can result. Even excluding NAPL, normally only a small fraction of the contaminant mass within the saturated zone will be in the dissolved phase. Therefore, this process must be designed to address the mass of contaminants that are adsorbed or entrained by the soil because the dissolved contaminant mass generally represents less than 1% of the total mass of contaminant distributed throughout the impacted area.

The remediation system must supply the necessary amount of electron acceptor to degrade the total mass of contaminant within the contaminated saturated zone and capillary fringe minus the mass of contaminant that is removed with the extracted groundwater. For remedial designs that include bioventing, the mass of contaminants removed or biodegraded through bioventing as a result of water table fluctuations should be estimated. When oxygen is used as the electron acceptor, between 1 and 3 kg of oxygen must be supplied for each kilogram of hydrocarbon not removed in the recovered water or through bioventing. In essence, the problem consists of engineering a system that can cost-effectively meet this requirement within an acceptable time frame and at a lower cost than other acceptable alternatives.

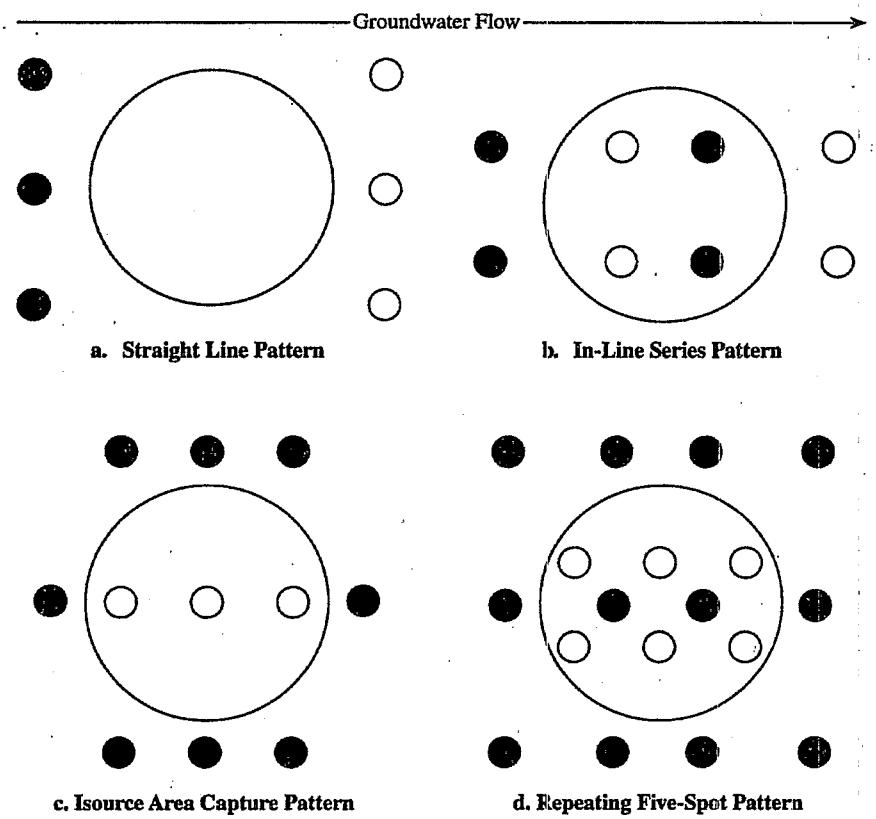
First, it is necessary to know that all constituents of interest are biodegradable, will be extracted, or will be addressed by an integrated design. Given that these conditions are met, the aquifer must be evaluated to determine unacceptable pH conditions, presence of inhibitory compounds, availability of electron acceptors and nutrients, contaminant distribution, and hydrogeology. The first two criteria can be functionally evaluated by standard plate count techniques that will identify conditions potentially deleterious to microbial activity. If electron acceptors and nutrients were already present at sufficient levels, there would be no need to design a system. Nutrients, especially phosphorus, may be sufficient to support biodegradation of the contaminant mass. However, electron acceptors are usually insufficient and their rate of introduction to the aquifer is normally rate-limiting for biodegradation during active remediation.

The critical feature of the design is the distribution of the electron acceptor(s). For design purposes, background levels of electron acceptors can be left out of the calculations. If background levels of electron acceptors are significant compared to the contaminant mass, let alone the uncertainty in the contaminant mass, then intrinsic remediation will, in all but a few cases, be the remedy of choice. Designing a system to meet the oxygen demand requires an understanding of the three-dimensional distribution of the contaminant mass and the details of the site hydrogeology. Mass distribution is determined from soil borings. Site hydrogeology is determined first from well logs, but must eventually include slug tests or preferably 24- to 72-hour pump tests and some level of modeling (Falatico and Norris 1990; Bedient and Rifai 1993). Two dimensional analytical flow models are frequently sufficient, require modest data input, and can be used to simulate numerous injection-recovery scenarios, thereby permitting selection of the most favorable combination of injection and recovery wells. Numerical models can account for heterogeneity and provide a more accurate representation of groundwater flow but require more input and are much more costly to develop and use.

Modeling is used to select the number and location of wells using patterns such as those shown in Figure 5.2, and to estimate groundwater injection and recovery rates. The groundwater injection rates are used along with the achievable concentrations of electron acceptors in the injection water to estimate the delivery rates of the electron acceptor and thus, the time that the system will have to operate to meet the remediation goals. The rate of physical removal also needs to be factored into the calculations. These calculations are discussed in more detail in Section 5.2.9.

Injection and recovery rates must be balanced so that injected nutrients and electron acceptors flow through the contaminated zone and can be captured by the recovery wells if not used by the microorganisms. For efficient capture, the injection rate typically needs to be less than the recovery rate by about 20% to 30% to satisfy regulatory agency concerns regarding residual levels of nutrients and to minimize the probability of spreading the contaminants. From a practical point of view, small excursions of contaminants are addressed through natural attenuation. To avoid recovering and treating excessive quantities of clean water, it may be necessary to recover less water than the wells could yield if pumped at full capacity. As shown in Figure 5.3, pumping at maximum recovery rates can extract water from outside the contaminated area, excessively diluting the feed to the aboveground treatment system, resulting in the need for a larger system than necessary to treat the contaminated aquifer.

Figure 5.2
Raymond Process Well Configurations

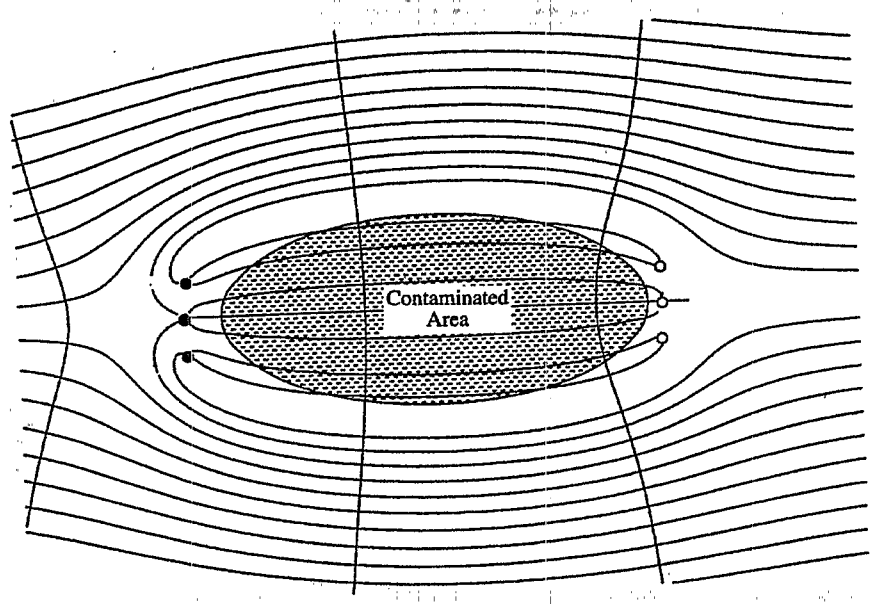


● Injection Wells
○ Recovery Wells

One common approach is to locate injection wells upgradient of the source area and recovery wells on the downgradient side as shown in Figure 5.2a and 5.2b (Brubaker et al. 1994). This takes advantage of the natural gradient and also serves to pull back some portion of the plume. Another approach is to place extraction wells within the center of the plume and inject through a ring of wells located near the perimeter of the source area as shown in Figure 5.2c. This design maximizes the recovery of dissolved-phase contaminants as well as residual LNAPL and creates a flow from the clean area to the impacted area. For large sites or for sites with relatively low hydraulic conductivity, a repeating five-spot pattern (Figure 5.2d) creates flow within the aquifer that reduces the travel time of

the injected water as compared to the previously discussed patterns. The last two patterns also lend themselves to subsequently reversing or otherwise modifying the flow directions. Reversing the flow direction reduces the average distance that electron acceptors and nutrients must travel and can eliminate dead spots (flow stagnation) that may occur (especially for the five-spot pattern).

Figure 5.3
Inefficient Groundwater Capture Resulting from an Excessive Pumping Rate



● Recovery Wells
○ Injection Wells

The interval over which the injection and recovery wells are screened is important. At a minimum, wells need to be screened across the smear zone and must allow for normal water table fluctuations. Screening over a larger (deeper) interval will allow higher recovery rates and may allow higher injection rates. The impact of the screened dimension will depend upon the details of the soil particle-size distribution in the vicinity of the wells. Increasing the groundwater recovery and injection rates will not be of benefit if the increased flow occurs primarily through deep, high-permeability channels where only a small fraction of the contaminant mass exists. Design of

injection/recovery systems must incorporate a three-dimensional picture of both the hydraulic properties of the aquifer and the distribution of the contaminant(s).

After an injection/recovery well pattern has been selected, it is necessary to estimate whether the configuration can deliver sufficient electron acceptors in a reasonable time to meet the demand created by the mass of contaminants. The mass of contaminants can be estimated from the volume of impacted soil and the average concentration, or more sophisticated estimating techniques can be used. The mass of oxygen required is adequately estimated as three times the contaminant mass associated with the soils. The time required to deliver the required oxygen is estimated by dividing the required oxygen mass by the oxygen flux, calculated from groundwater injection rate, the water density, and the oxygen (or other electron acceptor) concentration in the injected water.

Table 5.2 gives some examples of the time required to introduce various electron acceptor sources and blends at a series of injection rates to degrade 454 kg (1,000 lb) of contaminant mass. The estimated mass of contaminant to be biodegraded should be adjusted for the mass of the contaminant that would be extracted by the recovery system. For gasoline and jet fuels, this mass could be 20% to 40% of the total, depending upon the initial conditions and the proximity of the recovery wells to the highest soil contamination levels. For heavier molecular weight fuels, the mass recovered in the aqueous phase will be insignificant compared to the uncertainty in the estimations of the adsorbed-phase mass and the amount removed by groundwater recovery can be ignored for these calculations. If the estimated time to supply the electron acceptor is too long to meet project objectives, then the well pattern is not satisfactory. In some cases, the hydraulic conductivity of the aquifer will be insufficient to permit satisfactory rates of electron acceptor introduction without incorporating an excessive number of wells.

The above-described simple approach ignores heterogeneity in groundwater flow and contaminant distribution. Depending upon the type of well pattern used and the degree of heterogeneity, this approach may be satisfactory. Frequently, it is prudent, if not always practiced, to estimate treatment times for *individual areas* within the contaminated zone. This added level of complexity may lead to the inclusion of several additional wells located to more aggressively address areas of high contamination or low hydraulic conductivity.

An excellent approach is to include, as part of project design and budgeting, the installation of additional injection and/or recovery wells after the initial system has been operated long enough to learn how the aquifer is

actually going to respond. This observational approach provides the best opportunity to respond to the presence of permeable channels that have low-adsorbtivity capability and to low-permeability intervals that have greater adsorptive capacity and thus may contain the majority of the contaminant mass. Where this dichotomy is extreme, it may be best to use an active system to address the more transmissive soils and allow intrinsic remediation to address contaminants that will slowly diffuse from the less transmissive soils to the more transmissive soils. In many cases, natural attenuation will be sufficient to prevent significant migration of contaminant mass toward downgradient receptors. A discussion of intrinsic remediation for groundwater management is provided in Section 5.3.

Table 5.2
Treatment Time for Each 454 kg (1,000 lb) of Hydrocarbons*

Source	Electron Acceptor Concentration (mg/L)	Treatment Times (Days) at Indicated Injection Rates 4.5 m^3/s	45 m^3/s	450 m^3/s
In Well Aeration	8	55	5.5	0.6
In Well Pure Oxygen	40	11	1.1	0.1
NO_3+ Pure Oxygen	80	5.5	0.55	0.06
H_2O_2	200	3.5	0.35	0.04
H_2O_2	500	1.4	0.14	0.01

*Assumes 100% utilization and stoichiometric requirements.

One other important consideration is site-specific geochemistry (Norris 1992; Ward et al. 1995). The addition of oxygen sources to an aquifer can cause precipitation of reduced iron that is frequently present in contaminated groundwater or, worse, precipitation of iron from reinjected groundwater leading to plugging of wells or reduced permeability in the immediate vicinity of the injection well. Groundwater chemistry is also a critical issue with respect to nutrient selection. Calcium, iron, and magnesium will precipitate in the presence of ortho phosphate (salts of phosphoric acid). Therefore, it is preferable to use potassium tripolyphosphate (KTPP) because it can

sequester these metals and prevent precipitation in the vicinity of the well bore. Tripolyphosphate must be present in molar excess of the total moles of calcium, iron, and magnesium. The appropriate calculation for the minimum KTPP concentration is presented in Section 5.2.9. The use of potassium salts rather than sodium salts minimizes the possibility of swelling of clays. If the chemistry of the treated water is not appropriate for nutrient amendment and reinjection, it will be necessary to dispose all treated water and use water from another source, such as city water or water from a deeper aquifer for reinjection.

For planning purposes, the total amount of nutrient required can be estimated from a C:N:P ratio of 200:10:1 that is based on the ratio of those elements in cell material with the assumption that 50% of the contaminant is converted to cell mass. This is an overestimate because the soils and groundwater nearly always contain most of the required phosphorus and some nitrogen in usable forms and these elements are recycled when the cells die. On the other hand, transport of nutrients is retarded by the soil. In practice, nutrients are first added at a rate that would provide nutrients over the first 25% to 50% of the estimated treatment time. Nutrient addition is adjusted or terminated based on detection at downgradient monitoring locations; after nutrients reach the extraction wells, nutrient addition should be terminated so that nitrogen and phosphorus levels will not exceed regulatory limits at the end of the remediation process.

Extraction wells are designed as previously described. Installation techniques are the same as for any groundwater recovery system. It is important to pay close attention to well completion and development techniques to minimize loss in recovery rates from redeposition of fines and to maintain the design flow rates for long periods. Groundwater recovery can be accomplished with many different pump types. Pump selection and design depends upon the total flow, depth to water, and potential for silting. A good description of groundwater recovery pumps can be found in *Groundwater and Wells* (Driscoll 1986).

Groundwater treatment systems are designed based on the composition of the groundwater, requirements for offgas treatment or polishing of effluent, flow rate, regulatory compliance requirements, and level of operator attention. Table 5.3 lists types of groundwater treatment systems, the classes of compounds that can be treated, and the general level of operator attention required.

Monitoring well requirements and treatment of the extracted groundwater are discussed in Section 5.2.6. Treatment of extracted groundwater must take into account the chemistry of the water provided for reinjection. While regulatory requirements focus on removal of contaminants, the inorganic

Table 5.3
Common Groundwater Treatment Systems

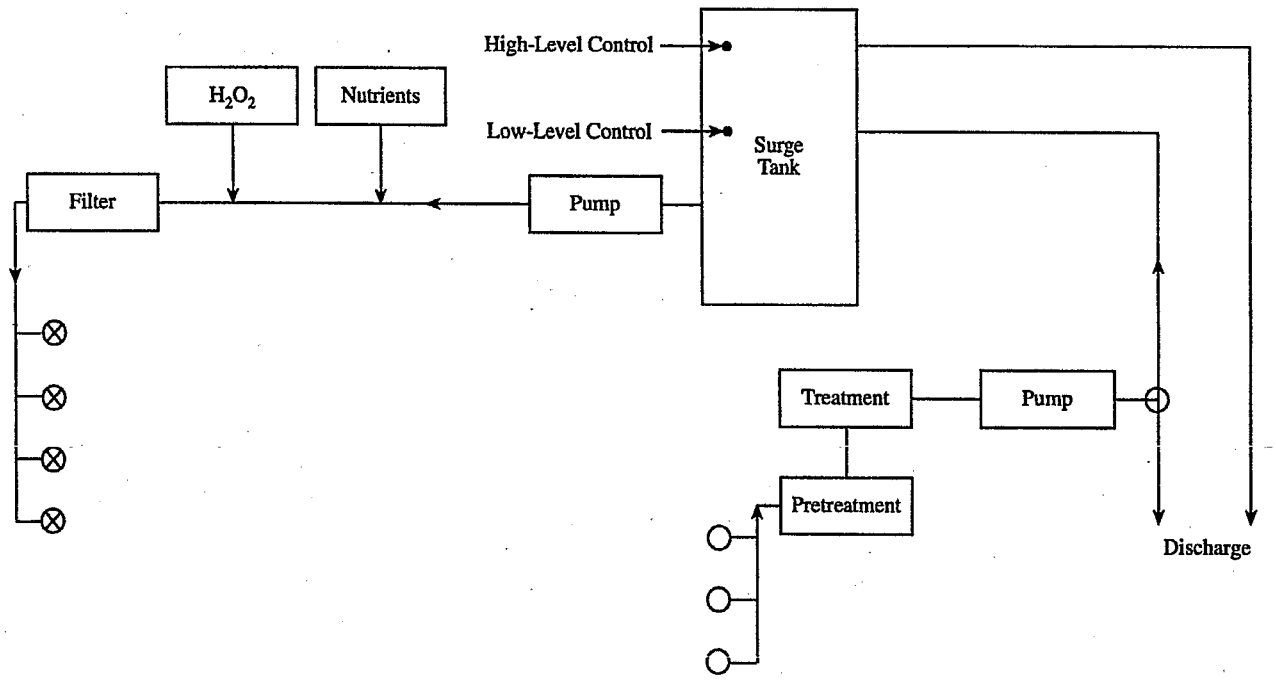
Treatment System	Contaminants Treated	Comments
Air Strippers	VOCs-BETX, gasoline, etc. TCE, PCE, MTBE	• Considerable maintenance • May need off-gas treatment • Iron removal may be necessary
Activated Carbon	Most organics; inefficient for highly water-soluble compounds	• Simple to operate • Costly O&M • Nondestructive technology • Filtration pre-treatment may be required
Bioreactors	Most organics; some chlorinated organics are less biodegradable	• Suspended growth for high concentrations (e.g., >100 mg/L as COD) • Fixed growth for low concentrations (e.g., <100 mg/L COD) • Nitrogen and phosphorus addition may be required • Sludge handling and disposal required
UV Oxidation	Most VOCs and organic ketones; alcohols are not readily oxidized	• Compound-specific treatment • May require catalyst (e.g., Fenton's Reagent) • Destruction to $CO_2 + H_2O$ possible for selected organics • Pre-treatment for iron required • Can create oxidation byproducts such as acetone
Membrane Separation	Most organics and inorganics	• High capital cost • High O&M cost • Nonselective treatment • High level of pre-treatment required

chemistry (calcium, iron, magnesium, carbons, etc.) will determine whether pretreatment is needed to prevent operational problems during remediation. Pretreatment for metals can add significantly to groundwater treatment costs.

5.2.3 Process-Flow Diagrams

Critical features that are frequently incorporated into the design of a Raymond Process system are shown in Figure 5.4. These include components for pretreatment for inorganics and metals, if necessary; treatment; a surge tank with controls unless none of the recovered groundwater is reinjected; addition of nutrients; addition of the electron acceptor; transfer lines; and filtration before injection. Process and instrumentation (P&I) drawings should be prepared for each major component including transfer lines as discussed in Section 5.2.8.

Figure 5.4
Groundwater Treatment, Amendment, and Recirculation



⊗ Injection Wells
○ Extraction Wells

5.2.4 Process Modifications

The Raymond Process, as first practiced, provided aqueous solutions of nutrients in batch additions to the injection wells. Oxygen was supplied by the use of air diffusers (air spargers) located at the bottom of the injection wells. Nutrients were dissolved in water on-site and added in batches. The simplest process modification was the inclusion of a storage tank and metering pump for continuous addition of nutrients. Three other modifications have been practiced: (1) alternate electron acceptor sources, (2) injection and recovery systems other than wells, and (3) air sparging directly into the aquifer as discussed in Section 5.5. The other oxygen and alternate electron acceptor systems include those discussed in the following paragraphs.

Pure Oxygen Systems. The use of pure oxygen in place of air offers the possibility of introducing the electron acceptor at a five-fold increase in rate and, presumably, a similar reduction in the treatment time. Oxygen is generated on-site or brought on-site in liquid (cryogenic) form (Prosen, Korreck, and Armstrong 1992). Other aspects of operation are virtually the same. Oxygen-generating units, such as those used in remote hospitals, can provide sufficient oxygen for modest systems at reasonable capital investments. If liquid oxygen is used, an evaporator and additional equipment are required and thus this approach is more applicable to larger systems. The injection system can be much the same as for air, using spargers or diffusers in the injection well. Oxygen utilization is more efficient if the injection water is saturated with oxygen aboveground in one of several types of systems. These systems provide high turbulence to allow dissolution with a short contact time. After the oxygen is dissolved in the injection water, the linear velocity of the water in the delivery system must be maintained above certain levels to minimize dissolution of the oxygen. The oxygenated water is then introduced through an annular pipe to the bottom of the injection well. Fully-pressurized systems where the well bore is maintained full of water reduces the hazard of high oxygen levels in the presence of flammable vapors.

Hydrogen Peroxide Systems. Hydrogen peroxide, H_2O_2, was first used in the mid-1980s because it is miscible in water and decomposes in the aquifer to yield oxygen and water (Brown and Norris 1988). Two kilograms of pure hydrogen peroxide produce almost 1 kg of oxygen. Hydrogen peroxide systems use metering pumps to transfer hydrogen peroxide (35 to 70%) from storage tanks for continuous addition to the injection water. Hydrogen peroxide at higher concentrations can serve as a bactericide and at too high a concentration, will yield oxygen too rapidly, leading to loss of oxygen to the unsaturated zone or gas blockage of the aquifer. Where applicable, hydrogen peroxide can be introduced at concentrations from 100 mg/L to

1,000 mg/L (typically, 200 mg/L to 500 mg/L). At 500 mg/L, oxygen is theoretically provided at a rate that is 25 times greater than that achieved by the sparging of air and more than 10 times faster than that achieved with pure oxygen. However, hydrogen peroxide stability is frequently a problem and must be evaluated before completing the system design (Flathman et al. 1991; Lawes 1991). If hydrogen peroxide stability and the groundwater flow rate under operating conditions are insufficient to permit hydrogen peroxide and/or elevated levels of oxygen to penetrate several meters into the aquifer, alternative designs will have to be implemented. Shorter remediation times should result if hydrogen peroxide utilization is efficient.

Nitrate Systems. Nitrate systems use metering pumps to transfer nitrate from tanks containing concentrates for continuous addition to the injection water (Hutchins et al. 1991). Nitrate can serve as a nutrient source and as an electron acceptor for aromatic compounds (except, reportedly, benzene) and some chlorinated solvents, but not for aliphatic hydrocarbons. Nitrate is highly soluble in water and is not retarded by soils. Thus, nitrate is technically an ideal electron acceptor for some organics. However, its use is regulated, and many regulatory agencies limit the nitrate concentrations in the injection water to 10 mg/L as N (46 mg/L as NO_3^-)

Sulfate Systems. Sulfate systems use metering pumps to transfer sulfate from tanks containing sodium or potassium sulfate concentrates for continuous addition to the injection water (Beeman et al. 1993). Sulfate has been used at a few sites for the reductive dechlorination of tetrachloroethylene (PCE) and trichloroethylene (TCE) under anaerobic conditions. Reductive dechlorination requires a degradable organic substrate/electron donor, such as sodium benzoate. Sulfate is highly water soluble and is not retarded by soils, so it is easily distributed through the aquifer. Apparently, there are no regulatory restrictions that would limit the amount of sulfate added; however, sulfide is an anaerobic byproduct that can be of concern, and sulfate concentrations greater than 250 ppm produces a laxative effect, and should be avoided.

Multiple Electron Acceptor Systems. Some designs have successfully incorporated more than one electron acceptor. Both oxygen and nitrate were successfully used at the French Limited site in Crosby, Texas (Thomsom et al. 1995). Nitrate penetrated more rapidly than oxygen and appeared to serve as an electron acceptor for the degradation of toluene and several chlorinated ethenes. Oxygen can be introduced downgradient of where sulfate is introduced to promote reductive dechlorination. Oxygen is then available to enhance biodegradation of vinyl chloride, which may be formed by reductive dechlorination.

Other Injection/Recovery Systems. Figure 5.5 shows alternatives to injection/recovery well systems (Cookson 1995). Systems that add amended water at the surface, beneath the surface but above groundwater (percolation systems), or beneath the groundwater surface (trench systems) have been used in various combinations, including combinations with recovery wells.

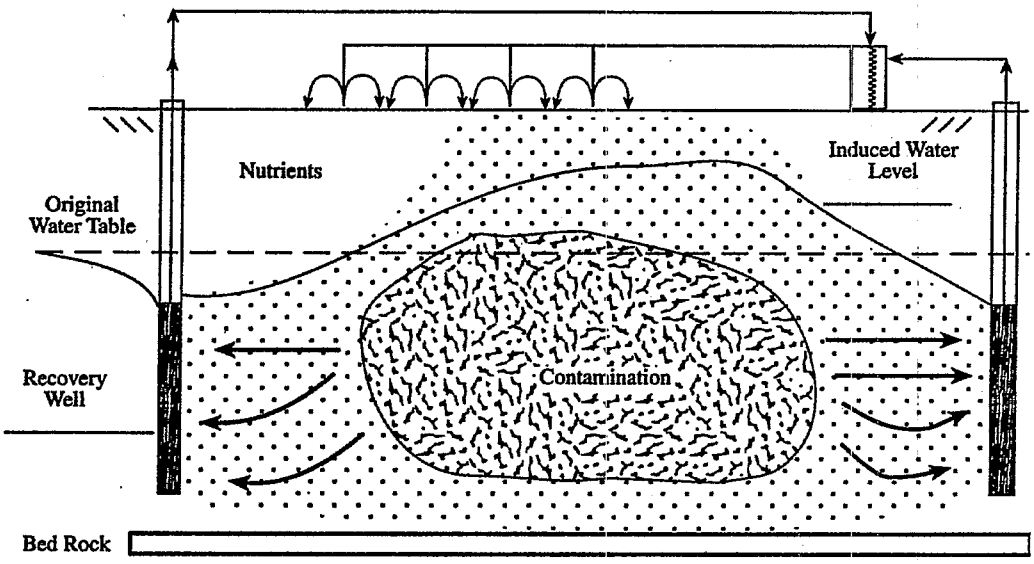
Percolation Systems. Introduction of amended water from the surface using percolation systems are limited to sites where the unsaturated zone consists of soils with adequate percolation rates. Sands and gravel are most appropriate. As the fines content of the soil increases, percolation rates decrease, adsorption of nutrients increases, and potential losses of electron acceptors, especially hydrogen peroxide, increase. A detailed discussion of these processes can be found in *Bioremediation Engineering: Design and Applications* (Cookson 1995).

The system shown in Figure 5.5a presents a number of permutations of the addition of amended water to unpaved surfaces using sprinklers, irrigation hoses, etc. This approach allows water to be added over a large area, usually in batch additions. Provisions need to be made to prevent run-off, and the surface should preferably be covered with a geomembrane to facilitate more homogeneous percolation by minimizing redistribution of fines.

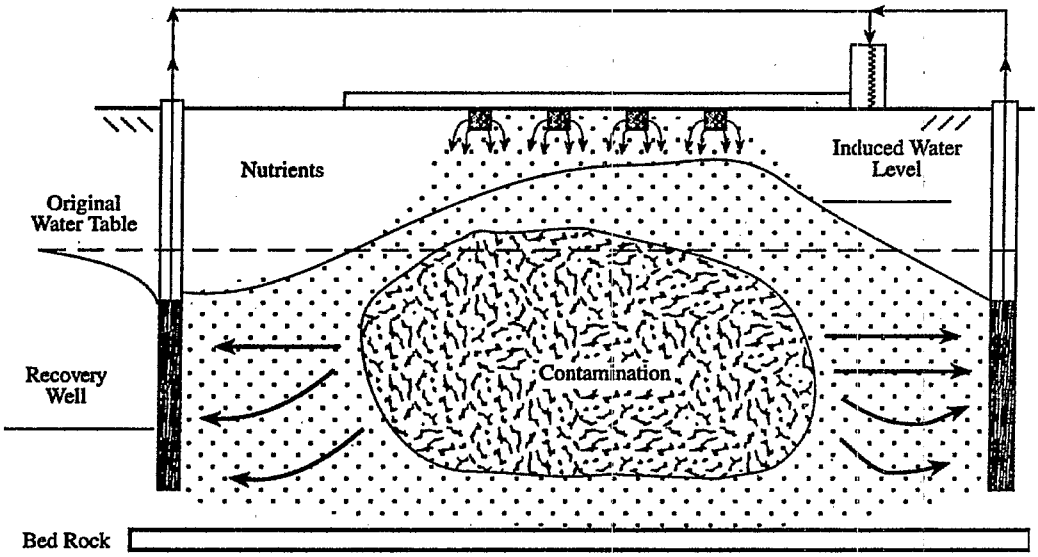
Systems that inject amended water below ground, but above the water table, include injection galleries. These systems have in common a gravel- or sand-filled void created by shallow excavations, trenches, or the bottoms of tank pits. They have advantages over surface addition systems in that they introduce amended water closer to the water table surface, have larger water retention capacity, are not subject to run-off, and are out of sight.

The introduction of water by percolation methods will result in groundwater mounding. Because the amended water is introduced from above the water table, nutrients and electron acceptors will be preferentially provided to the upper few feet of the aquifer and to the capillary and unsaturated zone soil. This may limit the rate at which nutrients and electron acceptors are provided to the deeper portion of the aquifer. Where most of the hydrocarbon mass is present in the smear zone, as is commonly the case, this type of delivery system introduces the amended water where it is most beneficial. As a result of normal water table fluctuations and possible intermittent addition of amended water, the interval over which the nutrients and electron acceptors are being provided will vary. One important difference between percolation and well systems is that in percolation systems the amended water is introduced over a wide area compared to well systems where introduced amendments must travel through the aquifer before reaching areas distant from the injection point. Thus, remediation is initiated over a wide

Figure 5.5
Alternative Injection/Recovery Well Systems for the Raymond Process



a. Spray Irrigation for Gravity-Feed System



b. Infiltration Trenches for Gravity-Feed System

Source: Cookson 1995

area as soon as amended water percolates to the water table in subsurface percolation systems.

Percolation systems generally incorporate groundwater recovery systems that capture the introduced amendments and contaminated groundwater to satisfy regulatory requirements or to protect downgradient receptors. First, it is necessary to calculate, determine, or estimate percolation rates and mounding effects (Cookson 1995) and, in some cases, account for retardation effects. For highly-porous, unsaturated soil with a shallow water table, percolation rates will probably exceed requirements. Where the aquifer is highly transmissive, mounding may be minimal. For less permeable soil and deeper water tables, percolation rates and mounding effects may limit this application method. The groundwater recovery system must then be designed, using modeling techniques discussed in Section 5.2.1, to capture contaminated and amended water. As with well systems, the rate of groundwater recovery must exceed the rate of introduction, and aboveground treatment will be required.

Systems using trenches extending into the aquifer operate much like well systems except that radius of influence limits no longer apply as long as the trench(es) traverse the entire treatment zone. Trenches also provide more surface area and are less prone to plugging than wells.

5.2.5 Pretreatment Processes

Recovery and reinjection wells must be developed or redeveloped prior to implementation to ensure maximum performance of the wells. Well development procedures differ depending upon the type of well and the characteristics of the formation. Procedures are described in *Groundwater and Wells* (Driscoll 1986).

Pretreatment of water to remove iron and calcium may be necessary to prevent fouling of the water treatment system. Removal of heavy metals may also be necessary for regulatory purposes. Typically, inorganics and heavy metals are removed through precipitation, although reverse osmosis or ion exchange may be used as discussed in Section 5.4.6. Depending upon the treatment method used for recovered groundwater, adequate metal removal may readily be achieved as discussed in Section 5.2.6.

Nutrient blends can be prepared on-site, but it is generally more economical to have the blends prepared off-site by a chemical distributor. The distributor should be required to filter the nutrient concentrate before shipment. The injection water should also be filtered downstream of where the nutrients and the electron acceptor are introduced and ahead of the injection

wells. If precipitates are introduced into the well, the well, gravel pack, and/or formation may become plugged, reducing well performance and increasing treatment times and cost.

5.2.6 Posttreatment Processes

Where the concentration of degradable compounds in the recovered water exceeds several mg/L, it is more cost-effective to treat the water aboveground because reinjection of untreated water will increase the demand upon the injection system to introduce electron acceptors, resulting in longer treatment time. Reinjection without treatment is not usually an option because contaminated groundwater typically must be treated before reinjection to meet regulatory requirements. One exception is where water can be discharged to a sewer or existing wastewater treatment plant and another source of water is used to introduce nutrients and electron acceptors.

Monitoring well locations and screened intervals need to be determined as part of the design. To modify operating parameters based on evaluation of performance as discussed in Section 5.2.18.2, the wells must be located to provide performance data in a timely fashion. Typically, this means locating monitoring wells or piezometers based on the travel time of the injected water. The monitoring points located closest to the injection wells should intercept the injected water at a point corresponding to one to two weeks groundwater travel time from the injection wells. Additional monitoring points need to be spaced at points corresponding to, for example, 25, 50, and 75% of the groundwater travel time between injection and recovery points.

Treatment of the recovered water is the same as for pump-and-treat systems. Air stripping towers or low-profile strippers, activated carbon, and bioreactors, as described in Section 5.4, are the most common treatment systems. Air-stripper towers may require an offgas treatment system. Air strippers are typically sized using computer software incorporating input parameters that include flow rate, temperature, volatile organic compound (VOC) concentration, and the Henry's Law constants for all constituents. Activated carbon system requirements can be estimated by suppliers based on known flow rates and groundwater quality data. The major problems in sizing either air strippers or activated carbon systems are obtaining good estimates of groundwater flow and the concentration of specific compounds in the recovered water. Usually systems are overdesigned to ensure compliance. Groundwater with mixtures of VOCs, semivolatiles, chlorinated solvents, and acetones or ketones may require two methods of treatment. Table 5.3 summarizes the commonly used groundwater treatment processes.

In addition to treatment of organics, it may be necessary to remove iron and/or heavy metals. Iron treatment is usually accomplished by oxidation and precipitation and includes filtering, drying, and sludge disposal. If heavy metals are present or if organics are removed with the iron, the sludge may need to be disposed as hazardous waste. Treatment of iron and/or heavy metals can easily exceed the treatment costs for the organic constituents.

For bioremediation at gasoline service stations and similar UST sites, the water treatment system must be able to operate for several days or weeks at a time without maintenance. At larger sites, such as many Superfund sites, daily or even around-the-clock operators may be required for other purposes, and thus, more labor-intensive treatment systems may be tolerable.

The treated groundwater may be discharged to sewers, surface water, and/or reinjected. Unless another source of water is being used for reinjection, the treated water stream is normally split between some form of discharge and nutrient/electron acceptor amendment and reinjection. Before reinjection, it is necessary to filter the water so that particulate matter is not being introduced to the well; even small amounts of solids can eventually reduce injection rates.

5.2.7 Process Instrumentation and Control

The main components of a Raymond Process system are listed in Table 5.4. In addition to the components common to a pump-and-reat system, Raymond Process systems include nutrient and electron acceptor delivery systems, transfer pumps and lines, injection wells, controls, and meters. The system components are designed to remove and treat water from the aquifer, amend the water, and reintroduce the water to the aquifer in a manner that does not lead to reduction in permeability. All of these processes need to be integrated so that water flow is balanced.

As shown in Figure 5.4, the effluent from the groundwater treatment system is split between discharge and recirculation. The recirculation water is typically sent to a surge tank which should hold several hours of flow. The surge tank is necessary because the rate at which injection wells will accept water fluctuates and typically decreases over time until the wells are treated or redeveloped. Transfer pumps are used to deliver water to the injection header. Injection wells are either gravity fed or pressure fed. Controllers are used to operate valves and/or the transfer pumps. Water level in the surge tank is maintained between specified limits with high/low switches. The system can be designed to automatically direct more of the treated groundwater to the sewer or other discharge point, rather than interrupt groundwater

Table 5.4
Major Raymond Process System Components

Recovery Wells	Groundwater Treatment System
Injection Wells	Surge Tank
Manifolds/Transfer Lines	Nutrient System
Force Mains	Electron Acceptor System
Transfer Pumps	Controllers
Valves/Meters	Programmable Logic Controller

recovery, thus maintaining groundwater capture patterns. The system design, in most cases, should call for operation at less than the maximum achievable injection rates so that the system can be adjusted to compensate for moderate losses in injection capacity over time.

The nutrient and electron acceptor feeds are located between the surge tank and the header(s) to the injection wells. The nutrient tanks should be sufficient to contain several weeks' supply of nutrients. Level indicators on the nutrient tanks document the amount of nutrient added. Totalizer readings and delivery records are used, as are periodic analyses of both the nutrient solution in the tank and samples collected at points sufficiently downstream of the nutrient feed, to document nutrient delivery to the aquifer.

The electron acceptor delivery system depends upon the total system design. Nitrate and sulfate addition is essentially the same as that for nutrients. Hydrogen peroxide delivery systems are similar except the properties of hydrogen peroxide place special demands on the materials of construction and require provisions for pressure release. Small remediation systems may use drums or other containers, while large systems use storage tanks up to 7,570L (2,000 gal). Transfer lines must not isolate hydrogen peroxide without pressure release, otherwise the slow evolution of oxygen gas as the hydrogen peroxide decomposes will rupture the line. It is imperative that a hydrogen peroxide supplier or a qualified distributor provide the delivery system and, for larger systems, install the system.

Gas delivery systems consist of an oil-free air compressor (to avoid introducing contaminants) and filter, along with pressure release valves, pressure gauges, and control valves. Molecular sieves can be used to remove nitrogen from air so that a higher oxygen content can be introduced into the aquifer. A more complete description of such systems is provided in Section 5.5.5.

If city water is used as a water source, it may be necessary to add a small amount of sulfur dioxide to destroy residual chlorine. Alternatively, a second groundwater system may be used to recover water from a deeper aquifer for supply purposes.

While temporary interruptions in service may not cause further environmental damage, they can be quite expensive. Thus, it is important to specify good quality equipment with a reputation for reliability. Appropriate materials of construction including piping that is compatible with the water source must also be specified. Downtime delays remediation and requires additional maintenance that will quickly exceed the savings realized from purchasing less reliable equipment. While it is not necessary or always preferable to buy the most expensive equipment, equipment is not the place to economize.

Enhanced performance and reduced labor costs can be achieved by the use of automated control systems. Programmable logic controllers (PLCs) have become quite sophisticated. PLCs provide standard relay-type operation for control of surge tank water levels and injection and recovery flow rates. Control can be based on response to meters or on a programmed time sequence of events. A computer program for the specific system is developed in conjunction with the system vendor. Modifications to the program are readily made in the field or by remote command. The return on the investment in PLCs can be substantial based solely on reduced labor costs. However, the biggest potential for return is the ability to maintain the system closer to optimum and reduce the time for required remediation.

5.2.8 Process and Instrumentation Diagrams

Process and instrumentation (P&I) diagrams are necessary to ensure design quality and to facilitate efficient and correct installation. The level of detail required depends upon whether the design firm is also doing the installation. If the work will be put out for bid, the level of detail needs to be greater because of the potential for misinterpretations and to limit the opportunity for change orders. For Superfund and RCRA projects, the P&I drawings will need to be highly detailed and will undergo review at several stages of the process.

Several types of P&I diagrams are necessary. These include the following:

- total system showing major components;
- injection, monitoring, and recovery wells showing screened intervals, grouting, and surface completion;

- water treatment system and offgas treatment system, if included;
- nutrient and electron acceptor delivery systems;
- piping from recovery well(s) to treatment system, to discharge and to surge tank, to injection well, and from delivery systems to injection water header;
- electrical systems; and
- meters, gauges, and controllers.

Figures 5.6, 5.7, and 5.8 show typical P&I diagrams for the total system layout, for the nutrient/electron acceptor delivery system, and for the piping system. Typical diagrams for wells, electrical, and groundwater treatment systems (Section 5.4.6) are adequate.

5.2.9 Sample Calculations

Many of the calculations involved in this process are used elsewhere or are relatively fundamental. These include calculations of contaminant mass, nutrient and electron acceptor requirements, and groundwater flow. The dissolved mass is estimated by multiplying the aquifer pore volume by the average dissolved contaminant concentration.

Total contaminant mass associated with the soils can be estimated from:

$$M(kg) = V(M^3) \bullet D(kg / M^3) \bullet \frac{C_{avg}(ppm)}{10^6} \tag{5.1}$$

or,

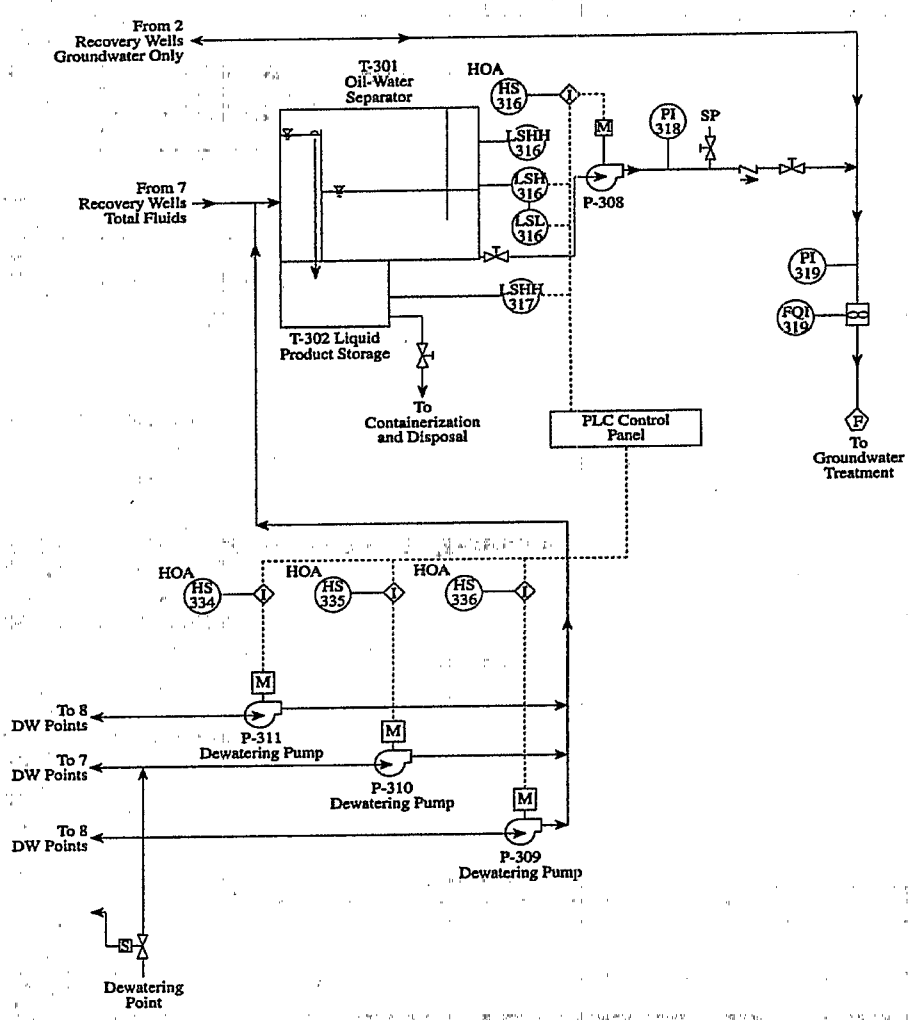
$$M(lb) = V(ft^3) \bullet D(lb / ft^3) \bullet \frac{C_{avg}(ppm)}{10^6} \tag{5.2}$$

where:

M	=	mass of contaminants;
V	=	soil volume;
D	=	soil density (typically 1,350 kg/m^3(105 lb/ft^3]); and
C_{avg}	=	average soil contaminant concentration.

The stoichiometric electron acceptor and nutrient requirements are presented in Table 5.5. These are only starting values and need to be adjusted for the factors discussed in Section 5.2.2, including the mass of contaminant removed through groundwater extraction.

Figure 5.6
Groundwater Recovery, Dewatering, and Oil-Water Separator Systems



The total volume of injected water that will be required is calculated from the concentration of the electron acceptor(s) and/or nutrients as introduced into the aquifer.

$$V_i = \frac{M_{ea}}{C_{ea}} \bullet 10^3 \qquad (5.3)$$

where:

M_{ea} = required mass of electron acceptor [kg (lb)];
V_i = volume of water to be injected [M^3 (ft^3)]; and
C_{ea} = concentration of electron acceptor in the injection water (mg/L).

Figure 5.7
Air Injection System

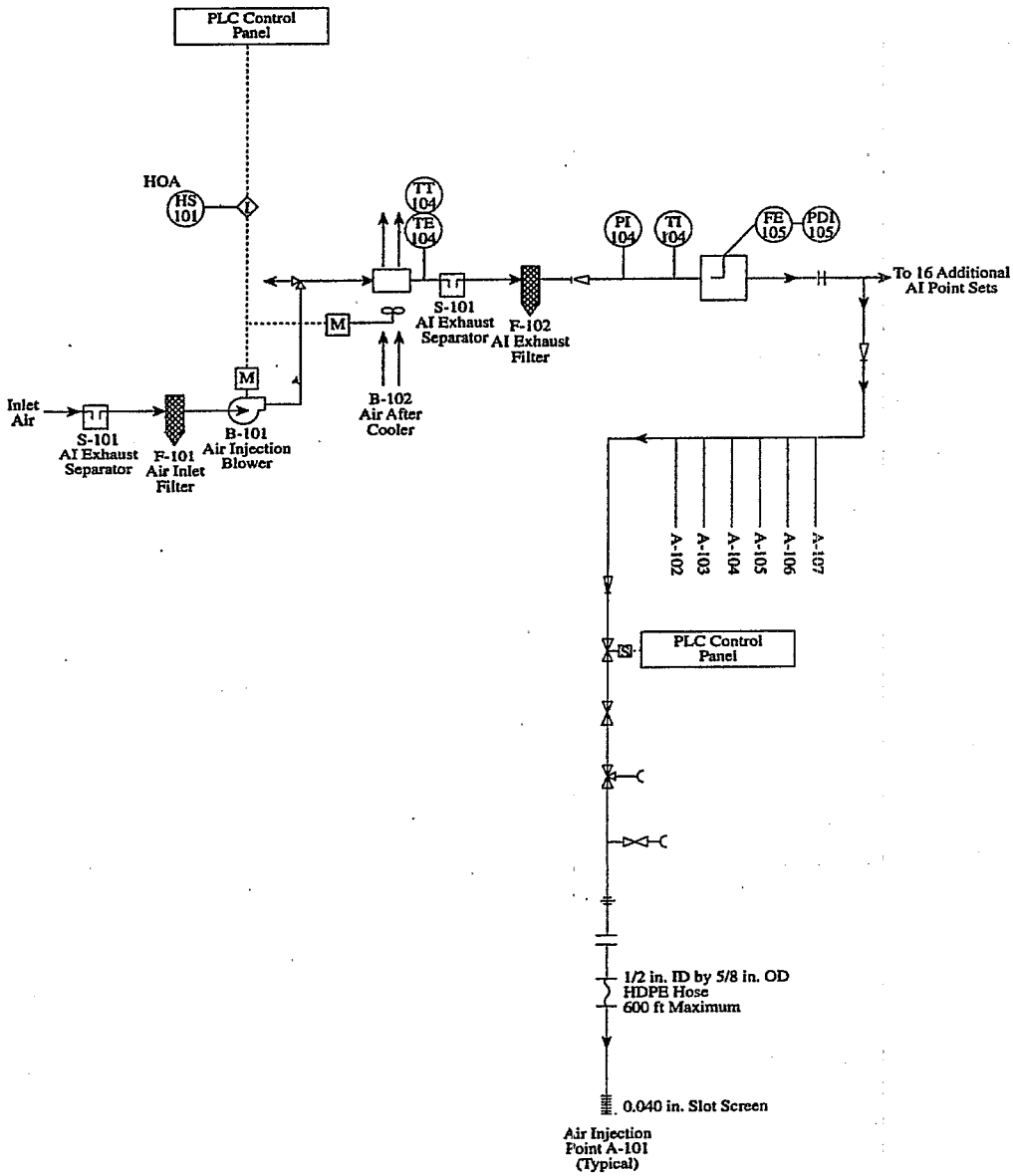


Figure 5.8
Water Treatment and Injection System

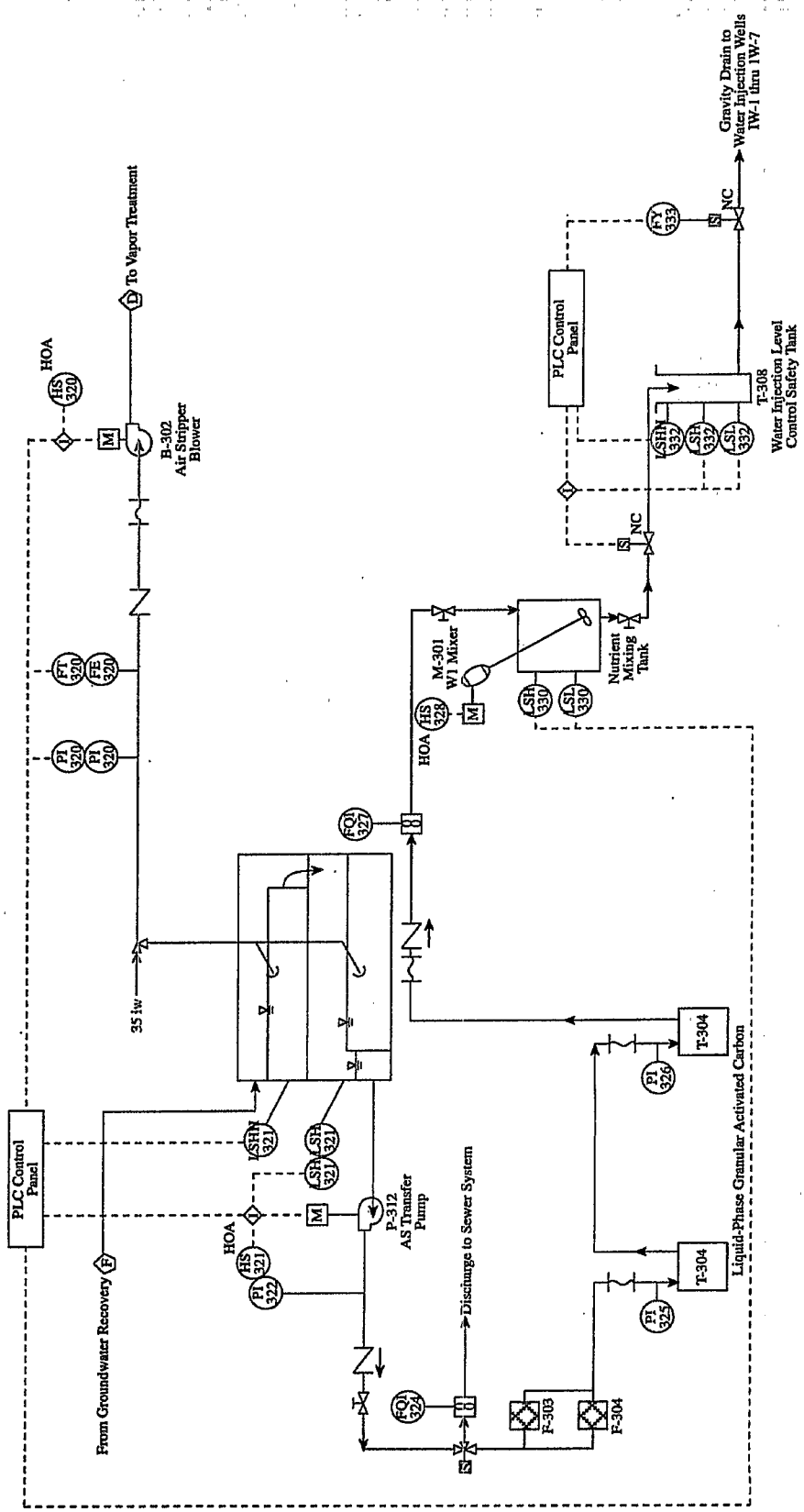


Table 5.5
Effective Range of Electron Acceptor Concentration and Cost for the Raymond Process

Electron Acceptor and Source	Effective Concentration (mg/L)	Kg Toluene / Kg electron acceptor source	Cost ($) for Electron Acceptor per kg Toluene
Air (O_2)	8	15	0.00*
Oxygen (O_2)	40	3	0.40
Sodium Nitrate (NO_3^-)	45	5.2	5.00
$H_2O_2(O_2)$	235	6.5	12.00

*Only costs are capital and O&M.

The rates of groundwater recovery and injection are determined by conducting pump tests and incorporating the results of the test in a groundwater flow model that can simulate capture and flow lines from the injection to the recovery well(s). Anticipated recovery rates can be estimated from soil classifications and tables found in books, such as Freeze and Cherry (1979). This process is highly dependent upon the judgment of the geologists who classify the soils. More often than not, this process overestimates sustainable yields. Further, unless the recovery well is within the source area and surrounded by injection wells, it may not be advisable to operate the well at maximum yield because significant volumes of clean water will be captured requiring a significantly larger groundwater treatment system than would otherwise be necessary. In general, injection wells will sustain lower flow rates than recovery wells.

Based on the anticipated injection rates and the concentrations of nutrients and/or electron acceptors, the mass of electron acceptor that can be introduced in one month or one year is calculated. It is then a simple matter to estimate the remediation time from this value and the demand calculated earlier.

$$T = \frac{V_i}{R_I} \tag{5.4}$$

where:

V_i = volume of water to be injected [M^3 (ft^3)];
R_I = injection rate [m^3/d (ft^3/d)].

The total volume of water that can be added over the estimated remediation time can then be used to determine the required average concentration of nutrients that will be needed to meet demand. The concentration of nutrients at startup should be two to four times this value, with the anticipation that the nutrient concentration will be adjusted based on observations made during operations. If precipitation of calcium, iron, and/or magnesium is indicated, the minimum concentration of KTPP is calculated from:

$$\frac{K_5P_3O_{10}(g)}{448} \geq \frac{Mg(g)}{24} + \frac{Fe(g)}{56} + \frac{Ca(g)}{40} \tag{5.5}$$

Jar tests can also be used to test the calculated nutrient formulation. Jar tests are conducted by adding a volume of water to each of several jars containing various amounts of nutrient concentrate. Visual inspection is used to determine the lowest concentration of nutrients that will not result in precipitate formation. If the calculated minimum concentration or that determined from jar tests exceeds the concentration based on demand, nutrients should be added intermittently at the higher concentration. Because water quality will change over time, the calculations and/or jar tests should be repeated after one pore volume of water has passed through the contaminated aquifer.

The time for injected water to reach the recovery wells or sweep through the contaminated zone should not be excessive. Long residence times equate to long remediation times because numerous pore volumes of injected water will be required for remediation. Additionally, long residence times result in greater loss of nutrients and electron acceptors through nonproductive reactions and adsorption. The loss of electron acceptors to other reactions is particularly critical when hydrogen peroxide is used. Long residence times are most easily addressed by closer spacing of wells as discussed in Section 5.2.2. Residence times can be approximated from the injection rate and the volume of soil through which the water will pass. First the velocity of groundwater flow is calculated as:

$$V(m/d) = \frac{Q(m^3/d)}{W(m) \bullet h(m) \bullet n} \tag{5.6}$$

or

$$V(ft/d) = \frac{Q(ft^3/d)}{W(ft) \bullet h(ft) \bullet n} \tag{5.7}$$

where:

Q	=	injection rate [m^3/d (ft^3/d)];
W	=	width of sweep zone [m (ft)];
h	=	depth of sweep zone [m (ft)]; and
n	=	porosity.

The time of sweep through a given zone is then calculated from the groundwater flow velocity and distance from the injection well to point of interest (i.e., a monitoring or recovery well).

5.2.10 Safety Requirements

In addition to the common health and safety considerations associated with environmental activities and covered by the OSHA the following must be addressed:

- electrical systems must meet local codes including ground fault protection;
- mechanical equipment must be supported on concrete pads;
- pressure release valves must protect each pressurized system and be located such that personnel cannot be struck by the discharge;
- fugitive emissions must be controlled through treatment or the use of stacks;
- chemicals must be stored properly, including segregation of noncompatible chemicals (e.g., hydrogen peroxide and combustible materials) with appropriate warning labels and first aid information clearly accessible;
- hydrogen peroxide systems must be designed by suppliers or distributors, constructed of appropriate materials, and contain adequate pressure relief. Lines should not be located over personnel access areas;
- liquid oxygen tanks should be placed on concrete rather than asphalt pads because of fire hazard;
- eyewash and first aid supplies should be kept in an accessible and easily identified location;
- project-specific health and safety reviews should be held along with personnel training (Hazard Communication); and

- site security must be sufficient to eliminate casual, unwanted visitors who may hurt themselves or damage equipment and increase potential harm to site workers and/or official visitors.

5.2.11 Specifications Development

The selection of all equipment, meters, valves, piping, controllers, and chemicals should be compared to the appropriate specifications. Vendors and suppliers should be required to provide the appropriate documentation regarding materials, quality, and performance.

5.2.12 Cost Data

The costs associated with a Raymond Process system are highly site-dependent and a function of the hydrogeology, treatment zone dimensions, contaminant properties, loading contaminant mass and distribution, clean-up targets, regulatory design limitations, and specific design used. Because of the large variability in costs among relatively similar sites, caution and engineering judgment must be used to extrapolate these representative costs to a specific site.

The cost of any system is a function of engineering, capital, and operation and maintenance (O&M) costs. O&M costs are associated with operations, maintenance, labor, chemicals, and electricity and can easily exceed other costs. Additionally, project management, and reporting costs can be significant. Designs that increase the rate of introduction and distribution of electron acceptors increase capital and monthly operating costs, but can shorten the duration of the remediation project.

The electron acceptor must be selected based on the contaminant and known metabolic pathways as discussed in Section 2.1. After this criterion is met, the selection is based on cost-effectiveness. However, the cost of supplying the electron acceptor may be less important than the impact of the selection upon total remediation time because this determines the number of months or years over that which O&M costs will be incurred. Table 5.5 shows the effective concentrations that might be achieved with oxygen sources, nitrate, and sulfate; the relative amounts of toluene that could be biodegraded; and the cost of the electron acceptor per kilogram of contaminant treated. Table 5.6 indicates typical durations of Raymond Process treatment applications using various electron acceptors along with an estimated total project cost for each application. The total cost consists of capital costs, O&M costs accrued over the lifetime of treatment, as well as the incidental costs, which may include limited use of the property or third-party

impacts. Table 5.7 provides a typical cost breakdown for a 3-year hydrogen peroxide treatment project.

Table 5.6
Typical Cost* of Aquifer Bioremediation Using Various Electron Acceptors in the Raymond Method

Source Electron Acceptor	Months	K$/Month	Total (K$)
Air 8 mg/L	100	10	1,000
O_2 30 mg/L	40	11	440
H_2O_2 200 mg/L	20	12	240
NO_3^- 50 mg/L	40	10.1	404
NO_3^- 200 mg/L	15	10.4	156
$O_2 + NO_3^-$ 30/50 mg/L	25	11.1	278
$O_2 + NO_3^-$ 30/200 mg/L	10	11.4	114
$NO_3^- + H_2O_2$ 200/200 mg/L	7	12.4	87

*Including capital, O&M, and incidental costs.

5.2.13 Design Validation

Design validation should include review of all calculations and equipment specifications including comparison with other projects. The design should also consider problems that have occurred at other sites. Sustainable recovery and injection rates should be tested at representative wells. Permits should be reviewed so treatment process discharges meet regulatory and permit limits including both air or water quality and flow rates if discharges are made to sewers.

Treatability studies do not always need to be conducted. Easily conducted tests including pH, bacteria counts, analysis of potential toxins, electron acceptors and nutrients, and degradation byproducts, as well as historical water quality data can provide a good indication of whether bioremediation is an appropriate remedial technology for a given site. Microcosm studies can validate that microbial populations capable of degrading the

Table 5.7
Typical Raymond Process Cost Breakdown

Cost Element	Unit Costs ($)	No. of Units	Costs ($)
ENGINEERING			
Work Plan	3,000	1	3,000
Aquifer Tests	10,000	1	10,000
Laboratory Tests	15,000	1	15,000
Modeling	5,000	1	5,000
Design	25,000	1	25,000
Subtotal, Engineering			**58,000**
TREATMENT COSTS			
Well Installation	2,000	20	40,000
Transfer Lines	20/ft	600	12,000
Pumps & Controls	7,000	3	21,000
Nutrients System	20,000	1	20,000
H_2O_2 System	20,000	1	20,000
Water Treatment System	25,000	1	25,000
O&M (annual)	110,000	3	330,000
Management (annual)	12,000	3	36,000
Reporting	10,000	5	50,000
Subtotal, Treatment Costs			**554,000**
CLOSURE			
Final Soil Sampling	5,000	1	5,000
Final Report	10,000	1	10,000
Site Restoration	3,000	1	3,000
Subtotal, Closure			**18,000**
GRAND TOTAL			**630,000**

contaminants of interest are present and can be stimulated. However, microcosm studies do not provide rate data that predict remediation times as remediation time is more a function of groundwater injection rates and mass loading of the contaminant, than the specific microbial population that can be enriched in a microcosm study. As a result, pump test results and computer fate and transport modeling (taking into consideration the mass loadings) are more meaningful than microcosm studies for the evaluation of expected remediation times under specific field-limiting conditions.

In general, requirements for design validation will be more strict for Superfund and RCRA sites than for state-mandated sites, such as UST sites at service stations.

5.2.14 Permitting Requirements

Permitting requirements vary among states and sometimes within states where local or regional agencies exist. Typically on Superfund and RCRA sites, permits are not required, but the conditions of the permit regulations must be met. The types of permits that apply include:

- well installation (some jurisdictions);
- discharge to groundwater;
- discharge to surface water bodies;
- discharge to sewers;
- air discharge;
- building;
- electrical;
- unique local regulations;
- wetlands; and
- coastal waters.

Most of these permits are obtained as for any other remedial technology. The discharge to groundwater permit may be stringent in some locations because nutrients and electron acceptors are being introduced. For instance, nitrate may be limited to concentrations below its maximum contaminant level (MCL) of 10 mg/L as N. Some states allow nutrient injection, but require that ammonium and phosphate levels not exceed background or regulatory levels at the completion of the project.

As part of the permitting process, public notification and hearings may be required.

5.2.15 Design Checklist

Table 5.8 provides a relatively comprehensive list of items that need to be addressed in the design and implementation of the Raymond Process for aquifer remediation.

Table 5.8
Raymond Process Design Checklist

Site Characterization	Type and distribution of contaminants
	Soil characterization
	Contaminated soil and groundwater volume
	Aquifer characteristics
	Groundwater chemistry
Site Features	Property lines
	Nearest power source
	Building/confined space locations
	Underground utilities
	Concrete/asphalt surfaces
	Normal use and traffic patterns
Aquifer Testing Results	Adequate hydraulic conductivity
	Appropriate microbiology
	Appropriate electron acceptors
	Nutrients compatible with groundwater
	Estimated treatment time acceptable
Well Design	Screened intervals
	Well locations
	Completion methods
Water Treatment	All regulated compounds treated
	Precipitation potential addressed
	Sufficient capacity
	Residuals addressed
	Discharge water quality acceptance
Groundwater Transfer System	Lines deep enough to avoid freezing/heat traced
	Valves, flow meters, control valves
	Surge tank controls
	In-line filters

Table 5.8 (cont.)
Raymond Process Design Checklist

Amendment Addition	Adequate storage
	Compatible materials of construction
	Check valves/pressure relief
	In-line filters
Health and Safety	HASP complete/kept on site
	Dig safe contacted
	Ground fault protection
	Electrical interlocks
	Fire Department notified (H_2O_2)
	Security
	Emergency shutdown procedures
Miscellaneous	Permits secured
	O&M manual reviewed
	Monitoring plan/schedule
	Treated soil placement
	Site restoration

5.2.16 Implementation

Implementation requires coordination of several activities. Wells must be installed using the appropriate drill rigs and installation techniques, and completed at the proper elevations for monitoring wells (e.g., surface or aboveground completion). Injection and recovery wells must be completed either at the surface or beneath ground in vaults depending upon where the force mains and transfer lines are placed. Force mains and underground transfer lines should be installed from well manifolds to points of connections to tanks and pumps.

Equipment support pads, treatment buildings, storage buildings, electrical service, security fencing and lighting, access roadways and paths, if needed, and grading should be completed before equipment is delivered. Equipment and tanks should be placed on support pads or in a building as specified.

Treatment equipment, pumps, meters, valves, and controllers should be installed and tested to the extent practical. Repairs or replacements should

be made immediately. The system should be inspected to ensure that specifications have been met. Finally, all appropriate local agencies should be notified.

5.2.17 Start-up Procedures

Start-up procedures vary somewhat with the design, electron acceptor used, and groundwater chemistry. Startup begins with checking the system to ensure that no installation-related problems exist.

Baseline measurements of water quality and bioremediation parameters are made prior to initiating groundwater recovery. A detailed list of wells to be sampled, parameters to be analyzed in each well, and sample preservation requirements should be prepared, reviewed, and used as a guide in the field. A similar list, including measurements of temperatures, flow rates, and pressures across the system, should be prepared for the duration of the start-up period.

Groundwater recovery is initiated with 100% of the treated water being polished with activated carbon and discharged to a sewer line or surface water body until water quality can be demonstrated to meet regulatory requirements. After this condition has been met, a portion of the groundwater can be diverted to the surge tank. When the level in the surge tank exceeds the "low level" the transfer pump is turned on and water is introduced to the injection wells through the manifold or header.

Groundwater recovery and injection are continued without nutrient or electron acceptor addition for a specified period depending upon the groundwater geochemistry. Nutrient addition is typically initiated prior to electron acceptor addition. If hydrogen peroxide is used, nutrient addition is maintained for 1 to 2 weeks prior to initiating hydrogen peroxide addition. Hydrogen peroxide is first added at a relatively low concentration, 20 to 50 mg/L, and successively increased about once per week until the design concentration of 100 to 500 mg/L is attained.

During the start-up period, the schedule for measuring and recording flow rates, taking meter readings, and collecting samples for analysis is followed. Samples of the influent and effluent to the groundwater treatment system are collected for analysis. Nutrient and electron acceptor concentrations in the feed solutions and in the injection water are determined.

Water levels are measured for evaluation and verification of the computer model used to design the system. This will allow periodic adjustment of the recovery and injection rates from individual wells to achieve the desired groundwater flow patterns.

During this period, flow rates and other parameters are modified to meet specifications and/or to optimize performance. Since the system will not behave entirely as expected, modifications to the O&M manual should be anticipated based on the outcome of this start-up period. Monitoring and documentation procedures are also evaluated and changed as necessary.

5.2.18 Performance Evaluation

Performance evaluation includes determining changes in groundwater quality, nutrient and electron acceptor concentrations at monitoring locations, groundwater recovery rates, injection rates, groundwater treatment efficiency, and changes in piezometer surfaces. In all but the smallest systems in relatively homogeneous formations, it is highly unlikely that the system, as originally designed, will provide the best practical remediation. The O&M plan should incorporate procedures to evaluate performance and modify operations. This requires that the monitoring plan be designed to identify optimization refinements as well as to satisfy regulatory requirements and measure progress of treatment. Potential changes in operational procedures include modifications to: (1) reduce operator time; (2) change requirements; (3) minimize monthly operating costs; or (4) better distribute nutrients and electron acceptors to reduce the treatment time. As discussed in Section 5.2.1, the project design and budget should provide for the installation of additional wells, if needed.

5.2.18.1 Operation Practices

Operations include injection and recovery well maintenance; balancing groundwater recovery, discharge, and reinjection; maintenance of groundwater treatment; management of nutrient and electron acceptor addition; evaluation and response to monitoring data; routine maintenance of equipment, controls, and monitoring equipment; and housekeeping.

Maintaining flow in the injection wells is frequently the most time-consuming activity listed above. The rate of remediation is closely linked to the rate of introduction of the electron acceptor. If the rate of water injection decreases, the number of months over which O&M, reporting, and management costs are incurred increases. Design and well completion procedures for injection wells are important, as is scheduling well redevelopment at a frequency based on experience with different types of aquifers, mass of organics to be degraded, and design flow rate. Performance of and anticipated problems with injection wells can be evaluated from changes in the cycling frequency of the high/low controllers for gravity-fed wells and by pressure changes in pressure-fed wells. Wells can be treated by surging to remove

fines. Biological growth and precipitation of calcium or iron can be addressed by adding dilute hydrochloric acid to the well and subsequently recovering the spent acid after several hours. This may kill bacteria within a few feet of the well, but this is not a concern as remediation of this area should have occurred within the first few days of operation. A better approach is to add a batch of 1 to 3% hydrogen peroxide to kill bacteria. This results in a more easily-removed (particulate) biomass than does the use of dilute acid which often results in a slimy biomass that is difficult to remove from the well.

To optimize the groundwater flow patterns, the model used to design the treatment system is used during operation to adjust flow rates based on the current piezometric surface. The model output is used to determine if nutrients and electron acceptors are being proportionally introduced based on the contaminant distribution. If not, model simulations can suggest modifications to flow rates at individual injection and recovery wells. The impact of the changes in flow rates can be evaluated within a few days by measuring the changes in the piezometric surface and again running the model. Use of the model provides operational guidance more rapidly than waiting months for monitoring data to indicate how to change well operation; however, the model must be used in conjunction with the field monitoring data.

The distribution of treated water between injection and discharge is controlled by the level of water in the surge tank. Manual adjustments to valves are made to prevent excessive cycling within the surge tank while ensuring adequate feed rates.

Operational practices of the groundwater treatment system depend upon the treatment process used. Groundwater treatment operational practices and monitoring are critical because of the potential to discharge water that is out of regulatory compliance to surface water, groundwater, or sewers, all of which can result in fines and poor relations with the regulatory agencies or the public. Operational practices for biological treatment systems are discussed in Section 5.4.16. Activated carbon systems are relatively simple. The principal activity consists of monitoring the water quality in the influent, effluent, and between the carbon units. The use of three units in series permits greater loading than using two in series, but requires an additional analysis to be performed. The first unit in series is removed when spent, and a new unit is placed at the effluent end of the series. Air strippers, either towers or low-profile strippers, routinely require maintenance to remove precipitates of iron and/or calcium and biomass.

5.2.18.2 Operation Monitoring

As with most remedial systems, monitoring includes baseline sampling and analysis. Monitoring is most intense during the first few days of operation and decreases in frequency over the first few months. To the extent practical, monitoring should be conducted with instrumentation and automatic recording devices. For remote sites, it is particularly advantageous to link these devices to an off-site location to reduce travel and labor costs.

Generally, for a Raymond Process system, the parameters listed in Table 5.9 are monitored. Initially, the most critical parameters are the influent and effluent water quality parameters from the groundwater treatment system. If the groundwater treatment system is not meeting the specified criteria, the entire system will need to be shut down. The groundwater treatment system influent quality is also used to cumulatively measure the mass of contaminant being removed as one indication of remedial progress.

Table 5.9
Required Monitoring Parameters Used in the Raymond Process

Parameters	Comments	Locations
Organics	Specific (e.g., benzene), and surrogate (e.g., TPH or TOX)	Monitoring/Recovery Wells Treatment System, and Influent/Effluent
Nutrients	Nitrogen (e.g., NO_3^-), NH_4^+, TKN, and Phosphorus (e.g., total phosphate)	Monitoring/Recovery Wells Storage Tanks, and Injection Header
Electron Acceptor(s)	DO, NO_3^-, or SO_4^{2}	Monitoring/Recovery Wells Storage Tanks, and Injection Header
Inorganic Ions	Fe, Ca, and Mg for Precipitation Concerns and Others if Fresh Water Supply is Injected	Monitoring/Recovery Wells, Treatment System Influent/Effluent, and Injection Header
pH, Temperature, eH, and Conductivity		Monitoring/Recovery Wells Treatment System Influent/Effluent Injection Header, and Storage Tanks
Groundwater Levels		All Wells
Recovery/Injection, Discharge Flow Rates, and Pressure		Injection/Recovery Wells and All Transfer Lines

Monitoring for groundwater quality changes is necessary to meet regulatory requirements and to evaluate remedial progress. Data interpretation requires a detailed understanding of the process — degradation will occur first near the injection wells, to some extent the more degradable compounds will be treated first, the more soluble compounds will be removed through groundwater extraction, and solubilization effects from biosurfactants will frequently result in increased dissolved-phase concentrations. Thus, these data need to be interpreted in the context of the mechanisms of remediation and the sequence of their occurrence along groundwater flow paths. It is important that the regulatory agencies understand that increased concentrations of various constituents in the groundwater may occur before improvements to groundwater quality are achieved.

Biodegradation parameters, especially nutrient and electron acceptor concentrations, are initially intensely monitored in the vicinity of the injection wells to evaluate flow patterns relative to contaminant distribution. Dissolved oxygen (DO), pH, conductivity, eH, and temperature can easily be measured on-site using readily available meters. (For DO values less than 1 mg/L, some practitioners prefer kits based on the Winkler method although there is some question of the benefit of accurate DO measurements for DO levels less than 1 mg/L). Phosphate, ammonium ion, nitrate, nitrite, carbonate, sulfate, magnesium, manganese, chloride, and iron can be measured using water analysis kits while on site. During startup, such rapid access to data can be beneficial. For routine operations, it is not always cost-effective to use the kits, and the results are often not as defensible as data obtained from an analytical laboratory.

It is equally important to measure the depth to water in monitoring wells frequently during the first several months of operation. As previously mentioned, the groundwater model used to design the well layout and flow rates can be used to evaluate groundwater flow patterns and to adjust flows from individual wells. The model should also be evaluated and calibrated as necessary during the course of the project based on measured field data.

The monitoring program should also include measurement of water flow rates from individual wells, headers, groundwater treatment influent, discharge line, and individual injection wells. The most practical method of obtaining these flows is to use totalizers and record the data on a predetermined schedule.

Nutrient and electron acceptor concentrations are measured in the concentrate tanks following deliveries and in the header at a location downstream of the mixing point. These values are compared to tank level records for consistency and to the O&M schedule to verify stable performance of the system over time.

5.2.18.3 Quality Assurance/Quality Control

Quality Assurance/Quality Control (QA/QC) procedures applicable to the Raymond Process include practices common to other bioremediation technologies (i.e., the use of blanks, blind duplicates, and spiked samples for laboratory and field measurements). Quality practices specific to the Raymond Process are:

- determination of composition of the nutrient and electron acceptor concentrates;
- comparison of current groundwater recovery flow rates and cumulative flow from individual wells to the current flow rates and cumulative flow from the injection header and discharge line;
- comparison of the distribution of nutrients and electron acceptor concentrations as indicated by monitoring data to those predicted from the groundwater flow pattern simulated by the computer model (tracers can also be used);
- comparison of biological parameter data with changes in groundwater quality and mass removed from groundwater extraction;
- review of health and safety practices;
- review of operating practices and training of new field personnel; and
- routine evaluation of monitoring and metering equipment, valves, etc.

5.3 *Intrinsic Remediation*

5.3.1 Principles of Operation

Intrinsic remediation is the process of site assessment, data reduction, and interpretation that quantifies the natural assimilative capacity of a given aquifer system to treat groundwater contaminants through physical, chemical, and/or biological means without human intervention. Through the intrinsic remediation plume management approach, the nature and extent of soil and groundwater contamination, and the extent and rate of natural contaminant degradation at a site are determined. This approach is appropriate if the plume has not impacted a downgradient receptor and the rate of

contaminant release from the source area is equal to or less than the contaminant degradation rate observed at a site. Dissolved plumes containing those compounds shown in Table 2.2 to be biologically transformed under aerobic and anaerobic conditions could potentially be managed using an intrinsic remediation approach.

A number of field sampling protocols are available from a variety of sources describing approaches for collecting and analyzing data necessary to verify that intrinsic remediation processes are taking place (Wiedemeier 1994; Wilson et al. 1994). The connection of these data with decisions regarding source removal activities or with estimates of source lifetime have generally not been presented in the literature. An approach for implementing intrinsic remediation concepts from data collection through source removal and source lifetime considerations has been developed for the US EPA and the U.S. Air Force (Dupont et al. 1996 , 1997; UWRL 1997). These concepts and procedures are presented in the following sections.

5.3.2 Process Design Principles

Intrinsic remediation assessment involves a seven-step process outlined in Figure 5.9. For a given site, this process involves: (1) determining whether steady-state plume conditions exist, (2) estimating contaminant degradation rates, (3) estimating the source mass, (4) estimating the source lifetime, (5) predicting long-term plume behavior with and without source removal, (6) deciding whether to use intrinsic remediation and/or source removal, and (7) developing a long-term monitoring strategy if intrinsic remediation is selected for plume management.

5.3.2.1 Determination of Steady-State Plume Conditions

Verifying that steady-state conditions exist for a contaminant plume at a given site is critical in establishing that intrinsic remediation processes are taking place and are likely to provide continued plume containment under current site conditions. Steady-state plume conditions occur when the rate of contaminant release from the source area is equivalent to the rate of contaminant assimilation by biotic and abiotic processes taking place within the aquifer. Steady-state conditions can be identified by observing contaminant concentrations at specific groundwater monitoring locations over time. However, a better approach is to evaluate contaminant concentration and contaminant mass distribution changes throughout the entire plume over time. This latter approach involves the collection of centerline concentration or total integrated mass and center of mass data within the delineated plume

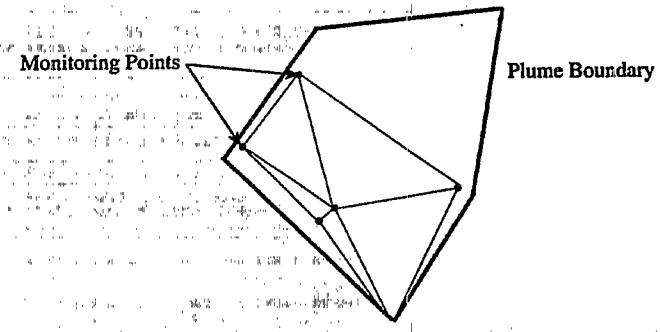
contaminant concentration and aquifer volume for each monitoring point is summed to yield a total dissolved mass for the plume.

Aquifer volume is determined from the product of the aquifer porosity, the average aquifer thickness (generally the length of the largest sampling interval used within the monitoring network at a given sampling time), and a plume surface area associated with each sampling point. One procedure that can be used to obtain an estimate of area associated with each sampling point is the Thiessen Polygon Method. This method was developed in the field of hydrology for estimating areas associated with point rainfall measurements within rain gage networks. The Thiessen method assumes that the concentration measured at a given sampling point is equal out to a distance halfway to the sampling points located next to it in all directions. The relative weights (areas) represented by each sampling point are determined by the construction of a Thiessen polygon network, the boundaries of which are formed by the perpendicular bisectors of lines connecting adjacent points (Chow 1988). The construction of an example polygon network is shown in Figure 5.11. The outer boundary of the Thiessen polygon network is estimated based on the outermost well locations. It is important for boundary definition to be consistent if mass calculations are to be comparable among sampling events. It is also important to note that this method can be used for estimating mass within a monitoring network consisting of as few as three monitoring wells. However, an increase in sampling point density throughout the plume will improve the accuracy of the plume mass calculations, as interpolation among data points will be improved due to the shorter interpolation distance. Ideally, from 10 to 20 monitoring points throughout the site, both inside and outside the contaminant plume, can be used to provide reasonable accuracy in plume mass estimates and plume delineation for a reasonable cost.

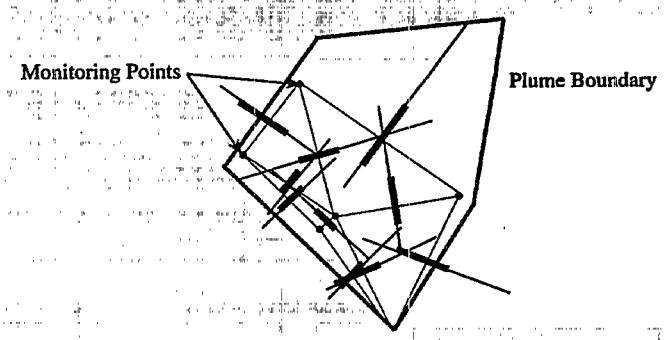
In addition to estimating the total mass of a compound within the dissolved plume at a given time, the representative center point of the combined plume mass can also be calculated. This representative mass center is termed the centroid of the mass (CoM) and is calculated by taking the first moment of inertia of the mass at each sampling location within the contaminant plume about specified X and Y axes. Example calculations for both dissolved plume mass and CoM are provided in Section 5.3.9.

These CoM calculations are useful for tracking and interpreting the movement of contaminants, reactants, and products within the contaminant plume over time. They can also aid in assessing the status of the plume and interpreting its migration pattern over time as indicated in Table 5.10.

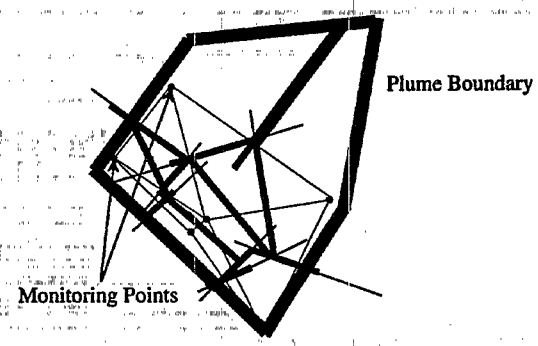
Figure 5.11
Example Thiessen Polygon Network Construction



a. The outer boundary of the sampling network is identified based on logical, physical boundaries of the problem. Each sampling location is then connected to all adjacent points to form a series of polygons with the sampling points as their corners.



b. The lines between these sampling points are bisected, and perpendicular lines are drawn at the bisection points. These perpendicular lines are then extended so that they intersect one another.



c. The intersecting lines are connected to form polygons associated with each original sampling location to yield unbiased and consistently generated areas. These areas can then be used to generate associated groundwater and soil volumes that allow the determination of the mass of contaminant within the assigned plume boundary and the changes in that mass over time.

— Bisectors
▬ Bisector Extension
■ Associated Area Boundary

Table 5.10
Changes in Contaminant Mass and Mass Center Coordinates and Corresponding Interpretation of Plume Mobility and Persistence

Contaminant Mass	Centroid of Mass	Interpretation
Increasing	Moving Downgradient	Continuous Source; Unstable Plume; Contaminant Migration
Constant (Steady State)	Moving Downgradient	Finite Source; Plume Migration; Minimal Natural Attenuation
Constant (Steady State)	Stable	Continuous Source; Stable Plume; Contaminant Attenuation
Decreasing	Moving Downgradient	Finite Source; Plume Migration; Contaminant Attenuation
Decreasing	Moving Upgradient	Finite Source; Plume Attenuation; Rapid Contaminant Attenuation; Optimal Intrinsic Bioremediation

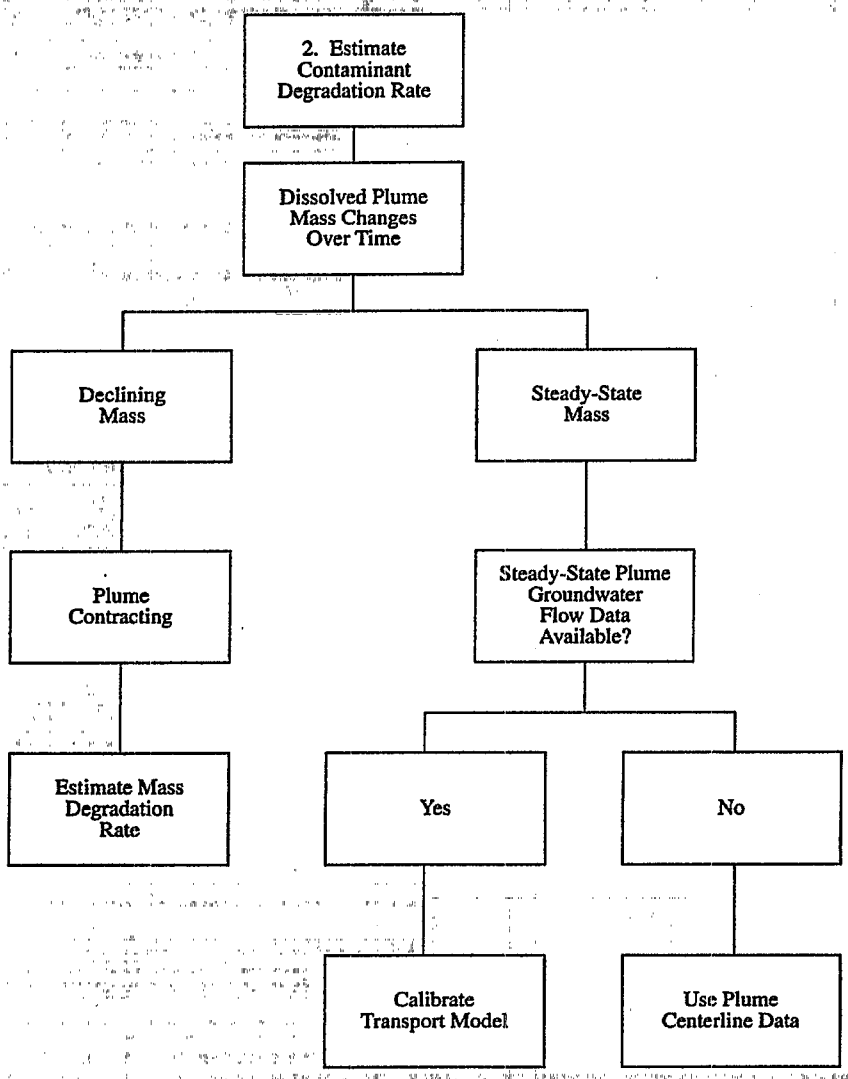
If plume centerline analysis and CoM calculations suggest that the plume is growing over time, steady-state conditions have not been reached, and either ongoing monitoring should take place to ensure future attenuation of the plume, or active source removal and/or site remediation should occur if a sensitive receptor is or will be impacted in the near term. If the contaminant plume is shown to have reached steady-state conditions, further quantification of the nature and extent of plume attenuation taking place under site conditions is warranted.

5.3.2.2 Estimation of Contaminant Degradation Rate

Contaminant degradation rates can be estimated based on dissolved plume contaminant mass data if a declining mass of contaminant is observed over time, or on contaminant groundwater concentration data if the source produces steady-state dissolved mass in the plume over time. If steady-state mass is indicated, degradation rates for the contaminants can be estimated directly from centerline concentration data or through the calibration of a contaminant fate and transport model to field groundwater data. Figure 5.12 presents the logic associated with the estimation of field-determined degradation rates and suggests that if aquifer flow data are available, the use of a fate and transport model accounting for advection, dispersion, sorption, and degradation is preferred over the use of plume centerline concentration data alone. In addition, the use of less degradable "plume resident tracer" compounds in the calibration process is desirable for the calibration of the transport component of the fate and transport model if data for these tracer

compounds are available. The use of the less-degradable tracers simplifies modeling because the transport components of a model can be calibrated without having to consider degradation reactions.

Figure 5.12
Decision Logic for Evaluating Contaminant Degradation Rates



Dissolved Plume Mass Changes Over Time. Dissolved plume mass changes over time can be used as an indicator of the type of plume existing at a site as summarized in Table 5.10. When the total mass of contaminant in the dissolved plume is decreasing over time, a finite source is suggested. Both its position and concentration profile would not be expected to be steady-state, and it would behave as a pulsed source. To estimate the degradation rate of contaminants within the plume resulting from this pulse source, the changes in total contaminant dissolved plume mass should be analyzed over time.

A classical approach to the evaluation of contaminant degradation rates in biological systems is to analyze the changes in contaminant concentration or mass over time to establish the relationship between concentration or mass versus reaction time using zero- or first-order reaction rate laws. Zero-order reactions are described by a contaminant reaction rate independent of contaminant mass (i.e., a constant mass degradation rate over time) or:

$$dM / dt = -k_o \tag{5.8}$$

where:

k_o = the zero degradation rate constant (mass/time). The integrated form of this equation is shown in Equation 5.9:

$$M = M_o - k_o t \tag{5.9}$$

where:

M = contaminant mass at time t (mass); and
M_o = the initial contaminant mass at time t = 0 (mass).

If the reaction is governed by a zero-order degradation rate law, a plot of contaminant mass versus time produces a linear relationship, the slope of which equals k_o and whose intercept value should equal M_o.

First-order reactions are described by a contaminant reaction rate that is dependent on contaminant concentration or mass (i.e., a mass degradation rate changing over time), or:

$$dM / dt = -k_1 M \tag{5.10}$$

where:

k_1 = the first degradation rate constant (1/time). The integrated form of this equation is shown in Equation 5.11:

$$M = M_o e^{-k_1 t} \tag{5.11}$$

A plot of contaminant mass versus time produces a non-linear relationship that can be linearized by plotting the natural log of contaminant mass versus time. The slope of this linearized relationship is equal to k_1.

Plume Centerline Concentration Data. Plume centerline concentration data can be used to quantify contaminant degradation rates if the dissolved plume mass does not change significantly over time (i.e., if a continuous steady-state source is indicated) (Table 5.10). Using the data reduction approach described above for dissolved plume mass, contaminant concentration data can be analyzed using zero-order reactions with Equation 5.12:

$$dC / dt = -k_o \tag{5.12}$$

where:

k_o = the zero degradation rate constant (mass/volume/time).

The integrated form of this equation is shown in Equation 5.13:

$$C = C_o - k_o t \tag{5.13}$$

where:

C = contaminant concentration at time t (mass/volume); and
C_o = the initial contaminant concentration at time t = 0 (mass/volume).

A plot of contaminant concentration versus time produces a linear relationship, the slope of which equals k_o and whose intercept value should equal C_o.

First-order reactions using contaminant concentration data are written as:

$$dC / dt = -k_1 C \tag{5.14}$$

where:

k_1 = the first degradation rate constant (1/time).

The integrated form of this equation is shown in Equation 5.15:

$$C = C_o e^{-k_1 t} \tag{5.15}$$

A plot of the natural log of contaminant concentration versus time is linear when first-order degradation is taking place, with the slope of this linearized relationship equal to k_1. This data analysis approach has been incorporated into an intrinsic remediation protocol developed by Chevron Research and Technology Company (Buscheck, Reilly, and Nelson 1993).

Calibration of Analytical Fate and Transport Groundwater Models. When a continuous source is observed at a site, calibration of analytical fate and transport groundwater models provides the best estimate of contaminant degradation rates as these models integrate transport, retardation, and degradation using site-specific contaminant and aquifer properties. An analytical, one-dimensional flow, three-dimensional dispersion model developed by Domenico (1987) is one such model that can be used in intrinsic remediation methodology. Use of this model accounting for flow and contaminant sorption characteristics, in addition to degradation yields, a "dilution-corrected" degradation rate. When calibrated with nondegradable "tracer" compounds (i.e., dimethylpentane or trimethylbenzene isomers) in the source area, the model provides improved degradation rate estimates for the more reactive compounds (e.g., benzene, toluene, ethylbenzene, and xylenes BTEX) of health significance. The use of this model for intrinsic remediation assessment is presented in a case study in Chapter 8 of this monograph.

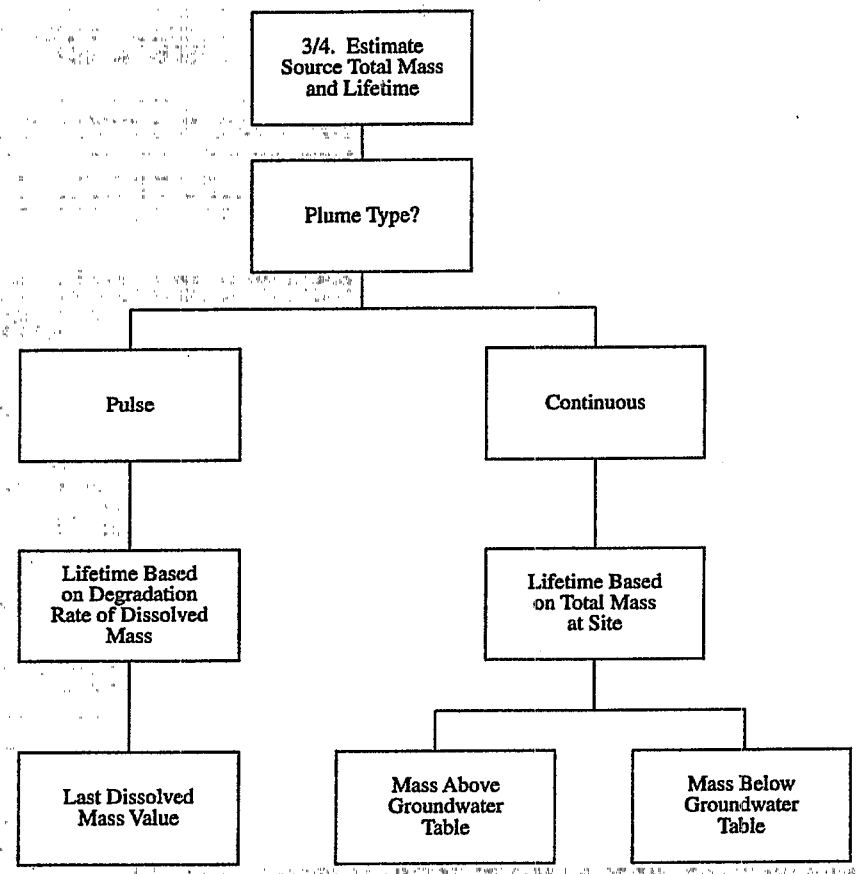
5.3.2.3 Estimation of Source Mass/Lifetime

With an estimate of the rate of contaminant degradation at a site, management decisions regarding the appropriateness of source removal actions and the effect of such actions on the projected lifetime of contamination at the site can be made. The logic associated with source mass and lifetime determinations is shown in Figure 5.13. Specific calculations for the estimation of contaminant source mass and lifetimes as a function of plume type are detailed below in Section 5.3.9.

If a continuous source is found at a site, contaminant mass within the source area will continue to contribute mass to the groundwater, maintaining the contaminant plume footprint that has developed over time. To estimate the potential lifetime of this plume, an estimate must be made of the mass of contaminant existing as residual saturation both above and below the groundwater table, along with that residing in any free product occurring at the site. Ideally, these estimates should be based on soil core and free product samples collected throughout the site. This total mass estimate requires that the soil and free product volumes associated with each soil core or monitoring location be defined using a procedure such as the Thiessen Polygon Method previously described.

If soil core data are unavailable, the source area mass can be estimated from groundwater concentration and free product measurements in observation wells and groundwater monitoring points. Concentrations of contaminants in groundwater above the equilibrium values expected based on Raoult's Law (water concentration = solubility • mole fraction in

Figure 5.13
Decision Logic for Evaluating Contaminant Source Mass and Source Lifetime



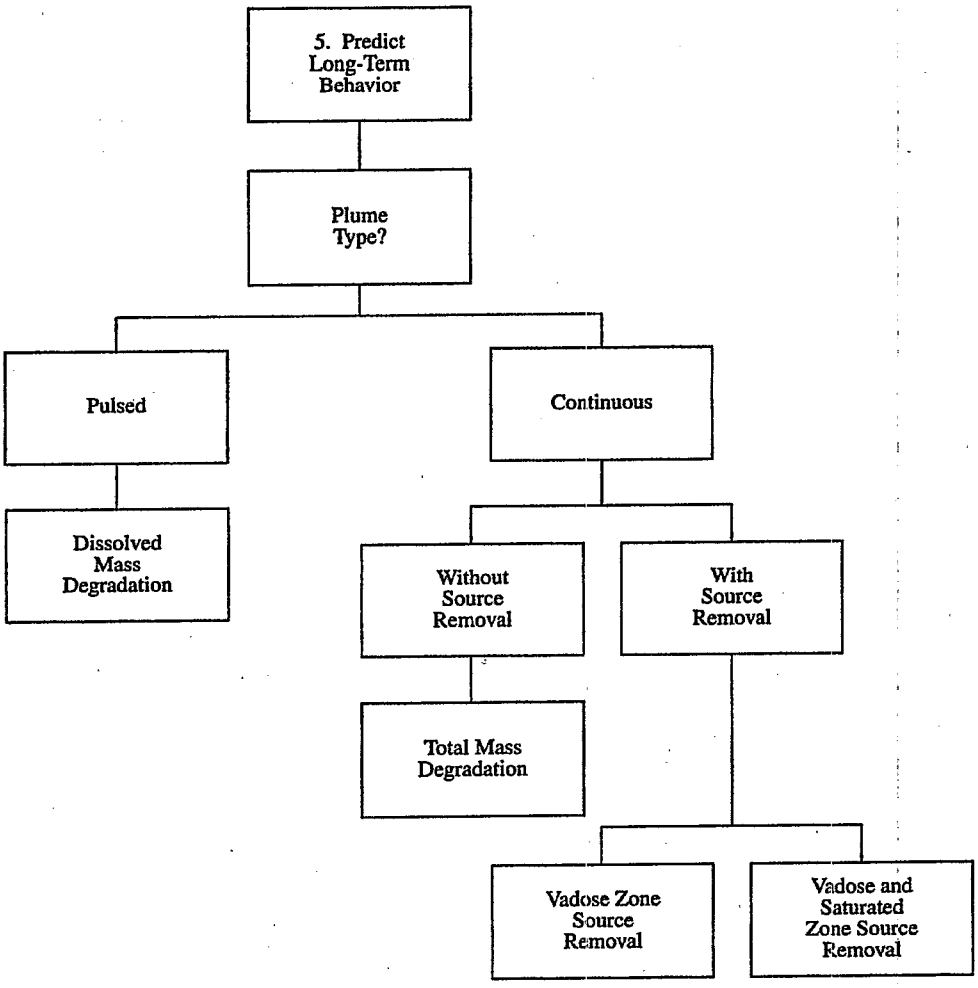
residual-phase product) suggest residual saturation in soils below the water table. With the extent of mobile product and/or residual saturation estimated based on groundwater measurements, and residual fuel saturation values as a function of soil type (Parker, Lenhard, and Kuppusamy 1987) available in the literature, source area mass can be estimated. An example of such calculations is provided in a case study in Chapter 8.

Once the total mass of contamination is estimated above and below the groundwater table, estimates for the total lifetime of the plume can be made based on the total mass disappearance rate described in Section 5.3.2.2. These calculations are presented in detail in Section 5.3.9.

5.3.2.4 Prediction of Long-Term Plume Behavior

The long-term behavior of a contaminant plume is impacted both by the characteristics of the source, which affect the duration of the release of contaminant into the aquifer, and by the characteristics of the aquifer itself, affecting the transport and degradation of contaminant once it is released from the source area. Figure 5.14 presents the decision logic related to long-term source behavior, identifying differences in analysis of the plume based on whether it is a pulse or continuous source.

Figure 5.14
Decision Logic for Evaluating Long-Term Contaminant Plume



If the plume is a pulsed source, no residual source area exists, and the long-term behavior of the plume is related to the projected lifetime of the plume. If the site contains a significant source area, producing a "continuous source" plume, long-term plume behavior can be evaluated based on various source removal scenarios. If no source removal is to be carried out, a worst-case scenario develops in terms of the length of time the plume will persist, as the plume lifetime calculations for the sum of vadose zone, saturated zone, and dissolved plume masses estimated above apply. If contaminant source removal is being considered, the effect on plume lifetime of mass removal from various locations at the site and at various levels of removal efficiency can be evaluated.

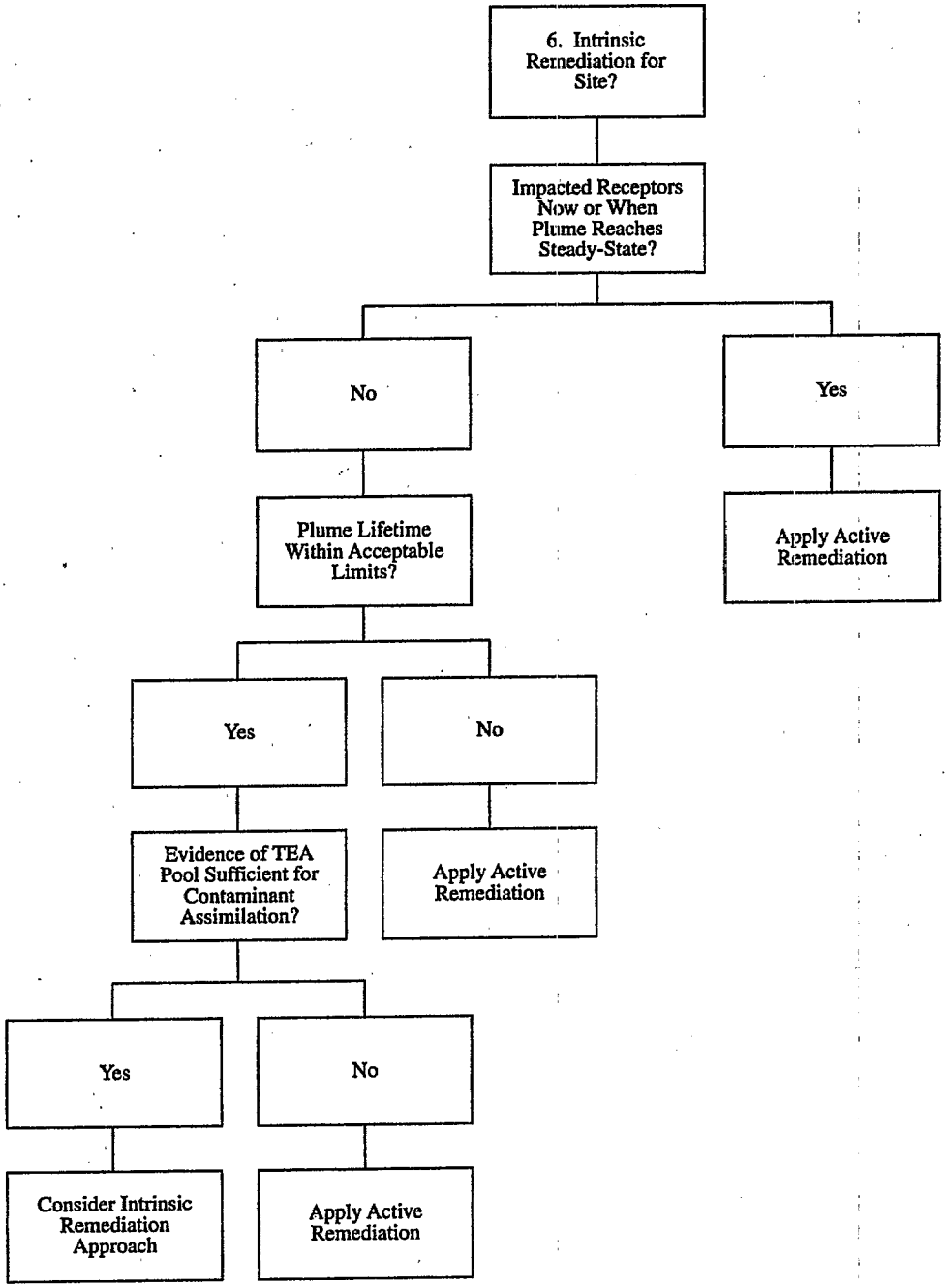
Once source removal strategies are investigated, the complete long-term behavior of the contaminant plume can be predicted using a groundwater fate and transport model. As indicated by Gorder et al. (1996), source removal activities can be modeled by superposing a "negative" continuous source plume on top of the existing steady-state plume concentration profile. This "negative" plume is generated using a source concentration equal to the negative of the initial source concentration at a point in time corresponding to the time of source removal. With this superposition, movement of the steady-state plume away from a source area that has been eliminated following source removal activities can be modeled. An example of such a modeling approach is provided in a case study in Chapter 8. It is important to note that the steady-state contaminant plume profile represents the highest downgradient concentration profile that would be expected at a given site. The concentrations at a given point in space will decrease over time following source removal activities if the plume is truly at steady-state and if all other site conditions remain the same.

5.3.2.5 Decision Making Regarding Intrinsic Remediation

The analyses described above provide a basis for making decisions regarding the applicability of an intrinsic remediation plume management approach for a site. Figure 5.15 provides a summary of the logic necessary to complete the decision-making process based on the impact the plume has on downgradient receptors and the potential for intrinsic attenuation reactions to contain and control the plume.

The final questions that must be answered regarding application of an intrinsic remediation management approach at a site are: (1) whether a sensitive receptor is being impacted now or in the future when the plume is projected to reach steady-state conditions and (2) whether the projected lifetime of the plume is acceptable to owners/operators, regulatory agencies,

Figure 5.15
Decision Logic for Evaluating Applicability of Intrinsic Remediation Plume Management Approach



and other interested parties. In general, if an existing or projected receptor impact exists, active source removal and plume control/remediation will be required unless institutional controls (i.e., deed restrictions, etc.) can be put into place to restrict the long-term use of contaminated soil and/or groundwater. The issue of plume lifetime tends to be more complicated. If significant contaminant mass remains in the source area of a site, the resulting plume may persist for decades. If remediation goals are established with shorter timeframes (i.e., for property transfer reasons, etc.), this assimilation time will likely be unacceptable and active remediation may be required.

The focus of the previous discussion has been on quantifying the transport and degradation of contaminants under actual site conditions. After a projected source lifetime is deemed acceptable and intrinsic remediation is considered viable at a site, final supporting evidence for verification that degradation reactions are biologically mediated must be provided through an analysis of the changes in background terminal electron acceptor (TEA) mass compared to that within the plume itself. If contaminant biodegradation is taking place, indigenous organisms will consume TEAs (O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}, CO_2) at a rate and to an extent that should correspond to contaminant loss observed at the site. The stoichiometry associated with microbial metabolism known to occur under various TEA conditions (Table 5.11) allows a determination of the potential contaminant assimilative capacity of background groundwater moving into the source area and available within the plume itself. If this theoretical assimilative capacity is equal to or greater than the level of contamination observed at the site, expressed both on maximum concentration and total mass of contaminant bases, biological intrinsic remediation processes can be expected to play a major role in contaminant attenuation. If assimilative capacity is limited, some source removal and/or active site remediation action is likely warranted. An example of the evaluation of potential site assimilative capacity is provided in Section 5.3.9 and in a case study in Chapter 8 of this monograph.

5.3.2.6 Long-Term Monitoring

If an intrinsic remediation management approach is selected for a given site, the last step in the assessment process is the development of a long-term monitoring strategy. Figure 5.16 shows that the requirements of the monitoring strategy are twofold: compliance monitoring and intrinsic remediation process monitoring.

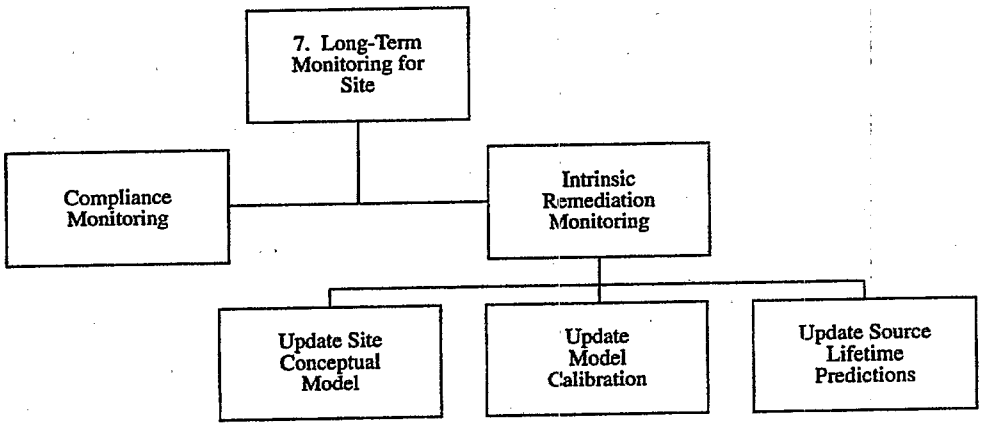
Compliance monitoring must be conducted to provide data to the regulatory agency to confirm that plume containment and risk management continue to take place at the site. Compliance monitoring normally involves an

Table 5.11
Potential Hydrocarbon Assimilative Capacity Relationships for Electron Acceptors of Importance at UST Sites*

TEA Indicator	Compound Degraded	Molar Relationship (gmol/gmol HC Degraded)	Mass Relationship (g/g HC Degraded)
Oxygen	Aromatic Alkane	-7.5 -9.5	-3.1 -3.5
Nitrate	Aromatic	- 6	- 1.07
Fe^{3+} to Fe^{2+}	Aromatic Alkane	+ 30 + 38	+ 2.15 + 24.7
Sulfate	Aromatic Alkane	-3.75 -4.75	-4.6 -5.3
Organic to CH_4	Aromatic Alkane	+3.75 +4.75	+0.77 +0.88

* These molar relationships were determined using the stoichiometric relationships presented in Weidmeier et al. (1994). No specific kinetic rate or metabolic pathway should be inferred from these data. Negative values indicate TEA use in reaction is quantified. Positive values indicate product generation is quantified. For solid-phase reactants (i.e., iron and manganese), quantification of product generation will normally underestimate the total assimilative capacity with these TEAs.

Figure 5.16
Requisite Components of a Long-Term Monitoring Approach at an Intrinsic Remediation Site

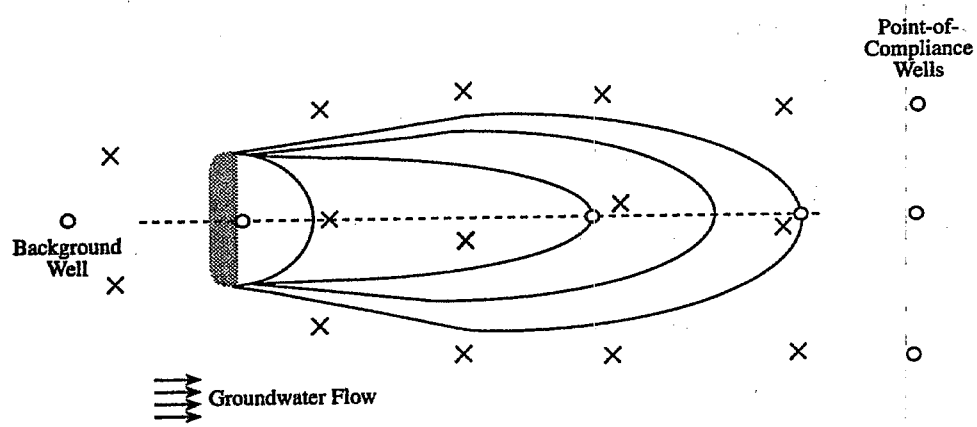


upgradient, background monitoring well; one to two monitoring wells within the contaminant plume; and one to two downgradient compliance wells used to detect contaminant migration toward potential receptors. Groundwater elevation, contaminant concentration, and minimal groundwater quality data (pH, temperature, total dissolved solids) are generally required to be reported for these monitoring wells.

Although the information generated for compliance monitoring is required, it is insufficient for intrinsic remediation process monitoring; data from additional monitoring locations and for additional analytes should be collected for process monitoring. Figure 5.17 shows a monitoring well network that is appropriate for initial intrinsic remediation evaluation during the site assessment phase as well as for long-term compliance and intrinsic remediation process monitoring. In addition to the data collection requirements for compliance monitoring, intrinsic remediation process monitoring should include analysis of TEAs that are consumed (O_2, NO_3^-, SO_4^{2-}) and products that are formed (Mn^{2+}, Fe^{2+}, CH_4) during contaminant biodegradation, and assessment of water quality characteristics (alkalinity and oxidation/reduction potential) that indicate of biological processes within the contaminated aquifer. Based on data collected from process monitoring, the conceptual model of the site (including land use assumptions) and model calibration results can be periodically updated to provide ongoing refinements to source lifetime predictions and to risk assessment considerations for the site.

Finally, the frequency of groundwater monitoring must be established as part of the long-term monitoring plan. Compliance monitoring schedules generally require quarterly to annual sampling. However, under most circumstances, annual sampling will be the shortest time interval necessary for intrinsic remediation process monitoring because the low groundwater velocities observed at most sites do not warrant more frequent sampling intervals. At a site with a groundwater velocity of 0.01 m/d (0.04 ft/d), unretarded groundwater moves less than 4.5 m (15 ft) in a year. With a retarded velocity 1/3 to 1/6 that of groundwater (appropriate for benzene and xylene, respectively) contaminant movement of less than 1 to 1.5 m (3 to 5 ft) would be expected over a 1-year time period. With a monitoring grid spaced at 10-m (30-ft) intervals, a 1-year change in plume position cannot be detected. Again, the sampling interval should be assessed on a site-specific basis, but generally, an annual to biannual sampling schedule should be sufficient to ensure that adequate data are collected while minimizing the sampling and analysis burden at intrinsic remediation sites.

Figure 5.17
Groundwater Monitoring Network for Both Compliance and Intrinsic Remediation Process Monitoring



× Shallow Groundwater Monitoring Points
o Monitoring Wells

5.3.3 Process-Flow Diagrams

Because intrinsic remediation is an in situ plume management approach that relies upon indigenous physical, chemical, and biological processes for the attenuation and destruction of contaminant mass, no engineered process flow scheme is involved. The major system requirements relate to contaminant plume delineation and long-term groundwater monitoring. A typical monitoring network to provide the necessary initial site assessment information and long-term monitoring of the mobility and transformation of contaminants within the groundwater plume is provided in Figure 5.17.

5.3.4 Process Modification

5.3.4.1 Hydrocarbon Plumes

The intrinsic remediation process design principles discussed in Section 5.3.2 apply primarily to dissolved contaminants that degrade under a variety of TEA conditions to short-lived intermediates. This situation is typical of fuel-contaminated groundwater where hydrocarbon constituents of the released fuels are degraded both aerobically and anaerobically to CO_2 and water with few intermediate products being detected in the plume. The

intermediates that have been observed are low-molecular-weight volatile fatty acids generated in the oxidation of monoaromatic hydrocarbon fuel constituents (Cozzarelli, Eganhouse, and Baedecker 1990; Cozzarelli et al. 1994). The presence of these intermediate compounds downgradient from a source area indicates biological fuel contaminant degradation, and quantification of such compounds may be warranted if additional evidence of intrinsic bioremediation is required. Cozzarelli et al. (1990, 1994) provide a detailed description of the analytical methodology for separation and quantification of these volatile fatty acids in groundwater.

Additional verification of the biological nature of contaminant degradation processes taking place in hydrocarbon-contaminated groundwater systems can be provided using plume-resident tracers (PRTs) as suggested in Section 5.3.2.2. To be an effective tracer, these compounds must be less degradable than the compounds of interest (i.e., the BTEX components) and must reside in the source area at concentrations high enough to produce a measurable downgradient plume. If these bioresistent compounds exist in the source, their relative concentration in the resultant groundwater plume should increase with respect to the more degradable BTEX components as the plume moves downgradient of the source area. The relative concentration (Wilson et al. 1994) or relative mass flux across the plume (Dupont et al. 1996) of the PRTs versus the BTEX components can be used to indicate the biodegradation of BTEX constituents in the plume. In addition, these PRTs have been used to calibrate the flow portion of a groundwater fate and transport model prior to calibration and degradation rate determinations for the BTEX components (Dupont et al. 1996, 1997; UWRL 1997).

A number of these PRTs have been reported in the literature, including 2,3-dimethylpentane; 2,4-dimethylpentane; 1,2,3-trimethylbenzene; 1,2,4-trimethylbenzene; and 1,3,5 trimethylbenzene. Again, the resistance of these compounds to biodegradation within aquifer systems provides additional evidence that biologically-mediated contaminant destruction is taking place at a site, and the quantification of these compounds may be necessary to provide additional verification to regulatory agencies that contaminant mass degradation, not simply dilution, is taking place.

5.3.4.2 Chlorinated Solvent Plumes

Industrial solvents, such as TCE, PCE, carbon tetrachloride (CT), and chloroform (CF) are some of the most common pollutants found at contaminated groundwater sites. Those compounds that are highly chlorinated (i.e., PCE and TCE), are also highly oxidized and cannot serve as a source of energy (electron donor) to indigenous microorganisms under aerobic

conditions. However, in the absence of oxygen and under highly-reducing conditions, these chlorinated solvents actually act directly as alternative electron acceptors through the process of reductive dehalogenation.

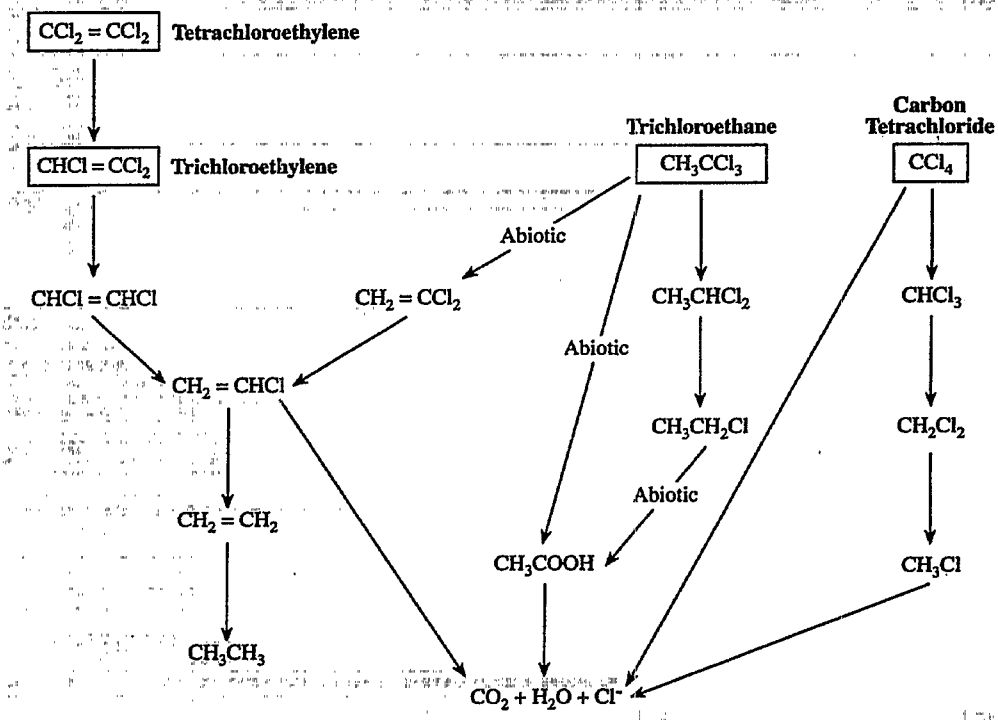
Reductive dehalogenation results in the degradation of TCE to environmentally acceptable products, such as ethylene (Freedman and Gossett 1989; de Bruin et al. 1992; DiStefano, Gossett, and Zinder 1992), ethane (de Bruin et al. 1992) and CO_2 in the laboratory through the general pathway shown in Figure 5.18. Mohn and Tiedje (1992) provide a review of microbial reductive dehalogenation research. Many studies, however, have reported the accumulation of intermediate products in the dehalogenation process, namely cis-dichloroethylene (cis-DCE) and vinyl chloride (Imbrigiotta, Ehlke, and Martin 1991), which pose a threat to human health and the environment. DiStefano, Gossett, and Zinder (1991) summarize of the literature in this area, and McCarty (1994) has presented a recent summary of the current state of knowledge regarding anaerobic transformations of chlorinated solvents in contaminated groundwater systems.

The pathway shown in Figure 5.18 describes the biologically-mediated, anaerobic transformation of PCE and TCE in contaminated aquifer systems. Within the framework of intrinsic remediation previously described, the detection of daughter products of these biotransformation reactions serves as supporting evidence to suggest the natural containment of chlorinated solvent groundwater plumes. In demonstrating the attenuation of these chlorinated solvent plumes, the following two primary aquifer characteristics must be shown:

- the aquifer is highly reducing (e.g., evidence of sulfate reduction and methanogenesis exists at the site) such that anaerobic dechlorination would be expected to take place under field conditions; and
- the PCE/TCE plume mass is stable (as determined according to procedures defined in Section 5.3.2.1) with daughter product mass data which indicate accumulation of intermediates from these dehalogenation reactions, or reduction in daughter product mass if further degradation of these intermediates can be verified.

To provide the information necessary to make these determinations, intrinsic remediation assessment for chlorinated solvent plumes should include sampling and analysis for water quality parameters indicative of aquifer oxidation/reduction status (dissolved oxygen, nitrate, sulfate, dissolved iron and manganese, dissolved methane, and dissolved hydrogen sulfide), parent and intermediate compound groundwater concentration data (PCE, TCE,

Figure 5.18
Pathway for the Anaerobic Dehalogenation of PCE and Various Intermediate Products



Source: McCarthy 1994

cis- and trans-DCE, vinyl chloride, and ethylene), and electron donor species driving the anaerobic dechlorination process (dissolved total organic carbon or chemical oxygen demand).

This last parameter is important due to the inefficiency of electron transfer, which has resulted in a requirement of as much as 150 times the estimated reducing equivalents to sustain dehalogenation. Gross parameter measurements for electron donor concentrations appear appropriate as numerous organic substrates including methane (Corapcioglu and Hossain 1991; Enzien et al. 1994); ethanol, acetate, and lactate (de Bruin et al. 1992; Gibson and Sewell 1992; Pavlostathis and Zhuang 1993); methanol and glucose (Freedman and Gossett 1989); and propionate, crotonate, and butyrate (Gibson and Sewell 1992) have been used by researchers to stimulate reductive dehalogenation in the laboratory. Fiorenza et al. (1994) reported

reductive dehalogenation of PCE and TCE at a manufacturing plant in Ontario, Canada, using organic contaminants, such as naphtha components and volatile fatty acids, as electron donors. An example of verification of the intrinsic remediation of a chlorinated solvent plume is provided in a case study in Chapter 8.

5.3.5 Pretreatment Processes

Since this is an in situ, plume monitoring approach, no engineered pretreatment processes are necessarily required. However, based on the assessment methodology presented above, some source removal and active source remediation may be recommended to accelerate site cleanup. Refer to Section 4.2 for information regarding the in situ treatment of contaminated source area soil; Sections 4.3, 4.4, and 4.5 for ex-situ source area soil treatment; and Sections 5.5 and 7.2 for integrated approaches for source area product recovery and soil and groundwater treatment.

5.3.6 Posttreatment Processes

Since this is an in situ, plume monitoring approach, no engineered posttreatment processes are required.

5.3.7 Process Instrumentation and Control

Since this is an in situ, plume monitoring approach, no process instrumentation or controls would be required. If source removal or treatment is being carried out at an intrinsic remediation site to accelerate site remediation, process instrumentation and controls for necessary soil handling and treatment systems would be required. Refer to the appropriate source area treatment technologies for their specific process instrumentation and control requirements.

5.3.8 Process and Instrumentation Diagrams

Since this is an in situ, plume monitoring approach, no process and instrumentation (P&I) diagrams would be generated. If some source removal and active source remediation is recommended based on the assessment methodology presented above, P&I diagrams appropriate for the selected technology would be required. Refer to the appropriate source area treatment technologies for their specific P&I diagram requirements.

5.3.9 Sample Calculations

5.3.9.1 Dissolved Contaminant Plume Mass and Center of Mass Calculations

The total mass of a compound within the dissolved plume at a given point in time is determined from the product of: (1) contaminant concentration associated with each sampling location (C_i); (2) aquifer porosity (θ); (3) average aquifer thickness (H); and (4) plume surface area associated with each sampling point generated from the Thiessen Polygon Method described in Section 5.3.2.1.2 as follows:

$$\text{Mass}_T = \sum \text{mass}_i = \sum C_i(\theta)(H)(A_j) \tag{5.16}$$

where:

mass_i = dissolved contaminant mass associated with sampling location i (mass); and

A_j = Thiessen Area j associated with sampling location i (length^2).

The representative center point of the combined plume mass (CoM) is calculated by taking the first moment of inertia of the mass at each sampling location within the contaminant plume about specified X and Y axes. Mathematically, this can be expressed as follows for the center of mass X and Y coordinates, respectively:

$$X = \frac{\sum_{i=1}^{n} x_i(\text{mass}_i)}{\sum_{i=1}^{n}(\text{mass}_i)} \tag{5.17}$$

$$Y = \frac{\sum_{i=1}^{n} y_i(\text{mass}_i)}{\sum_{i=1}^{n}(\text{mass}_i)} \tag{5.18}$$

where:

x_i and y_i = x and y coordinates of each sampling location within the Thiessen area network.

Table 5.12 summarizes typical calculations for total mass and center of mass results generated from a monitoring network for which contaminant concentration and Thiessen area values were obtained. Results from these calculations indicate a total dissolved benzene plume mass of 3,696 g, with CoM X and Y coordinates of +66.5 ft and -17.2 ft, respectively.

5.3.9.2 Estimation of Source Area Mass

When a continuous source plume is identified at a site, source area mass should be estimated based on soil core measurements above and below the groundwater table. Figure 5.19 indicates the configuration of soil cores and associated geometry used in Equations 5.19 and 5.20 for average borehole concentration, C_{ave}, and total contaminant mass, M_T, estimates in a source area:

$$C_{avg,j} = \frac{\sum_{i=1}^{n} C_{i,j} h_{i,j}}{\sum_{i=1}^{n} h_{i,j}} \tag{5.19}$$

where:

$C_{i,j}$ = soil contaminant concentration in core j at depth i in the core (mass contaminant/mass soil);

$h_{i,j}$ = core j interval thickness at depth i (length); and

n = total number of soil cores collected at the site.

Total source area mass is calculated as:

$$M_T = \sum_{j=1}^{n} A_j \left(\sum_{i=1}^{n} C_{i,j} h_{i,j} \right) \tag{5.20}$$

where:

A_j = Thiessen area associated with core j (length^2).

The denominator in Equation 5.19 is the thickness of vadose zone contamination for mass above the groundwater table, while it is the thickness of contaminated soil below the groundwater table for saturated zone mass determinations. Generally, total mass calculations provided via Equation 5.20 are carried out separately for mass above and below the groundwater table so that the vertical distribution of contaminant mass can be evaluated.

If soil core data are unavailable, then contaminant mass within a source area can be estimated based on a determination of the extent and composition of free product or residual saturation at a site. The extent of free

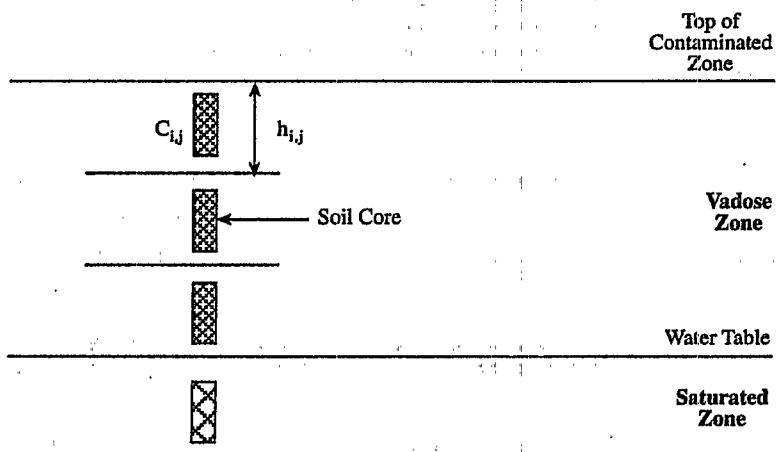
Table 5.12
Typical Total Mass and Center of Mass Calculation Using Field-Determined Groundwater Data from Shallow Groundwater Monitoring Points (CPTs) and Monitoring Wells (MWs)

Sampling Location	Sampling Number	X Coor. (ft)	Y Coor. (ft)	Associated Thiessen Area (ft^2)	Elevation TOC (ft)	Elevation BOC (ft)	Water Col. Depth (ft)	Volume (ft^3)	Benzene (µg/L)	Benzene Mass (g)	Mass•X (g-ft)	Mass•Y (g-ft)
CPT	1	-8.4	-80.6	1,490	97.43	6.71	4.24	4,967	0.0	0.0	0	0
CPT	2	54.6	-122.4			plugged				0.0	0	0
CPT	3	-47.5	-52.8	1,767	97.24	6.91	3.95	5,889	0.0	0.0	0	0
CPT	4	-4.5	-42.8	1,272	97.9	7.32	3.90	4,240	965	116	-518	-4,954
CPT	5	-36.3	-74.6	2,152	97.11	6.65	4.27	7,173	1.0	0.2	-7.4	-15.2
CPT	6	108.7	55.4		98.91	plugged				0.0	0	0
CPT	7	-41.9	-2.2	1,745	96.88	6.75	1.17	5,818	0.0	0.0	0	0
CPT	8	59.4	13.7	1,737	99.64	8.86	3.19	5,791	2,442	400	23,794	5,501
CPT	9	-51.3	24.9	2,669	97.10	7.33	2.77	8,895	0.0	0.0	0	0
CPT	10	63.4	58.1	1,600	98.23	7.58	3.70	5,333	0.0	0.0	0	0
CPT	11	-16.0	16.5	1,108	97.38	6.65	3.80	3,693	0.0	0.0	0	0
CPT	12	64.7	35.9	1,008	98.98	8.24	4.02	3,360	70.0	6.7	431	239
CPT	13	108.7	11.5	2,492	99.67	9.3	3.25	8,304	4,344	1,021	111,016	11,704
CPT	14	19.0	-8.9	1,207	98.45	7.68	3.32	4,023	71.0	8.1	154	-72

CPT	15	14.3	15.4	763	98.10	7.12	4.23	2,543	406	29.2	419	449
CPT	16	26.2	-35.4		98.63	plugged				0.0	0	0
CPT	17	9.1	33.8	2,479	97.68	6.80	3.90	8,261	2.0	0.5	4.2	15.8
CPT	18	-4.3	-61.9	693	97.65	7.00	5.23	2,311	2.0	0.1	-0.6	-8.1
CPT	19	52.0	-40.6	3,540	99.51	8.94	3.96	11,799	4,170	1,393	72,469	-56,570
CPT	20	28.5	-58.4	1,046	98.42	7.85	2.80	3,485	4,893	483	13,772	-28,202
CPT	21	37.8	-82.8	5,384	98.78	8.20	3.75	17,944	1.0	0.5	19.2	-42.1
MW	1	103.0	35.7	2,043	99.73	8.49	8.51	6,810	1,226	236	24,345	8,437
MW	3	0.0	0.0	791	97.48	6.70	10.30	2,637	3.0	0.2	0	0
MW	4	-17.2	-137.5	4,086	96.20	5.89	11.11	13,618	1.0	0.4	-6.6	-53.0
					Max Depth (ft) =		11.11		Σ=	3,696	245,890	-63,571
								CoM Coordinates (ft, ft)			66.5	-17.2

Source: UWRL 1997

Figure 5.19
Configuration of Soil Cores and Associated Geometry Used for Calculation of Average Borehole Contaminant Concentrations as Input to Total Mass Estimates



product can be estimated from observation well and monitoring point locations that contain free product during sampling. Because the thickness of product observed in a monitoring well can be substantially greater than that actually existing within the formation, care must be taken in interpreting monitoring well product thickness results. Attempts should be made, however, to estimate free product volume both above and below the water table so that the source contaminant(s) lifetime can be predicted. When the composition of contaminants within the free product, the lateral and vertical extent of free product distribution, and the formation total porosity are known, the mass of contaminant existing within the free product at the site (M_{fp}) can be estimated as follows:

$$M_{fp} = \text{Area}(\text{Thickness})\theta\rho_{fp}C_i \tag{5.21}$$

where:

Area	=	estimated areal extent of free product (length^2);
Thickness	=	estimated vertical extent of free product (length);
θ	=	formation total porosity (decimal);
ρ_{fp}	=	free product density (mass/volume); and
C_i	=	contaminant concentration within the free product (mass/mass).

If high dissolved contaminant concentrations but no free product is observed in monitoring wells, then product exists throughout the site as residual saturation. Estimates of the maximum amount of residual-phase product existing at a site can be made based on the characteristics of the soil at a site using the quantitative relationships presented by Parker, Lenhard, and Kuppusamy (1987) and Mobil Oil Corporation (1995). These relationships describe the typical residual hydrocarbon saturation within the smear zone at and below the groundwater table as a function of soil texture. For sands, a residual saturation of 25% of the total pore volume is suggested, while this value drops to 15% for sandy silts and fine sands, and to only 5% for silty clays.

With residual-phase product, the composition of the product can be inferred from groundwater concentration data assuming that equilibrium exists between the residual phase and the groundwater using the following relationships based on Raoult's Law, an assumed molecular weight of the residual product, and the known aqueous solubility of the individual compounds of interest:

$$\text{Equilibrium Concentration} = \text{Mole Fraction (Aqueous Solubility)} \quad (5.22)$$

$$\text{Mole Fraction} = \text{Equilibrium Concentration / Aqueous Solubility} \quad (5.23)$$

$$\text{Moles in Product} = \text{Mole Fraction } (M_{fp}) / MW_{fp} \quad (5.24)$$

$$\text{Mass in Product} = \text{Moles in Product} \bullet MW_{compound} \quad (5.25)$$

where:

$MW_{compound}$ = Molecular weight of compound (lb/lb mol), and

MW_{fp} = molecular weight of the product (lb/lb mol) = 120 lb/lb mol for typical gasoline.

This procedure for estimating residual-phase product and contaminant mass in the source area was used at a site where former gasoline tanks had released product to the soil and groundwater (Dupont et al. 1997). No free product, only light sheens, had been observed in soil core and ongoing groundwater monitoring samples. However, total petroleum hydrocarbon (TPH) and BTEX groundwater concentrations approaching levels in equilibrium with free product were observed throughout much of the site. These elevated groundwater data were used to delineate the apparent areal extent of residual-phase material — approximately 776.64 m^2 (8,360 ft^2). Based on this area, the volume of soil existing below the site that contained this

residual saturation and the vertical extent of potentially contaminated soil — 4.11 m (13.5 ft) [3.05 m (10 ft) of measured groundwater contamination and 1.06 m (3.5 ft) of capillary fringe and smear zone] — were estimated. It was assumed that 10% of the pore volume of the fine sand and clay soil at the site contained this residual product material based on the findings of Parker, Lenhard, and Kuppusamy (1987). Based on an estimated total contaminated soil volume of 3,197 m^3 (112,900 ft^3) and a total porosity of 0.38, a total pore volume of 1,215 m^3 (42,900 ft^3) was calculated for the source area. The actual residual product volume was estimated to be 121.5 m^3 (4,290 ft^3), resulting in an estimated 109,300 kg (241,000 lb) of TPH below the site. From this estimate of product mass and the measured concentration of specific components in equilibrium with the product in the groundwater, the mass of each contaminant of interest within the source area residual product was estimated using Equations 5.22 through 5.25 as summarized in Table 5.13.

Table 5.13
Summary of Estimated Total Residual Contaminant Mass Based on Residual Product Volume Estimates and Dissolved Plume Mass Measured at a Field Site

Compound	MW (lb/lb mol)	Aqueous Solubility (mg/L)	Measured Groundwater Concentration (mg/L)	Mole Fraction in Product	Mole in Product (lb)	Mass in Product (lb)	Mass in Plume (lb)
Benzene	78.1	1,780	4.9	0.003	5.5	431	8.1
Toluene	92.1	759	3.2	0.004	8.5	782	3.4
Ethylbenzene	106.2	135	1.9	0.014	28.5	3,025	1.9
p-Xylene	106.2	221	6.3	0.029	57.5	6,111	9.6
Naphthalene	128.2	30.6	0.79	0.026	52.1	6,681	1.2
TPH	120.0		86.1			241,000	172

Source: Dupont et al. 1997

5.3.9.3 Estimation of Source Mass Lifetime

Based on the logic presented in Figure 5.14, the specific procedure to be followed for source mass lifetime calculations is dependent upon the type of source at a site. If a pulsed source is identified, little residual contaminant

mass remains in the original source area, and the lifetime of the plume can be estimated based on the dissolved plume mass from Equation 5.16, along with the estimated contaminant degradation rate determined from Equations 5.8 through 5.11. A source lifetime (T_{pulse}) can then be estimated as follows for zero-order, and first-order degradation rates, respectively:

$$T_{pulse,zero} = (Mass_T) / k_o \tag{5.26}$$

$$T_{pulse,first} = -\ln(M / Mass_T) / k_1 \tag{5.27}$$

where:

M = final mass that is to be reached at the end of the calculated plume lifetime.

For a continuous source, the plume lifetime is the sum of the lifetime of the dissolved plume mass plus the mass remaining in the source area. The total mass disappearance rate is equated to the contaminant degradation rate determined from Equations 5.8 through 5.11 to yield an estimate of total plume lifetime ($T_{continuous}$), for zero- and first-order degradation rate relationships, respectively:

$$T_{continuous,zero} = (Mass_V + Mass_{SZ} + Mass_T) / k_o \tag{5.28}$$

$$T_{continuous,first} = -\ln[M / (Mass_V + Mass_{SZ} + Mass_T)] / k_1 \tag{5.29}$$

where:

$Mass_V$ = contaminant mass located above the groundwater table (mass);

$Mass_{sz}$ = contaminant mass located below the groundwater table in the source area (mass); and

$Mass_T$ = contaminant mass located in the dissolved groundwater plume (mass).

5.3.9.4 Estimation of Source Mass Lifetime with Source Removal

The effect of source removal efforts, either partial or complete, on the overall lifetime of contaminant mass at the site can be evaluated through a modification of Equations 5.28 and 5.29 presented above. For example, if a significant mass of contaminant exists above the groundwater table (i.e., $Mass_V$ is large relative to $Mass_T$), the effect of vadose zone source removal on the lifetime of the plume can be evaluated using Equations 5.30 or 5.31:

$$T_{continuous,zero} = [(1-p)Mass_V + Mass_{sz} + Mass_T] / k_o \quad (5.30)$$

$$T_{continuous,first} = -\ln\{M / [(1-p)Mass_V + Mass_{sz} + Mass_T]\} / k_1 \quad (5.31)$$

where:

p = % removal of vadose zone contamination (decimal).

The impact of various removal scenarios on the plume lifetime can be evaluated using this general approach. If 100% vadose and saturated zone source removal is assumed, the continuous source plume lifetime equation reduces to that of a pulsed source as shown in Equations 5.26 and 5.27. An evaluation of the impact of source removal on predicted plume lifetime and the duration of management activities required at a site is presented in a case study in Chapter 8.

5.3.10 Safety Requirements

No safety requirements beyond those associated with proper conduct during environmental sampling and monitoring covered by OSHA are necessary for implementation of intrinsic remediation at a site.

5.3.11 Specifications Development

Specifications required to properly conduct an intrinsic remediation study at a field site apply primarily to: (1) soil and groundwater monitoring point installation and construction and (2) soil and groundwater sample collection, handling, and analysis. Recommendations related to monitoring point installation can be found in US EPA RCRA groundwater and vadose zone monitoring guidance (US EPA 1986a, 1986b), while sample collection and analysis methodologies for a variety of analytes are described in detail in a variety of laboratory protocol documents available from US EPA (1984a, 1986c, 1986d, 1989b). Many of these field and laboratory methods specifically relevant to intrinsic remediation studies have been compiled by a number of authors representing both the public (Wiedemeier et al. 1994) and private sectors (Buscheck and O'Reilly 1995; Mobil Oil Corporation 1995; Yang et al. 1995). The U.S. Air Force protocol prepared by Wiedemeier et al. (1994) is the most comprehensive in terms of its treatment of monitoring and analytical approaches and should be consulted when preparing specifications for a field intrinsic remediation study.

The specification document for conducting intrinsic remediation field assessments should emphasize sampling and analysis activities and, at a minimum, contain the following:

- introduction to the site and test objectives;
- conceptual model of site and site contamination;
- sampling and analysis plan to be implemented at the site including:
  - hydrogeology assessment,
  - water and soil gas sampling point installation requirements,
  - soil core sampling requirements,
  - groundwater and soil gas sampling requirements,
  - field analytical requirements
  - fixed-base laboratory analytical support, and
  - sample handling, storage, transport, labeling, and tracking requirements;
- quality assurance plan (see Section 5.3.17.3);
- health and safety procedures to be followed during field and laboratory activities; and
- data summary and presentation requirements.

5.3.12 Cost Data

The costs associated with implementation of an intrinsic remediation plume management approach at a contaminated site involve initial site assessment (monitoring point installation and sampling) and intrinsic remediation process evaluation (data analysis, interpretation, and modeling) activities, followed by ongoing site monitoring and process model improvements during the life of the source area/plume. Significant additional expense can arise if active source removal efforts are undertaken to reduce the duration of monitoring required at a site. Table 5.14 provides a summary of costs associated with intrinsic remediation plume management. Other sections of this monograph discuss costs associated with free product recovery technologies and in situ and ex-situ remediation of the source area should such efforts be necessary.

5.3.13 Design Validation

Intrinsic remediation and natural containment of a contaminant plume are validated through multiple lines of evidence as indicated in the intrinsic remediation assessment protocol presented in Section 5.3.2. At a given site, validation of the intrinsic remediation plume management approach is supported by:

Table 5.14
Typical Intrinsic Remediation Plume Management Costs*

	Unit Cost	No. of Units	Cost
INITIAL SITE ASSESSMENT/CAPITAL REQUIREMENTS			
Prepare Work Plan	$4,000	Lump Sum	$4,000
Install MWs & MPs	$30/LF	600 LF	$18,000
Conduct Initial Site Assessment/Data Collection	$10,000	Lump Sum	$10,000
Data Analysis, Modeling, Intrinsic Remediation Verification	$15,000	Lump Sum	$15,000
TOTAL			**$47,000**
ANNUAL SITE MONITORING/DATA ANALYSIS COSTS			
Annual Monitoring and Sample Analysis	$500/well	20 wells	$10,000
Annual Data Reduction and Model Verification	$5,000	Lump Sum	$5,000
TOTAL			**$15,000**

*Typical costs for site where depth to groundwater table = 9 m (30 ft), 20 monitoring wells and/or groundwater monitoring points areinstalled, and annual groundwater monitoring is required. These values do not include source removal/treatment costs. Refer to cost data for specific active source treatment technologies for these source removal cost data.

- confirmation of biologically-mediated reactions in the contaminant plume from chemical indicators of groundwater quality;
- detection of biologically-generated chemical intermediates;
- relative loss of degradable versus non-degradable contaminants within the plume; and
- contaminant fate and transport modeling.

As previously indicated, ongoing monitoring and updating of the site conceptual model is an integral part of the intrinsic remediation management approach and should be used to validate and/or update contaminant fate and transport predictions throughout the life of the plume.

5.3.14 Permitting Requirements

Permitting requirements for intrinsic remediation systems are generally minimal unless active source removal is part of the overall management approach at a site. For the site assessment and ongoing monitoring phases of

the intrinsic remediation plume management approach, well construction permits will be required in some states. Permits may also be required for transport and disposal of contaminated drill cuttings from monitoring well installation and contaminated groundwater generated during monitoring well and shallow monitoring point purging prior to sampling. Depending upon local requirements, the time and cost of managing these sampling residues can be significant. In addition, as part of the permitting process for most remediation techniques, public notification and public hearings may be required to justify selection and implementation of intrinsic remediation for contaminant plume management.

5.3.15 Design Checklist

The previous sections provide detailed logic regarding the application of intrinsic remediation under site-specific conditions. The following is the sequence of activities in the assessment and implementation of intrinsic remediation for contaminant plume management.

- Determine steady-state plume conditions — evaluate plume centerline concentrations or estimate plume mass (CoM);
    - If the plume is stable or shrinking, intrinsic remediation is viable.
    - If the plume is growing, continue to monitor unless source removal or remediation is warranted due to receptor impact.
- Estimate contaminant degradation rates — evaluate dissolved plume mass changes over time;
    - If the plume mass is declining over time, a contracting plume is indicated. Estimate degradation rate from mass loss over time.
    - If the plume mass is steady-state over time, a continuous plume is indicated.
        - If groundwater flow data are available, calibrate fate and transport model to field data.
        - If flow data are not available, use plume centerline concentration data.
- Estimate the mass of contaminant in the source area;
- Estimate the source lifetime based on degradation rates;

    - If the plume is a pulsed source, base lifetime on dissolved mass degradation rate.
    - If the plume is a continuous source, base lifetime on source mass above and below groundwater table in source area and in plume.
- Predict long-term behavior of plume;
    - If the plume is a pulsed source, long-term behavior is controlled by plume degradation rate estimated from dissolved plume mass loss over time
    - If the plume is a continuous source, then:
        - Evaluate fate and transport with no source removal; and
        - Evaluate fate and transport with various levels of source removal.
- Determine applicability of intrinsic remediation; and
    - If a receptor will be impacted during the life of the plume, apply active remediation.
    - If the plume lifetime using intrinsic remediation is not acceptable, apply source removal.
    - If the pool of TEAs is insufficient to assimilate mass in the source area over the predicted life of the source area, apply active remediation.
- Develop long-term site monitoring plan including:
    - Compliance monitoring for regulatory purposes,
    - Intrinsic remediation process verification monitoring,
    - Update conceptual model of site, source lifetime predictions, contaminant degradation rates, and
    - Update assessment of intrinsic remediation at the field site.

5.3.16 Implementation

Implementation of the intrinsic remediation plume management approach primarily involves the installation of groundwater and soil gas sampling points and the collection and analysis of soil and groundwater samples from a contaminated site. Wells and monitoring points should be installed by a qualified driller with experience in environmental drilling, soil sampling procedures, and OSHA 40-hour safety certification. All appropriate local

and regional regulatory agencies should be notified. Refer to the appropriate sections of this monograph that discuss active treatment methods should such methods be necessary.

5.3.17 Start-up Procedures

There are no specific start-up procedures for an intrinsic remediation plume management approach as it is focused on site assessment, plume delineation, plume modeling, and long-term monitoring. Procedures appropriate for startup during the site assessment process include utility right-of-way clearance, monitoring well and shallow groundwater sampling point position identification, drill-rig mobilization, drilling, and soil and groundwater sample collection. There are no active system start-up procedures required unless source removal or treatment is implemented as part of the intrinsic remediation management approach. Refer to the appropriate sections of this monograph that discuss active treatment methods should such methods be necessary.

5.3.18 Performance Evaluation

Performance evaluation of the intrinsic remediation plume management approach was identified in the assessment protocol presented in Section 5.3.2. Performance of intrinsic remediation is based on the ability of natural processes taking place within the contaminated aquifer to attenuate and destroy the contaminants of concern before they migrate to downgradient receptors. Methods for verification of contaminant attenuation, which are detailed in previous sections, include the evaluation of plume steady-state conditions, determination of contaminant degradation rates, and quantification of the long-term assimilative capacity potential of the contaminated aquifer. An integral component of this methodology is the long-term monitoring of the contaminant plume to up-date the conceptual model for the site and verify contaminant degradation rates and assimilative capacity.

5.3.18.1 Operation Practices

Operations primarily involve routine soil gas and groundwater sampling throughout the contaminated site and data analysis, interpretation, and modeling for verification of contaminant attenuation. Standard protocols for soil, soil gas, and groundwater sampling are summarized by US EPA (1986a, 1986b), while methods for laboratory analyses required for documentation of intrinsic remediation are available from a number of sources (APHA 1989; Nelson and Sommers 1982; Olsen and Sommers 1982; US EPA

1986c, 1986d, 1989c). Refer to the detailed protocol prepared for the U.S. Air Force by Wiedemeier et al. (1994) for a comprehensive discussion of sampling and analysis methods appropriate for evaluation of intrinsic remediation processes at a site.

5.3.18.2 Operations Monitoring

Monitoring of intrinsic remediation involves the quantification of the degradation of the contaminants of concern, magnitude and distribution of chemical species serving as electron acceptors during microbial degradation of these contaminants, and general aquifer properties indicative of groundwater conditions relevant to microbial degradation processes. Table 5.15 summarizes these analytes along with methods used and the purpose for their determination. Refer to the detailed protocol by Wiedemeier et al. (1994) for a discussion of analytical methods appropriate for these analytes.

5.4 Aboveground Reactors

5.4.1 Principles of Operation

Biological treatment of domestic wastewater using naturally-occurring microorganisms for removal of contaminants has been practiced for years. Biological treatment using aerobic biodegradation has historically been the primary treatment process for domestic wastewater. Over the years, the process has been improved and enhanced to improve efficiency and performance. Several variations of the basic biological treatment process are in widespread use for treatment of domestic wastewater throughout the world, and are described in detail in numerous textbooks and design manuals written on the subject. The reader is referred to the first monograph in this series (Ward et al. 1995) for specific design and application details for biological reactors. A summary of key principles and issues related to the biological treatment of contaminated groundwater and solids in ex-situ reactors is provided below.

The basic biological treatment process involves the use of naturally-occurring aerobic, facultative or anaerobic microorganisms to metabolize organic material. The majority of organisms found in biological treatment systems are of the facultative type, that is, they can function in either an aerobic or anaerobic environment. Aerobic degradation uses oxygen as an electron acceptor while anaerobic processes use inorganic carbon

Table 5.15
Soil, Soil Gas and Groundwater Sample Analyses that can be used to Quantify Intrinsic Remediation Processes

Sample Type	Measurement	Method	Purpose
Groundwater	O_2	Field DO Meter	Electron acceptor
	Fe^{2+}, Mn^{2+}	Colorimetry	Biological product from electron acceptor
	pH	Field Glass Electrode	Env. conditions
	Redox	Field ORP Electrode	Redox potential
	Aromatic HCs*	Lab GC**	Substrate
	Total HCs	Lab GC	Substrate
	Boiling point splits	Lab GC	Substrate
	Chlorinated HCs	Lab GC	Substrate/co-substrate biological products & intermediates
	Dissolved Gases (CH_4, ethylene, vinyl chloride)	Lab GC	Biological products & intermediates
	COD	Lab Acid Chromate	Substrate/electron donor
Soil	Organic carbon	Lab Acid Chromate	Sorption
	pH	Lab Glass Electrode	Env. conditions
	Kjeldahl-N	Digestion	Nutrient
	Extractable P	Extraction	Nutrient
	Texture	Physical	Env. conditions, flow
	Aromatic HCs	Lab GC**	Substrate
	Total HCs	Lab GC	Substrate
	Boiling point splits	Lab GC	Substrate
	Chlorinated HCs	Lab GC	Substrate/co-substrate biological products & intermediates
Soil Gas	O_2	Field O_2 Meter	Electron acceptor
	CO_2	Field CO_2 Meter	Mineralization product electron acceptor
	CH_4	Lab GC	Biological product
	Aromatic HCs	Lab GC	Substrate
	Total HCs	Field/Lab GC	Substrate
	Boiling point splits	Lab GC	Substrate
	Chlorinated HCs	Lab GC	Substrate/co-substrate biological products & intermediates

*HCs = hydrocarbons
**GC = gas chromatograph

as an energy source. The anaerobic process is typically applied to wastewaters of high organic strength (>1,000 mg/L BOD or COD) or for degradation of specific chlorinated organics (e.g., trichloroethene). However, for most groundwater treatment applications, aerobic biological treatment is applicable due to the low organic loadings typically encountered, even in what is considered highly contaminated groundwater systems.

Aerobic biological treatment processes can operate as either suspended growth or fixed-film systems. Suspended growth systems, such as the activated sludge process, consist of free-floating microorganisms suspended in the liquid or solid slurry suspension being treated. The waste/microorganism mix (mixed liquor) is oxygenated in a tank (aeration tank) using mechanical or diffused aeration by the addition of either ambient air or pure oxygen. The microorganisms or the treated solid suspension are then separated from the treated liquid using sedimentation, filtration, or flotation processes. A portion of the separated solids are recycled back to the aeration tank in the liquid wastewater system to ensure that adequate microbial populations exist in the bioreactor to treat more waste. The portion of the microorganisms not recycled to the aeration tank are removed (wasted) from the system to account for organism growth and to maintain the desired microorganism concentrations within the biological reactor. Suspended growth systems are typically applicable to wastewaters with BOD concentrations of 100 to 1,000 mg/L, and are the only systems applicable for the treatment of soil slurries. At low BOD concentrations in liquid-phase bioreactors, insufficient growth rates due to a low food supply make it difficult to maintain a sufficient microorganism population to overcome losses in the separation process. As a result, washout of the microorganisms can occur, leading to process failure.

Fixed film treatment systems, such as submerged biological filters, biotowers, rotating biological contactors (RBCs), biological activated carbon (BAC) and fluidized-bed reactors (FBRs) are generally more applicable for treatment of dilute groundwaters than are suspended growth systems. In a fixed-film process, the microorganisms are attached to a media and the substrate is passed over the attached biomass. Oxygen is supplied in the RBC and biotower processes by diffusion from the atmosphere through the air-liquid interface on the reactor media in contact with the atmosphere. Oxygen then diffuses to the microorganisms in the attached biofilm while metabolic endproducts (i.e., CO_2, etc.) diffuse out of the biolayer, through the liquid-air interface and into the atmosphere. Oxygen is transferred to the wastewater to be treated in the FBR process by air or more typically, pure oxygen injection at the bottom of the reactor. This injected gas stream serves both as a source of electron acceptor, and as a means of mixing and fluidizing the bed within the reactor. Submerged biological filters can also

be aerated using diffused aeration. BAC units are typically aerated by saturating the influent with oxygen prior to its entry into the reactor.

Excess biomass is removed from fixed-film systems by the process of sloughing. As the biomass grows on the media, organisms attached to the media become starved as substrate diffusing from the surface of the biofilm becomes depleted before reaching them. Without electron donors these organisms die, the biofilm looses its attachment to the media surface, and the entire biofilm sloughs off of the media due to turbulence. This sloughed biomass is subsequently removed from the reactor effluent by sedimentation, filtration, or flotation. BAC units are periodically backwashed to remove excess biological growth as evidenced by excessive pressure drop across the carbon bed. In the case of the FBR process, a mechanical system is used to shear the biomass from the media when the density of the biomass/media particles decrease sufficiently due to biological growth to elevate the bed height above a predetermined point.

All biological treatment technologies are not applicable to the treatment of extracted groundwater. Generally, extracted groundwater is characterized as having relatively low biodegradable organic concentrations (e.g., BOD or COD) as compared to domestic or industrial wastewaters. Groundwater characteristics from several Superfund sites in the northeast are provided in Table 5.16 . These data demonstrate the variability in constituents and concentrations from different sites, thus indicating the importance of conducting treatability studies to evaluate the performance of biological treatment with a specific groundwater matrix. The importance of acclimation of the biomass to a specific groundwater to evaluate performance is evident from the range of influent characteristics that can be encountered. Of note are the comparatively low BOD and COD concentrations. Consequently, technologies developed for treatment of high strength wastewaters (e.g., pure oxygen activated sludge and most anaerobic processes) are not generally appropriate for groundwater treatment applications.

5.4.2 Process Design Principles

5.4.2.1 Technology Application

Figure 5.20 shows the range of organic strength at which potentially applicable aboveground biological treatment processes can typically operate. In general, suspended growth processes, such as activated sludge and Powdered Activated Carbon Treatment (PACT®), can effectively and efficiently treat contaminated groundwater streams only at a higher range of organic strength than fixed growth processes, such as submerged biological filters,

Table 5.16
Example Groundwater Influent Data

Parameter	Site A Influent	Site B Influent	Site C Influent	Site D Influent
West Chemistry (mg/L)				
BOD (total)		13	16	51
BOD (soluble)			16	
COD (total)	350		187	253
BOD (soluble)			179	
Chloride		4		
Total Cyanide			BMDL	
Amenable (Free) Cyanide)			BMDL	
TKN			49	
Oil & Grease			BMDL	
TPH			BMDL	
pH (s.u.)			6.85	
Phenolics			0.10	
TDS	445		954	4,688
TOC				
TSS			84	155
Hardness as $CaCO_3$			123	
Sulfate		14		
Sulfide			BMDL	
Volatile Organics (µg/L)				
Methyl methacrylate	57,184			
Acetone	302	557	450	40
Benzene	344	9	190	107
2-Butanone		524		35
Carbon disulfide	43	2		4
Chlorobenzene			250	1,736
Chloroform		1		
Chloroethane				7
Chloromethane				7
1,1-Dichloroethane	85	8		
1,2-Dichloroethane	42	1,652		57
1,1-Dichloroethene		2		

BMDL = Below Method Detection Limits
Blanks indicate the analyte was not detected at that site.

Table 5.16 (cont.)
Example Groundwater Influent Data

Parameter	Site A Influent	Site B Influent	Site C Influent	Site D Influent
1,2-Dichloroethene (total)				7
cis-1,2-Dichloroethene	193	141		
trans-1,2-Dichloroethene	43			
Total 1,2-Dichloroethene		141		
1,2-Dichloropropane		118		
trans-1,3-Dichloropropene				3
1,4-Dioxane		126		
Ethylbenzene	550	104	98	
4-Methyl-2-Pentanone		111	210	9
Methylene chloride	48	4		
Styrene	43			
Tetrachloroethylene				
Toluene	105	845	480	6
1,1,1-Trichloroethane				
Trichloroethene	48			3
Vinyl chloride	89	2		
Xylene (total)		453	380	62
Acid Extractable Compounds (µg/L)				
Benzoic Acid				10
2-Chlorophenol				14
2,4-Dichlorophenol				12
2,4-Dimethylphenol	48		11	10
2-Methylphenol	19			5
4-Methylphenol	18		16	19
Pentachlorophenol				25
Phenol	74	10	4.1	516
2,4,6-Trichlorophenol				19
Base Neutral Organics (µg/L)				
Acenaphthene			0.4	10
Aniline			200	
Benzo(b)fluoranthene				10

BMDL = Below Method Detection Limits
Blanks indicate the analyte was not detected at that site.

Table 5.16 (cont.)
Example Groundwater Influent Data

Parameter	Site A Influent	Site B Influent	Site C Influent	Site D Influent
Benzo(k)fluoranthene				10
Benzyl alcohol	2			13
Bis (2-Chloroethyl)ether			3.9	10
Bis (2-Chloroethoxy)methane			2.2	
Bis (2-Ethylhexyl) phthalate	22		U	10
4-Chloroaniline			42	2059
2-Chloronaphthalene				10
Chrysene				5
Dibenzofuran				10
Diethyl phthalate	28		1.1	
Dimethyl phthalate	2			
Di-n-butyl phthalate	19		0.6	
1,2-Dichlorobenzene			7.6	1,543
1,3-Dichlorobenzene			1.2	79
1,4-Dichlorobenzene	43		26	192
3,3-Dichlorobenzidine				
Fluoranthene				10
Fluorene				5
Isophorone			1.0	
2-Methyl naphthalene	20		13	10
Naphthalene	29		20	26
Nitrobenzene				543
N-Nitrosodiphenylamine			2.0	
Phenanthrene				10
Pyrene				10
1,2,4-Trichlorobenzene				703
Metals (µg/L)				
Aluminum (total)	253			
Aluminum (soluble)	66			
Antimony				
Arsenic (total)	23	3	37	377
Arsenic (soluble)	25		11	
Cadmium (total)	6		BMDL	4

BMDL = Below Method Detection Limits
Blanks indicate the analyte was not detected at that site.

Table 5.16 (cont.)
Example Groundwater Influent Data

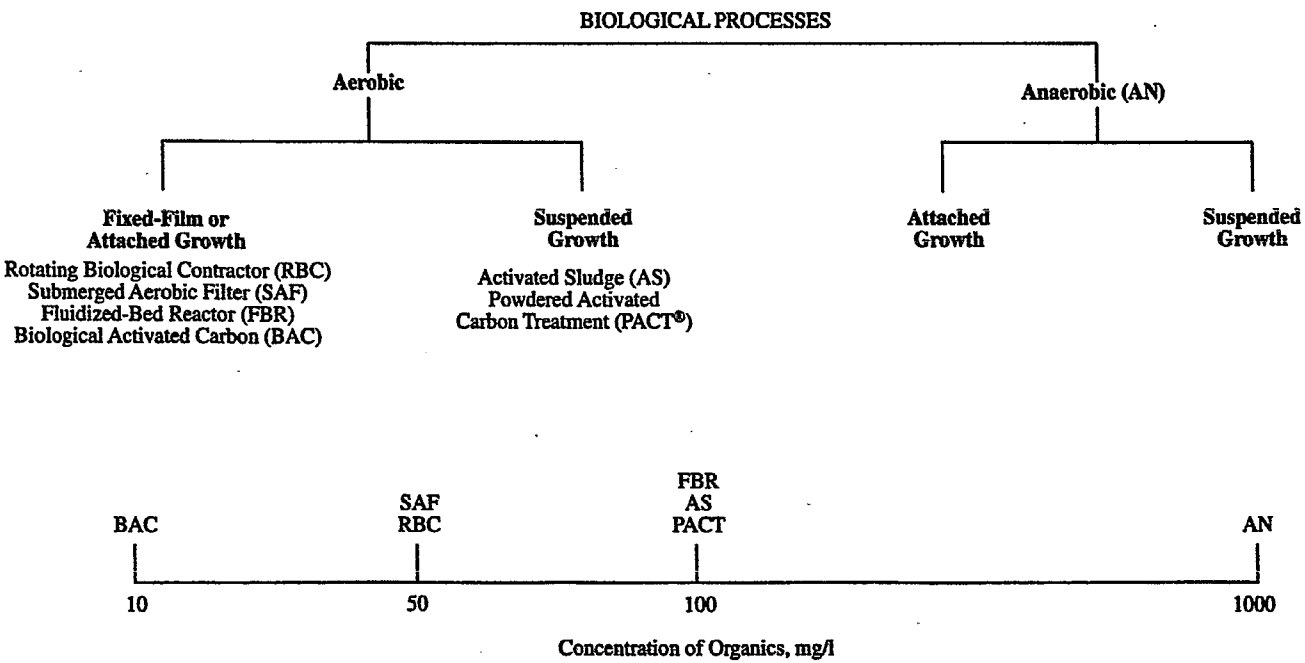
Parameter	Site A Influent	Site B Influent	Site C Influent	Site D Influent
Cadmium (soluble)	2		BMDL	
Chromium (total)		18	BMDL	108
Chromium (soluble)			BMDL	
Copper (total)		17	13	396
Copper (soluble)			8.7	
Iron (total)	104,426	46,858	318	52,200
Iron (soluble)	101,530		239	
Lead (total)	9	282	3.3	176
Lead (soluble)	5		BMDL	
Manganese (total)	76	167		
Manganese (soluble)	74			
Mercury (total)		1	BMDL	56
Mercury (soluble)			BMDL	
Nickel (total)			16	160
Nickel (soluble)			19	
Silver (total)			BMDL	2
Silver (soluble)			BMDL	
Zinc (total)		13,499	44	
Zinc (soluble)			56	

BMDL = Below Method Detection Limits
Blanks indicate the analyte was not detected at that site.

biological activated carbon, rotating biological contactors (RBCs) and fluidized-bed reactors (FBRs). Slurry reactors (high solids content suspended growth reactors) are applicable for highly concentrated solids streams and highly contaminated soils that are slurried prior to treatment.

Slurry reactors are liquid/solid contact biological reactors that are analogous to conventional biological suspended growth reactors, e.g., activated sludge systems. Slurry reactors are used to treat contaminated solid matrices, such as soils or sediments. They are employed to mitigate the environmental factors typically encountered with treating relatively recalcitrant constituents in soil or sediments. By suspending the soil or sediments in an

Figure 5.20
Overview of Biological Processes



aqueous system the availability of carbon sources, inorganic nutrients, and an electron acceptor (typically oxygen) are greatly improved by maximizing mass transfer rates and contact between the contaminants and the microorganisms.

Treatment of soils with a slurry reactor is nearly always considerably more expensive than treatment using a soil pile or by land farming. The use of this technology is generally limited to treatment of more recalcitrant compounds or highly contaminated soils or sediments. Typical wastes treated in this manner are oil refinery wastes, principally sludges from storage and treatment lagoons, and wood preserving wastes, such as impoundment sludges and the surrounding soils contaminated with creosote and/or pentachlorophenol (PCP).

Although aerobic reactors are most common, some systems are designed to operate under anaerobic conditions or to cycle between anaerobic and aerobic conditions. Slurry reactors can be operated in single or sequencing batch modes, or in either continuous or semi-continuous modes. Slurry reactors have been constructed in lined lagoons, unlined lagoons (for treatment of lagoon solids), or in constructed reactors.

In all systems, the two main design criteria are mixing and aeration. While mixing can, in some cases, be provided by aeration, it is typically achieved through mechanical means, especially for treatment of soils, which require more energy to maintain in suspension than do sediments.

Most of the constituents found in contaminated groundwaters can be removed using aerobic biological treatment. Any of several removal mechanisms including stripping, sorption, and biodegradation may occur alone or concurrently and contribute to overall contaminant removal. The fate of various organic compounds in aerobic biological treatment processes is shown in Table 5.17. The removal mechanisms are described below.

5.4.2.2 Stripping

Stripping can be a significant removal mechanism in aerobic treatment processes because the aeration process used to provide oxygen for aerobic degradation also strips volatile compounds. Depending on the particular constituent, both stripping and biodegradation may occur simultaneously. The proportion of removal that occurs due to either of these mechanisms depends on the constituent in question and, to a lesser extent, the type of treatment process being utilized. For example, vinyl chloride is extremely volatile and will generally strip before significant biodegradation occurs. However, a less volatile compound, such as acetone, will generally biodegrade readily with only minor removal due to stripping.

Table 5.17
Fate of Organic Constituents in Activated Sludge Systems

	Overall Percent Removal			Percent Volatilized to Air			Percent Partitioned to Sludge			Percent Biodegraded		
		Unacc.			Unacc.			Unacc.			Unacc.	
Pollutant	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %
2,4-D	90	60	50	0	0	0	7	5	4	83	55	46
Acenaphthylene	95	90	90	19	54	54	9	8	8	67	28	28
Acetaldehyde	95	95	95	0	5	5	10	10	10	85	81	81
Acetone	95	50	30	0	3	2	10	5	3	85	43	26
Acrolein	95	95	95	0	5	5	10	10	10	85	81	81
Acrylamid	90	62	50	0	0	0	9	6	5	81	56	45
Acrylic Acid	90	85	80	0	0	0	9	9	8	81	77	72
Acrylonitrile	90	75	70	0	4	4	9	8	7	81	64	60
Aldrin	90	90	90	0	0	0	33	33	33	57	57	57
Aniline	95	85	80	0	0	0	10	9	8	86	77	72
Anthracene	95	90	90	0	0	0	52	50	50	43	41	41
Antimony	60	60	60	0	0	0	60	60	60	0	0	0
Arsenic	50	50	50	0	0	0	50	50	50	0	0	0
Barium	90	90	90	0	0	0	90	90	90	0	0	0

Benzal Chloride	90	55	50	0	17	15	7	4	4	83	34	31
Benzene	95	90	90	24	72	72	2	2	2	69	16	16
Benzotrichloride	90	45	40	18	14	12	7	4	3	65	28	25
Benzyl Chloride	90	90	90	23	45	45	7	7	7	60	38	68
Bis-2-Chloroethyl Ether	90	50	30	0	3	2	9	5	3	81	43	26
Bis-2-Ethylhexyl Phthalate	90	90	90	0	0	0	66	66	66	24	24	24
Bromomethane	95	95	95	86	90	90	0	0	0	10	5	5
Butyl Benzyl Phthalate	95	90	90	0	0	0	43	41	41	52	50	50
Cadmium	27	27	27	0	0	0	27	27	27	0	0	0
Captan	90	50	30	0	0	0	7	4	2	83	46	28
Carbon Disfulide	95	85	80	76	77	72	1	1	1	18	8	7
Carbon Tetrachloride	90	85	80	72	77	72	12	9	8	6	0	0
Chlordane	90	90	90	9	9	9	33	33	33	48	48	48
Chlorobenzene	90	90	90	27	45	45	14	14	14	50	32	32

Acc = Acclimated sludge with constant loading Unacc = Unacclimated sludge with transient loads

Table 5.17 (cont.)
Fate of Organic Constituents in Activated Sludge Systems

Pollutant	Overall Percent Removal			Percent Volatilized to Air			Percent Partitioned to Sludge			Percent Biodegraded		
		Unacc.			Unacc.			Unacc.			Unacc.	
	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %
Chlorobenzilate	90	60	50	9	6	5	7	5	4	74	49	41
Chloroethane	95	90	90	76	81	81	1	1	1	18	8	8
Chloroform	90	80	80	63	72	72	2	2	2	25	6	6
Chloromethane	95	90	90	86	86	86	1	1	1	0	4	4
2-Chlorophenol	95	65	60	0	0	0	8	5	5	87	60	55
Chromium	70	70	70	0	0	0	70	70	70	0	0	0
Cresols	95	50	40	0	0	0	8	4	3	87	46	37
Cumene	95	95	95	38	57	57	4	4	4	53	34	34
Cyanide	60	60	60	0	3	3	57	57	57	3	0	0
Cyclohexane	95	95	95	10	86	86	4	4	4	82	6	6
Di-N-Butyl Phthalate	90	90	90	0	0	0	20	20	20	70	70	70
Di-N-Octyl Phthalate	90	90	90	0	0	0	7	7	7	83	83	83
Dibromomethane	85	80	80	43	64	64	13	12	12	30	4	4
1,2-Dichlorobenzene	90	87	85	45	78	77	32	9	9	14	0	0

1,3-Dichlorobenzene	90	87	85	45	78	77	3	3	3	42	6	6
1,4-Dichlorobenzene	90	87	85	45	78	77	23	9	9	23	0	0
1,2-Dichloroethane	90	50	30	45	45	27	5	3	2	41	3	2
1,1-Dichloroethylene	95	90	90	76	81	81	0	0	0	19	9	9
2,4-Dichlorophenol	95	55	50	0	0	0	8	4	4	87	51	46
1,2-Dichloropropane	90	70	70	45	63	63	0	0	0	45	7	7
Dichlorvos	90	50	30	0	0	0	9	5	3	81	48	27
Dicofol	90	90	90	45	45	45	8	8	8	37	37	37
Diethyl Phthalate	90	75	70	0	0	0	1	1	1	89	74	69
3,3-Dimethoxy Benzidine	80	30	20	0	0	0	8	3	2	72	27	18
2,4-Dimethyl Phenol	95	85	80	0	0	0	8	7	6	87	78	74
Dimethyl Phthalate	95	65	60	0	0	0	0	0	0	95	65	60
2,4-Dinitrophenol	90	75	70	0	0	0	9	8	7	81	68	63
1,4-Dioxane	90	50	40	0	0	0	9	5	4	81	45	36

Acc = Acclimated sludge with constant loading Unacc = Unacclimated sludge with transient loads

Table 5.17 (cont.)
Fate of Organic Constituents in Activated Sludge Systems

Pollutant	Overall Percent Removal			Percent Volatilized to Air			Percent Partitioned to Sludge			Percent Biodegraded		
		Unacc.			Unacc.			Unacc.			Unacc.	
	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %
Epichlorohydrin	87	59	25	0	0	0	9	6	3	78	53	23
Ethyl Benzene	95	90	90	24	72	72	6	5	5	66	13	13
Ethylene Thiourea	85	67	60	0	0	0	9	7	6	77	60	54
Formaldehyde	85	85	80	0	4	4	9	9	8	76	72	68
Hexachloro 1,3-Butadiene	95	90	90	0	5	5	9	8	8	86	77	77
Hexachloroethane	95	90	90	0	5	5	9	8	8	86	77	77
Hydrazine	95	85	80	0	4	4	10	9	8	85	72	68
Lead	70	70	70	0	0	0	70	70	70	0	0	0
Maleic Hydrazide	90	75	70	0	0	0	9	8	7	81	68	63
Mercury	50	50	50	0	3	3	48	48	48	2	0	0
Methanol	100	95	95	1	5	5	10	10	10	90	81	81
Methoxychlor	90	90	90	54	54	54	8	8	8	28	28	28
Methyl Ethyl Ketone	95	50	30	0	3	2	10	5	3	85	43	26
Methyl Isobutyl Ketone	90	50	30	0	0	0	9	5	3	81	45	27

Methylene Chloride	95	87	85	38	52	51	13	12	12	44	23	22
N-Butyl Alcohol	95	90	90	0	0	0	10	9	9	86	81	81
N-Nitrosodimethyl Amine	90	75	70	0	0	0	9	8	7	81	68	63
Naphthalene	95	75	70	0	4	4	27	21	20	68	50	47
Nickel	35	35	35	0	0	0	35	35	35	0	0	0
Nitrobenzene	90	25	20	0	0	0	9	3	2	81	23	18
2-Nitropropane	95	95	95	86	90	90	1	1	1	9	4	4
P-Benzoquinone	95	50	40	0	0	0	8	4	3	87	46	37
Parathion	0	55	40	0	0	0	0	4	3	0	51	37
PCB	92	92	92	9	9	9	22	22	22	61	61	61
Pentachlorophenol	95	25	20	0	0	0	17	5	4	78	21	16
Phenol	95	85	80	0	0	0	14	13	12	81	72	68
Phenylene Diamine	90	75	70	0	0	0	9	8	7	81	68	63
Phosgene	100	100	100	1	5	5	10	10	10	90	85	85

Acc = Acclimated sludge with constant loading Unacc = Unacclimated sludge with transient loads

Table 5.17 (cont.)
Fate of Organic Constituents in Activated Sludge Systems

	Overall Percent Removal			Percent Volatilized to Air			Percent Partitioned to Sludge			Percent Biodegraded		
		Unacc.			Unacc.			Unacc.			Unacc.	
Pollutant	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %	Acc. %	Med. %	Low %
Phthalic Anhydride	90	90	90	0	0	0	9	9	9	81	81	81
Pyridine	15	15	10	0	1	1	2	2	1	13	13	9
Selenium	50	50	50	0	0	0	50	50	50	0	0	0
Silver	90	90	90	0	0	0	90	90	90	0	0	0
Styrene	90	90	90	23	72	72	14	14	14	54	5	5
1,1,2,2-Tetrachloroethane	90	25	20	36	15	12	4	1	1	50	9	7
Tetrachloroethylene	90	85	80	45	68	64	3	3	2	42	14	14
Thiourea	90	75	70	0	0	0	9	8	7	81	68	63
Toluene	90	90	90	23	72	72	25	18	18	52	0	0
Toleune Diamine	90	75	70	0	0	0	9	8	7	81	68	63
Toxaphene	95	90	90	57	72	72	4	4	4	34	14	14
Trans-1,2-Dichloroethylene	90	80	80	63	72	72	27	8	8	0	0	0
Tribromomethane	65	35	30	36	21	18	5	3	2	24	11	10
1,2,4-Trichlorobenzene	85	85	85	43	51	51	8	8	8	35	26	26

1,1,1-Trichloroethane	95	90	85	76	81	77	1	1	1	18	8	8
1,1,2-Trichloroethane	80	25	20	40	20	16	0	0	0	40	5	4
Trichloroethylene	95	87	85	67	70	68	6	5	5	23	12	12
2,4,6-Trichlorophenol	95	55	50	0	0	0	8	4	4	87	51	46
1,1;2-TC 1,2,2-TF Ethane	90	85	80	63	68	64	4	3	3	23	14	13
Trifluraline	90	90	90	0	0	0	33	33	33	57	57	57
Vinyl Chloride	95	95	95	86	90	90	2	2	2	8	3	3
Xylenes	95	87	85	24	70	68	14	13	13	57	4	4

Acc = Acclimated sludge with constant loading Unacc = Unacclimated sludge with transient loads

Source: US EPA 1996

Stripping is also a concern with many slurry reactor designs as most use aeration to provide all or part of the energy required for solids suspension. Where heavy PAHs or other relatively non-volatile compounds constitute most of the contaminant mass, volatilization may not be a concern. Where solvents or low molecular weight hydrocarbons make up a substantial fraction of the organic loading, system design will normally include provisions for minimizing air emissions. This could include providing a reactor cover fitted with an air capture and treatment system. At the French Limited Superfund Site in Crosby, Texas, pure oxygen was introduced into a recycled liquid stream to provide sufficient oxygen to meet biological treatment requirements, but avoid the stripping action resulting from forced air systems.

The FBR concept is different from other aerobic processes in that stripping of organics is essentially eliminated due to the method of oxygen dissolution employed. The FBR process uses a pure oxygen bubble contactor which provides complete oxygen dissolution without release of any bubbles or off-gas. As a result, stripping is minimized and occurs only at the air-liquid interface at the reactor surface through diffusion.

5.4.2.3 Sorption

Although not a primary removal mechanism for most organic compounds, sorption on biological solids does occur, can contribute to organics removal, and may also affect waste sludge characteristics. As an example, pesticides (e.g., lindane) have been shown to be non-degradable with sorption providing the primary removal mechanism in biological reactors. Heavy metals also tend to sorb onto biological solids. Thus, concentrations of such compounds can accumulate in the waste biomass and can potentially produce a waste sludge that is classified as a hazardous waste. An evaluation of the potential for the accumulation of non-degradable, toxic constituents within the waste stream should be carefully made to make sure that complications related to handling and disposal of a hazardous solid waste stream are not unanticipated.

For slurry reactors, desorption rather than sorption generally controls the applicability and success of solid-phase treatment. The rate of biodegradation in many cases is limited by bioavailability, especially for heavier, less soluble compounds, such as five- and six-ring PAHs. The longer organic contaminants have been in contact with solids, especially silts and clays with high organic carbon content, the less available the compounds are for biodegradation, and the less successful biological treatment systems will be in yielding treated solids with low residual contaminant concentrations. Some

slurry reactor designs incorporate the addition of surfactants into a slurry preparation phase to improve contaminant desorption and bioavailability.

5.4.2.4 Biodegradation

Biodegradation is the primary removal mechanism for most organic compounds found in contaminated solids and groundwaters. Most organic compounds are biodegradable, although many of the constituents typically found at contaminated sites require an acclimation period before significant biodegradation occurs. For example, acclimation periods of 4 to 6 weeks have been reported for ethylbenzene and benzedrine, respectively, before municipal activated sludge achieved maximum removal rates for these compounds. Acclimation is generally performed by gradually increasing the concentration of a constituent over time while decreasing the base food source. This procedure is necessary to prevent possible shock or toxic effects to the biomass from the full-strength waste stream before complete acclimation of the biomass to the waste stream has been accomplished.

Addition of co-substrates, such as methanol or glucose must be added to increase the biodegradation rate of some compounds, chlorinated organics in particular. Studies have shown that the addition of methane, which promotes the growth of methanotrophic organisms, can significantly improve the removal of chloroform, trichloroethene, and other chlorinated organics through the stimulation of methanemonooxygenase (MMO) by methane oxidizing organisms. MMO is an extracelluar enzyme which has non-specific activity toward chlorinated solvents, resulting in their fortuitous oxidation under specific operating conditions.

5.4.2.5 Treatability and Pilot Studies

When first evaluating the potential feasibility of using ex-situ biological treatment, it is necessary to understand the biodegradability of the contaminants present. The reported biodegradability of typical groundwater and soil contaminants is provided in Table 5.17. Site characterization data should be used to estimate the nature and projected concentrations of contaminants that will exist in the extracted groundwater and excavated contaminated soil that must be treated from a site. If the waste composition, or the application of a particular reactor configuration have not been validated based on documented field-scale studies, treatability and pilot studies may be warranted. This is particularly true for slurry-phase reactors where only limited data currently exists defining their performance in the treatment of highly contaminated, complex waste constituent soil streams.

The first step in determining if biological treatment is feasible for the specific contaminant and matrix is to perform a biotreatability evaluation using representative samples of the material. Based on the data generated during the treatability studies, a pilot-scale study may be needed to further define operating conditions and parameters to optimize the cost-effectiveness of the proposed treatment scheme. Pilot-studies can be critical to demonstrating the technical and economic feasibility of slurry reactors before field implementation.

After it is determined that the constituents, or the majority of the constituents, are biodegradable, it is necessary to identify candidate technologies for further consideration. The technologies to be selected for further evaluation will depend on the characteristics of the contaminated media, most notably, the overall organic content as measured by BOD or COD and whether the media to be treated is groundwater or soil. Generally, for groundwater treatment applications, an aerobic fixed-growth process is preferred due to the relatively low organic content of the expected wastewater stream. Suspended growth reactors are required for treatment of contaminated solids in a slurry-phase application with high organic content, up to 250,000 mg/kg concentrations.

5.4.2.6 Oxygen and Nutrient Requirements

Aerobic treatment processes use oxygen as an electron acceptor and require adequate nutrients, in the form of nitrogen and phosphorus, to promote biological growth. Oxygen can be supplied passively as in an RBC or trickling filter process or actively as in an activated sludge or FBR process. The total amount of oxygen required depends on the organic content of the waste stream being treated and the endogenous respiration requirements of the biomass as follows:

$$O_2 = a' Sr + X_d b' X_v t \qquad (5.32)$$

where:

O_2 = oxygen demand (ML^{-3});
a' = oxygen consumption for biodegradation (M) O_2/(M) COD removal;
Sr = COD removal (ML^{-3});
X_d = degradable fraction of biomass;
b' = endogenous oxygen consumption (T^{-1});
X_d = volatile suspended solids concentration (ML^{-3}); and
t = hydraulic retention time (T).

The oxygen supply requirements can be estimated using the above formula or by empirical methods during treatability studies by measuring oxygen uptake rates. In any event, sufficient oxygen must be supplied to meet the maximum oxygen demand for biodegradation and endogenous respiration.

Nutrients generally must be added to groundwater and slurry-phase reactors to meet biological growth requirements because contaminated media are generally deficient in nitrogen and phosphorus. The nutrients may be added as individual compounds using aqueous ammonia, anhydrous ammonia, or ammonium salts to supply nitrogen and phosphoric acid to supply phosphorus. The use of individual compound addition is advantageous in that a specific addition rate for each nutrient can be controlled independently, thus minimizing costs. Alternatively, diammonium phosphate can be used to supply both the nitrogen and phosphorus in one step. Nitrogen and phosphorus requirements can be estimated based on a COD:N:P ratio of 100:5:1. The actual nutrient requirements should be determined during treatability studies and during actual operation by monitoring effluent nutrient levels. Nutrient addition should be adjusted to maintain effluent residual concentrations of nitrogen and phosphorus of approximately 0.5 and 0.1 mg/L, respectively.

Oxygen is typically provided to slurry reactors using submerged or floating aerators, by compressors and spargers, or by saturation of a recycled water stream with oxygen, which is then introduced into the reactor. Oxygen transfer and fugitive emissions from gas-sparged slurry systems can significantly limiteffective aerobic slurry bioremediation. Volumetric gas flows can be reduced by using pure oxygen rather than air to reduce volatile emissions associated with gas introduction. Evaporative cooling, foam formation, and energy costs attributable to mechanical aeration can also be reduced through the use of pure oxygen. More efficient mixing technologies with higher oxygen transfer efficiencies are required to offset the increased cost of pure oxygen addition (Storms 1993).

Nutrient addition is typically required as is pH control. Surfactants, dispersants, and cometabolites are sometimes added to improve substrate availability and to improve the physical characteristics of the solids.

Because slurry reactors are typically run in a batch mode, the more readily degraded compounds are removed relatively rapidly during the initial period of treatment. The more recalcitrant compounds subsequently degrade at a slower rate. Cell growth rates behave similarly, and as early formed cells die, they lyse, releasing internal cellular material, and recycling any nutrients they contain. Because of this nutrient cycling, nutrient addition rates during the initial phase of operation are relatively large and then taper

off over time during treatment. Typical cell densities may be 10^9 cells/mL or 1 g of carbon/L. This equates to an initial nitrogen requirement of approximately 100 mg/L.

5.4.2.7 Reactor Temperature

Biological reaction rates increase with increasing temperature, following the Arrhenius relationship of an approximate doubling of rate constants for each 10°C temperature increase up to a maximum tolerable temperature of approximately 35°C. Heating full-scale reactors is particularly important during cold season operation when biological degradation rates will fall. The decrease in treatment times achieved at higher reactor temperatures has obvious benefits, but requires additional capital and operating costs to insulate reaction vessels and heat incoming waste flows. One additional drawback to reactor heating is that elevated temperatures may also increase volatile emissions, requiring additional off-gas treatment that may not be needed at lower temperatures.

Reactor heating can be advantageous, however, as indicated by Woodhull and Jerger (1994) in the slurry reactor treatment of soils containing approximately 10,000 mg/kg of PAHs. Nine days were required to reach clean-up levels at 25 to 27°C versus only 6 days at 35 to 37°C. Overall treatment costs were 10% less at the elevated temperatures, despite increased operating costs for reactor heating because of the increase in reaction rate and decrease in treatment time.

5.4.3 Process-Flow Diagrams

Suspended growth processes that are applicable for treatment of contaminated groundwaters include the activated sludge process and several of its variations. Activated sludge consists of an aeration tank, clarifier, and return sludge pumps. The process can operate in a plug flow or complete mix configuration. A typical plug flow activated sludge system is shown in Figure 5.4.2. Biomass grows in the aeration basin where it contacts the substrate and removes organic constituents. Oxygen is supplied to the biomass in the aeration basin by diffused or surface mechanical aeration. The biomass is separated from the treated substrate in a clarifier by gravity sedimentation. Excess sludge is removed from the process to maintain the desired ratio of biomass to substrate. The majority of the biomass separated in the clarifier is returned to the aeration basin for reuse.

Fixed-film processes that are applicable to groundwater treatment include fluidized-bed reactors, biological activated carbon, rotating biological

contactors, and submerged biological filters. Trickling filters and biotowers have generally not been employed for groundwater treatment due to the potential for significant stripping of organics and associated air emissions concerns. In fixed-film processes, the biomass is attached to a media of some type. Media can be plastic in the case of submerged biofilter, plastic discs in the case of RBCs, GAC in the case of BAC, and sand or GAC in the case of an FBR process. The medium allows the biomass to be retained in the treatment process without relying on solids separation processes (e.g., sedimentation) as does a suspended growth process. The attached growth concept allows the system to operate effectively even at low organic concentrations where insufficient new biomass is produced to provide for flocculant settling conditions which are necessary for effective operation of suspended growth systems. Figure 5.21 shows a schematic of the FBR process, while Figure 5.22 shows a schematic of a suspended growth system containing fixed-film media in the form of powdered activated carbon, the (PACT®) process.

A process schematic of a commercial slurry-phase treatment system is shown in Figure 5.23. As indicated in this figure, the slurry-phase treatment process is similar in configuration and reactor layout to the PACT® process, but differs from it significantly in that in the slurry reactor the media in suspension is the contaminated soil to be treated, while in the PACT® process it is the treatment media itself.

5.4.4 Process Modifications

5.4.4.1 Suspended Growth Processes

Suspended growth processes applicable for treatment of contaminated groundwaters consist of the activated sludge process and several of its variations. Suspended growth processes, such as aerated or facultative lagoons are generally not applied due to concerns regarding air emissions, costs for lined lagoon construction, and the inability to develop and sustain an acclimated biomass on a one-pass system where the sludge is not retained and recycled in the process.

Conventional Activated Sludge. The standard activated sludge process may be applicable for treatment of comparatively high-strength organic concentrations, e.g., >500 mg/L as BOD, where air emissions are not of concern and the contaminants are readily biodegradable. Due to the aeration process, stripping may be a significant removal mechanism for many organics using this technology. In addition, BOD concentrations less than 100 mg/L are difficult to treat effectively in conventional activated sludge systems due to difficulties with solids-liquid separation that occur at the low aeration basin

Figure 5.21
Fluidized-Bed Reactor Process Schematic

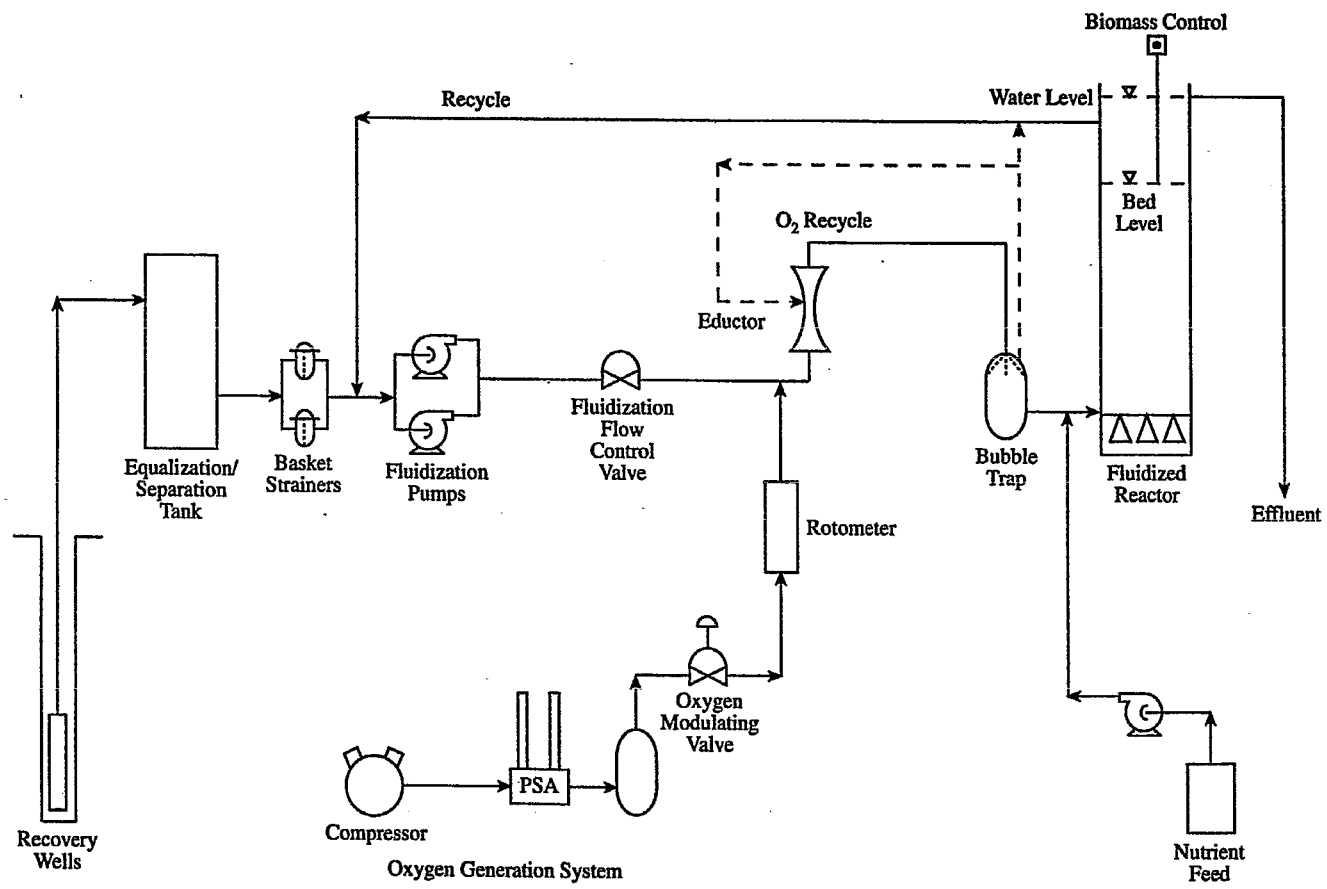


Figure 5.22
PACT® Flow Diagram

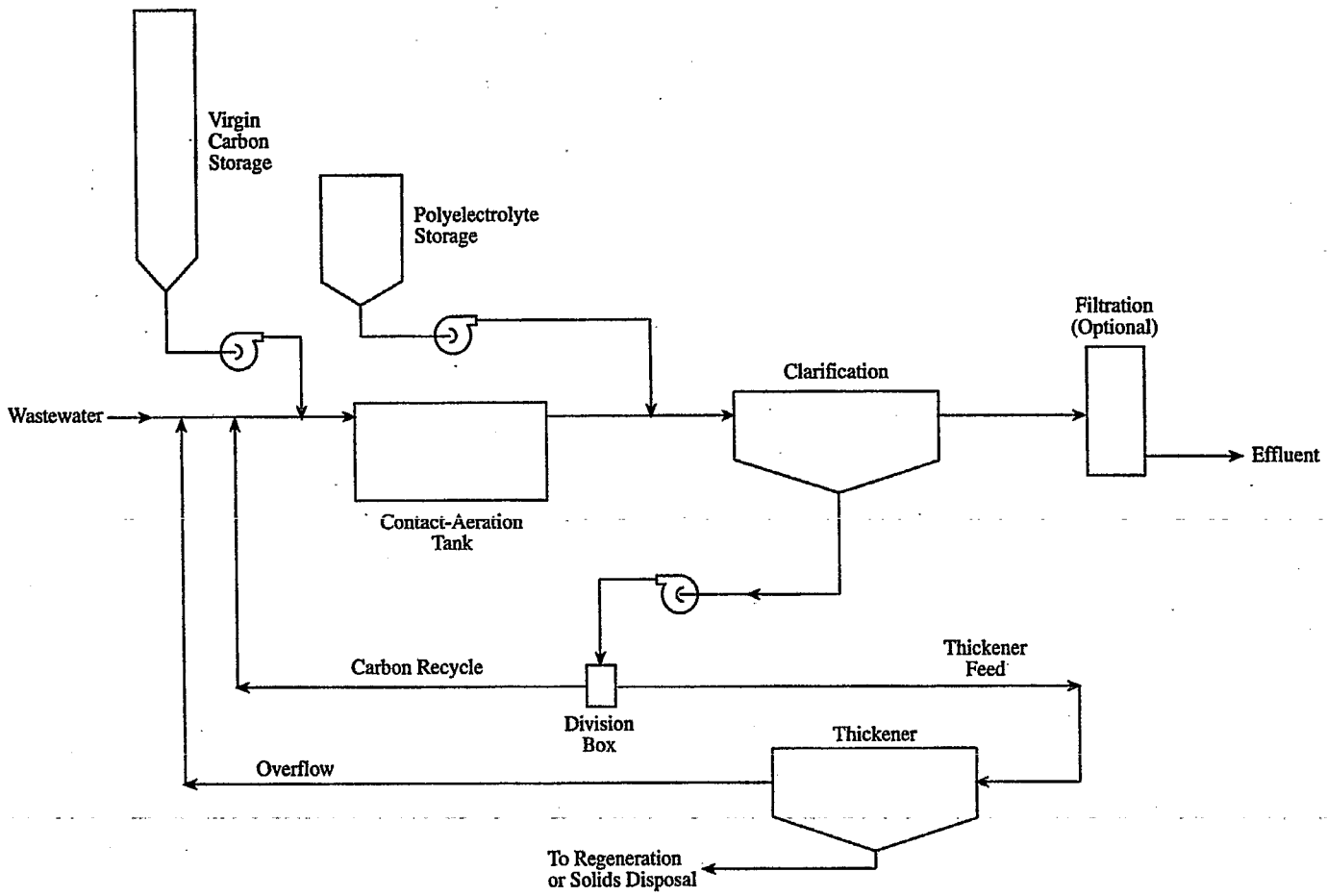
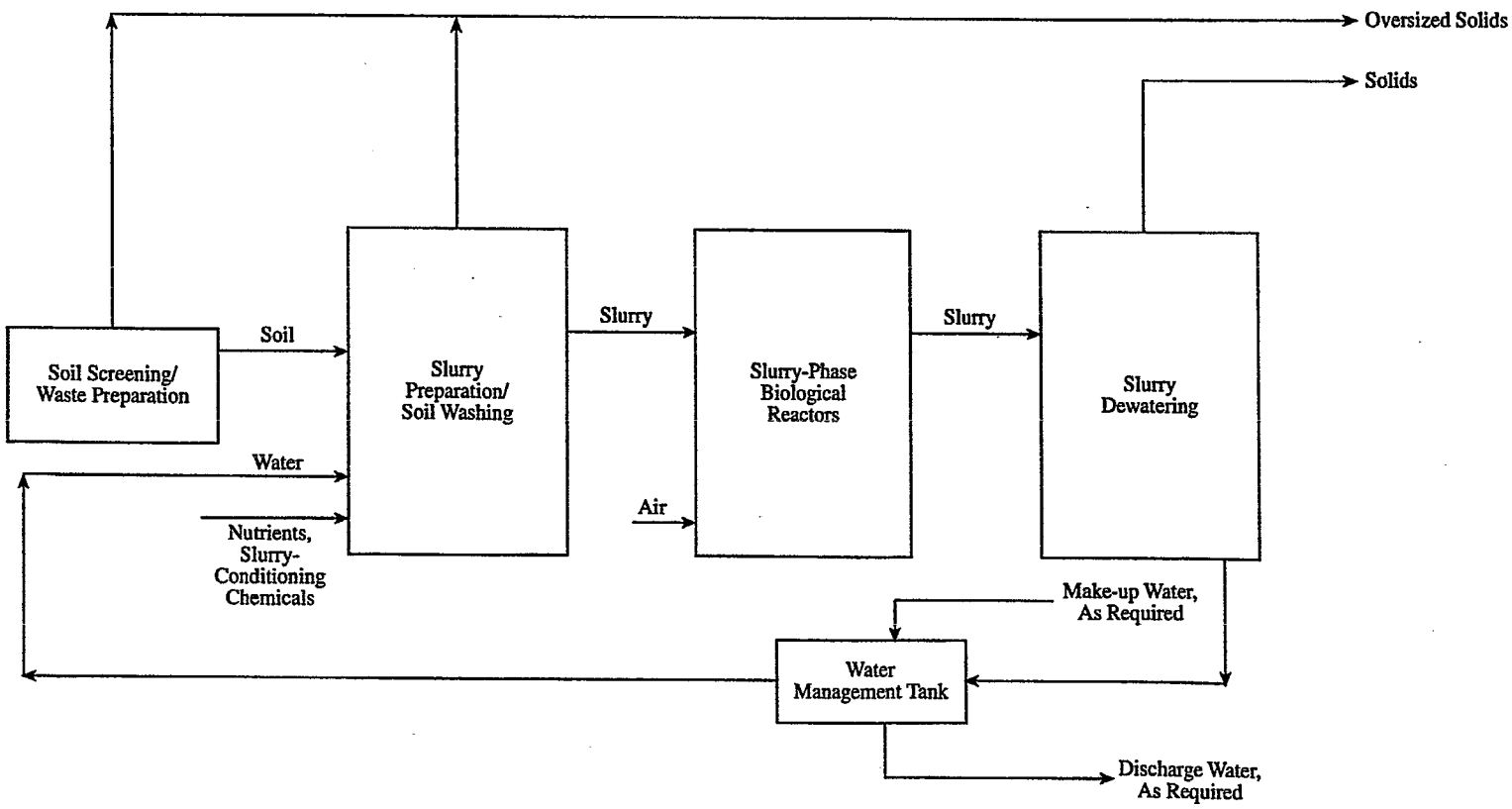


Figure 5.23
Full-Scale Slurry-Phase Biological Remediation Process



biomass concentrations that are generated from low strength waste. At low BOD concentrations, the biomass growth rate is low and only a dilute biomass concentration can be maintained in the aeration basin. At low biomass concentrations, flocculant settling does not occur and poor solids separation results in biomass carryover in the secondary clarifier, resulting in an ineffective treatment system.

The conventional activated sludge process can be configured to minimize air emissions by including an off-gas recycle system. The aeration basin is covered and the off-gas is collected, is recycled through the aeration blowers, and diffuses into the aeration basin. A small percentage, typically 10 to 15 percent by volume, of make-up air is added to provide adequate oxygen and to purge carbon dioxide. This approach effectively reduces off-gas emissions by increasing the contact of the stripped organic constituents with the liquid and biomass in the aeration tank where they can be biodegraded. Table 5.18 summarizes results of off-gas analyses from an activated sludge system equipped with off-gas recycle treating a contaminated groundwater consisting of Site A influent from Table 5.16. Performance data for this system is provided in Tables 5.19 and 5.20.

Powdered Activated Carbon Treatment. A variation of the activated sludge process is the powdered activated carbon treatment (PACT®) process (Figure 5.22) in which powdered activated carbon (PAC) is added to the aeration basin. This technology has been successfully applied to high strength and complex wastewaters, such as landfill leachate.

PACT® is a proprietary process offered by Zimpro that involves the addition of PAC to an activated sludge system. The PAC provides a medium for the biomass to attach to while also adsorbing refractory or toxic constituents. As a result, a higher level of effluent quality may be achieved in instances where there are refractory organics. Other benefits include improved sludge settleability, greater resistance to shock loads and potential for reduced effluent aquatic toxicity due to removal of refractory organics, and to some extent heavy metals. In cases where nitrification may be required, e.g., with a landfill leachate, the PACT® process can provide conditions suitable for sustaining nitrification where this would not be possible in a conventional activated sludge system due to inhibitory or toxic compounds.

PACT® can also reduce off-gas emissions by adsorbing volatile compounds. Table 5.21 presents off-gas emissions data from a PACT® system treating the same groundwater as described in 5.19. A comparison of the data indicates the PACT® process, with off-gas recycle, achieved comparable air emissions control. Effluent data and operational data for this PACT® system are provided in Tables 5.22 and 5.23, respectively.

Table 5.18
Mass Balance for VOCs in Activated Sludge Process With Off-Gas Recycle

Volatile Organic	Hc (µg/L)(µg/L)	Mean Concentration: Influent (µg/L)	Mean Concentration: Bio Effluent Liquid (µg/L)	Mean Concentration: Bio Effluent Off-Gas (µg/L)	Mean Mass Rate: Influent (µg/day)	Mean Mass Rate: Effluent (µg/day)	Mean Mass Rate: Stripped (µg/day)	Mean Mass Rate: Biodeg. (µg/day)	Mean Fraction of Influent Mass: Effluent	Mean Fraction of Influent Mass: Stripped	Mean Fraction of Influent Mass: Biodeg.
Methyl methacrylate	0.0102	1,010,000	0.3	0.0	12,120,000	3.6	1	12,119,996	0.000	0.000	1.000
Benzene	0.1456	18	0.0	0.0	216	0	0	216	0.000	0.000	1.000
1,4-Dichlorobenzene	0.1080	18	0.0	0.0	216	0	0	216	0.000	0.000	1.000
Cis-1,2-Dichloroethene	0.1096	15	10.5	1.15	180	126	249	-195	0.400	1.381	-1.08
Trans-1,2-Dichloroethene	0.3328	23	0.0	0.0	276	0	0	276	0.000	0.000	1.000
Ethylbenzene	0.1341	129	0.2	0.03	1,548	2.4	6	1,540	0.002	0.004	0.995
Styrene	0.0500	38	0.1	0.01	456	1.2	1	454	0.003	0.002	0.995
Trichloroethene	0.2463	28	1.9	0.47	336	22.8	101	212	0.065	0.301	0.631
Toluene	0.1364	35	0.1	0.01	420	1.2	3	416	0.003	0.007	0.990
Vinyl chloride	0.9040	2	0.1	0.09	24	1.2	20	3	0.050	0.814	0.136

Source: US EPA 1996c

Table 5.19
Example Activated Sludge with Off-Gas Recycle Performance Data

Parameter	Influent (µg/L)	Effluent (µg/L)
VOLATILE ORGANICS		
Methyl methacrylate	1,010,000	0.3
Acetone	1,000	8.0
Benzene	18	ND
Carbon disulfide	125	0.3
1,4-Dichlorobenzene	18	ND
Cis-1,2-Dichloroethene	15	10.5
Trans-1,2-Dichloroethene	23	ND
Ethylbenzene	129	0.2
Styrene	38	0.1
Trichloroethene	28	1.9
Toluene	35	0.1
Vinyl chloride	1.5	0.1
Methylene chloride	2,500	5.4
1,1-Dichloroethane	2,500	5.0
1,2-Dichloroethane	2,500	5.0
SEMI-VOLATILE ORGANICS		
Dimethyl phthalate	36	0.5
Diethyl phthalate	48	0.5
Di-n-butyl phthalate	11	0.7
Phenol	160	0.5
2-Methylphenol	47	1.0
Naphthalene	126	1.0
Benzyl alcohol	135	1.0
2-Methylnaphthalene	251	1.0
Bis (2-ethylhexyl) phthalate	6.4	3.3
4-Methylphenol	82	0.5
2,4-Dimethylphenol	102	1.0

ND = Not detected

Source: US EPA 1996c

Table 5.20
Summary of Operational and Performance Data for Conventional Parameters

Parameter	Operating Data
Process Parameters	
HRT (days)	1.6
SRT (days)	12
Temp (°C)	23
F/M (day $^{-1}$)	0.24
Aeration Basin Parameters	
MLSS (mg/L)	6,300
MLVSS (mg/L)	5,000
DO (mg/L)	5.3
pH (s.u.)	7.0-8.1
OUR [mg/(L-hr)]	24.3
SOUR [mg/(gVSS•hr)]	4.8
Air Recycle Ratio[a]	0.87
Influent	
Flow (mL/min)	7.6
TBOD (mg/L)	1,460
TCOD (mg/L)	3,320
SCOD (mg/L)	2,920
TSS (mg/L)	46
VSS (mg/L)	9
TDS (mg/L)	2,245
pH (s.u.)	6.3-7.2
NH_4-N (mg/L)	42
PO_4-P (mg/L)	21
Effluent	
TBOD (mg/L)	28
SBOD (mg/L)	15
TCOD (mg/L)	432
SCOD (mg/L)	288
TSS (mg/L)	85
VSS (mg/L)	80
TDS (mg/L)	1,660
NH_4-N (mg/L)	10
PO_4-P (mg/L)	3.4

[a] Recycle air flow/total air flow.

Source: US EPA 1996c

Table 5.21
Mass Balance for VOCs in a PACT® System without Off-Gas Recycle

Volatile Organic	Hc (µg/L)(µg/L)	Mean Concentration: Influent (µg/L)	Mean Concentration: Bio Effluent Liquid (µg/L)	Mean Concentration: Bio Effluent Off-Gas (µg/L)	Mean Mass Rate: Influent (µg/day)	Mean Mass Rate: Effluent (µg/day)	Mean Mass Rate: Stripped (µg/day)	Mean Mass Rate: Biodeg. (µg/day)	Mean Fraction of Influent Mass: Effluent	Mean Fraction of Influent Mass: Stripped	Mean Fraction of Influent Mass: Biodeg.
Methyl methacrylate	0.0102	1.010,000	12.2	0.12	6.060,000	73.2	27	6,059,900	0.000	0.000	1.000
Benzene	0.1456	18	0.3	0.01	108	1.8	9	97	0.017	0.087	0.898
1,4-Dichlorobenzene	0.1080	18	0.0	0.00	108	0	0	108	0.000	0.000	1.000
Cis-1,2-Dichloroethene	0.1096	15	6.7	0.43	90	40.2	159	-109	0.447	7.762	-1.211
Trans-1,2-Dichloroethene	0.3328	23	0.0	0.00	138	0	0	138	0.000	0.000	1.000
Ethylbenzene	0.1341	129	0.2	0.03	774	1.2	6	767	0.002	0.007	0.991
Styrene	0.0500	38	0.1	0.02	228	2.4	4	221	0.011	0.019	0.969
Trichloroethene	0.2463	28	108	0.44	168	10.8	96	61	0.064	0.570	0.363
Toluene	0.1364	35	0.2	0.03	210	1.2	6	203	0.006	0.028	0.967
Vinyl chloride	0.9040	2	0.1	0.09	12	0.6	20	-8	0.050	1.627	-0.667

Source: US EPA 1996c

Table 5.22
Example of PACT® Performance Data

Parameter	Influent (µg/L)	Effluent (µg/L)
VOLATILE ORGANICS		
Methyl methacrylate	1,010,000	12
Acetone	1,000	2.8
Benzene	18	0.3
Carbon disulfide	125	0.3
1,4-Dichlorobenzene	18	ND
Cis-1,2-Dichloroethene	15	6.7
Trans-1,2-Dichloroethene	23	ND
Ethylbenzene	129	0.2
Styrene	38	0.4
Trichloroethene	28	1.8
Toluene	35	0.2
Vinyl chloride	1.5	0.1
Methylene chloride	2,500	7.0
1,1-Dichloroethane	2,500	5.0
1,2-Dichloroethane	2,500	5.0
SEMI-VOLATILE ORGANICS		
Dimethyl phthalate	36	0.5
Diethyl phthalate	48	0.4
Di-n-butyl phthalate	11	0.6
Phenol	160	0.5
2-Methylphenol	47	1.0
Naphthalene	126	1.0
Benzyl alcohol	135	1.0
2-Methylnaphthalene	251	1.0
Bis (2-ethylhexyl) phthalate	6.4	20
4-Methylphenol	82	0.5
2,4-Dimethylphenol	102	1.0

ND = Not detected

Source: US EPA 1996c

Table 5.23
Summary of Operational and Performance Data for Conventional Parameters

Parameter	Operating Data
Process Parameters	
HRT (days)	1.6
SRT (days)	12
Temp (°C)	23
F/M (day $^{-1}$)	0.5
Aeration Basin Parameters	
MLSS (mg/L)	6,580
BIOMLVSS (mg/L)	4,300
Carbon TSS (mg/L)	1,558
DO (mg/L)	4.8
pH (s.u.)	7.2-8.1
OUR [mg/(L-hr)]	23.4
SOUR [mg/(gVSS•hr)]	5.3
Air Recycle Ratio[a]	0.87
Influent	
Flow (mL/min)	3.8
TBOD (mg/L)	1,460
TCOD (mg/L)	3,320
SCOD (mg/L)	2,920
TSS (mg/L)	46
VSS (mg/L)	9
TDS (mg/L)	2,245
pH (s.u.)	6.3-7.2
NH_4-N (mg/L)	42
PO_4-P (mg/L)	21
Effluent	
TBOD (mg/L)	43
SBOD (mg/L)	28
TCOD (mg/L)	682
SCOD (mg/L)	305
TSS (mg/L)	215
VSS (mg/L)	196
TDS (mg/L)	1,797
NH_4-N (mg/L)	6.0
PO_4-P (mg/L)	0.8

[a] Recycle air flow/total air flow.

Source: US EPA 1996c

5.4.4.2 Fixed-Film Systems

Media for biomass attachment includes random or structured plastic media, granular activated carbon, sand, wood, or rock, depending on the type of process and application. As the liquid flows across the substrate with the attached biomass, organics, nutrients, and oxygen diffuse from the liquid to the biomass. As metabolism of the organics occurs, byproducts and carbon dioxide diffuse out of the biomass into the liquid phase. As oxygen flows into the biological film, it is consumed through biological respiration. The zone in which oxygen is present is aerobic while deeper into the biofilm layer where oxygen does not penetrate, the metabolism becomes anaerobic.

Fluidized-Bed Reactor. The fluidized-bed reactor process is a highly robust treatment technology that is particularly applicable to groundwater treatment due to its broad operating range. The FBR process consists of a fluidized bed containing granular activated carbon or sand as the biomass support. The medium is fluidized using influent groundwater and, in cases of high organic concentrations, a recycle stream of treated effluent. A portion of the fluidization flow is passed through a bubble contact unit where pure oxygen is added under pressure causing complete dissolution of the oxygen. The oxygenated influent passes through the FBR where contaminants are removed by biodegradation and sorption. Stripping does not occur as the oxygen addition process eliminates the release of bubbles that could cause stripping. If GAC is used as the support mechanism, adsorption of recalcitrant organics will also occur. The recalcitrant organics are then biodegraded over time due to their increased contact time with the biomass attached to the media. Thus, the GAC is auto-regenerated and generally does not require replacement, except as makeup for attrition. Table 5.24 shows performance data for treatment of a contaminated groundwater. Typical design criteria are shown in Table 5.25.

Biological Activated Carbon. Biological activated carbon (BAC) is similar in concept to the FBR process except that the BAC process operates in a downflow mode. Biomass grows on the granular activated carbon and simultaneously biodegrades organics from the liquid phase and those that adsorb onto the carbon. Due to the potential for plugging of the GAC bed, this process is only applicable where the influent BOD concentration is less than approximately 10 mg/L and individual toxic organic concentrations are less than approximately 200 mg/L. Additionally, provisions for periodically backwashing the BAC column must be made to prevent complete plugging of the bed due to biological growth. Performance data are shown in Table 5.26. Design criteria are generally the same as for a GAC unit. The design

should provide for backwashing, for aerating the influent prior to the BAC unit, and for nutrient addition.

Table 5.24
Example Fluidized-Bed Reactor Performance Data

Parameter	Influent (µg/L)	Effluent (µg/L)
VOLATILE ORGANICS		
Methyl methacrylate	3,240	0.4
Acetone	80	34
Benzene	252	1.5
Carbon disulfide	17	0.5
1,4-Dichlorobenzene	0.9	0.0
Cis-1,2-Dichloroethene	61	3.4
Trans-1,2-Dichloroethene	1.2	0.0
Ethylbenzene	42	0.1
Styrene	2.0	0.1
Trichloroethene	23	0.2
Toluene	69	0.0
Vinyl chloride	94	27.0
Methylene chloride	131	4.0
1,1-Dichloroethane	131	4.2
1,2-Dichloroethane	131	4.4
SEMI-VOLATILE ORGANICS		
Dimethyl phthalate	2.3	0.5
Diethyl phthalate	1.3	0.4
Di-n-butyl phthalate	1.1	1.6
Phenol	0.5	0.5
2-Methylphenol	5.0	1.0
Naphthalene	4.4	1.0
Benzyl alcohol	1.0	0.8
2-Methylnaphthalene	0.8	1.0
Bis (2-ethylhexyl) phthalate	1.4	9.5
4-Methylphenol	0.5	0.5
2,4-Dimethylphenol	34	1.0

Source: US EPA 1996c

Table 5.25
Example Fluidized-Bed Reactor Operational and Performance Data

Parameter	Operating Data
Process Parameters	
HRT (hr)	2.1
DO (mg/L)	2.2
pH (s.u.)	6.6 to 7.3
Temperature (°C)	22
COD Loading (lb/1,000 ft^3)	160
Influent	
Influent Flow (mL/min)	16
TBOD (mg/L)	88
TCOD (mg/L)	223
SCOD (mg/L)	193
TSS (mg/L)	8
VSS (mg/L)	5
TDS (mg/L)	363
pH (s.u.)	6.4 to 7.2
NH_4-N (mg/L)	8.5
PO_4-P (mg/L)	6.8
Effluent	
TBOD (mg/L)	12
SBOD (mg/L)	9
TCOD (mg/L)	95
SCOD (mg/L)	52
TSS (mg/L)	36
VSS (mg/L)	24
TDS (mg/L)	295
NH_4-N (mg/L)	3
PO_4-P (mg/L)	1

Source: US EPA 1996c

Table 5.26
Example BAC Process Performance Data

Parameter	Influent (µg/L)	Effluent (µg/L)
VOLATILE ORGANICS		
Methyl methacrylate	2,660	0.6
Acetone	23	3.6
Benzene	35	ND
Carbon disulfide	1.4	0.9
1,4-Dichlorobenzene	0.2	ND
Cis-1,2-Dichloroethene	2.6	0.3
Trans-1,2-Dichloroethene	0.2	ND
Ethylbenzene	2.4	0.1
Styrene	0.8	ND
Trichloroethene	2.6	0.1
Toluene	6.2	0.1
Vinyl chloride	34	17
Methylene chloride	24	5.0
1,1-Dichloroethane	24	4.9
1,2-Dichloroethane	24	4.7
SEMI-VOLATILE ORGANICS		
Dimethyl phthalate	0.5	0.5
Diethyl phthalate	1.0	0.4
Di-n-butyl phthalate	1.5	1.2
Phenol	5.7	2.8
2-Methylphenol	1.4	1.0
Naphthalene	0.8	1.0
Benzyl alcohol	0.9	1.0
2-Methylnaphthalene	1.0	1.0
Bis (2-ethylhexyl) phthalate	4.0	3.3
4-Methylphenol	0.5	0.5
2,4-Dimethylphenol	26	1.0

ND = Not detected

Source: US EPA 1996c

Submerged Aerobic Filters. Submerged aerobic filters consist of a vessel with a random or structured plastic packing. Liquid flows through the vessel while oxygen is provided through diffused aeration. Biomass attaches to the media which is submerged in the vessel. This process can operate over a relatively broad range of influent concentrations and offers flexibility due to the attached growth concept. Excess biomass periodically sloughs from the media and must be removed by sedimentation, flotation, or filtration processes.

Rotating Biological Contactors. RBCs consist of a series of plastic wheels (drums) attached in parallel. The drums rotate slowly with typically 25 to 50 percent of the drum submerged at any one time in the influent being treated. Biomass attaches to the plastic drums and sorbs contaminants and nutrients from the influent while submerged. When not submerged, oxygen diffuses from the atmosphere into the biomass. Excess biomass is sheared from the media and is removed in a clarifier or filter. RBCs can treat groundwater over a broad range of concentrations by using a recycle stream to dilute high influent concentrations and by using multiple pass systems. However, due to mechanical problems with the shafts encountered in the past, this process has not been used significantly in groundwater treatment applications. An advantage of this process, however, is that volatilization of organics is minimized due to its passive mode of aeration.

5.4.4.3 Slurry Reactor Systems

In slurry reactors, soils or sediments are mixed with water to form as high a solid content as can be managed, up to 35% to 40% solids. The limiting factor is usually the density of the solids and the ability of the mixing equipment to maintain a well-mixed system. Sediments are generally less dense than soils and can be maintained in suspension more easily and at a lower energy requirement, ranging from 0.1 to 1 horsepower per 1,000 gallons. Mixing is provided by mechanical means, by aeration, or a combination of mechanical means and aeration. Although mixing is generally considered necessary, Remediation Technologies Inc. (RETEC)(US EPA 1990c) has reported a case where degradation rates were actually faster in an unmixed system than in a mixed system.

Oxygen can be provided through aeration below the surface which enhances mixing. However, this also increases emissions of volatiles which may require capture and treatment. Use of oxygen instead of air reduces the volatile emissions but also minimizes contributions towards suspension of solids, requiring more substantial mechanical mixing. Recovery of an aqueous stream, with subsequent saturation with oxygen prior to recycling of the

aqueous stream to the reactor, as was the case at the French Limited Superfund Site, nearly eliminates emissions.

Nutrients are added and chemicals are added for pH adjustment to the initial slurry reactor feed. During treatment, further nutrient addition and pH adjustment are typically added automatically as needed.

Slurry reactors are operated in one of two processing modes: batch or continuous/semi-continuous. Slurry reactors are operated in the batch mode by filling the reactor, treating for a fixed length of time, and discharging the slurry at the completion of treatment. Continuous/semi-continuous mode reactors have a constant influent and effluent stream with the slurry remaining within the reactor based on the design hydraulic residence time.

Batch operation is the most common configuration for slurry reactor operation and offers several advantages. Batch operation generally requires less sophisticated equipment, instrumentation, and control than a continuously-operated reactor, and is flexible in terms of solids processing rates it can achieve. The process can be sampled and monitored with relative ease and material can be held in the reactor until analytical results for treatment criteria are complete and desirable treatment endpoints are reached. Batch reactors also yield the highest conversion for a given reactor volume. The main disadvantages of batch reactors are the "down-time" to drain the reactor and refill it with slurry, and the fact that it does not operate under pseudo-steady-state conditions as does a continuous feed reactor that has stablized.

Continuous flow reactors require a greater degree of operational and monitoring sophistication. Both upstream and downstream process operations must be matched with the processing rate of the reactor. Depending on regulatory requirements for demonstration of treatment, the treated slurry may require out-of-reactor storage until laboratory data confirm treatment requirements have been met.

5.4.5 Pretreatment Process

5.4.5.1 Groundwater Treatment Systems

Pretreatment may be necessary prior to treatment in aboveground reactors to prevent toxicity to the biomass or accumulation of inert materials in the biomass that is generated during treatment. Typical pretreatment processes for groundwater include oil/water separation where free product may be encountered and chemical coagulation/flocculation/sedimentation for precipitation of toxic levels of heavy metals.

Oil/water separation typically consists of a corrugated plate or coalescing oil/water separator between the extraction well(s) and the treatment system. Product, either LNAPL or DNAPL, is separated based on differences in specific gravity between it and the groundwater to be biologically treated. Free product is removed either as a supernatant (LNAPL) or subnatant (DNAPL) and collected for off-site disposal. The aqueous phase is then pumped into the bioreactor for removal of dissolved phase organics.

Groundwater containing elevated concentrations of heavy metals generally must be treated either to meet final surface water discharge or groundwater reinjection requirements or to prevent biomass toxicity and accumulation in the biological sludge which would affect treatment plant operation, performance, and sludge handling and disposal (Table 5.27). In addition, elevated iron groundwater concentration (e.g., >1 mg/L) can cause fouling of aeration equipment and other downstream processes. Common technologies for metals removal include:

- hydroxide precipitation using lime or caustic soda,
- iron co-precipitation using naturally occurring iron or ferrous sulfate,
- sulfide precipitation,
- electrochemical precipitation, and
- ion exchange.

Achievable effluent concentrations for various metals using applicable technologies are summarized in Table 5.28.

5.4.5.2 Soil Treatment Systems

Like many solids treatment processes, the first step in the application of a slurry reactor is screening of the contaminated soil to remove material greater than a specific size, in general about 5 cm (2 in.), that is not effectively treated in the reactor. This soil screening equipment can also reduce the size of large soil clumps. The removal of large objects and the reduction in size of others enhances soil and sediment mixing and enables the contaminated material to be suspended and efficiently mixed within the slurry reactor. Further size reduction will occur by mixing to expose more soil/sediment surface to the aqueous phase.

Soil screening equipment is typically capable of processing 80 to 100 tons of excavated material per hour. The equipment is designed to reduce soil "clumps" prior to screening, remove material larger than 5 cm (2 in.) (e.g., concrete, rubble, timbers, etc.), and convey it into a debris stockpile. The

material less than 5 cm (2 in.) is conveyed into a separate stockpile. The soil screening equipment typically screens all of the soil independent of the downstream processing schedule.

Table 5.27
Threshold Inhibition Concentrations to Activated Sludge Processes

Constituent	Threshold Inhbition Concentration (mg/L)
Arsenic	0.1
Cadmium	1-10
Chromium (+6)	1-10
Chromium (+3)	15-50
Copper	1.0
Cyanide	0.1-5
Lead	1.0-5
Mercury	0.1-1
Nickel	1-2.5
Silver	0.25-5
Zinc	0.3-5

Source: US EPA 1996c

In soils which contain a range of particle sizes (e.g., sand through clay), a soil washing system should be considered because organic contaminants tend to concentrate in the humic and fine size fractions of the soil (i.e., organic matter, silt, and clay), while the contaminants associated with the coarse size fraction (i.e., sand and gravel) are primarily surficial. Soil washing, which separates soils by particle size, can separate the soils into several size fractions. The objective of soil washing then is to reduce the volume of soil requiring further treatment by concentrating the waste stream into a smaller volume of fine-grained material that can be effectively treated in the slurry-phase bioreactor while producing a washed, large particle size soil fraction which meets the site treatment criteria. In some instances, the sand fraction may represent 80 to 90% of the total contaminated soil mass, and can be treated to clean-up requirements by soil washing alone. This greatly

Table 5.28
Achievable Heavy Metals Removal Concentrations

Metal	Achievable Concentration (mg/L)	Technology
Arsenic (As)	0.05	Sulfide precipitation (pH 6-7)
	0.06	Carbon adsorption
	0.005	Co-precipitation (ferric hydroxide)
Barium (Ba)	0.5	Sulfate precipitation
Cadmium (Cd)	0.05	Hydroxide precipitation (pH 10-11)
	0.05	Co-precipitation (ferric hydroxide)
	0.008	Sulfide precipitation (pH 6-7)
Copper (Cu)	0.02	Hydroxide precipitation
	0.01	Sulfide precipitation (pH 8.5)
Lead (Pb)	0.01	Carbonate precipitation (pH 9-9.5)
	0.02	Hydroxide precipitation (pH 11.5)
Mercury (Hg)	0.01	Sulfide precipitation
	0.001	Co-precipitation (alum)
	0.005	Co-precipitation (ferric hydroxide)
Nickel (Ni)	0.12	Hydroxide precipitation (pH 10-11)
Zinc (ZN)	0.1	Hydroxide precipitation (pH 10)

Source: US EPA 1996c

reduces the volume of solids to be treated in the slurry reactor, and thus the size of the reactor required or the number of batches required for complete site treatment.

A slurry preparation/soil washing system processes the screened material at an average rate of 8 to 12 tons per hour. The process separates the stockpiled material into several size fractions utilizing several separation techniques. The unit operations include wet- and dry-screening, hydrocyclones, sand screws, and hydro classifiers. The slurry is treated with conditioning chemicals and the larger size fractions washed and separated from the slurry. The remaining slurry is generally amended with nutrients and pH adjusted prior to transfer to the bioreactors. (Refer to *Liquid Extraction Technologies: Soil Washing, Soil Flushing, Solvent/Chemical*, Mann et al. 1998 for details).

In some cases, chemical pretreatment has been used on contaminated soils prior to slurry reactor treatment to partially degrade relatively recalcitrant chemicals. Hydrogen peroxide has been used in conjunction with slurry treatment to pre-oxidize biologically recalcitrant targeted contaminants, forming oxidized intermediate compounds that are more susceptible to biological treatment than the parent compounds. Applications of this strategy have been predominantly targeted at polynuclear aromatic hydrocarbon contaminants found in gas station site pollution. There are some concerns with the use of hydrogen peroxide. High concentration can effectively disinfect the contaminated solids, likely requiring culture addition following pretreatment. Iron in the soil also limits the effectiveness of this pretreatment process because trace amounts of iron can autocatalytically decompose hydrogen peroxide. The oxygen formed by decomposition will be lost from the liquid phase and will have little effect on the treatment. Peroxide mixtures are available to avoid rapid decomposition, but notably these mixtures are less reactive than the pure hydrogen peroxide.

An integrated chemical/biological treatment process (MGP-REM) has been applied to manufactured gas plant (MGP) contaminated soil in New Jersey (Liu et al. 1994). The MGP-REM process combines chemical oxidation as a pretreatment for the difficult-to-degrade organics followed by aerobic slurry processing. Mild chemical oxidation with Fenton's reagent (hydrogen peroxide and ferrous ion) produces hydroxyl radicals which are expected to propagate a chain reaction of oxidation which leads to structural modification of the targeted organics. Bench-scale studies have shown that application of the MGP-REM process can enhance the rate and extent of treatment for the PAHs found in contaminated MGP soil. Field-scale implementation of this technology uses excavated soil which has been screened in two stages to the minus 20 mesh fraction. Conditions for the pilot treatment study are presented in Table 5.29, along with results of the study showing significant removals of 2- through 6-ring PAH constituents during treatment.

5.4.5 Posttreatment Process

5.4.5.1 Groundwater Treatment Systems

Effluent polishing from aboveground reactors treating contaminated groundwater may be required to comply with final discharge limits. Typical posttreatment processes include air stripping for removal of residual volatile organics, and granular activated carbon (GAC) for removal of volatile and semi-volatile organics, pesticides and herbicides, as well as biological process degradation products. Filtration is typically required prior to any

posttreatment process to prevent fouling of the treatment equipment or to prevent clogging of reinjection wells (if employed). Filtration may consist of sand filters or multi-media (e.g., anthracite and garnet) filters to reduce effluent total suspended solids concentrations below 1 to 5 mg/L. If greater filtration efficiency is required (e.g., for groundwater reinjection), bag filters, cartridge filters, or membrane filters can be used to provide essentially complete solids removal for solids with diameters as low as 1 µm. Chemical oxidation (e.g., UV/peroxide or UV/ozone) can be used as an effluent polishing step to remove recalcitrant organics in treated groundwater via chemical oxidation.

Table 5.29
MGP-REM Treatment Conditions and Performance

Factor	Operational Range
% Solids in Reactor	10 to 35
Slurry Residence Time (days)	8 to 20
% Hydrogen Peroxide Concentation (vol/vol)	0.5 to 2.0
Initial Soil PAH Concentrations (mg/kg)	100 to 2,000
Unit ProcessScheme	4 Stage Biological/Chemical

Pollutant Category	% Removal
Total	95
2 and 3-Ring PAHs	97
4, 5, and 6-Ring PAHs	93

Source: Liu et al. 1994

Final pH adjustment and removal of residual dissolved oxygen should be strongly considered for applications that use groundwater reinjection to prevent chemical incompatibility or induced biological growth in the aquifer which can lead to premature fouling and plugging of injection wells. Dissolved oxygen can be removed through chemical means (e.g., sodium sulfite) or by sparging nitrogen or carbon dioxide. Adjustment of pH can be accomplished with carbon dioxide or hydrochloric acid addition.

5.4.5.2 Soil Treatment Systems

At the completion of treatment in a slurry bioreactor, the soil and water making up the slurry must be separated for further handling. A number of options exist for liquid-solid separation including drying beds, gravity filtration, filter presses, centrifuges, and thermal dryers. Depending on project requirements, the aqueous or solid fractions may require further treatment, i.e., stabilization of metals in the solids, prior to discharge or disposal. Polishing processes for the aqueous effluent are the same as for groundwater treatment systems discussed above. The treated aqueous phase is typically transferred to a storage tank for re-use in the slurry preparation process, or can be discharged provided it meets permit limits for release into an appropriate receptor. The treated solids can be placed back into the ground or disposed at an appropriate landfill provided the requirements of the Land Disposal Restrictions (LDRs) have been met On-site disposal will require that moisture be adjusted to allow compaction requirements to be met. Some drying may be required to prevent water loss during transportation.

Off-gas treatment may also be necessary, especially for soils contaminated with a mixture of chlorinated solvents which degrade poorly or not at all under aerobic conditions, or with highly volatile petroleum hydrocarbons. Depending upon the concentrations of volatile species, the reactor temperature, the mode of oxygen supply, applicable local, state, and federal regulations, as well as nuisance considerations, off-gas treatment may be a significant factor in the design and cost of aboveground reactors. Reactors may be designed as enclosed vessels to facilitate the collection and treatment of gaseous emissions and may even be operated under reduced pressure conditions.

5.4.7 Process Instrumentation and Control

The instrumentation and control for biological treatment processes will vary depending on the type of process being used. For example, an anaerobic process requires careful monitoring of pH, alkalinity, methane production, and volatile fatty acids. An aerobic process requires monitoring of pH, dissolved oxygen, oxygen uptake rate, and nutrient (nitrogen and phosphorus) levels. Furthermore, different types of aerobic processes have different monitoring requirements. An activated sludge process requires measurement of return activated sludge (RAS) flow rate; however, this is not required for fixed-film processes, such as trickling filters or rotating biological contactors. Fluidized-bed reactor systems require monitoring of residual dissolved oxygen levels to control the oxygen dissolution system. The height of the fluidized-bed is also monitored to control the biomass wasting and fluidization pump flow rate.

In general, process monitoring and control can be as simple or as sophisticated as desired. Minimal automatic monitoring and control may be appropriate for smaller systems or where full-time operator coverage is available. Where minimal on-site operator coverage is desired, fully automated systems using a supervisory control and data acquisition (SCADA) process can be implemented. These systems typically use flow monitoring at multiple locations, level control algorithms, pH control, DO monitoring and control, and flow control valves. The computer control system can be programmed to achieve certain operating conditions with alarms to notify the operator (remotely) of problems. Set points for tank liquid or bed levels, chemical addition rates, pH, DO concentrations, and flow can be adjusted remotely using a computer interface connection. Data from selected monitoring points are collected and archived automatically.

5.4.8 Safety Requirements

The safety requirements for aboveground reactors are typical of any remedial or process industry system. System design must consider worker health and safety and meet all applicable OSHA requirements. Design, fabrication, installation, and operation codes and guidelines are summarized in Section 5.4.9. Large quantities of chemicals (i.e., nutrients, caustics, acids, surfactants, etc.) may also be present on a site so adequate worker and environmental protection must be provided during storage and handling of these potentially hazardous chemicals. Process control philosophy and instrumentation design is critical for monitoring process and equipment performance and providing adequate alarms or automatic shutdown to minimize endangering workers, discharging contaminants to the environment, or damage to equipment.

5.4.9 Specifications Development

In general, the applicable requirements of the following codes and standards will govern the design, fabrication, installation, and operation of aboveground biological treatment systems for bioremediation applications:

- Uniform Building Code (or governing local code),
- National Electric Code,
- National Electric Safety Code,
- Uniform Fire Code,
- National Electrical Manufacturers Association,
- Occupational Safety and Health Act,

- Instrument Society of America,
- Institute of Electrical and Electronics Engineers,
- American Society for Testing Material,
- ANSI Standard B31.1 - Petroleum Refinery Piping,
- ANSI Standard B31.6 - Chemical Plant Piping,
- American Society of Mechanical Engineers,
- American Welding Society, and
- American Petroleum Institute.

5.4.10 Costs

Costs associated with the treatment of groundwater contaminants in aqueous phase, aboveground bioreactors depend on the contaminants of concern and their concentrations in the influent stream. Full-scale bioreactors have been used for many years for the cost-effective treatment of domestic and many industrial waste streams at less than \$0.26/m^3 (\$1.00/1,000 gal). For contaminated groundwater systems designed to remove hazardous constituents in the waste stream, treatment is generally provided at less than \$0.79/m^3 (\$3.00/1,000 gal), including pumping costs. Off-gas treatment, if required, is expected to cost less than \$3.17/kg (\$7.00/lb) VOC removed (US EPA 1993b).

Cost estimates for slurry-phase reactors are not as well developed, so the following discussion provides a detailed cost estimate for a hypothetical slurry reactor treating 8,100 m^3 (10,000 yd^3) of contaminated soil. The costs were developed based on data collected from full-scale operating treatment systems using the following assumptions:

- 4,050 m^3 (5,000 yd^3) of contaminated soil are removed in the soil preparation/soil washing process.
- Four 720 m^3 (180,000 gal) (operating volume) slurry-phase reactors are operated at a 25% solids concentration.
- The reactors are operated in a batch mode with each batch requiring 30 to 35 days for biological treatment.
- The treated slurry is dewatered in a filter press and the recovered water is recycled to the slurry preparation/soil washing process.
- The treatment system is operated 7 days a week for the duration of the project.

A cost summary for this hypothetical treatment process is presented in Table 5.30. The system costs and capacity reflect actual full-scale systems. The labor costs include direct costs, benefits, overhead, and per diem for field personnel. Equipment costs include direct costs, depreciation, and operation and maintenance requirements. Materials, supplies, and utilities include direct costs plus a markup. The total estimated cost for a commercial slurry-phase biological process, operating under the above-mentioned conditions, is approximately \$250/m^3 (\$200/yd^3) of material as indicated in Table 5.30.

Table 5.30
Cost Analysis for Slurry-Phase Biological Treatment of 8,100 m^3 (10,000 Yd^3) of Contaminated Soil

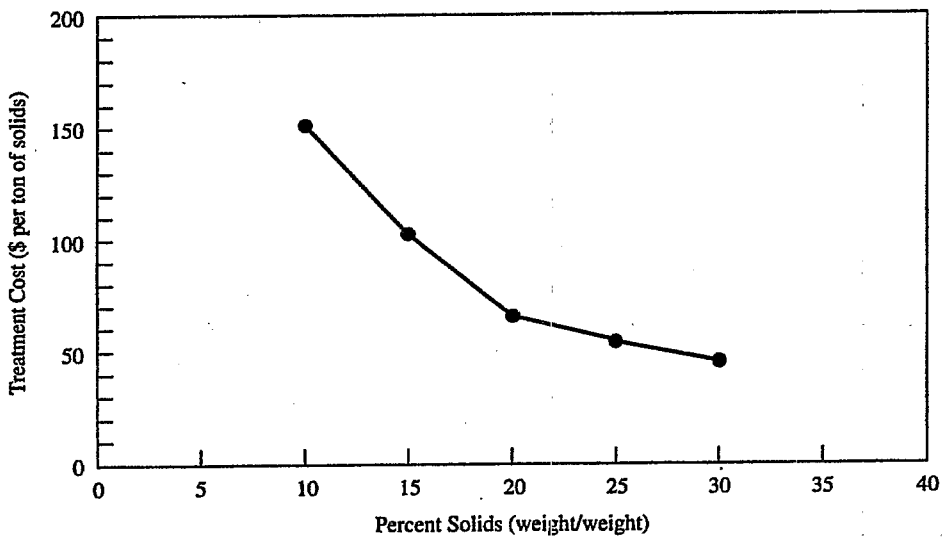
Cost Element	Cost (\$)
Engineering Design and Procurement	180,000
Treatment Costs	
Site Preparation and Equipment Setup	420,000
Soil Screening	80,000
Slurry Preparation	250,000
Slurry Biological Treatment	650,000
Decontamination and Demobilization	150,000
Subtotal, Treatment Costs	**1,550,000**
Project Administration	270,000
Grand Total	**\$2,000,000**

Three process variables have a significant impact on the total project cost of a slurry-phase treatment system: (1) reactor solids concentration, (2) residence time in the reactors, and (3) the percentage of material removed in the slurry preparation/soil washing system.

The effect of solids loading in the slurry reactors on treatment costs is shown in Figure 5.24. In general, for a given reactor configuration, the greater the slurry solids concentration, the lower the unit cost for the contaminated material. The upper solids concentration that can be effectively handled in a conventional slurry reactor configuration is limited to

approximately 30% to 35% solids, resulting in a minimum cost of approximately $56/tonne ($50/ton) of solids. The effect of reactor residence time on project costs is shown in Figure 5.25. An increased residence time reduces the through-put of the system, requiring additional labor and equipment costs to treat the same amount of material per batch. The effect on project cost of soil washing for removal of material from the feedstock is shown in Figure 5.26. The greater the quantity of material removed in the soil washing process, the less material requiring treatment and dewatering in the actual slurry-phase reactor.

Figure 5.24
Slurry-Phase Biological Treatment Effect of Solids Concentration on Treatment Costs



Modifications of operating temperatures can also affect slurry reactor economics. Using a full-scale slurry reactor treating PAH-contaminated soil as an example, the total capital and operating costs for the boiler system to heat the reactors were approximately $150/day/reactor. Using an average solids loading of approximately 152 tonnes/reactor (170 tons/reactor) (Woodhull et al. 1993), the cost of heating the reactors equates to approximately $0.96/tonne/day ($0.86/ton/day). Based on the data collected from the field reactors, heating the reactors from approximately 25 to 35°C

increased the kinetics for PAH removal by a factor of 1.6. For an initial concentration of 10,000 mg/kg PAHs, slurry-phase biological treatment at 25°C requires approximately 9 days to achieve the treatment criteria of 950 mg/kg, whereas biodegradation at 35°C requires only approximately 6 days to reach the same level of treatment. The cost to operate the unheated treatment system, adjusted for a 4-month shutdown period during the winter, is approximately $230/tonne ($205/ton) for a 9-day batch time (Woodhull and Jerger 1994; Woodhull et al. 1993). Operation of the treatment system without a winter shutdown at a 6-day batch time yields a total cost of approximately $202/tonne ($180/ton). Heating the reactors for 6 days requires an additional $5.60/tonne ($5/ton) in operating costs, raising the total costs to approximately $207/tonne ($185/ton); still lower than the $230/tonne ($205/ton) for the extended, unheated operation. This impact would be even greater as the ambient and slurry temperatures decrease to 15°C, causing even longer batch operating times to achieve treatment criteria. In this example, heating the reactor allows for continuous operation of the treatment system, reducing required operating times, increasing equipment utilization, and lowering overall life-cycle treatment costs.

Figure 5.25
Slurry-Phase Biological Treatment Effect of Solids Residence Time on Treatment Costs

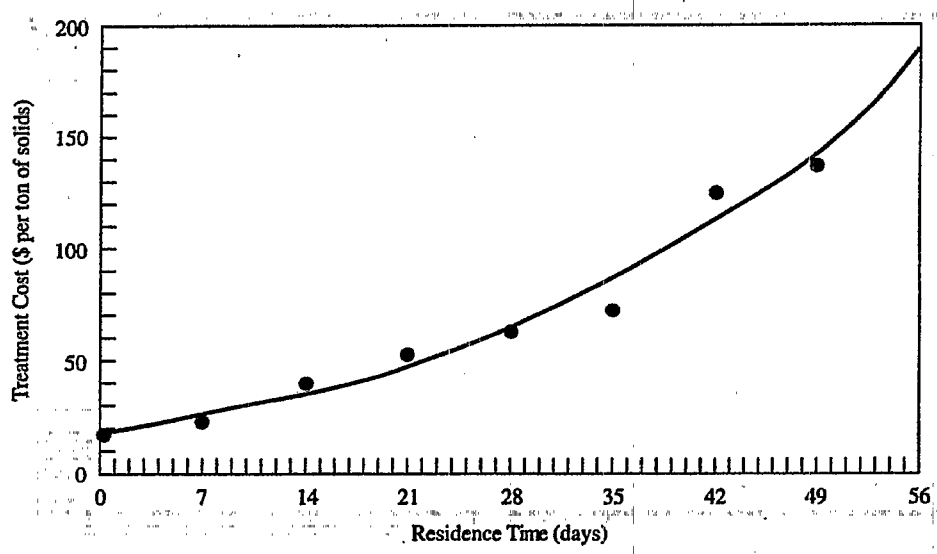
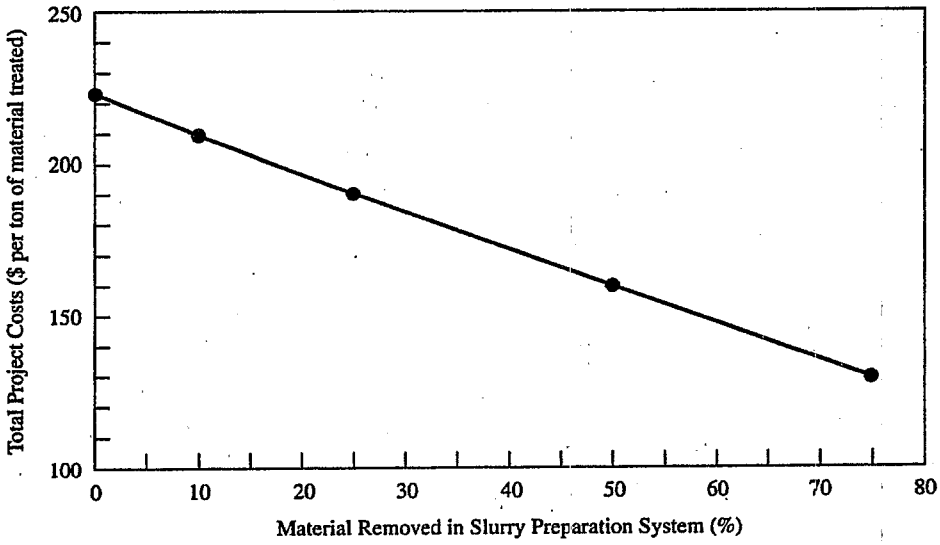


Figure 5.26
Slurry-Phase Biological Treatment Effect of Percent of Material Removed in Slurry Preparation System on Total Project Costs



5.4.11 Design Validation

The applicability of a biological treatment process should be evaluated by considering the types of constituents to be removed, the initial and long-term concentrations expected, the required effluent quality, and cost comparisons to other technologies. If the constituents present are readily biodegradable, the type of biological process to be employed will depend primarily on the contaminant concentrations. Groundwater or leachate with organic concentrations (as BOD or COD) up to 200 mg/L can be treated with FBR or fixed growth processes. Higher concentrations can be treated with FBR, activated sludge, or PACT® processes. For highly-contaminated soils and sludges that have contaminant concentrations ranging from 2,500 to 250,000 mg/kg, slurry-phase reactors should be considered. Specific design selection and validation are best determined by treatability studies.

Treatability testing for both aqueous and slurry-phase reactors is generally recommended as each individual groundwater and soil matrix will have specific organic removal rates dependent upon the specific constituents and concentrations in the matrix. For aqueous-phase reactors, testing should consist of operation for at least 8 weeks of bench- or pilot-scale systems so

that multiple sludge ages are achieved. Data collection during the treatability phase should focus on influent and effluent quality, as well as operational parameters, such as oxygen uptake rate, sludge yield, sludge settleability, etc. that will be important for design development. It is generally advisable to evaluate at least two operating conditions (e.g., organic loading rate, hydraulic residence time) for each process under consideration. For slurry-phase applications, bench-scale reactor studies can identify potential mixing problems with the contaminated solids and can aid in determining optimal solids concentrations for field-scale reactor operation. Temperature effects, bioaugmentation options, foaming control options, and surfactant enhancements can all be evaluated effectively at the bench-scale prior to initiating full-scale bioslurry remediation.

5.4.12 Permitting Requirements

In general, any unit that treats a hazardous waste is subject to RCRA operating permit requirements as a treatment, storage, and disposal facility, unless the system meets one or more RCRA permit exemptions. Some types of hazardous waste management units are exempt from RCRA permitting requirements because their operation is either regulated under federal and state programs or the operation of the unit should result in a minimal release. In addition, the system may meet the totally enclosed treatment facility (TETF) permit exemption criteria if the system is integrated into the production process to treat routinely-generated wastes. Enclosed aqueous- and slurry-phase reactors typically qualify for these exemptions.

Depending on the project location, air discharge permits may be required for operation of the reactors and any integral off-gas treatment systems that are used. Direct discharge of excess treated water from the process will typically require a National Pollutant Discharge Elimination System (NPDES) permit, or an agreement from the local wastewater treatment facility if it is discharged into a sanitary sewer system. Groundwater reinjection may require state or local injection permits. State and local regulations vary and need to be investigated as part of system design to ensure that all required permits are obtained without interfering with system design or operation.

5.4.13 Design Checklist

Prior to implementation of aboveground reactor design, the items listed in Table 5.31 should be reviewed.

Table 5.31
Aboveground Biological Treatment Design Checklist

	Aqueous-Phase Reactor	Slurry-Phase Reactor
Site Features	Property lines	
	Nearest power source	
	Building/confined space locations	
	Underground utilities	
	Normal use and traffic patterns	
Site Characterization	Type and distribution of contaminants	
	Contaminated groundwater volume	Contaminated soil volume
	Aquifer characteristics	Infrastructure near excavation
	Groundwater chemistry	Space for soil processing and stockpiling
Soil Characteristics	Aquifer properties	Soil type (particle-size distribution)
		Soil moisture content
		Volume/extent excavation
Test Results	Laboratory treatability study results	
	Aquifer hydraulic testing results	Processing/handling requirements
Design/O&M	Off-gas treatment	
	Electrical system	
	Monitoring system	
	Piping, valves, controls	
	Nutrient levels/source	
	Remedial goals achievable	
	Well design	Soil pre- and post-processing
	Groundwater transfer system	Soil transfer system
Health and Safety	HASP complete/kept on site	
	Personnel trained	
	Ground faults	
	Electrical system inspection	
	Security	
	Emergency shutdown procedures	
Miscelleaneous	Permits	
	O&M manual reviewed	
	Monitoring schedule	
	Site restoration	
	Treated water disposal	Treated soil storage & disposal

5.4.14 Implementation

Implementation of treatment using aboveground treatment reactors requires the coordination of a number of activities. For all aboveround systems, equipment support pads, treatment buildings, storage buildings, electrical services, security fencing and lighting, access roadways and paths, if needed, and site grading should be completed before any equipment is delivered. Equipment and tanks should be placed on support pads or in buildings as specified. The systems should be inspected to ensure that all construction specifications have been met. Notification should be made to all appropriate local agencies.

For aqueous-phase systems, wells must be installed using appropriate drill rigs and installation techniques. Wells must be completed using proper procedures to ensure their integrity over the duration of the project. Underground transfer lines must be installed from well manifolds to connect to all requisite tanks and pumps.

For slurry-phase systems, an important aspect of system implementation is management of soil during pre- and post-processing. Stockpile locations, as well as soil pre- and posttreatment areas, need to be located to minimize soil handling requirements. Equipment selection, both type and size, are important to the efficiency of the operation. Where rain may be heavy during pre- and post-processing, provisions need to be made to cover the contaminated soils within the pretreatment, stockpile and posttreatment areas. All soil processing and stockpiling areas should be located so that transportation requirements to the slurry reactor are minimized, and provisions should be made to minimize suspension and transport of contaminated soils away from the treatment area during process and transport.

5.4.15 Start-up Procedures

Start-up procedures vary with the design and the nature (i.e., suspended growth, fixed-film, slurry-phase reactor) of the aboveground reactor being used in a particular application. Startup begins with checking the system to ensure that no problems have developed since installation.

5.4.15.1 Groundwater Treatment Systems

For an aqueous-phase system, start-up procedures are identical to those described in Section 5.2 for the Raymond Process. Baseline measurements of water quality and bioremediation parameters are made prior to initiating groundwater recovery. A detailed list of wells to be sampled, parameters to be analyzed for each well, and sample preservation requirements should be

prepared, reviewed, and followed. A similar list will have been prepared for the start-up period and will include measurements of temperatures, flow rates, and pressures across the system. Prior to loading of the groundwater into the bioreactor, it normally is seeded with activated sludge from a local wastewater treatment plant. If contaminants to be removed from the contaminated groundwater are recalcitrant or inhibitory, seed organisms acclimated in pilot-scale reactors are added to the full-scale system.

Groundwater recovery is initiated with 100% of the treated water being polished with activated carbon and discharged to a sewer line or surface water body until water quality can be demonstrated to meet regulatory requirements. Once this condition has been met, activated carbon treatment is no longer required. If groundwater reinjection is to take place at the site, a portion of the groundwater will be diverted to a surge tank. When the level in the surge tank exceeds the "low level", the transfer pump is turned on and water is introduced to the injection wells through the manifold or header.

During the start-up period, the schedule for measuring and recording flow rates, meter readings, and collecting samples for analysis is followed. Samples of the influent and effluent to the groundwater treatment system are collected for analysis. Water level measurements are made for evaluation of the groundwater recovery system design so that adjustment of recovery and injection rates from individual wells can be carried out to achieve the desired groundwater flow patterns. During this period, modifications to flow rates and other parameters are made to meet specifications and/or to optimize performance. Because the system will not behave entirely as expected, modifications to the O&M manual should be anticipated. Monitoring and documentation procedures are also evaluated and changes are made to these procedures as necessary.

5.4.15.2 Soil Treatment Systems

For slurry-phase treatment systems, prepared soils are diluted and the slurry is transferred from the slurry preparation system to the reactor (normally multiple reactors are used with operating volumes typically 380 to 680 m^3 (100,000 to 180,000 gal) each). Feeding the reactor is initially done in small increments. Influent and effluent slurry and effluent water phase concentrations are monitored as the reactor solids content is raised to design levels to ensure that system performance is achieved during startup.

5.4.16 Performance Evaluation

Performance evaluation includes determining contaminant removal efficiency in groundwater and soil slurries, liquid/solid separation efficiency in clarifier units, oxygen transfer efficiency and dissolved oxygen levels in bioreactors, and throughput rates of the full-scale systems. It is highly unlikely in all but the smallest systems in relatively homogeneous formations or treating relatively uniform soil slurries that the system as originally designed will provide the best practical remediation. The O&M plan should incorporate procedures to evaluate performance and to modify operations as necessary to achieve overall optimal treatment. This requires that the monitoring plan be designed to identify optimization refinements as well as to satisfy regulatory requirements and to measure treatment progress. Potential changes in operational procedures include modifications to reduce operator time, to minimize monthly operating costs, to better distribute nutrients and oxygen, or to improve slurry mixing to reduce the required treatment time.

5.4.16.1 Operations Practices

Operations activities for aboveground bioreactors include: maintenance of the treatment system; management of nutrient and electron acceptor addition; evaluation and response to monitoring data; and routine maintenance of equipment, controls, and monitoring equipment, as well as housekeeping. For aqueous-phase reactors treating groundwater, additional operations activities are required for the groundwater recovery system that include: injection and recovery well maintenance and balancing groundwater recovery, discharge, and reinjection as appropriate. Slurry pre- and post-processing systems operations are needed in the preparation of contaminated soils prior to treatment and for dewatering soil slurries following treatment.

Maintaining flow in the injection wells is frequently the most time-consuming activity in an aqueous-phase treatment system. The rate of remediation is closely linked to the rate of introduction of the electron acceptor. If the rate of water injection decreases, the number of months over which O&M, reporting, and management costs are incurred increases. Design and well completion procedures for injection wells are important, as is scheduling well redevelopment at a frequency based on experience with different types of aquifers, the mass of organics to be degraded, and the design flow rate. Performance and anticipated problems with injection wells can be evaluated from changes in the cycling frequency of the high/low controllers for gravity feed wells and by pressure changes in pressure fed wells. Wells can be treated by surging to remove fines. Biological growth and precipitation of calcium or iron

can be addressed by adding dilute hydrochloric acid to the well and subsequent recovery of the spent acid after a few hours.

Treatment operational practices and monitoring are critical because of the potential to discharge water that is out of regulatory compliance to surface water, groundwater, or sewers, all of which can result in fines and poor relations with the regulatory agency or the public.

5.4.16.2 Operations Monitoring

As with most remedial systems, monitoring includes baseline sampling and analysis. Monitoring is most intense during startup, and decreases in frequency as the biological reactors reach steady-state operating conditions. To the extent practical, monitoring should be conducted with instrumentation and automatic recording devices. For remote sites, the ability to interface with monitoring equipment from an off-site location is particularly important as this can significantly reduce travel and labor costs.

Initially, the most critical parameters to be monitored are the influent and effluent water and/or slurry quality in the reactor treatment system. If the treatment system continuously does not meet performance criteria suggested from treatability studies during startup, the system should be shut down and the reason for poor treatment performance identified. If a source of microbial inhibition or toxicity is identified during full-scale system startup, additional treatability studies may be necessary to identify ways of reducing this inhibition via additional pre-treatment steps, through increased acclimation periods, or by decreased influent loading rates.

In aqueous-treatment systems, monitoring groundwater quality changes is necessary to meet regulatory requirements and to evaluate remedial progress. Interpretation of these data requires a detailed understanding of the process. Groundwater composition will change over time, and to some extent, the more degradable compounds will be treated first, as the more soluble compounds will be removed through groundwater extraction. Solubilization effects from biosurfactants will frequently result in increased dissolved-phase concentrations. Thus, interpretation of these data needs to be made in context of the mechanisms of remediation and the sequence of their occurrence along the groundwater flow path. It is important that the client and agencies understand that increased concentrations of various constituents in the groundwater may occur before improvements to groundwater quality are achieved.

The biodegradation parameters, especially nutrient and electron acceptor concentrations, are initially intensely monitored in the bioreactors to refine

nutrient and oxygen addition rates. DO, pH, and temperature can easily be measured on-site using readily available meters. Phosphate, ammonium ion, nitrate, nitrite, carbonate, sulfate, magnesium, manganese, chloride, and iron can be measured on-site using test kits. During startup, this rapid access to data can be beneficial. For routine operations, however, it is not always cost effective to use test kits and the results are not often as defensible as data obtained from an analytical laboratory.

Nutrients and electron acceptor concentrations are measured in the concentrate tanks following deliveries and in headers at a location downflow of the point of mixing in the bioreactors. These values are compared to tank level records for consistency and compared to the O&M schedule. Solids content measurements are also routinely monitored to ensure control of microbial biomass concentrations in aqueous-phase reactors, and slurry levels in slurry-phase reactors. As in aqueous-phase reactors, physical parameters are analyzed and evaluated as an indicator of process operation in slurry-phase systems. Specific parameters include slurry temperature, pH, total solids, slurry density, dissolved oxygen content, nutrient concentrations, etc. These parameters are used to operate and optimize slurry reactor performance.

For aqueous-phase reactors, it is important to gauge monitoring wells frequently during the first several months of operation to evaluate groundwater recovery system performance. Groundwater modelling is normally used to design the well layout and select groundwater recovery rates. Measured groundwater elevations are used to evaluate groundwater flow patterns and to adjust flows from individual wells using a model calibrated to site conditions.

Because of the nature of the contaminated material being treated in a slurry-phase reactor, to effectively and accurately monitor itsperformance it is particularly important that care be taken to collect representative samples at various points in the process and that these samples be analyzed for the appropriate chemical, physical, and biological parameters. Sample collection procedures are needed for collection from both the slurry reactors and the process equipment and piping. To collect representative samples, a statistically-based plan must account for the effect of variability in the feed characteristics, particle size distribution, and contaminant distribution on solids content. Statistically representative samples must be collected and must be tested for particle size density, total solids, and slurry density to determine how representative the sample is of the entire batch. Analytical results will be biased if samples are not representative, i.e., higher fraction of fines in sample, increased total solids, etc. In general, composite samples are preferable to discrete, grab samples. Once the samples are collected,

specific, repeatable procedures are required for sample handling, preparation, and extraction.

5.4.16.3 Quality Assurance/Quality Control

QA/QC procedures include practices common to the other bioremediation processes, including the use of blanks, blind duplicates, and spiked samples for laboratory and field measurements. Quality practices specific to both aqueous- and slurry-phase aboveground bioreactor processes include the following:

- control of composition of the nutrient and electron acceptor concentrations in the bioreactor systems;
- review of health and safety practices;
- review of operating practices and training of new field personnel; and
- routine evaluation of monitoring and metering equipment, valves, etc.

QA/QC considerations specific to aqueous-phase bioreactors treating contaminated groundwater include:

- comparison of groundwater recovery rate and totals with the rates and total from the injection header and discharge line; and
- consistency of biological parameter data with changes in groundwater quality and mass removed from groundwater extraction.

QA/QC considerations specific to slurry-phase bioreactors treating contaminated soils include:

- conducting solids mass balance calculations to compare influent soil and water rates with effluent oversize reject, slurry, treated solids, and treated liquid rates (Because the slurry density is not necessarily equal through out the reactor, sampling requirements and data interpretation are critical.; and
- consistency of biological parameter data with changes in soil slurry quality and mass removal during slurry treatment.

The key performance criteria is reduction in constituents of concern in the groundwater and contaminated solid matrix. Other measurements include pH, dissolved oxygen, and nutrient concentrations in addition to the appropriate analysis for the constituents of concern. Where applicable, surrogate analyses may be used for interim sampling events to reduce the total analytical costs.

5.5 Biosparging

5.5.1 Principles of Operation

Biosparging is an in situ remediation technology used for the remediation of groundwater contaminants. The process is sometimes referred to as *in situ aeration* or *in situ air sparging* (IAS). IAS can foster the removal of contaminants through a variety of physical, chemical, and biological processes. To promote the mass transfer of VOCs out of groundwater and the mass transfer of oxygen into groundwater, pressurized air is injected beneath the water table. Soil vapor extraction (SVE) is often used in conjunction with IAS to control the movement of contaminant-laden vapors migrating from beneath the groundwater table (Brown and Jasiulewicz 1992). IAS-enhanced aerobic biodegradation of contaminants can occur in both the saturated and unsaturated zones.

When pressurized gas is injected into water-saturated porous media, its behavior dependent upon media particle size and particle size distribution. Observations of injected air morphology and movement in a two-dimensional model aquifer, packed with various sizes and mixtures of glass beads, were made by Ji et al. (1993). In 4-mm beads, which correspond to medium or coarse gravel, "bubbly flow" was observed; air bubbles of one to three bead diameters in size migrated upward through the pores in a "stumbling" motion. In 0.75-mm beads or smaller, which correspond to sands, silts, and clays, "channeling flow" occurred, and the plume resulting from sparging was estimated to be 50% water and 50% air. In 2-mm beads, air was in the form of both bubbles and channels and it was concluded that this size is where the "transition between the flow regimes occurs."

In experiments using mixtures of bead sizes, small variations in the media resulted in distorted plume shapes. In experiments where confining layers of fine glass beads were placed above coarser beads, rising air migrated laterally upon encountering confining layers. These experiments demonstrated that air channels are sensitive to media heterogeneities.

Therefore, in soils with particle sizes equivalent to sands or smaller, air flow is restricted to discrete continuous air channels, and in natural soils, distorted air channels will predominate (Ji et al. 1993). In natural soils, the diameter of these air channels is estimated to be equivalent to a few grain diameters (Johnson et al. 1993).

It has been estimated that soil hydraulic conductivity of 0.001 cm/sec or greater is necessary for successful air sparging (Middleton and Hiller 1990;

Loden and Fan 1992). IAS appears to be best suited for remediation of uniform coarse-grained sands and gravel, free of confining layers, where air flow will be relatively uniform and more predictable (Marley, Hazelbrouck, and Walsh 1992; Marley and Bruell 1995). However, in highly-permeable soils, air flow will be primarily vertical, which limits the radius of influence (Nyer and Suthersan 1993).

In soils containing high percentages of silts and clays, often only minimal air flow rates can be achieved. In natural sediments, horizontal permeability can be several orders of magnitude greater than vertical permeability (Freeze and Cherry 1979). If the vertical movement of air is restricted by a confining layer, air will migrate in a horizontal direction, possibly spreading contaminants (Marley, Hazelbrouck, and Walsh 1992; Martin, Sarnelli, and Walsh 1992; Nyer and Suthersan 1993). If the injected air pressure should exceed the overburden pressure, then soil rupture and cracking can occur, short-circuiting air flow and reducing system effectiveness (Marley, Hazelbrouck, and Walsh 1992; Johnson et al. 1993). Therefore, IAS may not be appropriate where confining layers are present.

IAS has been used for the remediation of groundwater contaminants, such as BTEX, resulting from petroleum products and chlorinated solvents, such as TCE (Bass and Brown 1995). Biosparging is most often used to add dissolved oxygen (DO) to groundwater to facilitate the aerobic biodegradation of dissolved biodegradable contaminants. IAS can also be used to promote the mass transfer of VOCs from the groundwater to a vapor phase. Once volatile contaminants have entered the vapor phase, they may be transported to the vadose zone where biodegradation may take place. Alternatively, contaminant-laden vapors can be removed from the aquifer via SVE for subsequent treatment.

5.5.2 Process Design Principles

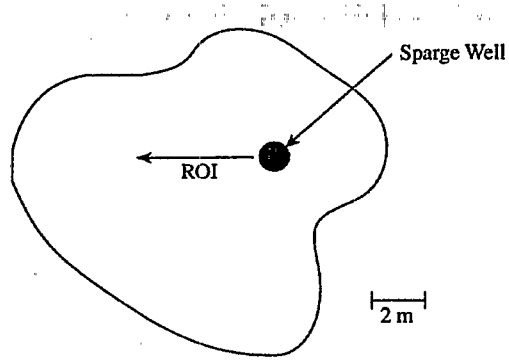
The potential for mass transfer of a contaminant from an aqueous phase to a vapor phase depends on the interfacial area between the phases and the contaminant's distribution at equilibrium between the phases. The interfacial area available for mass transfer is dependent upon the distribution and radial extent of air-filled channels during the sparging process. One method of estimating a dissolved contaminant's distribution at equilibrium is with the Henry's Law coefficient. Henry's Constant (H) describes the ratio of a contaminant's vapor pressure to its aqueous solubility as follows:

$$H = atm / (mol / m^3) = atm \bullet m^3 / mol \qquad (5.33)$$

A contaminant must have a Henry's coefficient of greater than 10^{-5} atm•m^3/mole to be stripped from an aqueous phase via IAS (Brown, Herman, and Henry 1991). Henry's Law coefficients of various groundwater contaminants commonly found at Superfund sites are listed in Table A-1. Additionally, the Henry's constants of selected gasoline additives at 25°C are as follows: tert-butyl alcohol (TBA), H = 1.20 • 10^{-5} atm•m^3/mol (Montgomery 1991); di-isopropylether (DIPE), H = 9.97 • 10^{-3} atm•m^3/mol (Montgomery 1991); and methyl tertiary butyl ether (MTBE), H = 5.72 • 10^{-4} atm•m^3/mol (Merck & Co. 1983).

The efficacy of IAS is highly dependent upon (1) the extent of contact of the injected air and the contaminated soil and groundwater, and (2) the magnitude of aquifer mixing (Bass and Brown 1995). One measure of the extent of contact is known as the *radius of influence* (ROI). ROI can be defined as the distance from an IAS well to a point where air flow can be detected or where the effects of air contact, groundwater mixing, or groundwater oxygenation are detectable and consistent (Marley and Bruell 1995). Radially symmetric air flow is unlikely in IAS system operation. Figure 5.27 shows a typical ROI obtained under field conditions.

Figure 5.27
Asymmetric "Real-World" Radius of Influence (ROI)



A field pilot-scale evaluation is usually conducted to determine an IAS-well ROI. However, no standard method exists to deduce the ROI from field data. In practice, the ROI is estimated from one or more experimental measurements. Several widely-used ROI monitoring parameters are described below.

Groundwater mounding is the upward movement of the water table in response to the injection of air into the saturated zone. Mounding indicates bulk water displacement and is often used as an indication of ROI because it is easily measured. However, caution should be used when employing groundwater mounding as a measure of ROI because mounding is transient, generally negligible under steady-state conditions, and extends beyond the region of air flow in the saturated zone (Lundegard 1995). New technologies that are being used to measure ROI on an experimental basis include the use of neutron probes and electrical resistance tomography (ERT). Neutron probes have been successfully used to measure changes in the percent of air saturation in a saturated sand (Acomb et al. 1995). ERT uses cross-bore-hole resistivity surveys to yield a multidimensional image of air distribution in the saturated zone (Schima, LaBrecque, and Lundegard 1994; Lundegard 1994; Lundegard and LaBrecque 1995).

Tracer gases, such as helium (He) or sulfur hexa-fluoride (SF_6) have been used to determine IAS ROIs. Generally, tracer tests are run with SVE wells in operation. A typical test consists of injecting a slug of tracer gas into the pressurized line connected to the sparging well. Tracer gas content is then measured in vadose zone monitoring points to determine the gas-phase tracer content in wells surrounding the IAS well. Portable instruments, such as the Mark Model 9820 He detector or TIF Model 5550 halogen detector, can be used to quantify gaseous He and SF_6, respectively (Johnson et al. 1995; Baker, Hayes, and Frisbie 1995). In a study using an He tracer, it was demonstrated that the ROI of a sparging well in both groundwater and the vadose zone were comparable (Javanmardian et al. 1995). Helium tracer has also been used to monitor the vapor capture capability of a combined IAS/SVE system (Johnson et al. 1995).

Measurements of pressure distributions in both saturated and unsaturated zones have been used as possible indicators of ROI. Pressures measured within the saturated zone are partially due to water table mounding and may result in overestimates of ROI (Acomb et al. 1995). Due to the nature of pressure propagation from an air source, the use of unsaturated zone pressures may also result in overestimates of the ROI.

Depleted groundwater DO content is often found in the vicinity of hydrocarbon spills as a result of biodegradation activity by naturally-occurring aerobic bacteria. After air sparging is initiated, DO levels may rise substantially at several monitoring wells. Oxygen transport may be occurring as a result of a combination of advection, dispersion, and diffusion. Increases in groundwater DO resulting from sparging activity is the most popular

indicator of air sparging well ROI and is a more direct measurement of whether oxygen is being supplied to the bacteria.

Figure 5.28 shows experimentally-measured ROI values from 37 sites (Marley and Bruell 1995). ROI values greater than 12 m (40 ft) were reported at only a limited number of sites; note that the testing procedures and analyses of data from sites exhibiting high ROI values were considered to be of questionable reliability. The majority of sites reported ROIs between 3 and 8 m (10 and 26 ft).

5.5.3 Process-Flow Diagram

The biosparging process is depicted schematically in Figure 5.29. The components of a typical biosparging process include the wells, a manifold, and a compressor system.

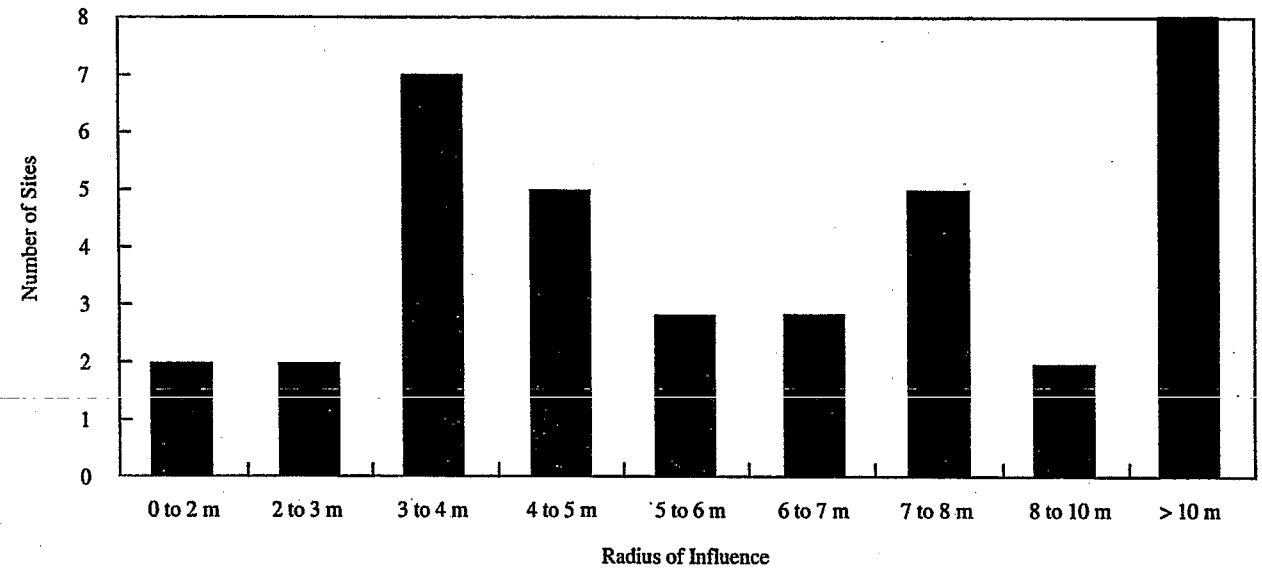
5.5.4 Process Modification

5.5.4.1 Air Injection Without Air Extraction

IAS systems are generally used in conjunction with SVE to prevent the migration of contaminated IAS gases. However, use of IAS without an SVE system has been documented at one research site (Beausoleil et al. 1993). Here, a low-flow (i.e., 4.25 m^3/hr [2.5 scfm]) IAS system used indigenous microbial populations in the adjacent vadose zone to degrade all contaminants. No significant downward or lateral dispersion of BTEX in the aquifer was observed, and no BTEX was volatilized to the atmosphere during the study period.

IAS systems can be designed and operated to optimize oxygen mass transfer into an aquifer or contaminant volatilization from an aquifer. Selection of the operational mode often depends on the relative biodegradability of the contaminant. In laboratory studies where an IAS system was operated primarily to add oxygen to a model aquifer, there was an optimum air injection rate above which further increases caused decreases in the rate of oxygen mass transfer (Rutherford and Johnson 1995). Oxygen mass transfer appeared to be affected by both air injection rate and groundwater flow. At low air injection rates, increases in air flow resulted in a higher density of air channels. A higher density of air channels, which constitutes an increase in interfacial area, increased mass transfer rates. At low injection rates, dye studies demonstrated that water still would flow through the zone of air travel. At air flows above the optimum flow rate, further increases in air flow rates did not cause further increases in air channel densities but,

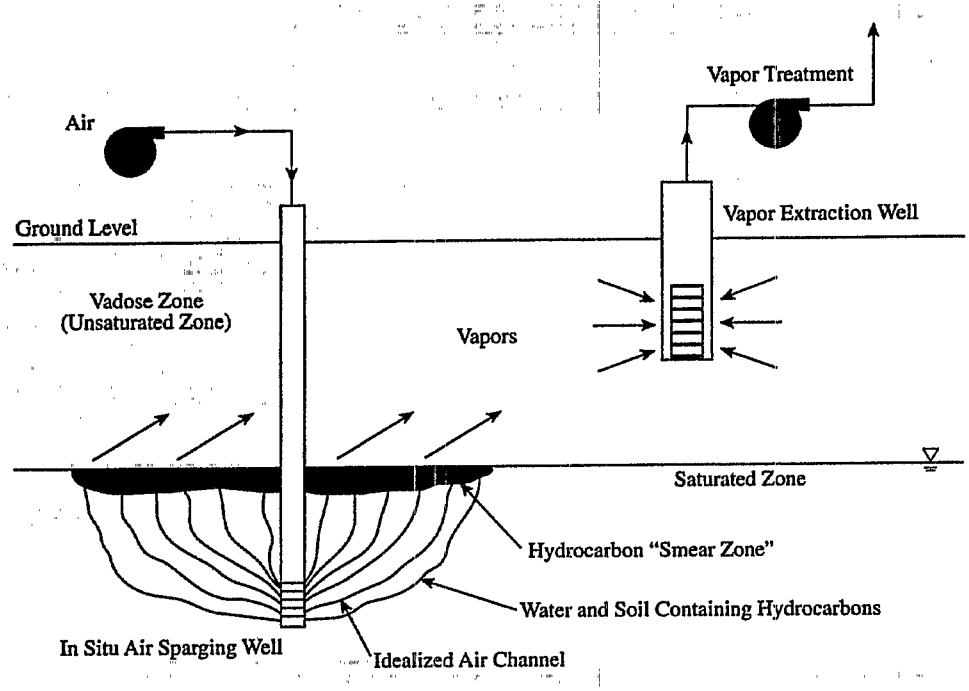
Figure 5.28
IAS ROIs Found at Numerous Sites



Total Sites = 37

Source: API Publication 4609, *In Situ Air Sparging: Evaluation of Petroleum Industry Sites and Considerations for Applicability, Design and Operation*, 1995. Reprinted courtesy of the American Petroleum Institute.

Figure 5.29
Biosparging Process-Flow Diagram Showing Biosparging Well Operating in Parallel with a Soil Vapor Extraction Well



Source: API Publication 4609, *In Situ Air Sparging: Evaluation of Petroleum Industry Sites and Considerations for Applicability, Design and Operation*, 1995. Reprinted courtesy of the American Petroleum Institute.

instead, caused reductions in relative permeability to the flow of water. In this case, water was forced to flow around the zone of air travel, and a decrease of mass transfer of oxygen into the water was observed. It is expected that the same qualitative trends will be observed in a field setting; however, specific correlations between laboratory results and field studies do not currently exist.

5.5.4.2 Pulsed Operation

Generally, an SVE system is used for several weeks to remove any residual hydrocarbons above the water table prior to initiating IAS activities. Figure 5.30 (top) shows an idealized response of hydrocarbon content in SVE stack gas for a system where SVE was initially conducted alone followed by continuous combined operation of SVE and IAS (Marley and

Bruell 1995). During SVE-only operation, the decrease in effluent hydrocarbon content follows a typical first-order decay. When IAS is initiated, hydrocarbon content increases as VOCs trapped beneath the water table are mobilized by the migrating air. However, a gradual first-order decay to asymptotic levels is again observed. It is theorized that this response to IAS in fine-grained soils is because the air-filled channels constitute select preferential pathways within the aquifer that directly impact limited portions of the aquifer. Therefore, contaminants contained in soils not directly impacted by the air-filled channels must diffuse or advect to these areas (Wilson, Norris, and Clarke 1996a).

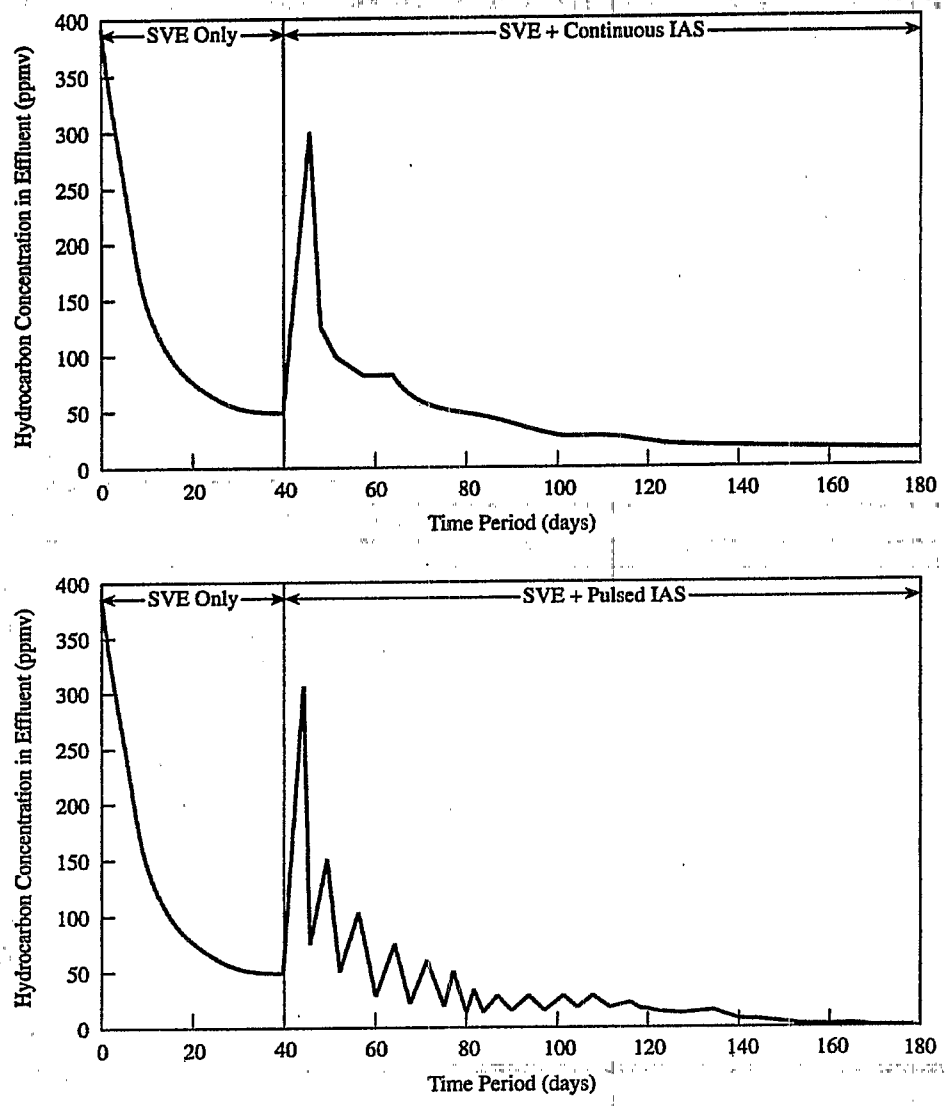
Cycling of an IAS system on and off for periods of time ranging from 12 hours to several days is known as "pulsed" operation. An idealized response of hydrocarbon content in stack gas for an IAS system which incorporates a continuous SVE system combined with pulsed IAS well operation is shown in Figure 5.30 (bottom)(Marley and Bruell 1995). Field data suggest that pulsed sparging greatly enhances groundwater mixing, which is necessary to overcome the diffusion limitations of sparging caused by air channeling (Clayton, Brown, and Bass 1995). Additionally, it is theorized that trapped air can be induced to dissolve by the action of sparging. The enhancement of dispersion resulting from pulsed IAS has been modeled (Wilson, Norris, and Clarke 1996b).

It is also theorized that selection of a pulse frequency depends on the desired mechanism of contaminant removal (i.e., volatilization versus biodegradation) (Rutherford and Johnson 1995). Trapped air remains after injection stops and continues to supply oxygen for biodegradation, while volatilization ceases when air injection stops.

5.5.4.3 In-Well Aeration Systems

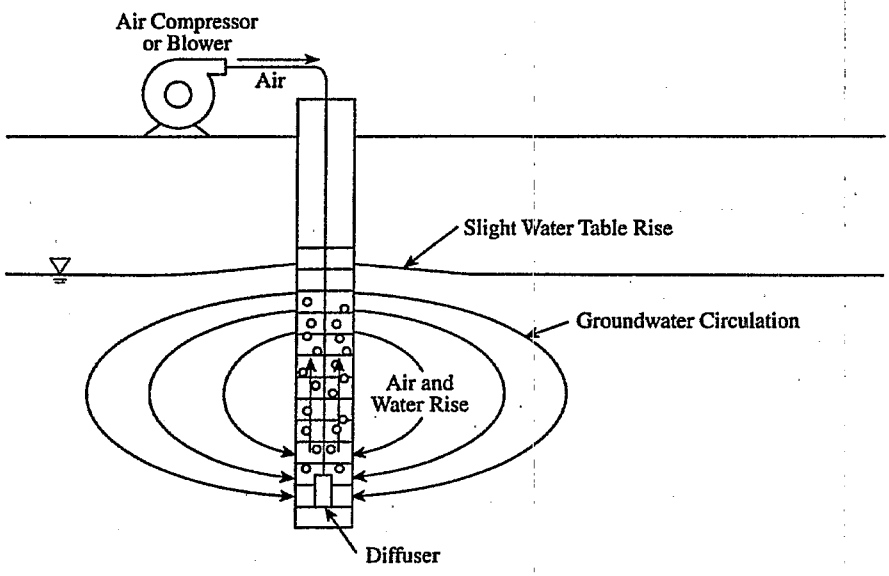
In-well aeration is the process of injecting a gas, usually air, into a well, resulting in an in-well airlift pump effect. In a typical application, illustrated in Figure 5.31, air is injected into the bottom of a well. The air travels upward, stripping volatiles and aerating the water. This upward movement of air results in an airlift pump effect causing water to flow into the well from the deeper screened portion of the well and out of the well from the shallower screened portion establishing a circulation pattern within the aquifer. If hydrogeologic conditions allow, in-well aeration creates a circulation cell that treats and aerates the water as it passes through the well. The airstream may also provide oxygen for biodegradation in both the saturated and unsaturated zones.

Figure 5.30
Idealized Hydrocarbon Removal Data Resulting from a Continuously Operated System (Top) vs. A Pulsed Operation (Bottom)



Source: API Publication 4609, *In Situ Air Sparging: Evaluation of Petroleum Industry Sites and Considerations for Applicability, Design and Operation*, 1995. Reprinted courtesy of the American Petroleum Institute.

Figure 5.31
Typical In-Well Aeration System



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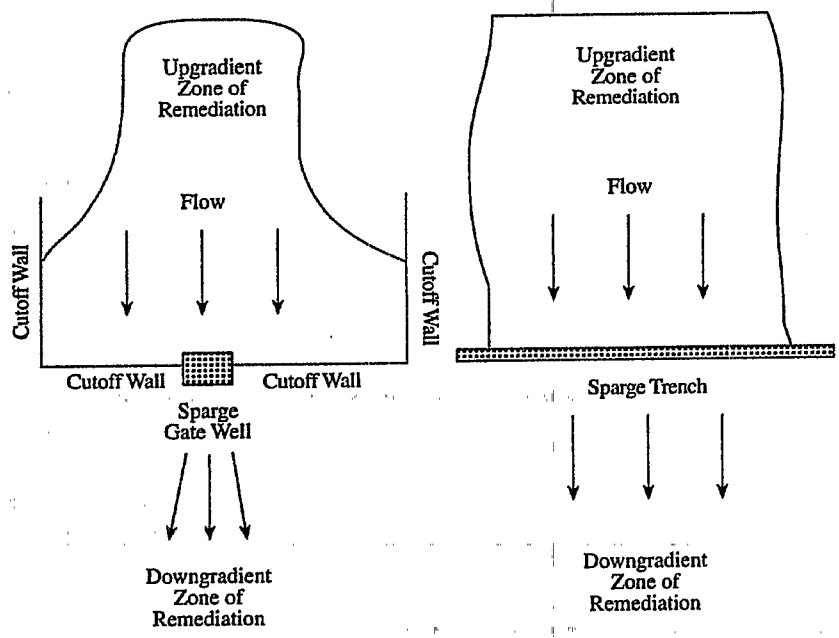
The operating principle of in-well aeration is relatively straightforward. Air is used to strip and/or oxygenate water by establishing an "in-well pump-and-treat" system. The advantage of this approach, compared to traditional pump-and-treat systems, is that it avoids removing water from the aquifer for aboveground treatment.

5.5.4.4 Sparging Gate-Wells, Trenches, and Curtains

A number of additional air sparging techniques have been used to contain and remediate VOC-contaminated groundwater, including the application of sparging gate-wells and trenches or "curtains" (Pankow, Johnson, and Cherry 1993; Marley et al. 1994). The concepts of sparging gate-wells and trenches are illustrated in Figure 5.32.

The sparging gate-well uses hydraulic barriers to direct contaminated groundwater flow through a treatment zone. The sparging trench is constructed perpendicular to the contaminated groundwater plume flow direction. The contaminants in the groundwater may be remediated while passing

Figure 5.32
Sparging Gate-Well and Trench Systems



Source: Pankow, Johnson, and Cherry 1993

through the sparging gate-well or trench, via volatilization, biodegradation, or other physical/chemical processes.

A sparging curtain resembles a sparging trench in that it is installed perpendicular to the flow of the contaminated groundwater plume. However, vertical sparging wells are generally spaced equally along the length of the curtain to emulate the performance of the sparging trench.

The main considerations in the design of a flow-through sparging treatment system are to ensure that:

- groundwater will flow through, not around the system;
- target VOCs can be removed to predetermined clean-up levels; and
- that relatively uniform air flow is provided over the entire system.

To achieve these criteria, the system design parameters (e.g., trench dimensions and fill material properties) and operating parameters (air injection flow rates, sparging manifold radius, port size, and manifold pipe lengths) must be established. In many cases, an associated passive or active SVE system may be required in conjunction with these systems.

5.5.4.5 Pure Oxygen

Delivery of oxygen is often the rate-limiting step controlling biodegradation. Air contains approximately 20% oxygen by volume. When using air as a sparging gas, the maximum DO concentration that may be obtained within an aquifer is 8 mg/L, based on partitioning described by Henry's Law at typical groundwater temperatures. Soils with low permeabilities may severely restrict the rate at which sparge gas, and therefore oxygen, can be introduced into an aquifer formation. When sparge gas flows are restricted to less than 3.4/m^3/hr (2 scfm), the use of pure oxygen as a sparging gas should be considered. With 100% oxygen as a sparge gas, the resulting DO level is 40 mg/L. Therefore, the amount of DO delivered and rate of biodegradation can be as much as five times faster than air when using pure oxygen as a sparge gas. This benefit may offset the lower sparge gas flow rates. Additionally, higher DO concentrations result in greater concentration gradients and higher rates of mass transfer to areas not directly contacted by sparging gas. Furthermore, in biosparging applications, the injection of pure oxygen can provide a means of effective sparging in geologic conditions not suited to traditional air sparging.

As an example, a biosparging pilot study was conducted for groundwater and soils contaminated with semivolatile organic compounds at a facility in Texas used to store wastes and wastewaters containing elevated levels of nitroaromatic and aromatic compounds. Site operations led to release of these compounds into the groundwater which was located in a confined sandy aquifer underlying a clay aquiclude. These site conditions prevented using a cost-effective SVE system for sparging gas capture. The pilot study demonstrated the successful application of pure oxygen into the aquifer. At an oxygen flow rate of less than 1.7 m^3/hr (1 scfm), a zone of influence in excess of 9.1 m (30 ft) was observed.

5.5.4.6 Addition of Methane to Sparge Air

Industrial solvents such as TCE, PCE, 1,1,1-trichloroethane (TCA), carbon tetrachloride, and chloroform are common environmental pollutants. Bacteria found in groundwater can biologically transform these chlorinated compounds via several pathways. Indigenous methanotrophic organisms can

be biostimulated with the addition of methane as an electron donor and oxygen as an electron acceptor. Methanotrophs produce the enzyme methane monooxygenase (MMO), which initiates the first step of methane oxidation when methane is used as the sole carbon source for energy and growth (Semprini et al. 1990). Under aerobic conditions, MMO can epoxidize alkenes. Aerobic TCE oxidation can be accomplished by mixed cultures of methanotrophic and heterotrophic organisms. TCE oxidation first involves the epoxidation of TCE by methanotrophs, an abiotic hydrolysis of the epoxide to nonvolatile products, followed by heterotrophic degradation of the products to CO_2, chloride, and water (Semprini et al. 1991).

Laboratory studies have shown that this process can be conducted aerobically with an air phase that contains as little as 0.6% natural gas (i.e., methane) by volume (Wilson and Wilson 1985). In microcosms, optimum gas-phase oxygen and methane content to promote TCE degradation were between 7.7% to 8.7% and 1.7% to 2.7%, respectively, which correspond to aqueous concentrations of 3.2 to 3.7 mg/L and 0.4 to 0.6 mg/L, respectively (Kane, Fischer, and Wilson 1996).

The addition of methane to simulate the growth of methanotrophs in the field has been investigated at the US DOE Savannah River Site, South Carolina (DOE 1991).

Methane can be added to sparging air by piping a methane line equipped with a check valve, isolation valves, and flow meter to a sparging well. The methane supply must produce sufficient line pressure to overcome pressure resulting from the air sparging compressor or blower. Methane content of sparging air should be maintained below the lower explosive limit (LEL) of 5% to prevent explosive conditions. The methane addition must occur only when a sparging blower is operating; this can be accomplished with an interlocked valve rated for natural gas service.

5.5.5 Pretreatment Processes

Pretreatment processes for IAS systems are related to the supply of air or oxygen. There are a number of methods of supplying oxygen for biosparging applications including liquid oxygen and oxygen concentrators. Oxygen concentrators use a dual-bed molecular sieve design to remove the nitrogen (and other non-oxygen components of air) from a compressed air stream. For example, a model AS 4000 oxygen concentrator can generate 11.3 m^3/hr (67 cfm) of 90% to 95% pure oxygen at 310.5 kPa (45 psi). The compressed oxygen from the concentrator is generally fed into a steel oxygen receiver tank, which can then be plumbed to the oxygen flow control

manifold. The oxygen flow control manifold system generally consists of pressure regulators, electric ball valves, electronic pressure and temperature transducers, and mass flow meters that are used to monitor and direct the oxygen flow to each of the biosparging manifold headers.

For air injection, only oil-less compressors or compressors outfitted with oil removal devices should be used to introduce contaminant-free air into the aquifer (see Section 5.5.11 for compressor selection).

5.5.6 Posttreatment Processes

Depending on site-specific conditions it may be necessary to capture and treat the gas emanating from the saturated zone as a result of the biosparging process. Ideally, if it can be demonstrated that the emanating gas is being degraded in the vadose zone and poses no significant risk, no collection or further treatment will be required. If collection is required, an SVE system is typically incorporated into the biosparging system design. Treatment of contaminants in the SVE offgas may consist of one or a combination of the following treatment technologies:

- activated or impregnated carbon sorption;
- thermal or catalytic oxidation;
- non-carbon based sorption (e.g., Zeolite);
- biofiltration; and
- membrane/separation technologies.

For thermal/catalytic options, the use of internal combustion engines (ICE) has shown promise. However, in some states a catalytic converter on an engine exhaust is considered an air-control device, and thus requires a permit. If target destruction efficiency can be achieved before the exhaust passes through the catalytic convertor then a permit is generally waived. As an additional control, the SVE/ICE system must shut itself off if the ICE goes down. This is generally achieved by using the vacuum created by the engine for the SVE. If additional blowers/compressors are used, then there must be a control system which shuts off these blowers/compressors if the ICE goes down.

The preferred technology for offgas treatment will be based on an evaluation of the most cost-effective process for the contaminants of concern. See Section 6.2 of this monograph for a detailed discussion of biofiltration for offgas treatment. See *Vapor Extraction and Air Sparging*, Holbrook et al. (1998).

5.5.7 Process Instrumentation and Control

IAS system instrumentation and controls monitor and regulate the flow of air (oxygen) at the source and at the individual injection wells.

5.5.7.1 Wells

In some cases, sparging wells can be driven from the surface to save installation costs. Limited experience indicates that driven points perform as well as drilled wells (Droste et al. 1994). However, the probability of short-circuiting along a driven well casing is higher than with a drilled well installation. In addition, special drive point techniques may be needed in fine-grained soils (clays) due to the potential for well screen smearing.

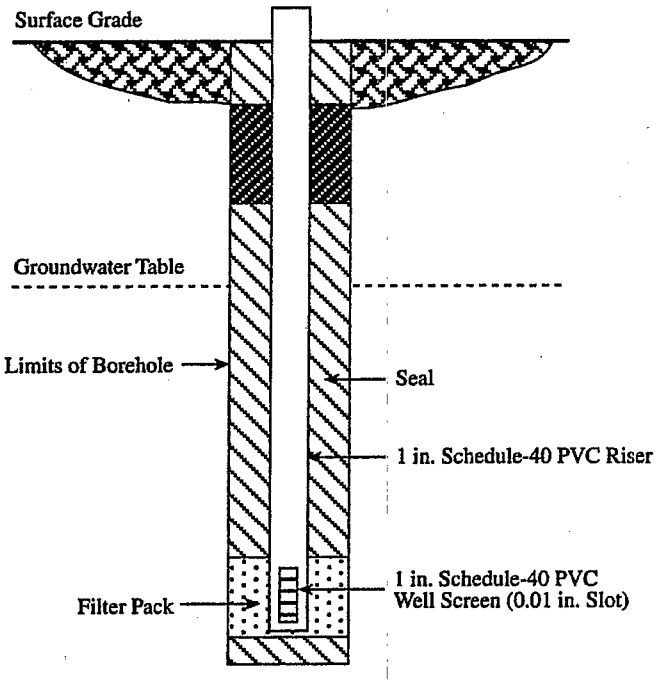
For drilled wells, the average grain size of the filter pack should be as close to the native soils as practical. Filter packs that have an average grain size larger than the native geologic materials may be more permeable than the native soil. While a highly-permeable filter pack is an advantage in wells constructed for other uses (e.g., monitoring or extraction), a filter pack that has a higher permeability than the surrounding formation enables the applied air to short-circuit up the borehole. A bentonite seal is used to seal the borehole and prevent short-circuiting of the air supplied. This seal should be placed from approximately 0.3 m (1 ft) above the IAS well screen filter pack to approximately 0.3 m (1 ft) above the seasonally high water table level and then hydrated. The annular space above the bentonite seal should be filled with a 5% (by weight) bentonite/cement grout mix.

Well-screen slot size should complement the filter pack design. Since air readily passes through well screens, a small slot size usually is sufficient; underestimating the slot size (by a small margin) relative to the filter pack is usually acceptable. In most cases, a 0.5-mm (0.020 in.) or 0.25-mm (0.010 in.) slot size is used.

A relatively short length of screen, such as 0.3 to 1 m (1 to 3 ft) is sufficient. Shorter screen lengths are not recommended. The well screen typically is flush-threaded slotted Schedule 40 or 80 PVC or CPVC pipe. A schematic of a typical drilled air sparging well is shown in Figure 5.33.

It is recommended that wells be developed to minimize accumulation of fines in the screened section and/or filterpack. Air sparging wells should be developed prior to operation because pulsed operation produces an effect essentially the same as well development, but without the removal of accumulated fines. In some cases, the reverse gradient created between pulses is sufficient to cause the fines to migrate into the well and the filterpack, causing clogging problems.

Figure 5.33
Typical Sparging Well with Grouting and Seal



Source: API Publication 4609, *In Situ Air Sparging: Evaluation of Petroleum Industry Sites and Considerations for Applicability, Design and Operation*, 1995. Reprinted courtesy of the American Petroleum Institute.

5.5.7.2 Manifold

The construction of an IAS manifold typically includes the following components: check valve, throttle valve, manifold piping or hose, quick-connect couplers, and plugs and sampling port(s) at the wellhead.

The manifold is typically buried underground below the frost level. If it is within the frost zone, it may need to be protected from frost with insulation and/or heat tape, and flexible connections may be needed to prevent damage from frost heaving. Once the main manifold run has been installed in the vicinity of a group of wells, hard piping or a high-pressure air hose equipped with couplers and plugs can be used for attachment to the well.

Check valves are recommended at the well (between each well and the manifold) to prevent temporary high pressure in the screened interval of the aquifer from forcing air and water back into the manifold after the IAS

system is shut down. A throttling valve should also be installed at each well to allow the isolation of the well from the system or for adjustments to the well air flow rate; gate valves and globe valves are effective throttle valves.

A manual or automatic pressure relief valve should be installed immediately downstream of the air compressor outlet. This valve exhausts excess air from the manifold to either the atmosphere or the compressor air inlet and acts to prevent excessive pressure from damaging the manifold or fracturing the aquifer soils in the event of a system blockage.

5.5.7.3 Compressor System

The selection of a suitable air compressor is typically based on the results of an in situ pilot study. The results of the pilot study are used to determine the optimal pressure and flow for a well installed within a specific geologic setting. The pressure capacity and flow rate of the air compressor should be designed based upon the maximum expected pressure and flow for any one group of wells and must consider manifold system head losses.

Compression of air can generate a significant amount of heat and noise. As part of the design, the air compressor exhaust temperature should be calculated based on manufacturer's data. Piping and manifold materials must be compatible with compressor discharge temperature and pressure.

The process of air compression can cause production of moisture in the air compressor and/or manifold line. In the winter months, precipitation in the manifold can freeze, restricting or blocking the flow from the compressor. Heat tracing can be used to winterize the piping/manifold. A receiver (air tank) with a manual or automatic drain to remove condensate from the receiver is recommended. For larger systems, moisture removal equipment may be installed upstream of the air inlet to the compressed air source. Common air compressor types are described in Section 5.5.11.

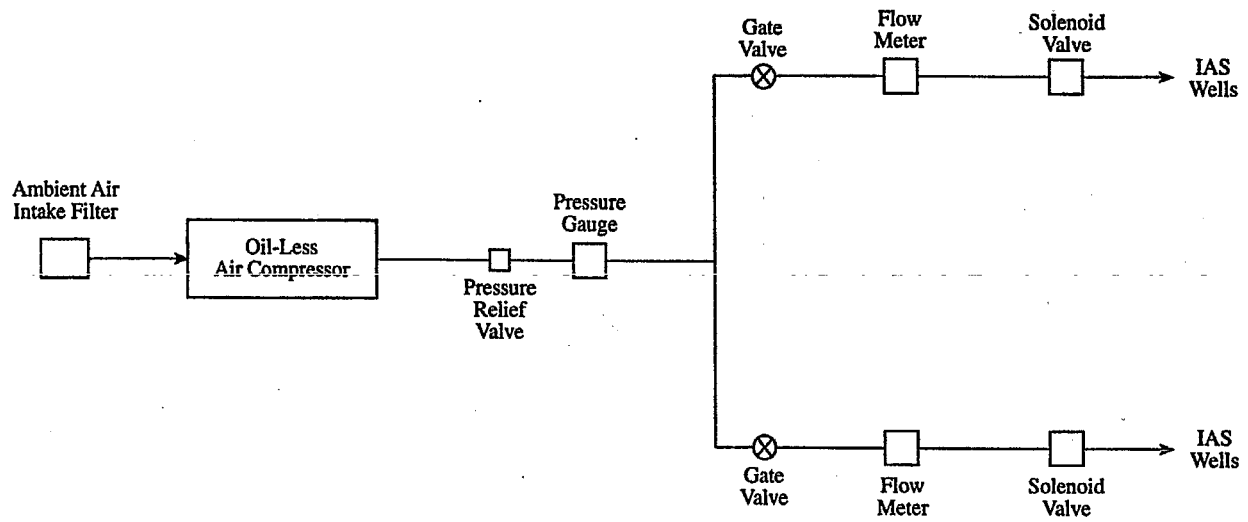
5.5.8 Process and Instrumentation Diagram

Figure 5.34 presents a typical P&I diagram for a biosparging application using a concentrator to provide pure oxygen. The concentrator can be eliminated when using air injection or replaced (including the compressor) with liquid oxygen tanks.

5.5.9 Sample Calculations

The use of excessive sparging pressures may cause soil fractures which short-circuit the air injected and compromise the effectiveness of the IAS.

Figure 5.34
Process and Instrumentation Diagram for a Typical Air Sparging System



The maximum air pressure that can be safely applied without producing soil fractures can be calculated based on an estimate of the overlaying pressure from the weight of the soil and water column above the top of the IAS well screen. Then, as a safety factor, only 60% to 80% of the overlying pressure should be applied to avoid soil rupture. This calculation is only a first approximation estimate because field conditions may vary (Marley and Bruell 1995). A sample calculation follows:

> Assume that the soil is unconsolidated medium-size sand with a 33% porosity (0.33) and a particle specific gravity of 2.65. The water table is located 5.49 m (18 ft) below the soil surface and the top of the sparging well screen is located 1.52 m (5 ft) below the water table. (Note: all calculations use gauge pressure.)

<u>In SI units</u>

$$\text{water pressure} = (1.52\text{m}) \bullet 0.33 \bullet \frac{9.81\ \text{kN}}{\text{m}^3} = \frac{4.9\text{kN}}{\text{m}^2} \text{ or } 4.92\ \text{kPa} \quad (5.33)$$

$$\text{soil pressure} = (5.49 + 1.52) \bullet 2.65 \bullet (1 - 0.33) \bullet \frac{9.81\ \text{kN}}{\text{m}^3} = \frac{122.10\ \text{kN}}{\text{m}^2} \quad (5.34)$$

or 122.10 kPa

$$\text{total pressure} = 4.92 + 122.10 = 127.02\ \text{kPa} \quad (5.35)$$

$$\text{Maximum pressure to avoid soil fractures} = 0.6 \bullet 127.02 = 76.2\ \text{kPa to } 0.8 \bullet 127.02 = 101.6\ \text{kPa} \quad (5.36)$$

<u>In English units</u>

$$\text{water pressure} = 5\ \text{ft} \bullet 0.33 \bullet 62.4\ \text{lbs/ft}^3 = 103\ \text{lbs/ft}^2 \quad (5.37)$$

$$\text{soil pressure} = (18 + 5) \bullet 2.65 \bullet (1 - 0.33) \bullet 62.4\ \text{lbs/ft}^3 = 2{,}548\ \text{lbs/ft}^2 \quad (5.38)$$

$$\text{total pressure} = 103 + 2{,}548 = 2{,}651\ \text{lbs/ft}^2 \bullet 1\ \text{ft}^2 / 144\ \text{in}^2 = 18.4\ \text{psi} \quad (5.39)$$

$$\text{maximum pressure to avoid soil fractures} = 0.6 \bullet 18.4 = 11.0\ \text{psi to } 0.8 \bullet 18.4 = 14.7\ \text{psi} \quad (5.40)$$

When sparging is initiated, the pressure required to establish flow is always greater than the pressure required to maintain air flow. This is because sparging air will displace a portion of the overlying water from the sparge well and soil column, and subsequent air flow will require lower pressures. Over-pressure can be defined as the pressure in excess of that required to overcome hydrostatic head at the top of the well screen, which is measured once flow has been established.

Assuming an operating over-pressure of 34.5 kPa (5.0 psi) for 8.49 m^3/hr (5 cfm) of air flow in a medium sand, the pressure required to maintain flow in the system can be estimated as follows:

<u>In SI units</u>

$$\text{hydrostatic head} = 1.52\ \text{m} \bullet \frac{9.81\ \text{kN}}{\text{m}^3} = \frac{14.9\ \text{kN}}{\text{m}^2}\ \text{or } 14.9\ \text{kPa} \qquad (5.41)$$

$$\text{pressure required to maintain flow} = 34.5\ \text{kPa} + 14.9\ \text{kPa} = 49.4\ \text{kPa} \qquad (5.42)$$

<u>In English units</u>

$$\text{hydrostatic head} = 5\ \text{ft} \bullet 62.4\ \text{lbs}/\text{ft}^3 \cdot 1\ \text{ft}^2 / 144\ \text{in}^2 = 2.2\ \text{psi} \qquad (5.43)$$

$$\text{pressure required to maintain flow} = 5.0\ \text{psi} + 2.2\ \text{psi} = 7.2\ \text{psi} \qquad (5.45)$$

This pressure is much less than the maximum pressure to avoid soil fractures. Pressure required to establish flow may be somewhat higher (i.e., 10 to 20 kPa [1.5 to 2.9 psi]).

Dissolved oxygen must be supplied in sufficient quantities to satisfy stoichiometric requirements for the aerobic biodegradation of contaminants. In the case of gasoline, which contains hundreds of hydrocarbons, benzene can be used as a surrogate for approximate calculation purposes. The oxygen requirement for the complete aerobic biodegradation and mineralization of benzene to carbon dioxide and water can be calculated as follows:

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O \qquad (5.45)$$

$$78\text{kg}C_6H_6 + 240\text{kg}O_2 \rightarrow 264\text{kg}CO_2 + 54\text{kg}H_2O \qquad (5.46)$$

$$\frac{240\text{kg}O_2}{78\text{kg}C_6H_6} = 3.1\text{kg}O_2 / \text{kg}C_6H_6 \qquad (5.47)$$

Therefore, every 1 kg of benzene will require 3.1 kg of DO for biodegradation. The time required for the delivery of oxygen is often the rate-limiting step that controls the rate of biodegradation. It should be noted that approximately 1% of the available oxygen from injected air is actually used in biodegradation with 99% not transferred to the groundwater during sparging (Newman et al. 1994).

5.5.10 Safety Requirements

IAS system technology health and safety considerations are primarily mechanical, electrical, and chemical.

Air compressors often have the capability of producing in excess of 621 kPa (90 psi) air pressure. This pressure can easily cause injury to personnel and equipment damage if not properly controlled. IAS systems should be designed using only suitable materials that are rated for expected operating pressures and should have properly operating pressure relief valves located at appropriate locations. Proper grouting is essential to avoid the launching of pressurized wells from the ground, putting personnel in the vicinity at risk; this phenomenon has been observed at one site. Air flow and pressure should be gradually applied to avoid pressure surges that could lead to soil rupture (see Section 5.5.9 for calculation of maximum sparging pressures).

Electrical hazards are always present when using electrical equipment under field conditions. All equipment should be wired by qualified technicians according to local electrical codes. Proper grounding of all equipment, such as compressors, vacuum pumps, catalytic converters, monitoring equipment, etc., is required to prevent the possibility of electrocution. Equipment that is outfitted with automatic ground fault protection should be used whenever available.

Movement of chemical contaminants resulting from IAS activity must be strictly controlled. Proper IAS/SVE system design, layout, installation and operation are required to prevent spreading of contaminants, migration of contaminants into buildings, or fugitive emissions to the atmosphere. All NAPLs should be removed prior to the startup of an IAS system. A properly designed SVE system with vapor treatment is generally operated prior to the startup of the IAS system. A comprehensive site survey should be conducted to identify any buried utilities that are present that could serve as possible conduits for gas migration. If present, such utilities should be isolated from the IAS/SVE system via interceptor wells or trenches.

If flammable gases are being vented from the soil by the SVE system, it is possible to approach LELs in the pipe network without dilution. Care should be taken to provide dilution valving at the wellheads so vapor mixtures within the piping above the surface is well below the LEL.

5.5.11 Specification Development

The following information on the selection of air compressors and piping materials is provided only as an initial guide. To prevent injury to personnel and damage to equipment, always consult manufacturers concerning the proper application of their products.

A pilot test using a portable air compressor is generally conducted to determine site-specific pressure and flows. Typical over-pressure and flows are 34.5 kPa (5 psi) and 1.7 m^3/hr to 17m^3/hr (1 to 10 cfm), respectively (see Section 5.5.9 for calculation of maximum pressure to avoid soil rupture and Table 5.32 for sizing information).

Air compressors are typically quite noisy and if they are to be near residential areas they should be located in enclosures outfitted with noise abatement equipment and insulation. Air compressors can also generate significant heat; therefore, it is necessary to use piping material that is compatible with expected discharge pressures and temperatures. This is often accomplished by using several lengths of metal piping to allow for heat transfer and system cooling before coupling to piping made of polymeric materials.

Air compression leads to the production of water in the compressor receiver tank and manifold lines. Therefore, air tanks should be drained regularly to prevent condensate buildup. It may be necessary to winterize the compressor system and heat trace exposed piping to avoid system icing and blockage.

Only continuous-duty, oil-less air compressors should be used. Most commonly available compressors do not meet these specifications. Oil-less compressors are necessary to avoid introducing hydrocarbons to the aquifer. Rotary-vane pumps or regenerative blowers can be used only when low air pressures (i.e., up to 69 kPa [10 psig]) are required. Rotary-lobe blowers can be used for sparging sites when air pressures do not exceed 103.5 kPa (15 psig). Reciprocating compressors are generally required for IAS pressures in excess of 103.5 kPa (15 psig). Reciprocating compressors can generally achieve over 621 kPa (90 psig) pressures and often use Teflon® components to avoid the use of lubricants. Other types of compressors (i.e., rotary screw) can be used if provisions are made to keep hydrocarbon lubricants from entering the air stream.

Table 5.32
Typical Air Sparging System Design and Operational Parameter Specifications

Parameter and range	Most often used value (no. of sites)	Second-most often used value (no. of sites)	Third-most often used value (no. of sites)	Total number of sites
Screen length	0.61 m	0.91 m	1.52 m	
0.15 to 3.05 m	(2 ft)	(3 ft)	(5 ft)	
(0.5 to 10 ft)	16 sites	8 sites	7 sites	40
Well diameter	5.08 cm	10.16 cm	2.54 cm	
2.54 to 10.16 cm	(2 in.)	(4 in.)	(1 in.)	
(0.35 to 18.2 psi)	17 sites	7 sites	5 sites	37
Overpressure	2.41 to 34.45 kPa	34.5 to 68.90 kPa	68.90 to 103.35 kPa	
2.41 to 125.67 kPa	(0.35 to 5 psi)	(5 to 10 psi)	(10 to 15 psi)	
(0.35 to 18.2 psi)	14 sites	9 sites	5 sites	31
Well screen depth below water table	1.52 to 3.05 m	3.05 to 4.57 m	0.61 to 1.52 m	
0.61 to 8.08 m	(5 to 10 ft)	(10 to 15 ft)	(2 to 5 ft)	
(2 to 26.5 ft)	10 sites	8 sites	6 sites	31
In situ sparging flow rate	2.21 to 8.50 m^3/hr	8.50 to 16.99 m^3/hr	25.48 to 33.98 m^3/hr	
2.21 to 67.96 m^3/hr	(1.3 to 5 cfm)	(5 to 10 cfm)	(15 to 20 cfm)	
(1.3 to 40 cfm)	16 sites	9 sites	5 sites	49
In situ sparging pressure	34.45 to 68.90 kPa	68.90 to 103.35 kPa	137.80 to 172.25 kPa	
24.11 to 172.25 kPa	(5 to 10 psi)	(10 to 15 psi)	(20 to 25 psi)	
(3.5 to 25 psi)	17 sites	8 sites	6 sites	40
(SVE ROI) (IAS ROI) ratio	1 to 2	0.16 to 1	3 to 4	
0.16 to 7.42	12 sites	6 sites	3 sites	26

Source: Marley and Bruell 1995

In all cases, compressor air inlets should be located to avoid the introduction of airborne contaminants. Therefore, inlets should not be located within service garages or in close proximity to SVE stacks.

The selection of piping materials depends upon the site-specific operating conditions, including gas pressures, gas temperatures, ambient temperatures, potential for shock, and chemical compatibility. Pipes that are 2.5 to 5 cm (1 to 2 in.) in diameter are generally more than sufficient to carry air flow rates of 3.4 to 17 m^3/hr (2 to 10 scfm). While smaller pipes may be used, head losses associated with smaller pipe diameters and smaller fittings should be carefully considered.

Technically, Schedule 40 PVC is often rated for operating temperatures up to 60°C (140°F) and nonshock operating pressures for liquids in excess of 690 kPa (100 psig). However, air is a compressible fluid, and striking a blow to any pressurized PVC pipe could potentially cause the pipe to burst, possibly resulting in injury. Therefore, when a sparging air compressor discharge is at pressures greater than 276 kPa (40 psig) or at temperatures greater than 38°C (100°F), the use of steel pipe that has been protected from corrosion or galvanized steel piping is recommended. When a sparging air compressor discharge is at pressures less than 276 kPa (40 psig) and at temperatures less than 38°C (100°F), the use of Schedule 40 or 80 PVC pipe should be investigated. Threaded fittings sealed with Teflon® tape are preferred over glued fittings on pressurized IAS plastic pipe lines to prevent the introduction of solvents associated with glues into the groundwater system.

Well screens used for IAS systems generally use 0.25- to 0.5-mm (0.01- to 0.02-in.) slots. Microporous bubblers have also been used at IAS sites (Kerfoot 1995). Typical design parameters from the API-IAS Database are presented in Table 5.32.

5.5.12 Cost Data

Based on pilot- and full-scale applications of this technology, the total cost of source area biosparging generally ranges between $13 and $55 per m^3 ($10 and $42.30 per yd^3) of soil remediated. The upper range of general cost can increase to $80 per m^3 ($61.50 per yd^3) when an SVE vapor capture/treatment system is required. On larger sites (greater than 10,000 m^3 [13,080 yd^3] of impacted soil), costs of less than $13 per m^3 ($10 per yd^3) can be achieved. On small sites (less than a few hundred m^3 of impacted soil), costs in excess of $80 per m^3 ($61.50 per yd^3) are common because of the fixed costs involved in project planning, permitting, drilling wells, and installing the required system equipment. Table 5.33 provides typical costs for

Table 5.33
Typical Full-Scale Sparging System Cost[a,b]

	Cost Element	Unit Cost ($)	No. of Units	Cost ($)
Pilot Testing & System Design	Conduct Pilot Testing	20,000	Lump Sum	20,000
	Data Analysis/Full-Scale Design	20,000	Lump Sum	20,000
Full-Scale Installation	Install SVE Blower and Off-Gas Treatment Systems (300 scfm)	100,000	Lump Sum	100,000
	In situ Sparging System (150 scfm)	20,000	Lump Sum	20,000
	Electrical	10,000	Lump Sum	10,000
	Manifold & System Installation	125,000	Lump Sum	125,000
	Start-up Report	8,000	Lump Sum	8,000
	Annual O&M Expenses	32,500	2 Years	65,000
Posttreatment Cost	Posttreatment Soil and Groundwater Sampling	12,000	Lump Sum	12,000
	Site Closure Report	3,000	Lump Sum	3,000
Total Project Cost[c]		**33.3 (24.6)[d]**	**11,500m^3**	**383,000**

[a]Costs are for large sparging site with >11,000 m^3 of impacted soil.
[b]System includes an SVE component with off-gas controls. Significant SVE component costs have been separately labelled.
[c]CERCLA sites will generally cost up to three times the projected expenditures due mainly to the additional deliverables and analytical and QA/QC measures required.
[d]Cost in parentheses is without major SVE components.

planning, design, installing, and operating a full-scale sparging system for a large site (11,000 m^3 [14,387 yd^3]) impacted by petroleum hydrocarbons.

5.5.13 Design Validation

Over the first few months of operation, the performance of the IAS system should be monitored to validate the design parameters. It is important to detect, quantify, and, if necessary, correct flaws in the system that may arise from unforeseen environmental factors, limited historical/background information, etc.

Discussions on many of the monitoring techniques used to validate the design are presented in Section 5.5.2. Monitoring individual well performance is recommended. Comparisons with the design operating pressures and flows will provide the necessary data to balance the system and ensure optimal distribution of flow across the target remediation area.

Further, monitoring of groundwater quality (as described in Section 5.5.18) will allow validation of the design ROI. It is important to ensure that monitoring points are located at discrete vertical intervals (it is recommended that vertical intervals be 0.3 to 0.6 m [1 to 2 ft] in length) and in areas most likely to be least impacted by the sparging system (e.g., midway between sparge points or in a lower permeability strata). The groundwater quality data in conjunction with the SVE discharge data (or vadose zone monitoring data if no SVE system is used) should be used to evaluate the projected rates of volatilization/biodegradation of the contaminants at the site.

5.5.14 Permitting Requirements

Permitting requirements vary significantly on a state-by-state basis. Generally, permits may be required for construction and operation of a remedial system, for discharge of any offgases from a remedial system, and where specialty gas injection (e.g., methane) is proposed. Local authorities should be consulted for information regarding permitting requirements at a specific site.

5.5.15 Design Checklist

The following is a list of items that need to be addressed in the design and implementation of sparging technology for aquifer remediation at a given site:

- develop a geologic cross-section with contaminant distribution overlay;
- determine radius of influence of sparge well (provide reasoning);

- determine number of wells required;
- determine injection pressures and flow rates;
- determine pulsed or continuous injection (pulse interval?);
- define well details (superimposed on geologic cross-section):
  - screen length and diameter;
  - slot size/filterpack; and
  - screened interval;
- design Manifold:
  - type and size;
  - headloss calculations;
  - valving and instrumentation;
  - P&I diagram;
- develop equipment specifications;
- complete required permits; and
- develop design validation/system monitoring plan.

5.5.16 Design Implementation

Implementation considerations for in situ biosparging systems and associated components are provided in Sections 5.5.3, 5.5.7, 5.5.8, and 5.5.18.

5.5.17 Start-up Procedures

Extensive site definition and baseline measurements should be made to determine the extent and distribution of contaminants. All NAPL should be removed prior to the initiation of IAS to avoid spreading of contaminants. SVE systems, where required, should be operated first to remove any product and vadose zone contamination. These systems should be interlocked with the IAS system.

If any chemical adhesives were used in constructing the system, the volatiles from the manifold system should be purged by opening IAS wellheads and injecting air into the manifold lines and running the air compressor for a minimum of 10 minutes and up to 2 hours. A portable hydrocarbon "sniffer" should be used to determine when the lines have been purged. After purging the manifold lines (if appropriate), he following procedures should be implemented for each of the IAS well groups:

- Turn on the air source. Adjust the throttling valve from a lower pressure to the necessary pressure to attain the design air flow rate for the chosen well group. (Do not exceed the maximum recommended air pressure);
- Balance the flow to each well since each well may behave differently;
- Develop a flow versus pressure (F/P) curve for each well. The generated F/P curve allows determination of well flow rate based upon wellhead pressure measurements. This approach reduces the effort required during routine site measurements;
- After balancing the wells, verify the air compressor and manifold line pressure and total injection flow rate. Also, determine the agreement between total air compressor flow and the cumulative flow as measured at each of the wells. Any design deficiencies will be apparent at this time;
- Sample the SVE system inlet and exhaust streams and analyze each over the start-up period;
- Check for bubbling in piezometers at the site. If bubbling is observed, operators should install air-tight caps on these wells to prevent fugitive VOC emissions;
- Record periodic groundwater table measurements to document the site-specific impacts of operating the IAS well group on groundwater mounding/mixing; and
- If any positive subsurface air pressure readings and/or high levels of vapor-phase contaminants are measured in vadose zone monitoring points adjacent to buildings or other structures that may accumulate potentially hazardous vapors, system operators should immediately re-evaluate the operational parameters of the sparging system. Discontinue operation of the air sparging system if conditions are deemed unsafe.

5.5.18 Performance Evaluation

5.5.18.1 Operation Practices

Following system startup and balancing, two simple methods are available for responding to changing conditions:

- vary air injection rates per well; or

- vary pulse frequency and pulsed well groupings.

As part of the system evaluation, these two optimization methods should be explored to provide site-specific system enhancements over the first six months of system operation. If monitoring of the system suggests that certain impacted areas of the site are not being effectively remediated, incorporating additional sparge wells into the system — potentially, the most effective optimization strategy available once the system is installed — should be considered.

5.5.18.2 Operation Monitoring

Monitoring of various physical parameters associated with the IAS and SVE processes is necessary to ensure optimal system performance. Typically, IAS and SVE pressures and flow rates for the system are measured and recorded. Individual wells are also monitored to balance the system. Groundwater levels should be monitored to ensure that the SVE well screens *are not* submerged and that the IAS well screens *are* submerged. Additionally, groundwater levels can serve as an indicator of possible impacts of IAS and SVE activities on regional groundwater flows.

Previously, monitoring of various chemical parameters (e.g., DO levels) was used to determine ROI in relatively short evaluation periods (i.e., <1 day). Over longer time periods, monitoring of parameters, such as relative abundance of hydrocarbon-utilizing bacteria and measurements of hydrocarbon content in water samples is warranted. Typically, BTEX measurements in groundwater samples are conducted on a quarterly basis. However, the minimum monitoring frequency depends upon local regulatory agency requirements.

Contaminant removal rates can be monitored by observing the hydrocarbon content of the gases captured by the SVE system. When contaminant levels have dropped to non-detectable (ND) in the vapor phase, groundwater BTEX levels should then be monitored. Following several months of IAS, groundwater BTEX levels will also often show at non-detect levels. This is especially likely if measurements are made while an IAS system is still in operation or immediately after IAS activities have been terminated. However, after extended periods, a rebound in BTEX levels may occur. This may coincide with high groundwater levels in the spring and probably results from the mobilization of trapped NAPLS that were not within the zone of influence of the sparging system.

A review of 21 IAS sites revealed that rebound generally occurs within 6 to 12 months and in some cases can take as long as 16 months to develop

(Bass and Brown 1995). This study showed that IAS was especially effective at sites where there was a dissolved phase alone (i.e., an absence of NAPLs). When petroleum-based LNAPLs were present, such as in source areas, the highest incidence of rebound was observed. Petroleum- contaminated sites also exhibited a higher level of rebound than chlorinated solvent sites.

The efficacy of IAS is highly dependent upon: (1) the extent of contact of the injected air and the contaminated soil and groundwater; and (2) the magnitude of aquifer mixing. Therefore, rebound was minimized by adequate treatment times (>10 months for source areas and 4 to 6 months for dissolved plumes), high air flows (>17 m^3/hr/well [>10 scfm/well]), close well spacing (<6 m [<20 feet]), and a high sparge well density covering the entire area (Bass and Brown 1995).

5.5.18.3 Quality Assurance/Quality Control

See Section 5.5.13, Design Validation.

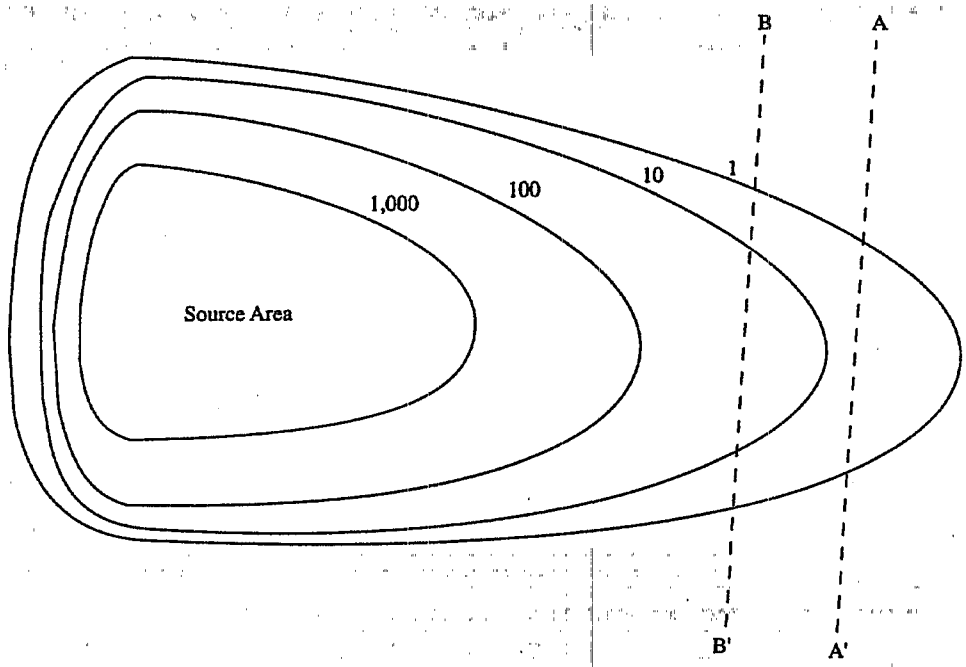
5.6 Emerging Technologies — Permeable Migration Barriers

Traditional methods of source area remediation are increasingly being replaced or augmented by emerging and recently-established technologies. In the last several years, alternatives for addressing downgradient migration or controlling contaminant plumes have also gained attention. Traditional methods of preventing migration (i.e., slurry walls and pump-and-treat systems) have been effective, but are expensive. Alternative approaches of plume containment include intrinsic bioremediation (Section 5.3) and migration barriers. Migration barriers can consist of air sparging wells, wells containing slow-release oxygen compounds (or other electron acceptors), and interceptor trenches.

5.6.1 Biological Barriers

The primary goal of biological migration barriers is to reduce the concentrations of groundwater contaminants at locations downgradient of the barrier. The barrier is placed to intercept the groundwater contaminant plume as shown in Figure 5.35. Placing the barrier along transect A-A' increases the potential for preventing contaminants from passing through the barrier as compared to placing the barrier further upgradient (e.g., along Transect B-B').

Figure 5.35
Migration Barrier Concept



In one sense, biological barriers have been used longer than any other method. As demonstrated several years ago by studies at a wood treatment facility in Conroe, Texas, natural biodegradation can be the controlling factor with respect to how large a plume grows (Wilson et al. 1985). At many sites, natural attenuation has controlled or limited migration during the period prior to discovery of the contamination and during the often lengthy period of site investigation through remedy implementation.

Recently, intrinsic bioremediation (as discussed in Section 5.3 of this monograph) has been adopted as the solution for many sites. Several well-documented studies identifying the factors controlling natural attenuation, pressure on responsible parties to control costs, and increased awareness of regulatory agencies concerning costs associated with UST reimbursement programs have all contributed to the rapid increase in use of this approach.

Intrinsic bioremediation will always play an important and appropriate role in site remediation. However, as with other technologies, it will not always be the most appropriate technology after all factors are considered.

For instance, at many service stations, the annual costs for monitoring and reporting may range from $10,000 to $25,000 per year. Under the right conditions, some active form of remediation may have a lower life-cycle cost if active remediation can be completed within several months for less than the cost of one or two years of monitoring and reporting (Norris, Dey, and Shine 1993).

At sites where intrinsic bioremediation cannot control the plume or where property boundary, receptor locations, or other considerations dictate that the edge of the plume not be allowed to extend as far as it does under intrinsic bioremediation conditions, an engineered system is appropriate.

Engineered biological migration barriers take many forms. These include:

- air sparging wells;
- wells containing slow-release oxygen compounds; and
- interceptor trenches with sparged air or some other method of adding an electron acceptor.

All of these systems create a zone containing elevated levels of one or more electron acceptors (usually oxygen) through which the contaminated groundwater must flow. In addition, air sparging results in physical removal of VOCs.

Initially, it was thought that the point of compliance should be immediately downgradient of the barrier. This led to the practice of installing barriers at locations along transect A-A' where the concentration of the biodegradable compounds was fairly low. At this point, the electron acceptor flux provided by the barrier would be sufficient to reduce the constituents of concern to below regulatory levels within a short distance of the barrier. While this approach has merit, it does not give full credit to the natural assimilative capacity of aquifer systems and tends to be an overly conservative approach.

If the barrier is located relatively close to the source area (e.g., along transect B-B'), the contaminant flux may overwhelm the electron acceptor flux from the barrier, and dissolved biodegradable compounds will emerge from the downgradient edge of the barrier. However, the mass of biodegradable constituents will be diminished downgradient of the barrier compared to what it would have otherwise been. As a result, the demand on the aquifer's natural assimilative capacity will be lessened. This will result in compliance levels being achieved at points closer to the source than would occur without the barrier.

Placing the barrier further upgradient may actually improve the efficiency of the barrier by introducing the electron acceptor flux where it has the greatest opportunity to be consumed by beneficial reactions.

Further, since the plume may expand in the downgradient direction, a smaller barrier (shorter trench or fewer wells) might be required. In the following sections, three types of biological migration barriers are discussed and corresponding results of laboratory and field tests and modeling are provided where available.

5.6.2 Air Sparging Barriers

Biosparging is the basis for one approach to plume containment. A treatment zone or curtain is created by introducing air into the solute plume (Gudemann and Hiller 1988). This provides VOC removal by mechanical stripping and subsequent migration of the vapor phase into the vadose zone, where attendant biological degradation of the contaminants in the presence of introduced air and possibly nutrients can take place. Degradation may also occur in the sparged groundwater.

Several configurations of the treatment curtain concept can be constructed. Basically, all of the approaches involve the introduction of a gas, usually air, into the saturated zone below the deepest level of the plume. The subsequent upward migration of the air strips the volatiles from solution converting them to the vapor phase. Once in the vapor phase, the contaminants migrate upward to be collected by vapor extraction pipes or wells or, alternatively, treated in situ by the addition of amendments (primarily nutrients) to enhance their in situ vapor-phase degradation (bioventing). One fortuitous, but confounding, factor in the engineering design of such installations is the potential bioenhancement effects of the air introduction itself. Biodegradation and stripping will occur simultaneously but at different rates, depending upon several geophysical and chemical factors of the aquifer system. This situation represents a basic and fundamental trade-off between the optimal rate of gas flux required in the saturated zone to reduce the solute concentrations to the design level and the proper residence time or retention time required in the vadose zone (and saturated zone) to achieve sufficient in situ biodegradation of the stripped vapors so that sufficiently low emission levels at the site are achieved. This is a conflicting trade-off, since a higher rate of gas flux is normally needed to strip the volatiles, while a lower flux rate may be required to yield sufficient retention times to achieve desired metabolic action by the indigenous soil organisms.

5.6.2.1 Background

In situ stripping by gas (air) injection into the saturated zone, both alone and combined with soil venting technology, has successfully removed dissolved hydrocarbons from groundwater. Applications usually require

extensive arrays of sparge and vent wells and secondary treatment of recovered soil vapors before discharge, as described in detail in Section 5.5 of this monograph. These systems are designed primarily for treatment of the source area. The use of an air-injection curtain, a continuous linear array of injection points transecting a contaminant plume, for interdiction of dissolved hydrocarbon, could reduce construction and operating costs compared to either more extensive source area treatment or pump-and-treat systems. Focusing on bioremediation rather than physical removal of VOCs could further reduce the construction and operating costs.

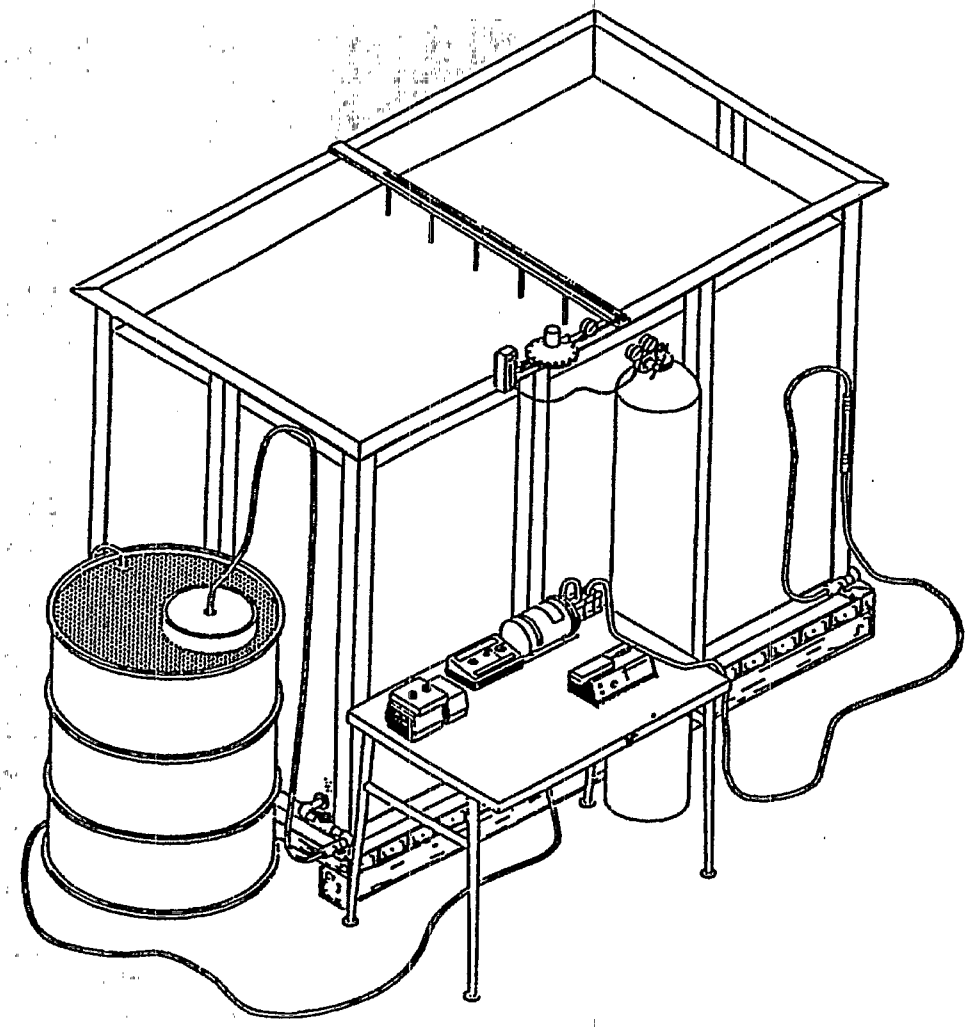
To successfully apply the air injection curtain technology for in situ plume interception and treatment, several design parameters need to be determined. They include the air flow rates required to remove the dissolved contaminants from the water; the location, number, and depth of the injection points; the oxygen loading rates required for biological degradation of the contaminants; and the relationship of these parameters to in situ aquifer properties including water chemistry, groundwater velocity, and soil characteristics. Quantifying these items enables the proper design of the air injection wells required for the curtain, and optimizes the field-scale application of this technology.

5.6.2.2 Bench-Scale Tests

In 1991, the U.S. Air Force funded a prototype demonstration project to explore the use of treatment curtains or zones to contain groundwater plumes. The demonstration project described here included design, construction, and operation of a prototype aquifer model to determine the effects of variations in design criteria on air injection and interdiction curtain performance. A typical sand aquifer with simulated groundwater velocities of 0.3 and 1 m (1 and 3 ft) per day was simulated in a 1.7 m (5.5 ft) long by 1 m (3 ft) wide by 1.3 m (4 ft) high Plexiglas® model (Figure 5.36). Several tests were performed using the prototype aquifer model. Bromide tracer and toluene volatilization studies were used to hydraulically characterize the aquifer physical model. Following these characterization tests, air sparging studies were conducted with and without toluene addition and with sodium azide, a biological inhibitor. Biodegradation was clearly present when the biological inhibitor was not in the prototype aquifer. The concentrations and distributions of toluene and DO were the main performance indicators used to evaluate the performance of this bench-scale test unit.

Approximate steady-state conditions for toluene were usually reached within 3 days under abiotic conditions (Figure 5.37). The baseline conditions were satisfactorily reached between sparging at each air flow rate event.

Figure 5.36
Bench-Scale Aquifer Model



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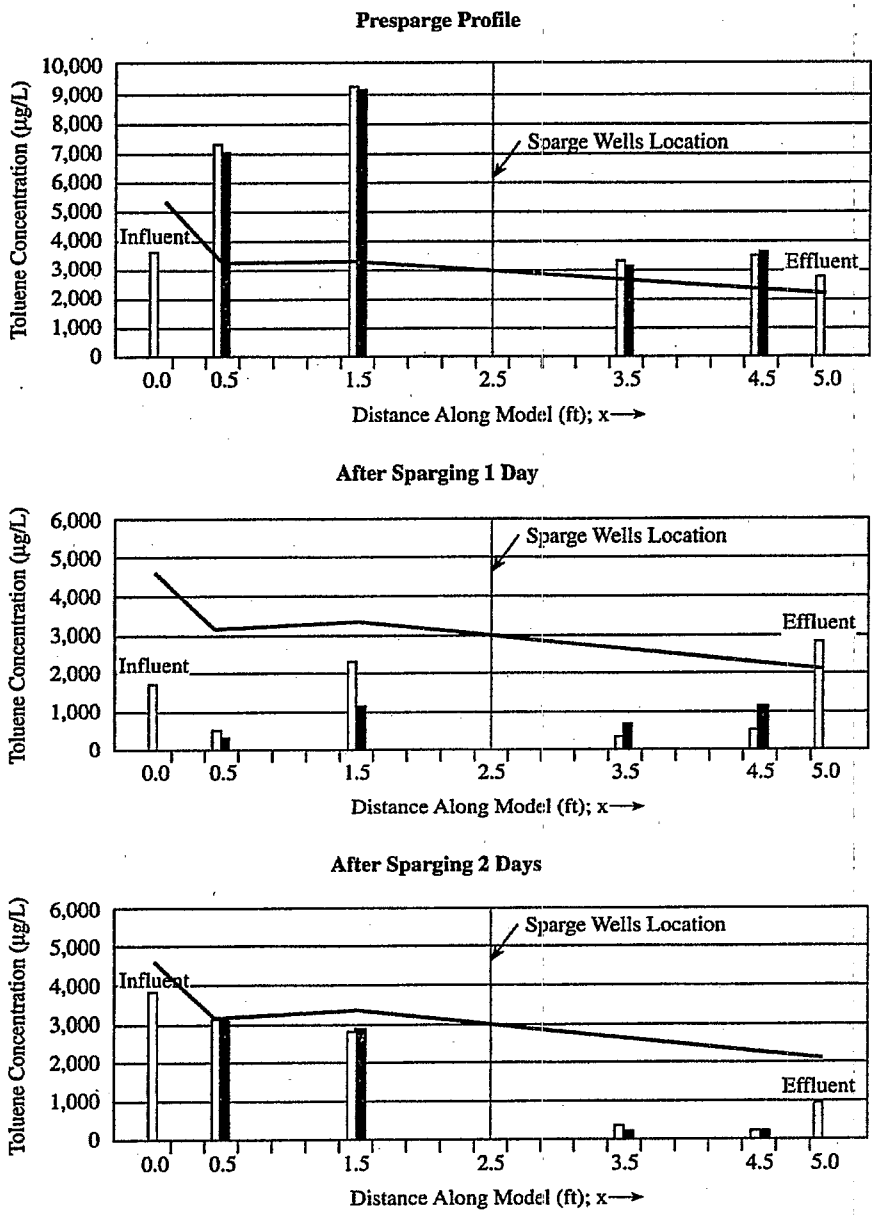
Methodology. Aquifer model characterizations were compared under five operating conditions to investigate the role of groundwater velocity, air sparging rate, and DO concentration and spatial distribution in affecting sparge interdiction curtain performance. The five operating conditions and their parameters were:

Figure 5.37
Toluene Concentration Profile Sparging at an Air-to-Water Ratio of 11



Row 1
Row 2
Row 3
Row 4
Approximate SS

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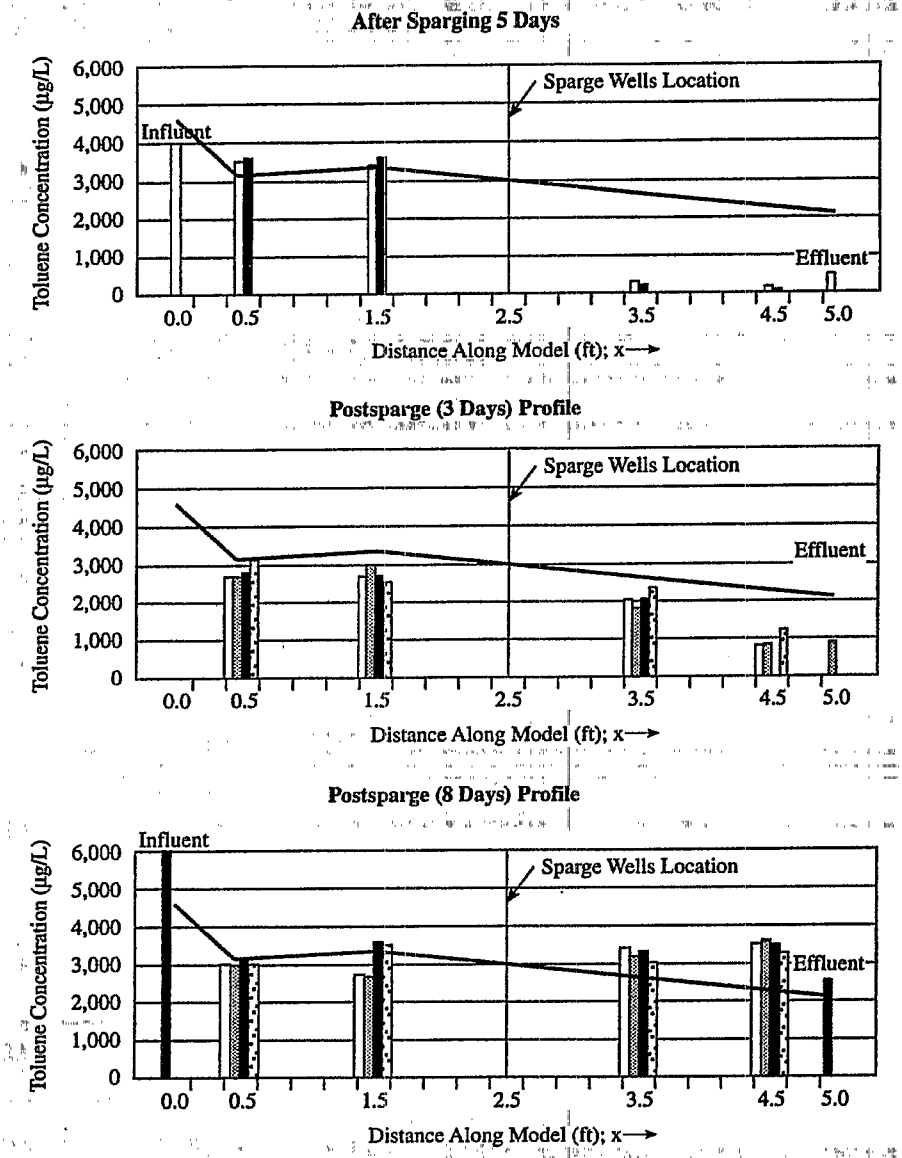
Figure 5.37 cont.
Toluene Concentration Profile Sparging at an Air-to-Water Ratio of 11



Row 1
Row 2
Row 3
Row 4
Approximate SS

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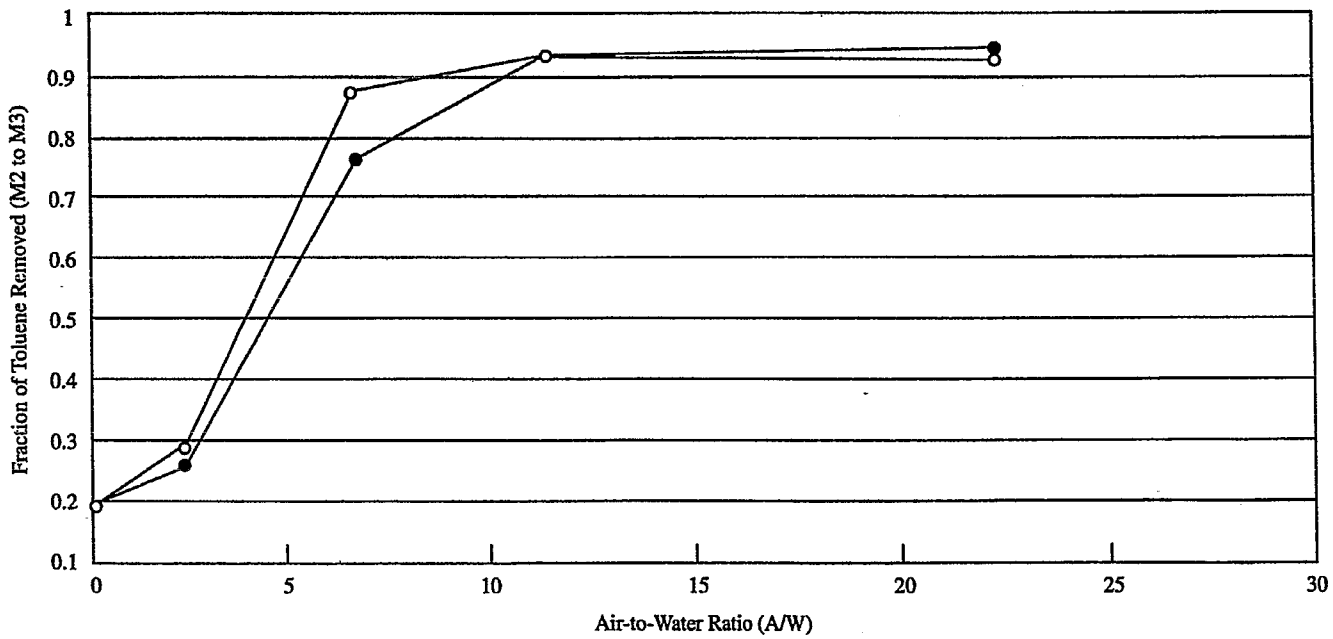
1. A simulated groundwater velocity of 1 m (3 ft) per day, no toluene addition, and sparging at various air flow rates to examine effects on DO concentrations;
2. A simulated groundwater velocity of 0.3 m (1 ft) per day, no toluene addition, and sparging at various air flow rates to examine the effects on DO concentrations;
3. A simulated groundwater velocity of 1 m (3 ft) per day, toluene addition, no inhibition of biological activity, and no sparging to establish pre-sodium azide addition baseline conditions;
4. A simulated groundwater velocity of 1 m (3 ft) per day, toluene addition at two concentrations, inhibited biological activity conditions, and no sparging to establish post-sodium azide addition, or presparge, baseline conditions; and
5. A simulated groundwater velocity of 1 m (3 ft) per day, toluene addition, inhibited biological activity conditions, and sparging at various air flow rates to examine effects on hydrocarbon and DO concentrations.

Baseline measurements were obtained by water sampling at approximate steady-state conditions before, during, and after operating the typical model at each condition listed above. Influent and effluent aqueous toluene concentrations measured under several conditions were used to conduct a mass balance on toluene.

Early observations revealed that the toluene disappeared rapidly after injection into the model aquifer even before sparging, due either to significant biological activity or volatilization. To examine and isolate the physical effects of air sparging on toluene removal, the aquifer model was treated with sodium azide to discourage biological activity. The unsaturated zone was eliminated by raising the water table to prevent the biodegradation of toluene in the vapor phase. The effects of the biological inhibitor on the model toluene concentrations were quantified and recorded for comparison to non-inhibited conditions where the biodegradation effects were clearly observed.

Results of Air Sparging Tests. Results of the air sparging studies under abiotic conditions verified that toluene removal was enhanced to 90% as it passed the air sparging interdiction curtain at air-to-water ratios of 11 and 22. A minimum air-to-water ratio of approximately 10 was required to effect the 90% removal of toluene as it moved through the interdiction curtain (see Figures 5.37 to 5.39). Subsequent increases in the air-to-water ratio did not yield increased toluene removal.

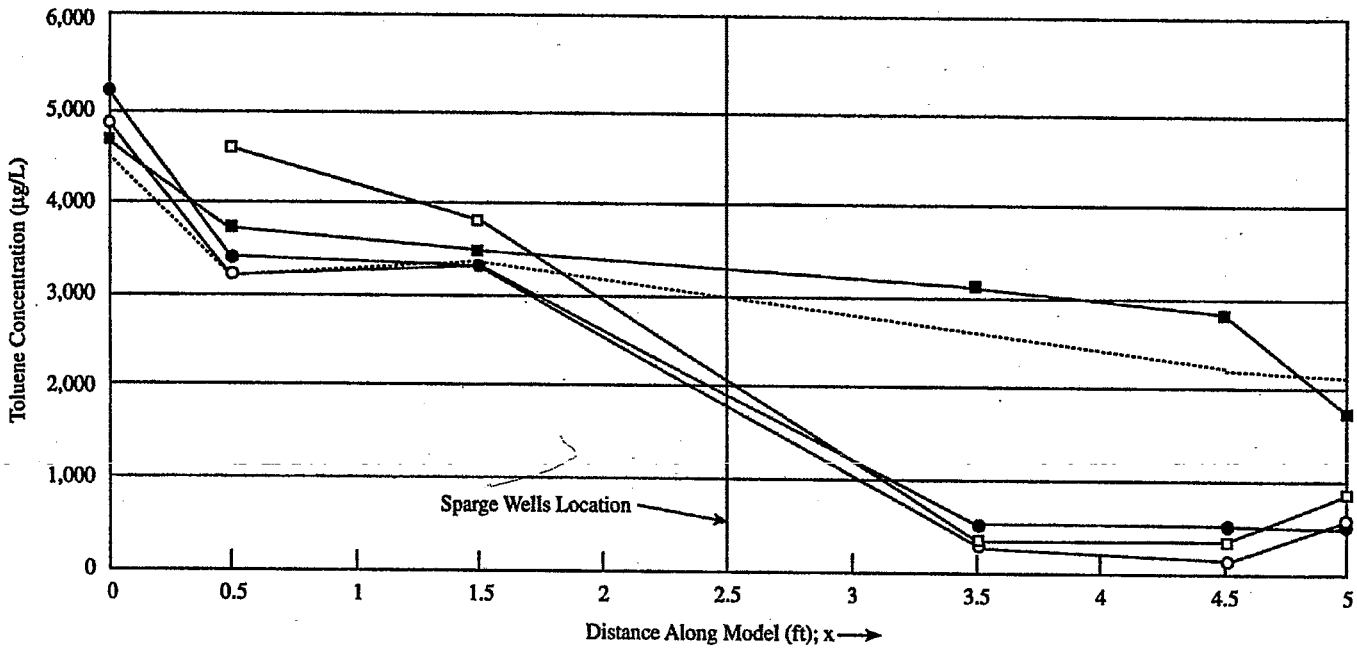
Figure 5.38
Effect of Air-Water Ratio (Volume/Volume) on Toluene Removal



● M3/Steady State M2
○ M3/M2
At 3 days after sparging initiated

Reproduced courtesy of Traverse Group (1993)

Figure 5.39
Effect of Air-Water Ratio (Volume/Volume) on Toluene Concentrations Along Flow Path



■ 2.2 A/W
● 6.6 A/W
○ 11 A/W
□ 22 A/W
----- Approx. SS
Average of Rows 1 and 3 each distance; after sparging 3 days

Reproduced courtesy of Traverse Group (1993)

Even though these air sparging studies were conducted under abiotic conditions, toluene removal was significantly enhanced by relatively low air-to-water ratios. There appears to be a limiting air-to-water ratio that can produce a certain level of treatment under abiotic conditions. Removal by biodegradation must be enhanced by a prescribed level of oxygen dissolved in the water; the air flow required to deliver the optimum amount of oxygen could prove to be greater than the minimum air-to-water ratio for enhanced volatilization alone. However, the oxygen delivered at the minimum air-to-water ratio to effect enhanced volatilization was theoretically sufficient to degrade the remaining 10% toluene. If this holds true for field-scale applications, retention times (controlled by sparge well depth and soil characteristics) must be recognized as a critical parameter in specifying the design air-to-water ratio.

Downgradient DO concentrations increased with each successive increase in the air-to-water ratio. However, DO movement through the model appeared retarded under biologically-inhibited conditions, leading to the premise that "trapped gas pockets," possibly augmented by sodium azide, could have continually leaked DO into the groundwater.

Summary of Air Sparging Barrier Results. The feasibility of air injection curtains as an interdiction method was demonstrated in laboratory-scale tests. Air sparging was effective as a migration barrier even under abiotic (worst-case) conditions. Approximate steady-state conditions with respect to the toluene profiles were reasonably confirmed, which allowed a relative mass balance on toluene to be performed.

The minimum air-to-water ratio required to achieve an enhancement of toluene loss of 90% through the interdiction well field in the aquifer model was 10. Subsequent increases in the air-to-water ratio did not increase toluene removal. The enhanced volatilization capability of the interdiction field appeared limited by the depth of the air injection wells in the laboratory-scale model.

The air injection DO profiles showed that DO increased downgradient of the injection wells in sandy soil, with a groundwater velocity of 1 m (3 ft) per day under abiotic conditions. Under these conditions, the size and location of the biodegradation treatment zone depended on groundwater velocity and the degree of potential biological activity inside the treatment zone, which would have depleted the DO under biotic (field) conditions.

Several criteria were identified for the design of air injection interdiction curtains. These include the minimum air-to-water ratio required to adequately remove contaminants, the depth of the air injection points to ensure

optimum removal of volatile contaminants, and the spatial location of the air injection points to maximize the biological treatment zone and prevent contaminants from passing through the injection well field.

The identified operational problems include increased surface monitoring as compared to soil venting systems; possible fouling of the injection wells (both inorganic and biofouling) that could affect aquifer characteristics; and the occurrence of channeling, that may be increased at higher air flow rates.

5.6.2.3 Field-Scale Systems

In the last few years, numerous air sparging-based migration barriers have been employed. The following examples were implemented by Remediation Technologies Inc. (RETEC). One example is a site where the remediation of the release of 150,000 L (40,000 gal) of unleaded gasoline to the soil and groundwater at an operating marketing terminal is ongoing. The site is situated on river alluvium composed of silt, sand, and gravel deposits. The unconfined aquifer that was affected by the release has a water table that fluctuates between 7 and 10 m (20 and 30 ft) below the ground surface because of regional irrigation.

A previously-installed groundwater containment system was not effective at recovering free-phase product. Therefore, soil venting was selected to remediate the subsurface contamination in the vadose zone above the water table and to remove the immiscible free-phase product on the water table. The soil venting system consists of three main components: (1) soil venting wells; (2) a vacuum blower and piping; and (3) a thermal oxidizer air treatment system. Permanent soil gas monitor probes were installed throughout the area to monitor organic vapors, vacuum, and oxygen levels.

A microbial fence in situ bioremediation system was installed to contain the dissolved hydrocarbon plume by establishing a zone of enhanced biodegradation activity at the leading edge of the plume. A total of 14 air injection wells were installed to provide the oxygen necessary to stimulate aerobic hydrocarbon biodegradation. An air compressor delivers air to the air injection wells at a design flow rate of 5 m^3/s (3 cfm) per well.

Soil venting costs included $140,000 for construction, $15,000 for compliance and air permits, and $5,000 per quarter for air sampling and reporting. Construction and startup of the microbial fence system cost $90,000, which included operator training and preparation of a comprehensive O&M manual.

In the first 19 months of operation, the soil venting system removed the equivalent of 61,000 L (16,000 gal) of gasoline vapor. Concentrations of BTEX in the groundwater downgradient of the microbial fence have

consistently been below detection limits, indicating that the microbial fence is effectively containing the dissolved hydrocarbon plume. The remediation strategy has achieved a faster rate of product recovery than could be obtained through pumping, without excavation or disruption of existing facilities or operations. The microbial fence system, in conjunction with source area treatment, has successfully halted plume migration without the need for groundwater extraction, expensive aboveground treatment, or the need for a NPDES permit.

A second example involves the design and construction of an in situ bioremediation system to eliminate off-site migration of oil at a refinery. The refinery, along with a neighboring facility, were required by court order to cease off-site migration of oil within 1 year. Off-site migration included contaminated groundwater and oil seeps to a stream. To comply with the order, the refineries cooperatively installed a product barrier wall and diverted the stream to a channel capable of handing a 10-year flood event. Additional groundwater pumping wells were installed to locally reverse the groundwater gradient. A biosparging/soil venting system was designed to remove hydrocarbon constituents from soils and groundwater and to prevent the off-site migration of dissolved hydrocarbons along the former stream channel downgradient of the product barrier wall. Approximately 0.4 km (0.25 mi) of former stream channel was targeted for remediation and plume containment.

The system consists of 78 biosparging wells to inject air and provide oxygen to the saturated zone. The injection air is produced by a 50-hp compressor at a total rate of 5.8 m^3/min (180). The soil venting portion of the system includes over 310 m (1,000 ft) of horizontal extraction wells and 11 vertical vapor extraction wells and a combined flow of 25.6 m^3/min (800 cfm) from a 50-hp positive displacement vacuum pump. The exhaust air is treated with a catalytic oxidizer capable of achieving 99% removal efficiency at a lower operating cost than normal thermal treatment.

Concurrent with the design, a treatability study was conducted to optimize the biodegradation rates at the site. This study determined that nitrogen availability would limit the rate of biodegradation under field conditions. Consequently, a system was incorporated to periodically add low concentrations of nutrients to existing wells within the area of the biosparging system. Data have shown that the system reduced hydrocarbon constituents to below action levels and has effectively halted the migration of dissolved contaminants.

At a third site, various alternative technologies were evaluated for groundwater extraction and treatment to control the migration of dissolved organic

constituents at a chemical plant. Based on the contaminants of concern and the geological/hydrogeological conditions at the site, an in situ microbial barrier (microbial fence) was selected using biosparging as a potentially effective, low-cost approach to plume containment.

The project was initiated by performing laboratory treatability studies to determine the oxygen and nutrient requirements of naturally-occurring microorganisms in the saturated zone soils to maximize the biodegradation of phenolic compounds in the groundwater. The treatability study demonstrated that the constituents of concern could be effectively biodegraded by the microorganisms at the site and also demonstrated that the rate of contaminant biodegradation was increased through the addition of supplemental inorganic nutrients.

Based on the results of the treatability study, a detailed work plan for the pilot-scale in situ microbial barrier system was prepared. A detailed engineering design for the system was completed, specifying three groundwater aeration wells, an array of nested monitoring wells upgradient and downgradient of the line of aeration wells, and vapor probes to assess the effectiveness of the groundwater aeration system. The system is designed to deliver air to each aeration well using an oil-free air compressor at a rate of up to 0.1 m^3/min (3 cfm) (actual air injection rates are less than 0.03 m^3/min [1 cfm]). Inorganic nutrients, consisting of a blend of ammonium chloride and phosphate salts, are supplied through periodic addition to an upgradient injection well. A bromide tracer study was performed to verify the rate of groundwater flow through the aeration zone.

During the first 2 months of system operation, concentrations of VOCs in the groundwater within the treatment area were reduced by an average of 84%, while SVOCs, primarily phenolic compounds, were reduced by an average of over 85%. The pilot study is expected to operate for 12 months. If the pilot system is effective at halting the downgradient spread of the dissolved contaminant plume, a full-scale system will be designed for implementation along the downgradient property boundary, eliminating the use of groundwater recovery for plume containment. In situ bioremediation techniques may then be applied to remediate contaminant source areas within the plant boundaries. The application of this innovative in situ bioremediation process is expected to save the client several million dollars during the course of the remediation program as compared to a conventional pump-and-treat approach.

5.6.3 Oxygen Release Compound Barriers

Passive migration barriers can consist of one or more rows of wells containing an oxygen release compound (ORC) as shown in Figure 5.40. The wells are placed perpendicular to the direction of groundwater flow. The release of oxygen into the aquifer creates a zone of increased oxygen through which the contaminated groundwater must flow.

The distribution of oxygen around the well is controlled by diffusion and dispersion. To serve as a barrier to contaminant migration, the wells must be closely spaced. Depending upon site conditions, the spacing might range from 1 to 2 m (3 to 6 ft).

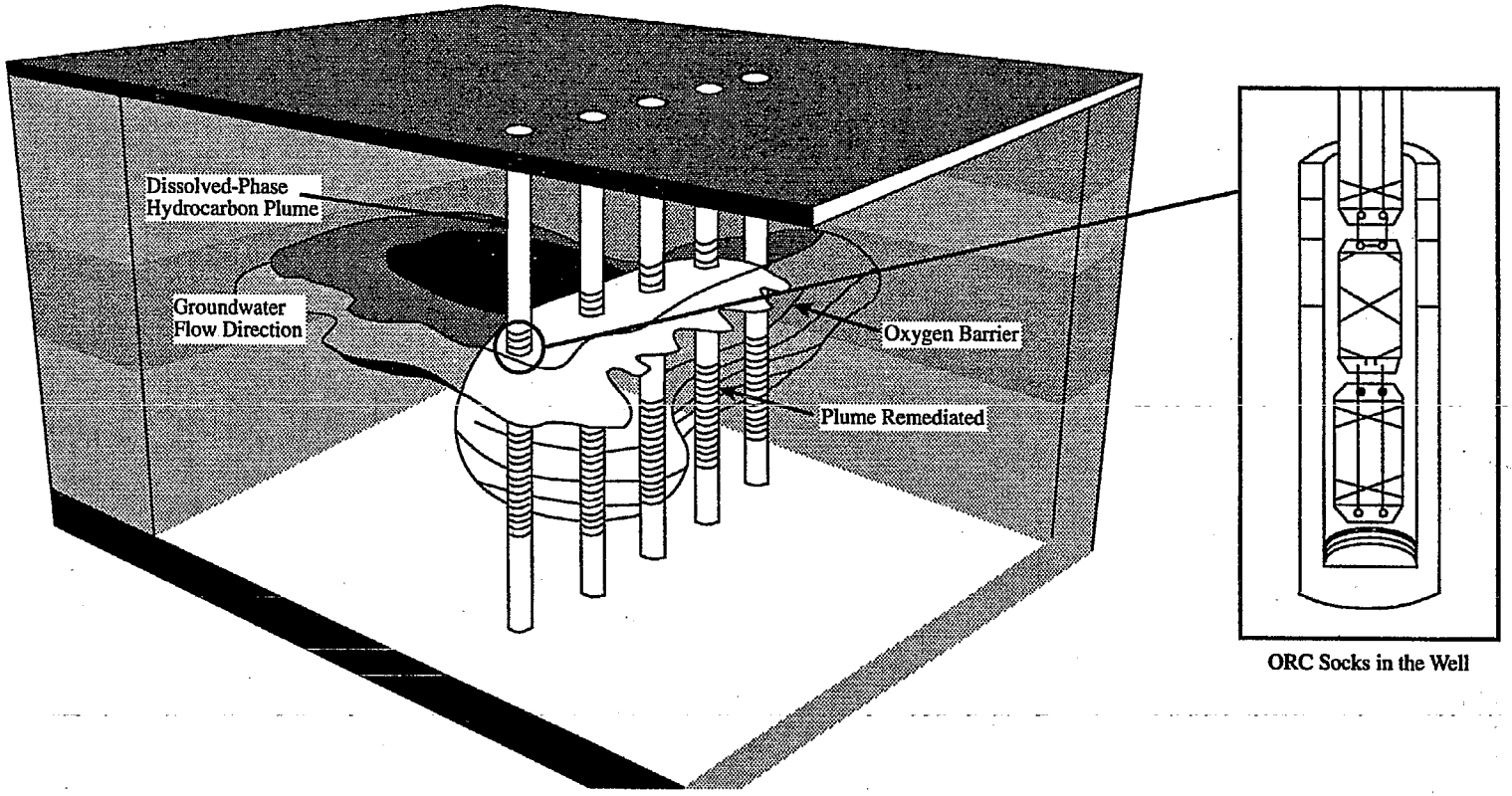
The rate at which oxygen must be supplied depends upon the contaminant mass throughput which is the product of the average contaminant concentration and the groundwater flow through the treatment zone. The migration barrier must release oxygen at a rate that equals or exceeds the demand based on the reduction in contaminant mass that is required to meet the clean-up criteria.

The rate of oxygen release depends upon the mass of the ORC and the oxygen release profile (e.g., the rate of conversion of a given mass of ORC to a given mass of oxygen).

Various derivatives of hydrogen peroxide have been evaluated for use as migration barriers or for other biodegradation processes (including soil cells) where a continuing source of oxygen is required for aerobic biodegradation processes. These peroxide compounds include magnesium peroxide, calcium peroxide, sodium carbonate peroxide, and urea peroxide. Magnesium peroxide and calcium peroxide have oxygen release profiles appropriate for migration barriers. Sodium carbonate peroxide and urea peroxide release oxygen much too rapidly to be of practical use. As a result, most bioremediation studies to date have been conducted with either magnesium peroxide or calcium peroxide. Nearly all of the studies involving migration barriers have been conducted with magnesium peroxide by or in conjunction with Regenesis™.

For oxygen release barriers to be effective, the constituents of interest must be aerobically biodegradable. Secondly, it is necessary to determine whether the contaminant mass throughput can be managed by a cost-effective amount of ORC. In general, this means intercepting the plume where its oxygen demand does not exceed 20 mg/L of dissolved hydrocarbons. The actual maximum concentration of hydrocarbons that can be biodegraded varies depending on groundwater flow rate, mass of ORC used, and oxygen release profile of the specific ORC product.

Figure 5.40
ORC Barrier Concept



For a specific site, engineering design parameters for these barriers include location of the rows of wells within the plume; well spacing and screened interval; diameter of wells; and characteristics of the specific ORC product. Location of the barrier relative to the contaminant concentration gradient will determine the oxygen demand it must meet. The spacing, screened interval, and diameter of wells determine the mass of ORC that can be placed in the aquifer. Thus, the rate at which oxygen is provided can be engineered into the system.

The advantage offered by passive migration barriers is that no mechanical or electrical equipment is required, and no trenches are needed to conduct water or air. As a result, these systems require no maintenance other than periodic replacement of the ORC, which can be incorporated in a concrete matrix contained in sleeves. Thus, one or more times a year, a technician can remove the old sleeves and replace them with new sleeves. As with other systems, periodic monitoring is required.

To date, a number of field trials have been conducted to evaluate and demonstrate the use of magnesium peroxide as a biological migration barrier. These include a controlled release test at the Bordon Landfill in Waterloo, Ontario; gasoline release sites in North Carolina and New Mexico; and a mixed fuels release site in Alaska. Each of these tests demonstrated that oxygen could be provided at and downgradient of the ORC-containing wells and that monoaromatic hydrocarbons could be degraded downgradient of the source area using oxygen released from these barriers.

The controlled release experiments in Canada involved the release of benzene and toluene through a row of wells located parallel to and upgradient of a row of wells containing magnesium peroxide in a concrete matrix and control wells (Bianch-Mosquera, Allen-King, and Mackay 1994). Test data presented in Tables 5.34 and 5.35 demonstrate that increased DO levels and degradation of toluene occurred downgradient of the ORC-containing wells. The tables show oxygen and benzene concentrations upgradient, at, and downgradient of the oxygen source and control wells.

The North Carolina study evaluated the performance of a biological migration barrier at an existing spill site (Kao and Bordon 1994). A row of wells spaced 1.6 m (5 ft) apart intercepted the plume approximately 46 m (150 ft) downgradient of the source area. Increased DO levels and decreased BTEX levels were observed in monitoring wells 3 m (10 ft) downgradient from the ORC-containing wells (Tables 5.36 and 5.37). Less clear results were observed from monitoring wells located further downgradient. It has been speculated that small amounts of free-phase gasoline may have existed near some of the ORC-containing wells. If so, this would have resulted in a

Table 5.34
Oxygen Release Barrier Controlled Release Test Results—Dissolved Oxygen

	Dissolved Oxygen Levels at Day 26			
Distance from Source	Control	Concrete (2nd Control)	ORC/Concrete	ORC/ Pencils
0.6 m[a]	<0.5	<0.5	<0.5	<0.5
1.0 m[b] (ORC Wells)	<0.5	<0.5	8	1
1.5 m[c]	<0.5	<0.5	11	<0.5
2.0 m[c]	<0.5	<0.5	8	1

[a]0.4 m downgradient of toluene source and 1.0 m upgradient of oxygen source.
[b]Oxygen source.
[c]Downgradient of oxygen source.

Adapted from Bianchi-Mosquera, Allen-King, and Mackay 1994

Table 5.35
Oxygen Release Barrier Controlled Release Test Results—Benzene

	Benzene Levels at Day 26			
Distance from Source	Control	Concrete (2nd Control)	ORC/Concrete	ORC/ Pencils
0.6 m[a]	2,000	1,600	1,500	1,500
1.0 m[b] (ORC Wells)	1,500	1,800	500	1,500
1.5 m[c]	1,300	1,800	<50	300
2.0 m[c]	1,500	1,800	<50	50

[a]0.4 m downgradient of toluene source and 1.0 m upgradient of oxygen source.
[b]Oxygen source.
[c]Downgradient of oxygen source.

Adapted from Bianchi-Mosquera, Allen-King, and Mackay 1994

larger oxygen requirement than initially anticipated. This test also produced some evidence of iron precipitation immediately downgradient of the ORC-containing wells. Studies of methods for predicting conditions under which iron precipitation might occur, whether it is a significant potential problem, and methods for mitigating the impact of iron precipitation are in progress.

Table 5.36
Oxygen Release Barrier at Spill Site—Dissolved Oxygen

	Dissolved Oxygen Levels			
	Day 0	Day 23	Day 38	Day 115
Background	4.4	3.4	3.0	–
Upgradient of ORC wells	0.7	0.3	0.02	0.4
Downgrandient of ORC wells				
3 m	0.7	2.5	0.2	2.8
8 m	0.7	1.0	1.0	1.0
23 m	0.7	0.0	0.0	0.3

Adapted from Kao and Borden 1994

Full details of the first oxygen barrier were reported by Marlow et al. (1995). This migration barrier was installed in Homer, Alaska, after a pilot study that compared the ORC method with air sparging. The shallow depth to groundwater, 1.5 m (5 ft), and dissolved iron concentrations in excess of 100 ppm accounted for the limited effectiveness of air sparging at this site. Also, with air sparging, contaminant levels rebounded during treatment, indicating that channeling may have occurred and/or diffusive transport from low-permeability layers (clay lenses, etc.) was rate-limiting.

The barrier was installed on a former utility site at which approximately 2,150 m^3 (2,500 yd^3) of soil contained as much as 13,130 ppm of diesel- and gasoline-range organics (DRO/GRO) and 32.8 ppm of BTEX. The groundwater dissolved-phase concentrations were as high as 6.8 ppm for DRO/GRO and 3.1 ppm for BTEX. After soil excavation, which removed most, but not all, of the free product, the barrier was installed. Normally, all free

Table 5.37
Oxygen Release Barrier at Spill Site—BTEX

	Total BTEX mg/L			
	Day 0	Day 23	Day 38	Day 115
Background	0	0	0	–
Upgradient	6	10	11	29
Downgradient				
3 m	6	1	5	1
8 m	3	4	6	1
23 m	7	6	12	–

Adapted from Kao and Borden 1994

product should be removed; however, in this case, free product could not be removed from areas under a warehouse. Nevertheless, regulators allowed the migration barrier to be installed as the next most reasonable action to take in order to pull the control point back to the source. The barrier consisted of a series of short treatment barriers installed sequentially downgradient within a trench running parallel to the direction of groundwater flow.

Groundwater velocity at the site varied by two orders of magnitude, from less than a 0.3 m (1 ft) per day to several meters per day, as affected by freeze-thaw cycles. During the winter, when flow was minimal, excellent control was achieved, and DRO/GRO and BTEX were significantly attenuated. At the furthest downgradient point, DRO/GRO was reduced from 7.4 ppm to below detection limits, while BTEX was reduced from 1.36 ppm to 0.017 ppm.

The barrier was recharged just after the spring thaw. As the water table rose into treated pockets of sorbed material and as the groundwater velocity increased dramatically, the barrier once again proved to be an effective control mechanism. When measured in the summer, the control point outside the barrier had a BTEX concentration over 50 times the previous measurement at the time of recharge of the ORC wells. By contrast, groundwater that passed through the barrier zones showed increases in BTEX concentrations only 9 times and 1.5 times higher than previous measurements at the first two sequential points, respectively. At the final downgradient point below the final barrier series, BTEX levels were actually reduced by 40%. Based on these results, the site owners chose to again recharge the barrier.

The most extensive field demonstration to date was conducted by GRAM, Inc. in Belen, New Mexico. The site involves an abandoned service station that required remediation due to the presence of gasoline-impacted soil and groundwater as well as small intermittent pockets of free-phase hydrocarbons. The site is a state-lead site, and the study was conducted in close coordination with the New Mexico Environment Department (NMED).

A BTEX plume extended across property boundaries for a distance of greater than 30 m (100 ft). The soils consisted of a heterogeneous mixture of clays, silts, and sands. The depth to groundwater ranges from 1.2 to 1.5 m (4 to 5 ft) below grade. USTs at the site were removed in 1982 and the site and surrounding properties were the subject of separate investigations from 1991 to 1994. These events led to the use of the site for a pilot test followed by a full-scale oxygen barrier installation.

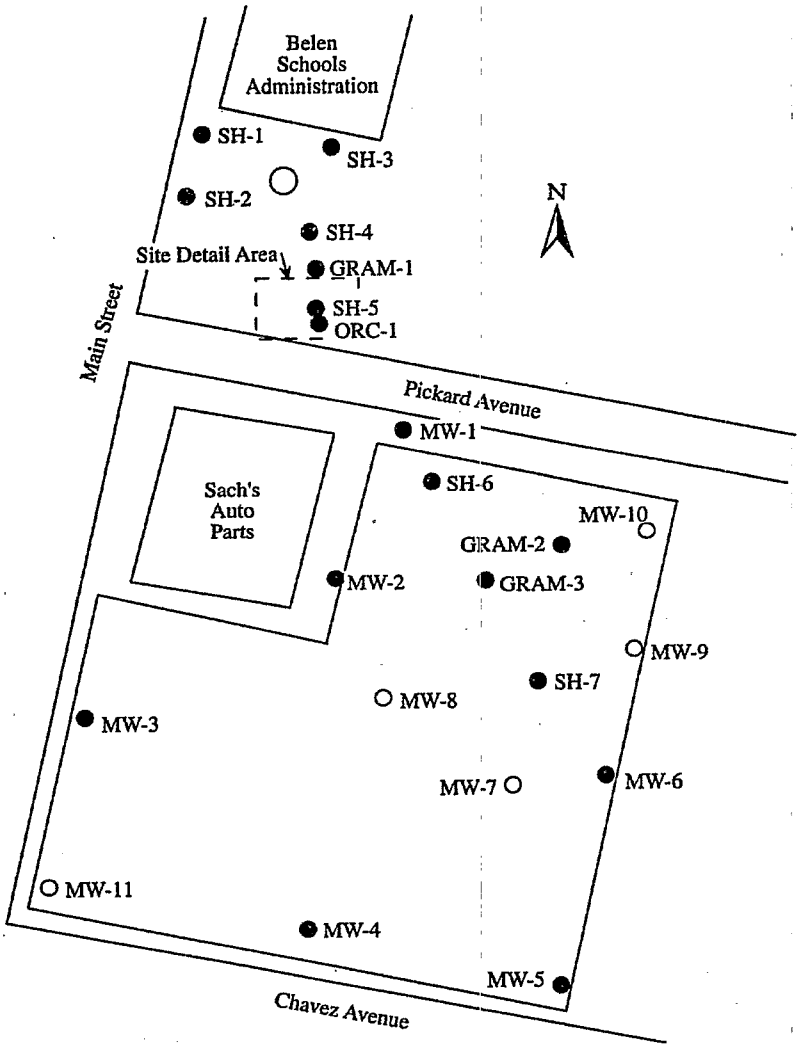
The pilot study was carried out primarily to determine oxygen dispersivity from a single point source and to record, with lesser frequency, the status of dissolved-phase hydrocarbons. ORC was installed in a single 15 cm (6 in.) well and monitored downgradient at 26 monitoring points and several existing monitoring wells. This well is designated ORC-1 in Figure 5.41, and is referenced in the legend of Figure 5.42. DO and BTEX levels were monitored from October through December 1994. The results showed that oxygen from the ORC was able to disperse readily downgradient and remediate hydrocarbons. Based on these results, the NMED approved the installation of a full-scale oxygen barrier.

The full-scale barrier consisted of 20 15-cm (6-in.) ORC wells. The downgradient sampling array was increased to 54 points as presented in Figure 5.42. Vertical distribution of DO and BTEX were monitored with probes at 1, 3, and 6 m (3, 10, and 17 ft) below the water table in the barrier zone and at various single and multiple depths at the downgradient points. A total of 342 ORC socks were installed on April 3, 1995, and the system has been monitored extensively since. Over a thousand oxygen and BTEX readings have been taken. Oxygen was measured using a modified Winkler titration (Hach test kit) because the NMED considered chemical methods, such as this, to be superior to oxygen electrodes. Ohmicron BTEX immunoassays were made, and over 50 of these measurements were supported by conventional laboratory GC analysis to establish needed correlations between the methods; about a dozen immunoassays can be performed for the cost of one GC analysis.

Oxygen distribution was estimated by contouring the areal and vertical distribution of initial and subsequent oxygen concentrations at 10 sampling times over a 3-month period. BTEX levels were evaluated using the same

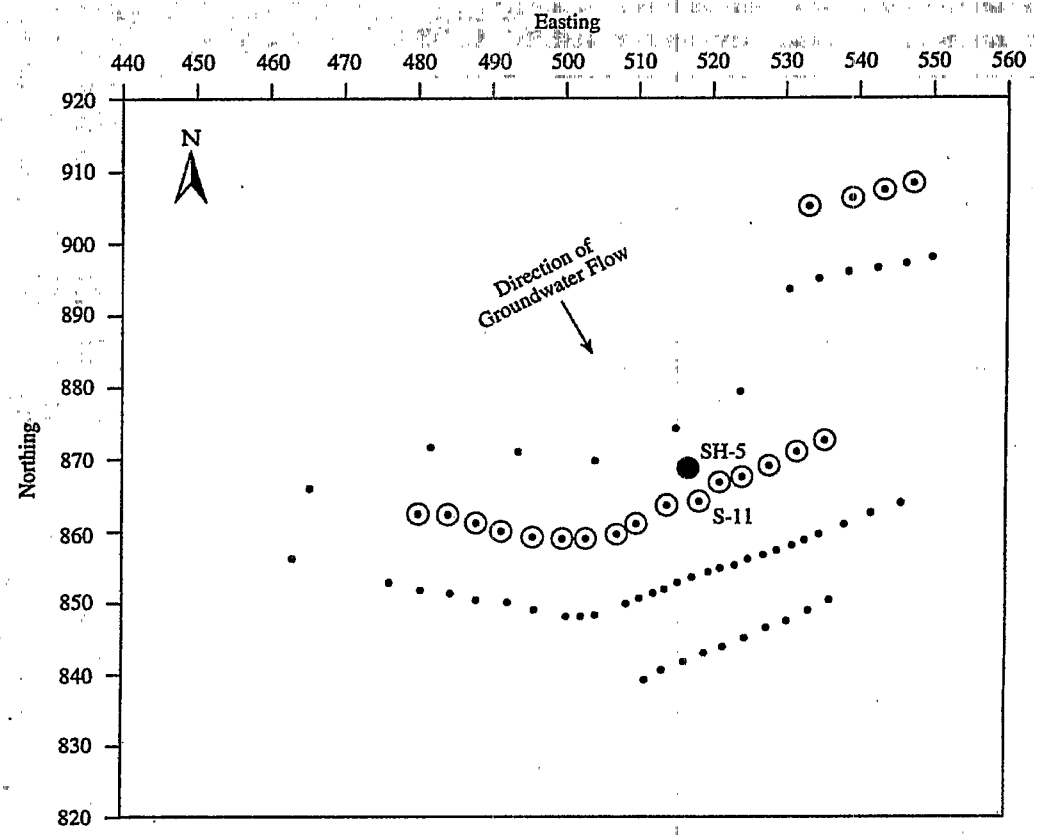
methodology. Figures 5.43 and 5.44 are concentration contours generated from these measurements for DO and BTEX, respectively. Rapid increases in DO can be observed following ORC barrier installation. It is clear that an oxygen barrier forms across the wells and rapidly moves downgradient from them.

Figure 5.41
New Mexico ORC Barrier Site
(not to scale)



● Permanent Monitoring Well
○ Temporary Monitoring Well

Figure 5.42
Oxygen Source Wells and Monitoring Points

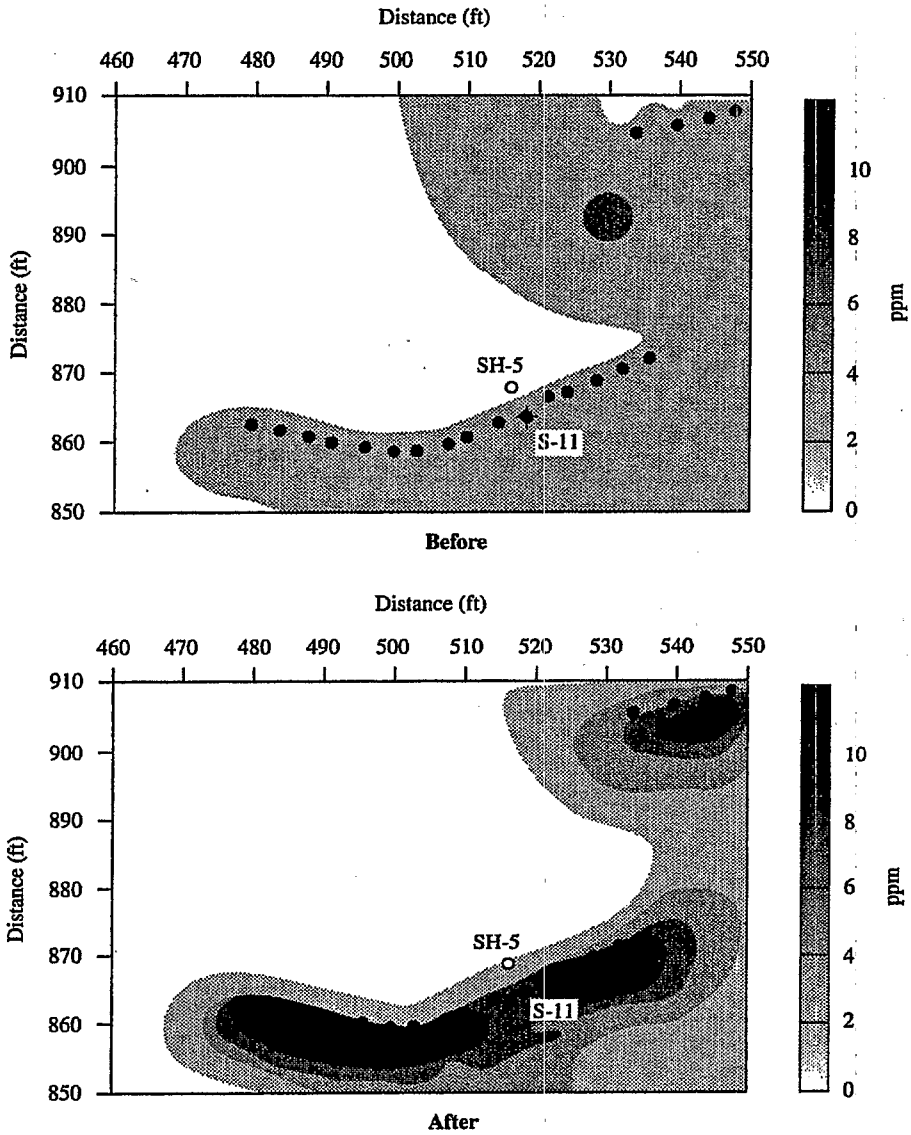


ORC Source Well
Pilot Study ORC Source Well
Existing Upgradient Monitoring Well
Monitoring Points

Oxygen levels remained fairly constant for the first 47 days following ORC barrier installation while BTEX levels dropped significantly. At Day 47, a significant rise in BTEX was noted and oxygen began to be consumed more rapidly. Subsequent to this event, BTEX concentration levels continued to decline with the corresponding use of DO through Day 93.

The presence of the BTEX spike can be understood in relation to the impact of additional work at the site. The NMED had directed that the contaminated source area be excavated before the barrier was installed. The

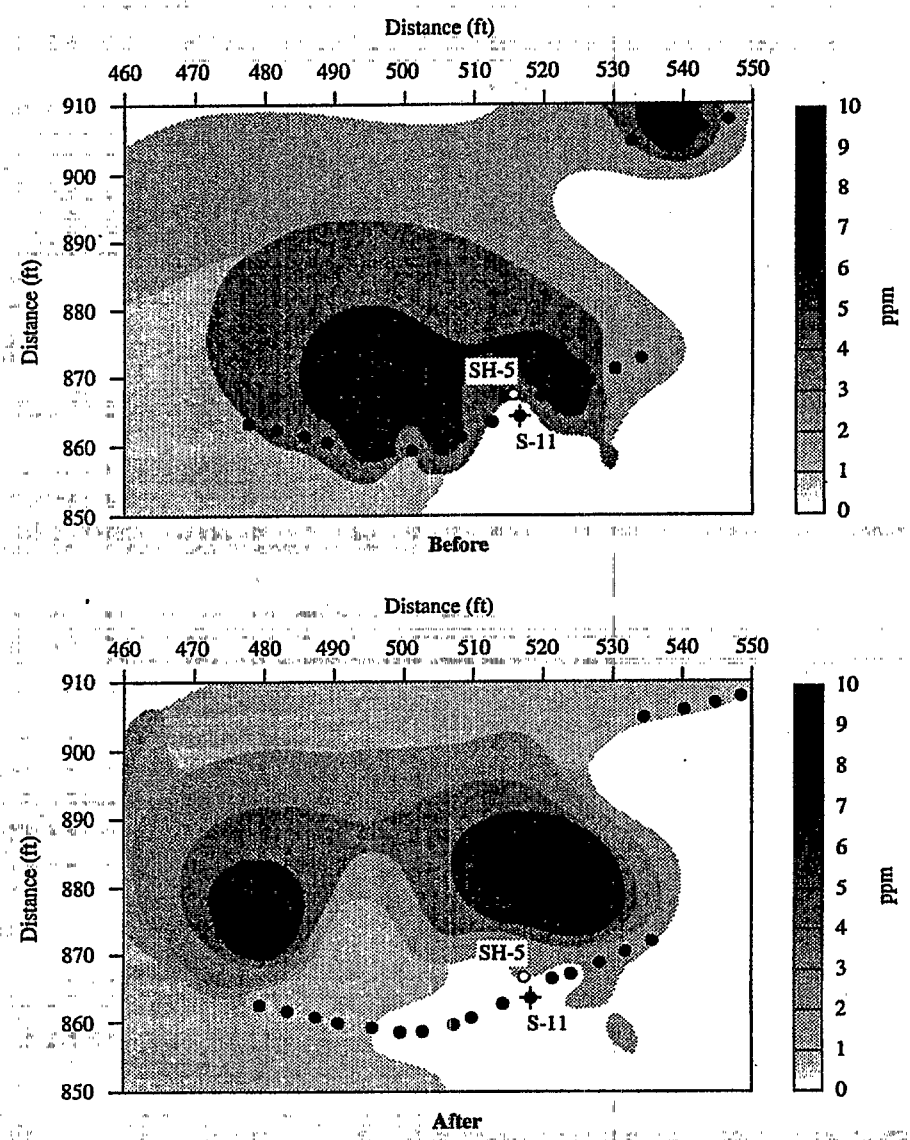
Figure 5.43
Dissolved Oxygen Concentrations Before and After Barrier Installation



excavated soils were located in the vicinity of well SH-4 (Figure 5.41), about 15 m (50 ft) northwest of the barrier. This physical disturbance, that reached the surface of the water table, impacted the equilibrium of the soil/ groundwater system and is presumed to have increased the dissolved-phase BTEX load moving toward the barrier. The rise of BTEX at Day 47 is

consistent with the observed groundwater velocity of 0.3 m (1 ft) per day. Detailed chemical analysis of the specific hydrocarbon distribution in groundwater was also consistent with the introduction of fresh material. Figure 5.44 presents the plan view of the study area with BTEX contours at the time of ORC installation and at Day 93.

Figure 5.44
BTEX Concentrations Before and After Barrier Installation



At the end of the 3-month experimental period, the impact of added dissolved oxygen on BTEX levels was observed in well SH-6 located 37 m (120 ft) downgradient of the barrier. BTEX levels decreased from several hundred ppb to ND. In essence, natural attenuation had previously resulted in BTEX levels of less than 1 ppm at SH-6 compared to about 10 ppm in the vicinity of the barrier. Following ORC installation, BTEX levels further decreased to ND despite the impact of the increased dissolved-phase BTEX generated by source excavation. This particular result serves as a graphic example of the principle of enhanced intrinsic bioremediation; the presence of the oxygen barrier served to pull the control point back toward the source with respect to well SH-6.

The system continues to operate. The available oxygen in the ORC filter socks was about half consumed after 3 months, so replacement charges were scheduled to be installed after 6 months of operation. Based on other studies, the life span of the ORC filter socks should increase as the BTEX mass reaching the barrier decreases.

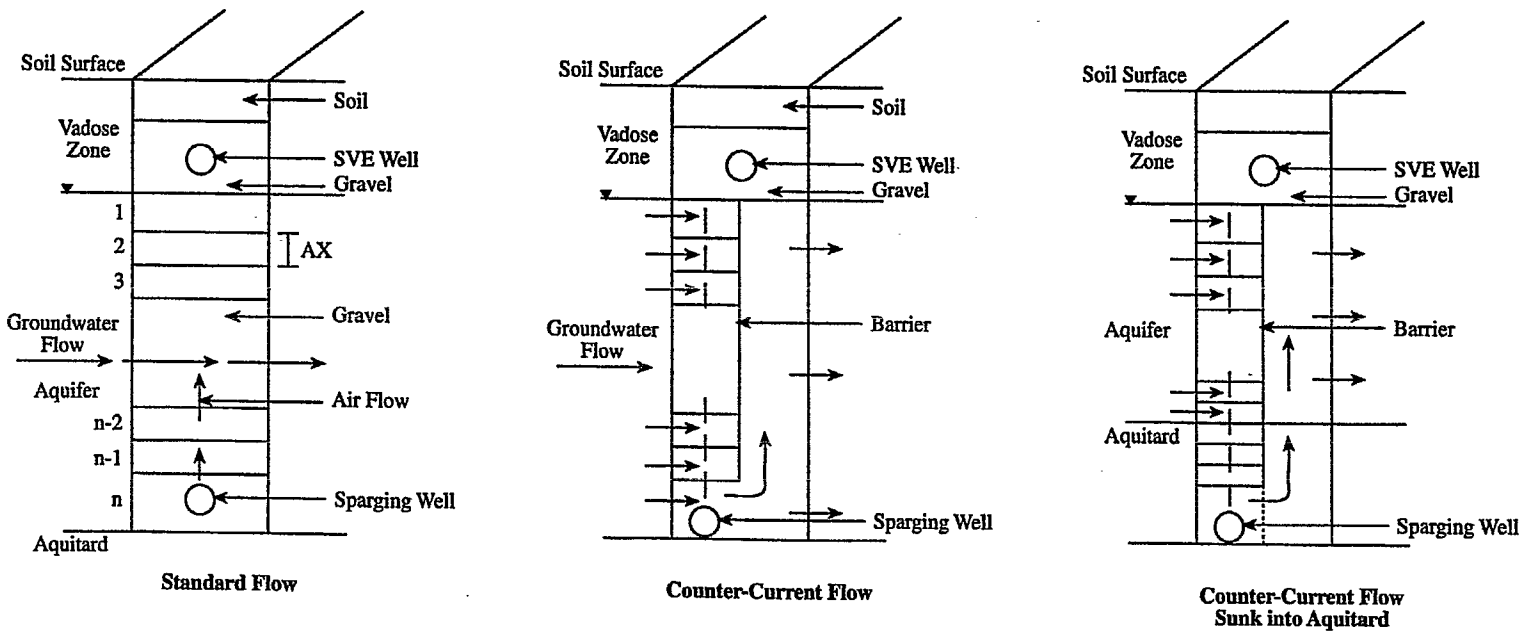
5.6.4 Interceptor Trenches

Aeration trenches (curtains) represent another form of barrier for the containment of plumes (Gudemann and Hiller 1988; Wilson et al. 1992). In this technology, the water entering the trench is sparged with air, stripping VOCs and providing oxygen for the degradation of biodegradable compounds. In air stripping, it may be possible to use the overlying vadose zone as a bioreactor for treatment of the VOC-laden air, or if some of the VOCs are not easily biodegraded (e.g., chlorinated compounds), the offgas will need to be captured by an SVE system for treatment.

Three aeration barrier trench configurations are presented in Figure 5.45. All involve the injection of a gas (usually air) into the saturated zone below the deepest level of the plume, followed by upward movement of the air, during which volatile contaminants may be stripped and oxygen transferred to the groundwater to support biodegradation. In addition, nutrients may be added to the aqueous phase as it moves through the trench. The extent to which bioremediation and/or air stripping will take place is controlled by several factors:

- biodegradability of the contaminant(s);
- volatility (Henry's constant and vapor pressure) of the contaminant(s);
- residence time of the water in the trench;

Figure 5.45
Three Interceptor Trench Configurations



Source: Mutch, Norris, and Wilson 1997. Used with permission.

- air flow rate;
- system design factors (configuration, bubble size, etc.); and
- temperature.

Both biodegradation and air stripping are enhanced by longer residence times, higher air flow rates, and higher temperatures within the sparging trench. Rapid biodegradation competes with air stripping; however, the contribution of biodegradation is reduced if the constituents are highly volatile. Maximum biodegradation rates are typically achieved with relatively modest air flow. Generally, therefore, the fraction of the VOCs that are biodegraded can be maximized by operating the system at the minimum air flow rate at which the level of contaminant removal is satisfactory; much less air is needed to strip most VOC constituents than to provide oxygen for biodegradation. Maximizing the fraction of constituents biodegraded may permit operation with no vapor recovery and treatment, greatly reducing remediation costs. System configuration has relatively little effect on oxygen transport to the aqueous phase; all three of the aeration barrier trench configurations shown in Figure 5.45 provide adequate oxygen transport. For biodegradation alone, therefore, the extra expense involved in the counter-current flow configurations (the second and third configurations in Figure 5.45) would not be justified. However, if it is necessary to air strip one or more biologically-refractory VOCs, the third configuration should be implemented as it is the most efficient of the three for air stripping.

Removal of TCE by the three configurations in Figure 5.45 was modeled under standard conditions of trench depth, air and water flow rate, and VOC mass transfer rate coefficients (Mutch, Norris and Wilson, 1997). The first configuration (cross current) air stripped 88.4% of the TCE in the influent, the second (cross current/counter current) removed 96.4%, and the third (cross current/counter current with a purely counter-current section at the bottom) removed 99.97% of the TCE.

Air bubble size should be small to increase air-to-water surface area and bubble residence time, thereby enhancing mass transport of oxygen and VOCs at the air-to-water interface. Excessive air flow rates will result in large bubbles, undesirable turbulence in the trench, and even reduced hydraulic conductivity across the trench. This latter effect may lead to changes in the plume flow pattern and may actually cause bypassing of the plume around the ends of the trench.

The air injection trench must be of sufficient length and depth to intercept the entire plume with some modest safety margin. Its width must provide adequate contact time under conditions of maximum groundwater flow rate;

the actual value will depend on both biodegradation and air stripping rates. If refractory VOCs are present, air must be provided at a rate to guarantee adequate stripping; this point can be readily explored by mathematical modeling of direct field testing. Provisions must also be made for offgas recovery and treatment if necessary. If the intent is to minimize air stripping and maximize biodegradation, the air flow must be sufficient to provide a stoichiometric excess of oxygen for the oxidation of the constituents of concern, as well as for the oxidation of nontarget compounds. However, higher air flow rates may cause excessive air stripping of VOCs and the need for costly offgas collection and treatment.

Monitoring wells should be located short distances upgradient and downgradient of the migration barrier. These are used to demonstrate the barrier's effectiveness in removing/destroying contaminants and in providing downgradient oxygen concentrations sufficient for degradation of residual organics. Residual organics should be degraded by intrinsic bioremediation processes in the aquifer between the barrier and the point of compliance. Monitoring wells should also be located at either end of the trench to make sure that contaminants do not bypass the barrier. Finally, monitoring wells should be placed farther downgradient from the barrier and somewhat upgradient from the point of compliance to ensure that the system is operating satisfactorily.

5.6.5 Summary

Field and pilot tests have demonstrated the potential use of migration barriers based on air sparging and ORCs. Both methods provide a low-cost alternative to pump-and-treat methods and in some cases, intrinsic bioremediation. Site conditions, contaminant properties and concentrations, and regulatory considerations will impact the selection of methods to be implemented at a particular site.

Biological migration barriers have a place in the continuum of bioremediation technologies that may be applied to contaminated sites. To properly apply this technology, it is necessary to understand what is required to meet site-specific objectives. In some cases, source area remediation may be required during which the downgradient regions of the aquifer must be protected; migration barriers are one approach to providing this protection. In other cases, active source remediation may not be required, intrinsic remediation may be inadequate, and some level of engineered bioremediation may be appropriate to meet the overall site remediation objectives.

One approach to selecting a remedy consisting of one or more bioremediation technologies is to use modeling techniques to evaluate remedies beginning with the least intrusive/costly and working successively toward more intrusive/costly solutions until an acceptable remedy is identified. Recently, Dupont et al. (1996) discussed the use of a model developed by Demenico (1987) that provides a three-dimensional description of contaminant transport taking into account the dispersion, sorption, and first-order decay of the constituents of interest. A methodology applying the Demenico model at sites by first simulating intrinsic remediation and then conditions where the original mass loading of contaminants has been reduced by various remedial strategies has been presented by Dupont, Noris, and Gorder (1996). Migration barriers, combined with intrinsic remediation, were considered the least intrusive/costly technique incorporating proactive remedies that can be evaluated at contaminated sites using this methodology.

6 VAPOR TREATMENT SYSTEMS

6.1 Introduction

Biofiltration is an ex-situ technology designed to degrade contaminant vapors that are generated in manufacturing, waste treatment, or site remediation activities. As such, the technology is not affected greatly by site, soil, or waste characteristics except as they relate to: (1) the relative volatility of the contaminant (the contaminant must move into the vapor phase but not be so volatile that it cannot be sorbed within the biofilter reactor), and (2) the air permeability and water content of the contaminated soil (low moisture content is necessary to maximize vapor recovery and contaminant removal for treatment in the biofilter). The technology is unaffected by conditions adverse to microbial activity in the site itself (i.e., nutrient limitations and non-ideal soil, water, and pH conditions) because these can be easily modified in a controlled-reactor environment. However, the technology is affected by waste constituent characteristics that affect the toxicity, biodegradability, and bioavailability of contaminant vapors. Toxicity and biodegradability limitations can be controlled in a biofilter reactor through dilution, addition of carbon sources to stimulate co-metabolic degradation, etc. The biofilter relies on contaminant mobility in the vapor phase so it can be collected for treatment, making a contaminant's volatility and solubility (i.e., its Henry's constant, see Appendix A) important in assessing the potential effectiveness of this method to treat a specific contaminant vapor. Site, soil, and waste constituent characteristics that are important in the evaluation and design of the biofilter vapor treatment system technology are summarized in Table 6.1.

Table 6.1
Impact of Various Site, Soil, and Waste Constituent Characteristics on Biofilter Vapor Treatment Technology Performance*

	Characteristic	Impact on Biofilters
Site	Climatic conditions	I
	Groundwater table fluctuations	N
	Surface structures	I
	Layered formation	I
	Product existence/distribution	I
Soil	Fine grained	I
	High-water content	I-
	Low-water content	N
	Nutrients	N
	pH	N
Waste Constituent	Volatility	V
	Biodegradability	V
	Bioavailability	V
	Water solubility	V
	Toxicity	V-

*BF = biofilter process
N = not important related to the performance of the technology
I = important related to the performance of the technology
V = very important related to the performance of the technology
+ = characteristic positively impacts the performance of selection of the technology
- = characteristic negatively impacts the performance or selection of the technology

6.2 Vapor Treatment Systems

6.2.1 Principles of Operation

Vapor treatment systems are based on the same principles as bioventing. The major difference is that the contaminants are contained within the vapor phase and delivered to the reactive zone as opposed to providing air to contaminated soil. Biological vapor treatment technology has been used for a number of years, primarily in Western Europe.

The work of Michelsen (1995), which appears in a comprehensive text entitled *Handbook of Air Pollution Control Engineering and Technology* was the primary basis for this section. In addition to the previous monograph in this series (Ward et al. 1995), other comprehensive references include International Process System (IPS) (1990); VDI (1991); Leson and Winer (1991); Bohn (1992); Michelsen (1992); Michelsen (1993); and Frechen (1993).

Biological vapor treatment systems or biofilters use microorganisms immobilized on wet organic packing material, through which the air stream is passed, to remove pollutants from offgas streams. Biodegradable organic and inorganic compounds are adsorbed by the packing material and the moisture coating the packing. Once adsorbed or absorbed, the odoriferous, volatile organic or inorganic compounds are oxidized by microorganisms to carbon dioxide, water, and/or inorganic salts. The process consists of the following steps:

- collection of raw gases;
- pretreatment to remove particulate, adjust temperature, and increase relative humidity; and
- dispersion throughout the biofilter.

The basic process requires that: (1) the compounds to be treated be biodegradable under aerobic conditions; (2) the combination of adsorption and rate of biodegradation be adequate to permit efficient treatment; (3) the packing material hasadequate adsorption characteristics; (4) there is adequate oxygen, moisture, and nutrients; and (5) there is adequate retention time.

Suitable vapor streams must contain degradable compounds at concentrations that are neither toxic nor too high for the capacity of the biofilter. Some compounds, such as formaldehyde, are readily biodegradable at low concentrations but toxic to microorganisms at higher concentrations. Other problems that may arise at higher concentrations include excessive biomass accumulation and acidification.

6.2.2 Process Design Principles

In general, the compounds most suitable for biofiltration are water soluble and of low molecular weight. Water solubility contributes both to rapid absorption by the moisture coating on the packing material and to biodegradability. Volatile organic compounds (VOCs) with functional groups containing nitrogen, sulfate, and/or oxygen typically are water soluble and therefore, are rapidly degraded. Odorous inorganic compounds such as hydrogen

sulfide, ammonia, and sulfur dioxide are also suitable (Eitner and Gethke 1987; Don and Feenstra 1984; Propkop and Bohn 1985; and Ziminski and Ferrara 1993).

Michelsen has developed the following general conclusions based on pilot-scale studies regarding the capability of biofiltration systems to treat various classes of VOCs (Yavorsky 1993):

- Aliphatic compounds with less than seven carbons, such as ethanol, acetone, isopropyl alcohol, methyl formate, and methyl ethyl ketone (MEK), are very degradable. These compounds can be treated with high efficiency at concentrations of greater than 1500 mg/m^3. Control efficiency of greater than 95% is possible with less than 1 minute retention time.
- Aliphatic compounds with more than six carbon atoms or aromatic compounds, such as toluene, xylene, phthalates, and mixtures of aromatic paint solvents are moderately degradable. These compounds are degraded at a slower rate than the VOCs listed above. A control efficiency of 95% is possible with inlet concentrations of 500 mg/m^3 and moderate retention times. Utilizing biofiltration to treat higher inlet concentrations or to achieve higher destruction efficiency is possible, however, a longer retention time is required.
- Some compounds, such as benzene, degrade poorly, and treatment by biofiltration is normally limited to an inlet concentration of 20 mg/m^3. In some cases, where there is a mixture of organic compounds, biodegradation can be improved by co-metabolism.
- Chlorinated hydrocarbon compounds with one or two chlorine atoms, such as methyl chloride and 1,2-dichloromethane, can be treated by biofiltration. Inlet concentration is normally limited to a maximum of 20 mg/m^3 and the filter material must contain a buffering agent to neutralize the hydrochloric acid formed by the biodegradation process.

Table 6.2 summarizes the relative applicability of biofiltration technology to classes of compounds and industrial sources.

In addition to considering the biodegradability of individual compounds, it is necessary to evaluate the impact of the specific mixture of compounds present in the offgas stream. The complexity of this task is increased for the treatment of sources, such as soil vapor extraction systems, because the concentrations and relative composition of the various constituents changes over

Table 6.2
Proven Applications of Biofiltration

Industry	Odor	Organic Compounds: Aliphatic Hydro-carbons	Organic Compounds: Aromatic Hydro-carbons	Organic Compounds: Containing Oxygen	Organic Compounds: Containing Sulfur	Organic Compounds: Containing Nitrogen	Organic Compounds: Halo-genated	Inorganics: H_2S	Inorganics: NH_3	Aromatic Oils
Used oil	X	X	X		X		X	?		X
Aroma extraction	X									X
Beer yeast drying	X			X		X				X
Fat processing	X			X	X	X		X	X	
Gelatin production	X			X	X					
Foundries	X	X	X	X					X	
Coffee roasting	X			X	X	X				X
Cocoa roasting	X			X	X	X				X
Sewage treatment (municipal)	X	X	X	X	X	X	X	X	X	
Sewage treatment (industrial)	X	X	X	X	X	X	X	X	X	X
Composting	X	X			X	X	X	X	X	
Plastics processing	X	X	X	X	X	X				
Adhesives	X		X	X						X
Polyester	X				X	X				
Tobacco processing	X		X		X	X				
Tank farms	X	X	X							
Rendering	X			X	X	X	X	X	X	

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time, especially during the first several weeks of operation. For some mixtures, the consumption of readily-degradable compounds may increase the biomass, improving treatment of marginally-degradable compounds. In other cases, co-metabolism may aid the degradation of compounds that might otherwise be poorly treated.

For continuous influent flow velocities with relatively consistent compositions, microorganisms can acclimate to the feed and achieve relatively high efficiency. Where the flow is intermittent or variable in either rate or composition, the system may never fully acclimate and might not achieve high efficiency. However, adequate treatment might still be achievable through process design modifications to accommodate the specific gas stream. Examples of such system modifications include providing longer residence time or providing intermittent makeup feed to the bioreactor.

The design of biofiltration systems must consider that the process is a combination of absorption and biodegradation. As shown in Figure 6.1, a biofilm surrounds the filter particles. The biofilm must be moist so that the contaminant can be absorbed into the aqueous film surrounding the filter particle as shown in Figure 6.2. Once in the aqueous phase, the microorganisms can use the contaminant as a carbon and/or energy source. As the contaminant is degraded, more molecules can be absorbed. Byproducts of metabolism, such as carbon dioxide, increase in concentration in the biofilm and then diffuse into the gas phase which escapes the biofilter.

Figure 6.1
Schematic Representation of the Biofilm Surrounding the Filter Particle

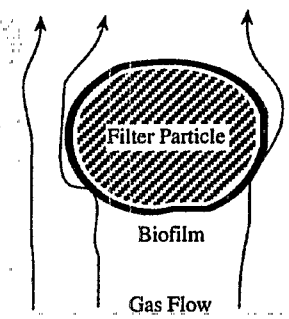

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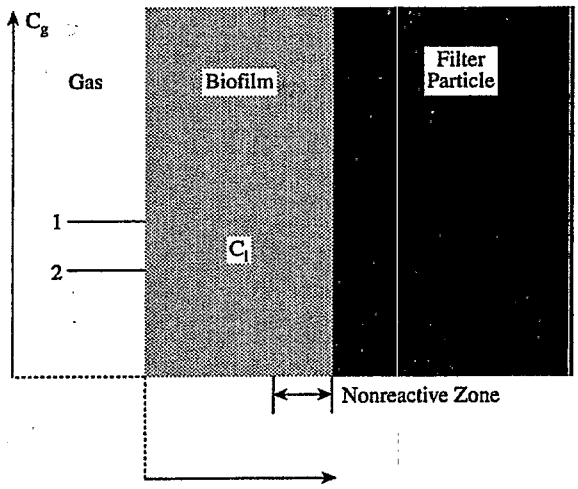
Figure 6.2
Biophysical Model for the Biolayer C_g is the Concentration in the Gas Phase



The two concentration profiles shown in the biolayer (C_l) refer to (1) Elimination Reaction Rate-Limited and (2) Diffusion-Limited

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The gas to be treated must reside within the biofilter for sufficient time to achieve a high sorption efficiency. The system must also be designed to promote biodegradation, which requires moisture and temperature conditions that are not optimal for absorption. Thus, designs must account for this contradiction by providing more retention time than is typically required for absorption alone. As a result, biofilters are relatively large and are best suited for relatively low concentrations of VOCs. Residence time requirements are typically 15 to 60 seconds, but are frequently longer. The minimum size of the biofilter system (volume of filter material) is governed by the residence time required. This volume is equal to the volumetric flow rate times the residence time.

The required residence time depends upon the water solubility and biodegradability of the compounds being treated, their concentrations in the gas stream, the filter material, the microbial community, and the required removal efficiency. The characteristics of the flow stream are generally determined by the application, although soil vapor extraction and bioventing systems can be operated in a fashion that provides more favorable offgas streams for treatment.

For given gas stream characteristics, biofilter design is first based on the filter material and the source of the microbial community. The material must provide a favorable environment for metabolic activity and must have adequate sorptive capacity. Materials that have been used include soils and compost produced from leaves, bark, wood chips, activated sludge, paper, etc. Other filter materials used include peat, heather, and inert materials. Wood chips, plastic spheres, and ceramics, have been added to the primary material to provide greater structural integrity to the biofilter bed. Some systems have incorporated activated carbon. For treatment of compounds with acidic degradation products (e.g., sulfuric acid from treatment of H_2S or SO_2), lime, limestone, or dolomite can be added to the filter matrix.

Necessary properties of the filter material include:

- high surface area for microbial attachment and transfer of the gas-phase constituents to the aqueous phase;
- good water retention capacity;
- good water drainage;
- low-rate microorganism attrition;
- a source of inorganic nutrients;
- a permeable structure that provides a low pressure drop during filtration; and
- minimal compactibility to avoid cracks and minimize pressure drops.

To achieve a low pressure differential across the filter material, the height of the filter bed is typically limited to 1.0 to 1.5 m (3 to 5 ft) with a maximum height of 2 m (6 ft) for materials that exhibit a low pressure drop. A minimal pressure drop across the filter is necessary to achieve uniform gas distribution; this requires a minimum height of about 0.5 m (1.5 ft). Where space is limited, separate biofilter segments can be stacked to reduce the footprint of the total system.

Microorganisms suitable for biofiltration are typically present in soils and compost and are typically capable of degrading the classes of compounds shown in Table 6.2. After the gas stream has been introduced into the biofilter, the microorganisms will acclimate to the specific substrates and their relative concentrations. If the gas stream remains constant in flow and composition, the microorganisms that can most efficiently use the substrates as a carbon and energy source will predominate. Where acclimation is not effective, it may be beneficial to add an exogenous source of microorganisms.

It is not possible to determine the optimum residence time, and thus biofilter size, based solely on the composition and volumetric flow rate of the gas stream. For gas streams containing a single contaminant or similar easily-degradable and readily-sorbed compounds, it is possible to determine an appropriate residence time based on experience with similar gas streams. For complex mixtures, the only practical approach to designing treatment systems is to conduct pilot studies to evaluate acclimation times as well as residence times. Where variability in composition or volumetric flow rates is expected, it may be advisable to incorporate activated carbon in the filter to prevent immediate breakthrough in response to increased flow rates or concentrations.

System designs include pretreatment for particulate removal and gas preconditioning, primarily for moisture and temperature adjustment, as discussed in Section 6.2.5. The air distribution network, filter material, and offgas discharge must also be included.

The gas distribution system's primary function is to evenly distribute the influent gas into the biofilter at rates appropriate for the loading of the filter medium. In upflow systems, additional functions that may be performed by the gas distribution system include drainage collection, leachate containment, and structural support. For soil beds, the gas distribution system consists of a ductwork header that feeds waste gas through a horizontal network of perforated pipes usually located 0.75 to 1 m (2 to 3 ft) below ground level. Other systems have been constructed from slotted or vented plates consisting of interlocking concrete or plastic blocks, concrete slabs, or metal grating. The materials of construction must be compatible with the characteristics (corrosiveness) of the waste gas and byproducts.

The gas distribution system must discharge gas at relatively equal flow rates across the entire system. Some systems include unaerated spaces along the outer edges of the filter to prevent short circuiting of gases along the side of the filter. The pressure drop across the network must be minimized by using adequate diameter piping and by limiting the length of perforated pipe sections.

Pilot studies should mimic the planned final design as closely as practical (Dragan 1993). Because the total height of biofilters typically ranges from 1 to 2 m (3 to 6 ft), pilot systems do not have to be very large to adequately mimic full-scale systems. However, the diameter should be large enough to simulate heat loss/gain within the reactor. In essence, the pilot system should be a complete, small-scale system with inlet gas temperature and humidity control. In addition, the closer the composition of the feed is to the gas stream to be treated by the full-scale system, the better the design data

will be. Where the gas stream already exists, a side stream should be used for the pilot test. It is also important to use the same filter bed material and source of microorganisms that will be used in the full-scale system for maximum representativeness of pilot study results.

The pilot study data should be used to develop full-scale system design details after conducting an economic evaluation to ensure that a biofilter is the most cost-effective gas treatment technology available. Provided a biofilter remains the preferred approach, the degradation data should be fit to a kinetic model that the design provides adequate capacity to accommodate variations in feed gas composition, temperature, and flow rate velocity. The design should incorporate volumetric flow rate, gas composition, degradation rates of all compounds present in the gas stream, variability of flow rates and composition, required destruction efficiency, biofilter capacity based on the field test, and available space for the bioreactor.

6.2.3 Process-Flow Diagram

A general flow diagram for biofilter treatment systems is presented in Figure 6.3. Specific systems vary based on the filter-bed design which may include moist packing material in constructed cells, subsurface soils, or a bed through which a continuous flow of water percolates. Typically, multi-bed systems are used.

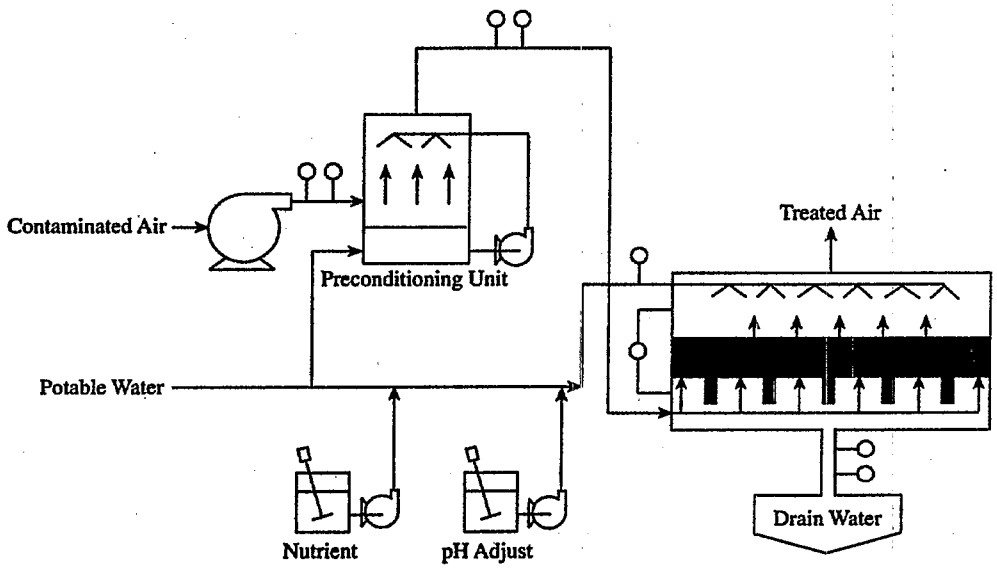
In addition to the systems outlined in Section 6.2.2, biological vapor treatment can be implemented in the form of: (1) trickling filters and (2) below ground, native-soil-based filter networks. Both are discussed below.

6.2.4 Process Modifications

Biotrickling filters contain conventional scrubber packing material instead of compost, soil, peat, or wood chips as described in Section 6.2.2 and operate with liquid flow over the packing to facilitate mass transfer (Yang and Alibeckoff 1995). Air flow can be in the same direction as water flow; however, performance is usually improved with countercurrent flows.

Preconditioned contaminated air is introduced at the bottom of the packing material and flows upward through the packing. Water inoculated with microorganisms and amended with nutrients is introduced through sprayers located at the top of the packing and percolates counter-current to the air flow. After a biofilm is established on the packing material, further inoculation is no longer required. Drainage water is recirculated, reducing the requirement for fresh water to replace evaporation losses. Drainage water recirculation also returns microorganisms to the top of the packing.

Figure 6.3
General Flow Diagram for Biofilter Systems



The counter-current flow provides efficient transfer of compounds from the gas phase to the aqueous phase and permits easy addition of nutrients and control of pH. Control of pH is particularly important when the gas to be treated consists of compounds containing chlorine, sulfur, or nitrogen that bio-oxidize to yield hydrochloric, sulfuric, or nitric acid, respectively. A potential advantage of biotrickling filters is that they generally have a smaller footprint than conventional biofilters.

Trickling biofilters have been used to treat the classes of compounds listed in Table 6.3. Recently, Envirogen introduced a modification of this system that is being developed to treat chlorinated solvents. The primary new feature is the introduction of strains of bacteria that can be "turned on" by toluene to degrade chlorinated ethenes such as trichloroethylene.

Another type of biofilter was developed by S.C. Johnson, Inc. for use at a manufacturing facility in Racine, Wisconsin (Kampbell et al. 1987). Vapors containing aromatic hydrocarbons from an indoor processing area are fed to a network of perforated pipes located several feet below the ground surface. The hydrocarbon-laden vapors pass through native soils which have been fertilized using standard landscaping fertilizer mixes. Other than

monitoring, the major operating activity is somewhat more frequent mowing of the grass located above the filter.

Table 6.3
Relative Biodegradation Rate of Individual and Classes of Volatile Compounds

Inorganic	Organic			
Rapid	Rapid	Moderate	Slow	Very Slow
Hydrogen Sulfide	Alcohols	Esters	Aliphatic	Many Halogenated
Ammonia	Methanol	Ethylacetate	Hydrocarbons	Hydrocarbons
Sulfur Dioxide	Butanol	Ketones	Methane	1,1,1, Trichloroethane
	Aldehydes	Acetone	Pentane	Polyaromatic
	Formaldehyde	Phenols	Cyclohexane	Hydrocarbons
	Acetaldehyde	Aromatics		
	Amines	Benzene		
	Organic Acids	Styrene		
	Butric Acid	Mercaptans		
		Methyl		
		Mercaptan		

6.2.5 Pretreatment Processes

Pretreatment of the raw gas is essential and fairly straightforward. Pretreatment commonly includes particulate removal, temperature adjustment, humidification, and, if necessary, toxin removal.

Particulates such as dust, oils, or other aerosols can add to biofilter biodegradation requirements as well as obstruct or clog pore spaces of the filter media or the air distribution network. Filter systems such as fabric filters, venturi scrubbers, or electrostatic precipitators, alone or in combination, can be used to remove particulate matter before the gas is passed through the filter media. Filter systems are described in detail in Chapters 4 to 8 of a recent book by Mycock, McKenna, and Theodore (1995).

The temperature of the influent gas largely controls the temperature of the biofilter. The optimum temperature of the biofilter is a trade-off between maximizing biodegradation rates and reducing contaminant water solubility. Typically, biofilters use mesophilic bacteria whose optimum temperature is approximately 35°C (95°F). At lower temperatures, the rate of biodegradation decreases by about a factor of one half for each 10°C (50°F). Above 40°C (104°F), mesophilic bacteria are inhibited and eventually die. Fungi tolerate a somewhat broader temperature range than do mesophilic bacteria. Bacteria found in cold climates can achieve reasonable biodegradation rates at low temperatures, while thermophilic bacteria are active at temperatures of 40 to 65°C (104 to 149°F).

Treatment of relatively water-soluble compounds such as oxygen, nitrogen, and sulfur-containing compounds is rapid because the compounds are efficiently absorbed and rapidly biodegrade. Temperature control is more important for alkanes, alkenes, and aromatic hydrocarbons. Also, relatively low water solubilities limit their rate of transfer into the aqueous phase making their biodegradation rates somewhat slower than those of more polar compounds.

Depending upon the microorganisms used in the filter and the temperature of the raw gas, either heating or cooling may be necessary. Cooling increases the relative humidity of the gas stream passing through the filter which may lead to condensation ahead of the biofilter and create the potential for drying of the filter material. If the filter becomes too dry, transfer of compounds to the aqueous phase is reduced, the filter material can shrink, and cracks and channels can form. Furthermore, filter dryness is undesirable as the microorganisms require moisture at levels of 50% to 75% of field capacity for survival and efficient metabolism.

Humidification of the gas stream is generally achieved by use of a water spray humidifier which can also serve to remove particulate matter and adjust temperature (Allen and Yang 1992). Moisture and nutrients can also be provided by spraying water on the surface of the filter material. As degradation proceeds, exothermic reactions increase temperatures across the bed and drying of the filter material. This moisture can be replaced through the use of automatic sprinkler systems. However, use of this method alone can cause localized drying and thus cracking and channeling. For gas streams that contain compounds at levels that are toxic to the microorganisms either pretreatment or dilution may be required, at least until the microbial community can acclimate or until the composition of the influent changes.

6.2.6 Posttreatment Processes

Posttreatment processes address water drainage from the biofilter bed, disposal of the spent filter material, and in a few cases, treatment of residual VOCs not treated in the biofilter.

While most systems recycle water that drains from the filter bed to the humidifier, periodic discharge of the leachate is necessary to remove nonbiodegradable contaminants. The discharge can be treated by activated carbon, chemical treatment, etc.

The filter material will degrade over time and typically will need to be replaced after a maximum of 5 years of operation (Leson and Winer 1991). Normally, systems are constructed of several cells so that individual cells can be shut down for addition of nutrients or lime, or addition or replacement of the filter material. If the filter material does not contain hazardous or listed compounds, it can be used beneficially. If hazardous compounds are present, the filter material must be properly disposed.

6.2.7 Process Instrumentation and Control

Process instrumentation includes the following:

- monitoring equipment for gas velocity on the inlet and effluent sides of the biofilter;
- temperature and humidity sensors and controllers in the pretreatment subsystem;
- pressure gauges on the influent and effluent side of each cell;
- thermocouples within each cell; and
- meters for total VOC, oxygen, and carbon dioxide concentrations in the effluent and VOC concentrations in the influent.

Continuously-recording monitoring equipment is preferred. Alarm systems are advisable to notify operators if the temperature, humidity, or offgas quality exceed prescribed limits.

6.2.8 Process and Instrumentation Diagrams

Process and instrumentation diagrams should be prepared for the filter bed, pretreatment system, electrical system, and controls, and should illustrate the following:

- dimensions of filter including height, length, and width;

- electrical system and controls highlighting flow and pressure measurement upstream and downstream of the filter; temperature within the filter; and temperature, flow, pH, and humidity in the pretreatment system; and
- monitoring system highlighting contaminant measurement upstream and downstream of the filter and in the filter drain water, and bioprocess monitoring (oxygen and carbon dioxide) in the filter effluent stream.

Details should include the location and type of pressure gauges, flow meters, humidity sensors, thermocouples, valves, sampling ports, meters, and controller sensors.

6.2.9 Sample Calculations

The capability and efficiency of an operating biofilter in eliminating pollutants in a waste gas is a result of both physical and biological factors. The physical factors include mass transfer processes, flow behavior of the vapor phase, and residence time. The microbiological phenomena involve the rate of pollutant elimination by microbial oxidation.

Because interaction between the physical and microbiological phenomena is complex, simplifying assumptions are necessary to model the system. Published research describes a theoretical model for the degradation of organic compounds in a biofilter (Ottengraf and Van der Oever 1983; Ottengraf 1986; Dragt & Ottengraf 1987). The biophysical model of the phases in a biofilter are schematically represented in Figure 6.2. As the gas flows through the biofilter, soluble compounds partition from the gas to the biofilm. The mass balance for a compound in the liquid biolayer is described by the Equation 6.1:

$$D(d^2C_1 / dx^2) - R = 0 \qquad (6.1)$$

where:

D	=	the diffusion coefficient (L^2T^{-1});
C_1	=	concentration in the liquid phase (ML^{-3});
x	=	distance (through biolayer) (L); and
R	=	the substrate utilization rate ($M^{-3}T^{-1}$) (biodegradation reaction rate).

Ottengraf (1986) described the reaction rate due to microbial degradation using the Monod kinetic model, which is widely used for biological processes. Ottengraf's model assumes:

- biodegradation occurs in the liquid phase of the biofilm and is the only substrate elimination reaction;
- the biofilm thickness is small compared to the diameter of the coated filter particle (This assumption treats the biofilm geometry as flat).;
- the flow of gas through the packed filter bed is plug flow;
- the concentrations of each component in the gas and liquid phases are described by Henry's law and are at equilibrium at the phase boundary; and
- the modeled compound is the only rate-limited substrate (no interaction between compounds in a gas mixture).

The reaction rate, (R), is described by the Monod (or Michaelis-Menten) substrate utilization relationship:

$$R = R_{max} C_l / (C_l + K_m) \qquad (6.2)$$

where:

K_m = the Monod (Michaelis-Menten) constant (ML^{-3});
R_{max} = the maximum substrate utilization rate ($ML^{-3}T^{-1}$).

R_{max} is a function of the concentrations of active microorganisms in the biomass layer:

$$R_{max} = X\mu_m / Y_i \qquad (6.3)$$

where:

X = the cell concentration of the active microorganisms (ML^{-3});
μ_m = the maximum growth rate (T^{-1}); and
Y_i = the cell yield coefficient, ($M_{cells}/M_{substrate}$).

Ottengraf and Van der Oever (1983) conducted intensive laboratory and pilot-scale experiments with several common VOCs to determine the overall kinetics of the biofiltration process. Two kinetic cases were distinguished in the experiments:

- *Reaction (Biodegradation) Rate Limited (Zero-Order Kinetics)*: the biofilm is fully saturated (no diffusion limitation) and fully active at high pollutant concentrations. In this situation, C_l is much greater than K_m. Since K_m is insignificant, the reaction rate, (R), is maximized and there is a linear relationship

(zero-order) between the reduction in pollutant concentration and bed height; and

- *Diffusion Rate Limited (First-Order Kinetics)*: at lower pollutant concentrations, the biofilm is not saturated or fully active. In this situation, K_m is greater than C_l. The conversion rate is controlled by the rate of diffusion in the biofilm. The rate of reduction in pollutant concentration decreases with height in the filter bed.

Ottengraf and Dever's experiments with various VOCs (including toluene, ethyl acetate, butyl acetate, and butanol) determined that the concentration where the biofiltration kinetics shifts from zero- to first-order is specific to an individual compound and varies widely among chemicals.

Ottengraf's kinetic model can provide a reliable basis for sizing a biofilter in the case of a single-component offgas. However, this model has limited utility for offgases with a mixture of pollutants. Complications due to interactions among compounds can have either a positive or negative impact on the biodegradation rate. These interactions include co-metabolism, which can increase the degradation rate of recalcitrant compounds (Kampbell et al. 1987); cross-inhibition, which can diminish degradation rates; and vertical stratification, where the most readily degradable compounds are metabolized at the inlet portion of the biofilter while less degradable compounds pass through to be metabolized at upper levels of the bed. As mentioned in Section 6.2.2, pilot-scale testing is generally required to correctly size a biofilter treating a multicomponent waste gas stream.

6.2.10 Safety Requirements

Since biofilters are used to treat relatively low concentrations of volatiles, explosion hazards are minimal. However, it is still advisable in any setting to incorporate only intrinsically safe blowers and other equipment into full-scale system design. This is particularly true as interest grows in developing biofilters to treat low flow, high concentration gas streams. If the volatile compounds in the influent gas are toxic, it is important to: (1) provide detectors at locations where leaks might occur; (2) locate the intake side of blowers as close to the filter as practical so that transfer lines operate under a partial vacuum; and (3) to schedule regular inspections of equipment and transfer lines.

6.2.11 Specification Development

System designs must specify the filter material, microbe source, pretreatment system, gas flow network, and residence time. The gas volumetric

flow rate and composition and the required destruction efficiency are the major inputs to system specifications. Filter materials, microbe sources, pretreatment systems, and gas flow networks are discussed in earlier sections; this section focuses on residence time.

The residence time is dependent upon biodegradation capacity, which is determined by kinetic modeling and/or pilot testing. Pilot testing, which is almost always required, determines degradation rates expressed as grams of compound degraded per volume (cubic yards or cubic meters) of filter material per hour. Typical rates are between 10 and 100 g/m^3-hr (0.02 and 0.2 lb/yd^3-hr) for the most common air pollutants — approximately five times the rates commonly achieved in bioventing systems.

Residence times can be calculated from the biodegradation rate. From this value, the size of the biofilter can be calculated using an appropriate height and the composition of the influent gas. The resultant area is dependent upon the filter material. The pressure drop varies with the filter material, and thus, different heights can be achieved with various filter packing. Soil beds are limited to heights of approximately 0.6 m (2 ft), while beds made from higher permeability materials, such as compost, wood chips, or bark chips can be 1 to 2 m (3 to 6 ft) high depending upon the gas flow rate.

The size of a biofilter can be expressed as the surface loading ratio, in which the influent gas volumetric flow rate (m^3/hr or cfm) is divided by the biofilter surface area (m^2 or ft^2). Surface area loads typically range from about 30 to 300 m^3/hr/m^2 (1.6 to 16 cfm/ft^2) depending on the characteristics of the influent gas and removal efficiency required. Maximum achievable surface loading rates can be as ranges to 500 m^3/hr/m^2 (27 cfm/ft^2) with optimized, low-pressure drop material. Modest fluctuations in volumetric flow rates or gas composition can be tolerated because of the sorptive capacity of the filter material.

Residence times can be as short as 15 seconds for low concentrations of easily sorbed and readily biodegradable compounds, such as those usually found in offgases from food processing, and as long as 15 minutes for high concentrations of less soluble and less readily degradable compounds.

6.2.12 Cost Data

Costs vary widely among systems based on design, contaminant treatability, and gas concentration. Costs are frequently estimated based on capital and operation and maintenance costs per volume of gas to be treated. As a result, costs are approximately directly proportional to the required system retention time. Michelsen (1995) surveyed published data on biofilter costs

and arrived at a range of capital costs of $3 to $30 per m^3/sec ($5 to $50 per cfm). The low range is for low concentrations of readily-degradable compounds that are easily sorbed. Typical annual operating costs are on the order or $4 per m^3/sec ($7 per cfm).

Table 6.4 provides a summary of typical costs for aromatic hydrocarbon-laden air based on several years of experience of one of the few U.S.-based firms that specializes in biofilters. The total cost of $20,400 includes routine laboratory tests, design, construction, and one year of operation. Permitting costs are not included and vary widely depending upon local and state regulatory requirements. These costs also do not include preparation of the treatment area prior to construction of the biofilter and are based on the assumption that electrical service is available.

Table 6.4
Typical Soil Biofilter Process Costs[a]

Cost Element		Cost ($)
ENGINEERING		
Prepare Work Plan		2,000
Laboratory Tests		1,000
Design		5,000
Subtotal, Engineering		**8,000**
TREATMENT COSTS		
Materials	170 m^3 @$20/$m^3$	3,400
Construction		5,000
O&M[b]		2,000
Analytical		1,000
Management		1,000
Subtotal, Treatment Costs		**12,400**
GRAND TOTAL		**$20,400**

[a]Treatment of 250 m^3 /hr (140 cfm) of air containing between 0 and 2,000 ppm (v/v) aromatic hydrocarbons with a removal efficiency of 90%. The biofilter contains approximately 170 m^3 (210 yd^3) of soil.
[b]O & M includes electrical power and 30 minutes of maintenance per week by the owners' employees.

Courtesy of Bohn, Biofilter Corp.

6.2.13 Design Validation

Pilot test results and experience with similar systems, if available, should be reviewed and compared to the anticipated flow rates, retention times, influent flow velocities, and influent gas composition to ensure that the biofilter has sufficient volume to treat the influent and meet regulatory requirements.

All control and monitoring equipment, piping, blowers, humidifier, heating coils, etc., should be reviewed to confirm that they have been sized correctly and are constructed of materials compatible with the influent raw gas and expected effluent products.

6.2.14 Permitting Requirements

As with any gas treatment system, air emissions are subject to air permitting requirements according to state and, possibly, local regulations. Unless federally-enforced regulations apply, individual state regulations will dictate permitting requirements. Offgas treatment requirements for biofilters are no different than for any other air emission control system. Typically, the compliance process includes obtaining permits to conduct a pilot study, construct the system, and operate the system. The discharge can be regulated based on: (1) percent reduction in emissions, (2) specific concentrations in the discharge or at the property line in which case the height of the discharge point and the distance to the property line may have to be used in the calculation of allowable discharge concentrations, or (3) a specific rate (e.g., pounds per day) for each compound. If the discharge exceeds the discharge limit for short periods of time, the regulating agency must be informed, but generally, operation can continue.

6.2.15 Design Checklist

Checklists will vary somewhat with design, but must include those items listed in Table 6.5.

6.2.16 Implementation

The contaminated gas collection system, if not already existing, must be constructed, and piping must be installed to transfer the gas to the pretreatment system. The pretreatment system should be located close to the filter bed inlet to minimize heat and moisture loss due to condensation. The filter bed may require a concrete pad for support. Pad construction must allow for adequate sampling access and ease of service to re-fluff or replace the filter material.

Table 6.5
Biological Vapor Treatment Design Checklist

Feed (Influent Gas) Characterization	Contaminant identification
	Range of concentrations
	Variability in composition
	Temperature range/patterns
	Humidity range/patterns
Site Features	Operation schedules/variability of influent source
	Location of source
	Location of treatment system
	Path from source to treatment system
	Normal "plant" operations/activities
Pilot Test Results	Flow rates/bed size
	Vapor composition
	Degradation rates
	Percent contaminant reduction
	Humidity, pH, temperature ranges
Design	Retention time
	Filter bed size
	Blower(s) size
	Piping heating, if needed
	Pretreatment, filter, humidify/dry heat/cool
	Filter bed moisture, pH (buffer)
	Nutrient source/levels
Health and Safety	HASP complete/kept on site
	Groundwater protection
	Electrical codes
	Emergency shutdown procedures
	Emission excursion alarm
Miscellaneous	Permits
	O&M manual
	Monitoring plan/schedule

A monitoring and control panel should be centrally located. Instrumentation should include components to measure: (1) temperature and humidity of influent gas before and after pretreatment and biofilter effluent; (2) pressure drop through the filter; (3) gas flow through each cell; (4) temperature within each cell; and (5) influent and effluent composition including oxygen, carbon dioxide, and VOC concentrations.

6.2.17 Start-Up Procedures

Acclimation of the microorganisms and establishment of conditions that can be maintained over long periods is important for both offgas and recovered water treatment because treatment must occur in a relatively short period compared to in situ systems. In almost all cases, destruction efficiencies will be lower immediately after startup than following a period of acclimation. Microbial populations will adapt to the composition and concentrations of biodegradable materials in the feed gas. Acclimation times can vary from a few days to a few months (Dragan 1993).

Microbial populations will adapt most rapidly to readily biodegradable compounds. Provided the filter material contains a source of an active indigenous culture, acclimation should occur within a few days, and seeding with exogenous cultures will not be necessary. For other moderately-to-easily degraded compounds, acclimation may require 10 to 15 days, depending upon the source and condition of the indigenous culture (Ottengraf 1986).

Where the compounds in the gas feed are less easily biodegraded or the filter material lacks the appropriate cultures, seed from cultures obtained from wastewater treatment sludge, soils that have been impacted for an extended time by the compounds to be treated, or a commercial source will have to be blended into the filter material. Documentation of the ability of these cultures to degrade the compounds in the gas feed is necessary, and such cultures should be tested in the pilot phase. Seeding of the filter material can also be used to shorten the acclimation time.

During the start-up phase, it is essential to provide a backup treatment system for the biofilter to ensure that discharge limits are not exceeded. Also during this period, the temperature and moisture content of the air entering and discharging from the reactor must be carefully monitored, and appropriate changes should be made to the operating conditions as temperature and moisture balance can be expected to change throughout the acclimation period.

6.2.18 Performance Evaluation

Operating and monitoring procedures are relatively minimal compared to many other treatment technologies; however, they are critical to maintaining performance. These procedures relate to maintaining optimum conditions for the sorption of the volatile compounds and for microbial activity.

6.2.18.1 Operation Practices

Moisture must be maintained in the proper range (Eitner 1990-1991). If the moisture level is too low, microbial activity will decrease. However, excessive moisture content will hinder air flow, increasing the pressure drop across at least some portions of the filter and forming pockets which the volatile compounds cannot reach and where anaerobic conditions may develop. Typically, moisture should be maintained between 30% and 60 % by weight (50% to 75% field capacity). Optimum conditions may vary for individual filters and should be determined as part of the pilot study or during operation refinement.

Moisture can be adjusted by either increasing or decreasing the amount of water introduced during humidification of the feed gas. If moisture levels cannot be maintained by humidification of the inlet gas, the filter will have to be irrigated.

As with all biodegradation processes, nutrients must be sufficient to sustain the formation of new cell material; typically, a C:N:P ratio of 350:10:1 is adequate. A portion of the nutrients required may be present in the filter material. Nutrients can be added as necessary during preparation of the filter bed, intermittently during operations through irrigation, or during periodic servicing of the filter bed.

Control of filter bed pH is important to maintain microbial activity. Degradation of hydrocarbons generates carbon dioxide, which may lower pH. Degradation of chlorine-, sulfur-, and nitrogen-containing compounds generates strong acids which require greater buffering capacity. In some cases, it may be necessary to add lime or limestone during periodic servicing of the filter bed to maintain desirable pH levels in the biofilter.

Unique to biofilters is the need to maintain gas flow resistance in the proper range. Conditions that impede flow or create channeling will reduce treatment efficiency. Use of the filter material by the bacteria as either a food source or nutrient source will result in decomposition of the filter material. Fines formed by this process will fill the void spaces between larger particles, resulting in blockage of the gas flow in some regions and channeling in others. If this occurs, treatment of volatile compounds will be greatly

reduced in both regions. Increased gas flow caused by channeling can be detected by a reduction in pressure drop across the system.

Periodic servicing is required to re-fluff the filter material, or after several years, the filter material may need to be replaced. Systems should be designed to include several treatment cells so that the system can continue to operate while one cell is being serviced. During servicing, nutrients and/or buffering agents can be added if needed.

Cessation of operation for more than a few days may result in detrimental changes to the microbial populations and may require another period of acclimation before optimum performance is achieved (Eitner 1990-1991). At a minimum, a low flow of moist air should be maintained through the filter to prevent anaerobic conditions. Such a flow can be accomplished by intermittent operation of the inlet fan to provide fresh air. To supply carbon for maintenance of the biofilter population, one possible approach is to introduce a source of gas containing a low level of the same volatile compounds found in the contaminated gas source during intermittent operations.

6.2.18.2 Operation Monitoring

Operation monitoring is performed to ensure that permit requirements are being met and to identify changes in performance that may warn of a decrease in treatment efficiency. This is accomplished by sampling and analyzing influent and effluent gases on a routine basis and periodically sampling the liquid effluent from individual cells. Additionally, oxygen, carbon dioxide and volatile byproduct concentrations, moisture levels, and temperature of the influent and effluent gases should be determined. VOCs, oxygen, and carbon dioxide (and other volatile byproducts) should be plotted and trends evaluated over time.

Periodically, the filter material should be sampled and analyzed for moisture content, pH, nutrient availability, microbial populations (plate counts), total organic carbon content, and filter particle density/porosity. These data should also be plotted and trends compared to trends in performance to evaluate long-term changes in biofilter media and the impact on biofilter contaminant removal efficiency.

6.2.18.3 Quality Assurance/Quality Control

Quality assurance and quality control (QA/QC) practices include those common to other remediation technologies, including the use of blanks, blind samples, and spiked samples for monitoring of influent and effluent air, and review of data for consistency to identify potential labeling

problems, etc. Field monitoring equipment should be routinely tested, calibrated, and serviced. In general, quality control practices resemble those appropriate for bioventing as discussed in Section 4.2.18.3.

7 INTEGRATED TECHNOLOGIES

7.1 Introduction

On many sites, both soil and groundwater have been contaminated by past chemical releases, so an integration of soil and groundwater treatment methods is often required for effective site remediation. Proper integration of treatment systems will reduce overall treatment costs and required treatment times. For example, there is little value using an in situ groundwater treatment system when the soils overlying the aquifer are contaminated with concentrated, residual-phase contamination which continues to leach soluble contaminants into the underlying groundwater. In this case, source remediation must be implemented before or during groundwater remediation if the rate of site remediation is to be accelerated above that which occurs naturally due to source area weathering. On the other hand, there may be little value in treating low levels of soil contamination when the primary risk at a site is from groundwater which is migrating toward an off-site receptor. Knowing when and how to integrate soil and groundwater treatment systems must be based on the distribution of contamination and the overall clean-up objectives for the site. On most sites, the objective will be to reduce the risk of contamination at the lowest possible cost within an acceptable timeframe, i.e., to accelerate the rate of contaminant removal to reach specific target levels in each medium in the shortest time that is economically acceptable.

Sites which contain concentrated amounts of free-phase product or residual saturation are often remediated in sequential phases, with each phase focused on a particular contaminated media. For example, free product removal normally precedes the installation of a groundwater biological treatment system. Optimized remediation systems will focus on removing the most accessible mass of risk-related contaminants first, and then shift to more dilute contaminants during a later phase. In this way, the greatest potential risk is removed for the least cost while each additional increment of

risk reduction is achieved at a higher cost. With the development of new remediation technologies and the growing acceptance of intrinsic biological remediation (Section 5.3) as a "polishing" step for impacted groundwater, more sites are being remediated using either a parallel or sequential treatment train approach.

The parallel treatment of impacted soil and groundwater media has historically been carried out using separate technologies (Brown and Sullivan 1991). Contaminated soils are often treated in place using bioventing (Section 4.2) at the same time that in situ groundwater treatment is enhanced using the Raymond process (Section 5.2). A treatment train that is becoming standard practice is the use of bioventing to reduce the long-term leaching of degradable contaminants in the vadose zone, while intrinsic biological remediation (Section 5.3) is used to complete risk reduction in a stabilized groundwater plume. For sites with small quantities of contaminated soils, excavation and aboveground biological treatment of the source (Sections 4.3 and 4.4) are also effective methods of reducing contaminant loading to the groundwater and accelerating natural biodegradation of the dissolved plume.

A summary of possible technology combinations for the biological treatment of soil and groundwater contamination is provided in Table 7.1 as a function of the nature and distribution of contamination existing at a site. The specific selection of a given component within the treatment train depends upon the magnitude of the impact on a given media, i.e., concentrations above MCL or risk-based action level, and whether a receptor is or will be impacted, i.e., concentrations above MCL or risk-based action level at a downgradient well, within a basement or utility corridor, etc. A more aggressive treatment component is generally selected if recoverable, free-phase product exists at a site or if concentrations of contaminants of concern are high in one or more media, and if an existing or imminent threat to a sensitive receptor can be demonstrated. Table 7.2 summarizes a number of studies that have recently been presented in the literature that demonstrate the integration of product recovery, soil, and groundwater remediation technologies for accelerated and enhanced site remediation.

Several technologies have been developed during the past decade to treat more than one media with concurrent processes. Bioslurping technology described in Section 7.3 is a good example of concurrent treatment designed into a single treatment technology. Using the bioslurping technology, contaminated groundwater and free product can be removed while air is drawn through contaminated unsaturated soils to stimulate in situ bioventing. Biosparging (Section 5.5) is another example of concurrent treatment using a single technology. Air introduced below the water table provides some

Table 7.1
Technology Combinations for Biological Treatment of Soil and Groundwater Contamination

Nature and Distribution of Contaminants	Free Product Recovery	Soils Treatment	Groundwater Treatment
Recoverable free-phase product and soil and groundwater contamination	Dual-phase extraction wells; OR Bioslurping; AND	Bioventing; OR Partial excavation and landfarming/biopiles; AND	Raymond Process; OR Biosparging; OR Pumping and aboveground air stripping or biological treatment; AND/OR Natural attenuation
Little free-phase product, residual-phase soil contamination, and groundwater contamination	Product skimmers; OR Passive wicking	Bioventing; OR Partial excavation and landfarming/biopiles; AND	Raymond Process; OR Biosparging; OR Oxygen release compounds; AND/OR Natural attenuation
No free-phase product, residual-phase soil contamination, and groundwater contamination	Not needed	Bioventing; OR Partial excavation and landfarming/biopiles; AND	Raymond Process; OR Biosparging; OR Oxygen release compounds; AND/OR Natural attenuation
No soil contamination, moderate groundwater contamination	Not needed	Not needed	Biosparging; OR Oxygen release compounds; AND/OR Natural attenuation

oxygen to enhance the aerobic biodegradation of dissolved hydrocarbons. In addition, contaminants volatilized with the injected air enter the unsaturated zone where they can be degraded by aerobic organisms which use the oxygen not transferred to the sparged groundwater in a bioventing mode.

Table 7.3 provides a matrix summarizing site, soil, and waste constituent characteristics that are considered important in the evaluation and design of a number of selected integrated technology treatment trains and the bioslurping technology listed in Table 7.2. For the treatment trains, Table 7.3 was generated using the site, soil, and waste limitations identified for each individual technology in the treatment train from the corresponding soil and groundwater treatment technology tables in previous sections of this monograph, Tables 4.1 and 5.1, respectively.

The bioslurping technology is an in situ one, and as such, the technology is affected greatly by site conditions that negatively impact the uniform distribution and transport of product being recovered and reactants (air) being distributed throughout the contaminated site (i.e., groundwater table fluctuations and heterogeneous layered soil lenses both above and below the water table). This technology uses high vacuum to assist in free product and

Table 7.2
Example Case Studies Demonstrating the Use of Integrated Technologies for Biological Treatment of Soil and Groundwater Contamination

Technology Combinations	Contaminant Type	References	Operating Mode: Parallel or Series
SVE/Bioventing	JP-4	Dupont et al. 1990	Series
Raymond Process/Liquid Bioreactor/Intrinsic Remediation	BTEX Chlorinated VOCs TOC	Thompson et al. 1995	Series + Parallel
SVE/Free Product Recovery	Gasoline	Norris et al. 1990	Parallel
Raymond Process/Soil Cell	Gasoline	Dey et al. 1990	
Air Sparging/Bioventing	Mixed Fuels	Lord et al. 1995	Parallel
	Toluene	Brown et al. 1995	
	Diesel and Gasoline	Ratz et al. 1993	
	Mixed Fuels	Jarvanmardian et al. 1995	
	Gasoline	Martinson et al. 1993	
	Diesel	Rhodes et al. 1995	
SVE/Raymond Process	Gasoline	Norris et al. 1993	Parallel
Biopiles/Raymond Process	Oil Refining	Ellis 1994	Parallel
Biopiles/Liquid Bioreactors/Raymond Process	PCP/PAHs	Piotrowski et al. 1994	Parallel
Vapor Bioreactor/Liquid Bioreactor	BTEX	Marsman et al. 1994	Parallel
Raymond Process/Biosparging	Natural Gas Site	Raetz and Scharff, 1995	Parallel
SVE/Bioventing/Biosparging Raymond Process/Soil Cells	Gasoline, Varsol No. 2 Fuel Oil	Dey et al. 1996	Parallel
Bioslurping Technology Applications	Jet Fuel	Leeson et al. 1995	Parallel
	Gasoline and Diesel	Connolly, et al. 1995	Parallel
	Jet Fuel	Hoeppel et al. 1995	Parallel
	Jet Fuel	Kirshner et al. 1996	Parallel

groundwater recovery, while also moving air through the vadose zone. It incorporates bioventing into its operation, and as with bioventing, air permeability and high water content in the vadose zone are both important soil characteristics affecting system performance. Finally, performance of the technology will be affected by additional soil conditions impacting microbial activity (i.e., non-ideal water content and soil pH limitations), and by waste constituent characteristics that affect a contaminant's toxicity, biodegradability, and bioavailability.

The following section provides additional discussion of applications and limitations of bioslurping technology identified in Table 7.1 for the integrated treatment of a site containing free product, residual-phase material, and contaminated soil and groundwater.

Table 7.3
Impact of Various Site, Soil and Waste Constituent Characteristics on the Performance of Various Treatment Trains and Bioslurping Technology Performance*

		SVE/BV	AS/BV	SVE/RP	SC/RP	BSI
Site	Climatic Conditions	N	N	N	I	N
	GW Table Fluctuations	I-	I	I-	I	I
	Surface Structures	I+	I	I+	N	I
	Layered Formation	V-	V-	V-	V-	V-
	Product Existence/ Distrubtion	V+	V+	V+	V+	V+
Soil	Fine Grained	I	V-	V-	V-	I-
	High Soil Water Content	V-	N	V-	I	V-
	Low Soil Water Content	I-	N	I-	I-	I
	Nutrient Limitation	N	I	I-	I-	N
	Adverse pH Conditions	I-	I	I-	I-	I
Waste Constitutent	Volatility	I+	V	I+	I	V+
	Biodegradability	I	V	V	V	V
	Bioavailability	I	V	V	V	V
	Water Solubility	I-	I	I-	I-	I
	Toxicity	I	V-	V-	V-	V

*SVE = soil vapor extraction
BV = bioventing
AS = air sparging
RP = Raymond process
SC = soil cells
BSI = bioslurping
N = not important related to the performance of the technology
I = important related to the performance of the technology
V = very important related to the performance of the technology
+ = characteristic positively impacts the performance or selection of the technology
- = characteristic negatively impacts the performance or selection of the technology

7.2 Bioslurping

7.2.1 Principles of Operation

Bioslurping is an integrated in situ process that combines vacuum-enhanced dewatering and free product recovery techniques with bioventing for the simultaneous recovery of LNAPL, contaminated groundwater, and contaminated soil vapor; and the transfer of oxygen to stimulate the aerobic degradation of contaminants within the dewatered capillary fringe and unsaturated zone. A typical configuration of a bioslurping system is shown in Figure 7.1.

As indicated in Figure 7.1, a typical bioslurping system consists of the following components:

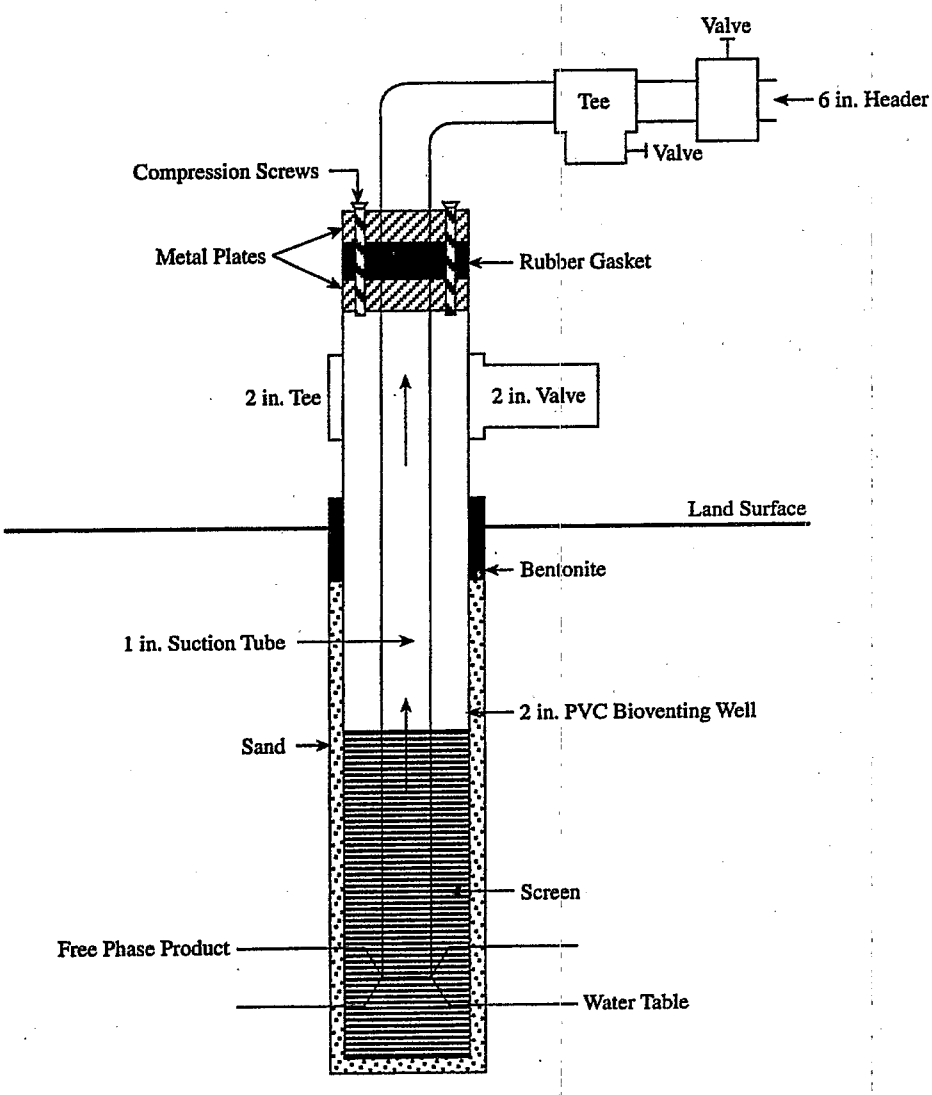
- a small diameter (typically 5-cm (2-in.)) PVC bioventing well screened across the vadose zone, capillary fringe and groundwater table; and sealed at the surface for maintenance of a vacuum within the well;
- a smaller diameter (typically 2.5-cm (1-in.)) PVC suction tube located within the bioventing well, and placed for extraction at the LNAPL/groundwater interface;
- a high vacuum liquid ring pump for extraction of liquids and vapors;
- an oil/water separator (OWS) for the gravity separation of recovered LNAPL and groundwater;
- OSW effluent holding tanks for recovered product and separated groundwater; and
- groundwater and vapor treatment systems as required.

7.2.1.1 Vacuum-Enhanced Free Product Recovery

Vacuum-enhanced free product recovery (FPR) uses a vacuum on a well point to increase the hydraulic gradient and improve the transmissivity of the aquifer in the capillary fringe to increase rate of flow of LNAPL and soil vapor into the well (AFCEE 1995). Vacuum-enhanced FPR is an improvement over conventional FPR systems using single or dual pumps, as conventional systems increase hydraulic gradients by creating a cone of depression around the extraction well, causing smearing of product and reducing the saturated thickness of the formation. With vacuum-enhanced FPR, minimal liquid drawdown occurs due to the production of reduced pressures around

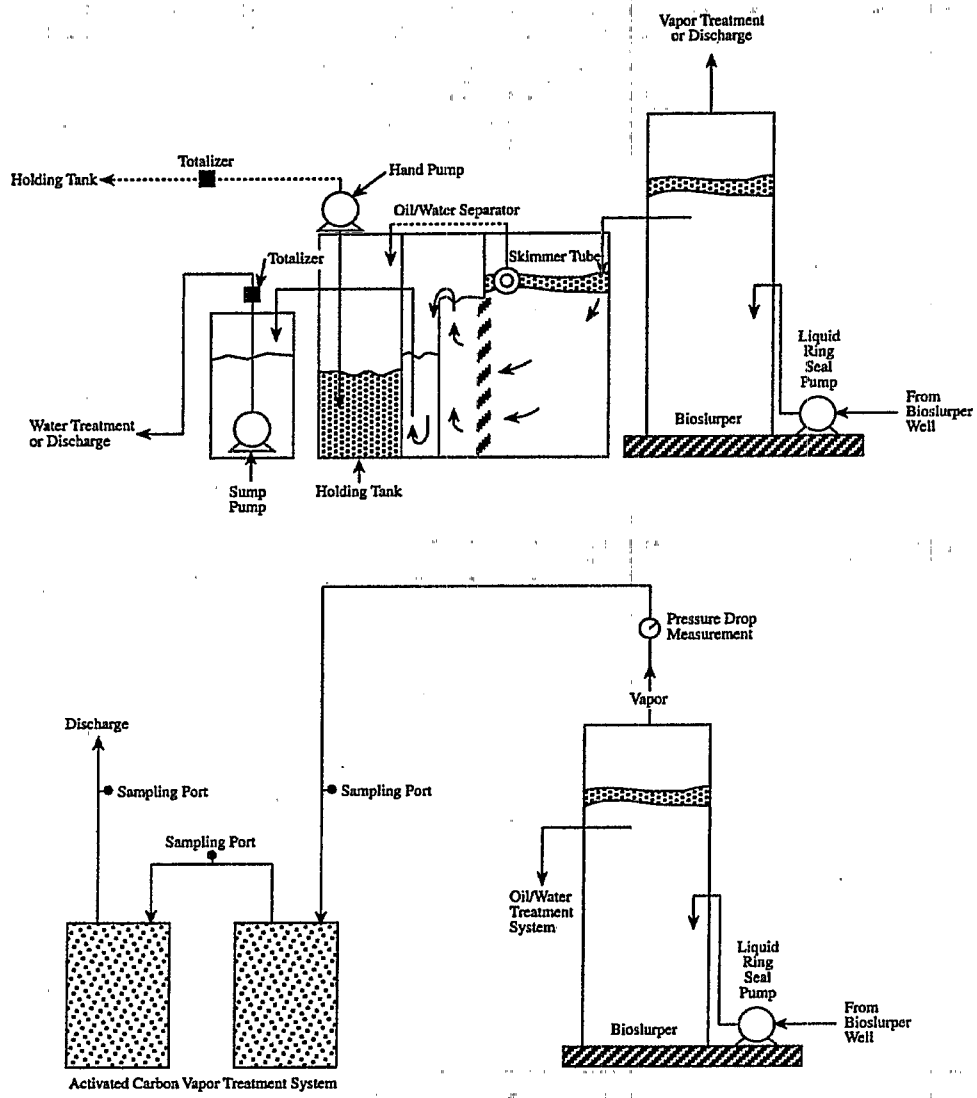
the extraction well, resulting in horizontal rather than diagonal flow through more permeable horizontal flow paths. Increased hydraulic gradients without a reduction in saturated thickness using vacuum-enhanced FPR results in improved liquid flow rates and improved LNAPL recovery.

Figure 7.1
Schematic of a Typical Bioslurping System



Source: AFCEE 1995

Figure 7.1 cont.
Schematic of a Typical Bioslurping System



Source: AFCEE 1995

7.2.1.2 Bioventing

The principles of operation and design of bioventing systems have been detailed in Section 4.2. As in a strict bioventing system, bioventing processes integrated into a bioslurper system use a vapor extraction system to

move oxygen through the unsaturated zone and enhance the aerobic degradation of contaminants within the unsaturated zone and throughout the capillary fringe. The use of conventional air extraction bioventing results in upwelling of the groundwater table and a reduction in air flow through the capillary fringe, the area typically containing high residual masses of contamination. Groundwater upwelling is eliminated with the use of the center suction or "slurp" tube incorporated into the bioslurper system design. This design addition allows the bioventing of the capillary fringe in extraction-mode bioventing systems, and significantly improves bioventing system performance when air injection bioventing systems cannot be utilized at a site.

7.2.1.3 Integrated Bioslurper Technology

As indicated above, bioslurper technology combines both vacuum-assisted FPR and bioventing technology concepts to provide an integrated approach for the removal of free product, contaminated groundwater, and contaminated soil vapors — while enhancing the recovery of mobile and residual-phase product and the in situ, aerobic treatment of unsaturated zone and capillary fringe contamination through the application of a high vacuum and use of a slurper tube in a small diameter extraction well.

The bioslurping system is designed to minimize the extraction of groundwater and soil gas by operating at low extraction rates with minimal product and groundwater drawdown using the slurper tube to extract mixed groundwater and soil gas vapors at the groundwater interface in the characteristic "slurping" mode. A comparison of a conventional dual pump LNAPL recovery system to that of a bioslurping well is presented in Figure 7.2. The slurping action describes the movement of slugs of air/groundwater/product mixtures up the center slurper tube as high vacuum (up to 51 cm (20 in.) of mercury) is applied to the extraction well. This slurping action also increases the theoretical maximum suction lift ≈ 8m (≈ 25 ft) of liquid from the groundwater table since the extracted fluid is a mixture of groundwater, soil gas, and free product, resulting in liquid fluid entrainment.

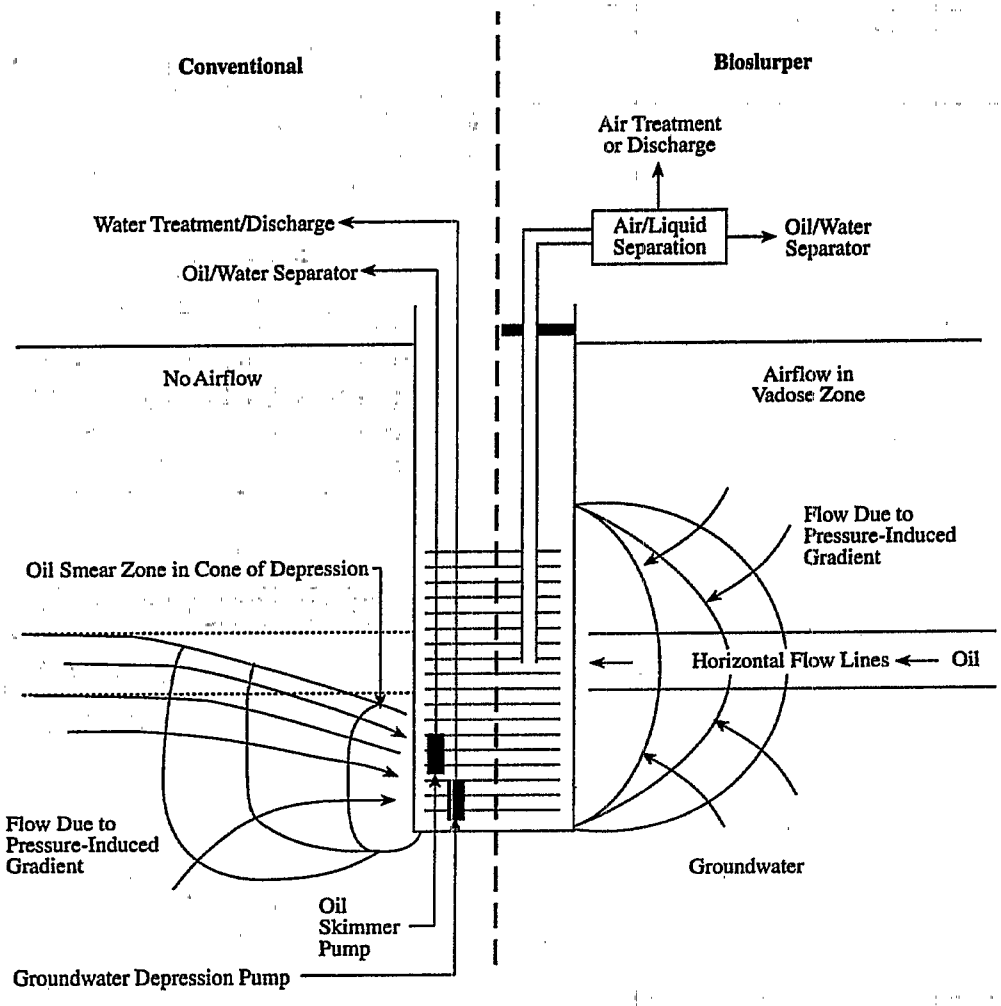
7.2.1.4 Technology Applications and Limitations

Keet (1995) summarized the applicability of the bioslurping technology as follows:

- recovery of free product from the groundwater table in fine- to medium-fine sediments and fractured rock;

- enhanced recovery of free product in formations where NAPL mobility is limited; and
- enhanced removal of aerobically degradable contaminants in the unsaturated zone and capillary fringe overlying free product layers via bioventing.

Figure 7.2
Comparison of Conventional LNAPL Recovery and Bioslurping



Source: AFCEE 1995

The bioslurping technology has the following advantages over conventional free product recovery and remediation techniques that are characteristic of innovative technologies designed with technology integration in mind (Keet 1995):

- free product recovery is enhanced in all medium-grained materials, particularly medium- to fine- grained materials, due to high vacuum operations;
- groundwater depression is practically eliminated due to the use of the slurper tube, resulting in little or no change in the relative permeability of the capillary fringe to residual product, producing enhanced product recovery rates compared to conventional FPR systems;
- operation under a vacuum results in recovery of residual product not mobile under atmospheric pressure conditions; and
- operation under a vacuum results in the movement of soil gas through the vadose zone and capillary fringe, stimulating volatilization of contaminants and oxygen transfer for the stimulation of in situ aerobic degradation of contaminants in a bioventing mode. Significant improvements in system performance can be expected in a bioslurper system as compared to conventional air extraction bioventing despite operating at high vacuums, particularly in the capillary fringe, due to the control of groundwater levels in a bioslurper system with the use of the slurper tube.

Two disadvantages of the bioslurping system have been identified (Keet 1995) as follows:

- high velocity extraction of groundwater/vapor/NAPL mixtures can form emulsions that are difficult to separate in post-extraction OWS units; and
- bioslurping systems generate not only a groundwater and free product stream, but also a contaminant-laden vapor stream that must be treated prior to discharge at many sites (see Figure 7.2), adding to the complexity of a free product recovery system.

7.2.2 Process Design Principles

Most of the information regarding bioslurper design comes from the AFCEE Test Plan and Technical Protocol document (AFCEE 1995) describing field treatability testing of the technology. The reader is referred to this document for complete details regarding recommended procedures for

conducting a field treatability test for bioslurping prior to final field-scale design. The following information is a summary of recommendations from the AFCEE protocol document, augmented with additional reference material as noted.

7.2.2.1 Extraction Well and Slurper Tube

A bioslurper extraction well consists of a 5- to 10-cm (2- to 4-in.) Schedule 40 PVC well (Figure 7.1) with a slot size allowing free soil gas flow without transporting fines into the well. In applications where the groundwater table is greater than 10 m (30 ft) below ground surface, a 10-cm (4-inch) diameter well is recommended. The screened interval begins a maximum of 1 m (3 ft) above the water table and generally extends 3 or more meters (10 or more feet) into the water table depending upon the thickness of contamination within the saturated zone and the seasonal fluctuation in groundwater table elevation.

Extraction well installation via hollow-stem auguring is recommended, with the diameter of the auger hole at least two times the outside diameter of the vent well. The annular space surrounding the slotted section of the extraction well should be filled with silica sand, with the annular space above the screened interval completed with bentonite grout to seal the well from the surface and prevent short-circuiting within the well annulus. A minimum 1 m (3 ft) grout seal is recommended.

A 2.5-cm (1-in.) PVC suction or slurper tube is placed within the outer extraction well and is sealed in some fashion with O-rings or compression gaskets to produce an air-tight seal on the surface at the wellhead. Figure 7.1 shows a typical bioslurper well with metal plates, rubber gaskets, and compression screws to complete the airtight seal around the slurp tube. This figure also suggests the use of a "T" and valve on the wellhead so that a variety of operating modes can be evaluated for the bioslurper well during field treatability testing (Section 7.2.2.5).

7.2.2.2 Liquid Ring Pump

Liquid ring pumps are suggested for bioslurper applications because of their efficient performance at high vacuums, i.e., 74 cm (29 in.) of mercury, and they are inherently explosion-proof. This latter characteristic is very important as bioslurping systems yield combinations of water, NAPL, and vapors that potentially can be explosive. A variety of pump sizes are available from a variety of vendors, ranging from 3-hp to 10-hp models, and should be selected based on site-specific needs. Single bioslurper well

installations with groundwater depths less than 7.6 m (25 ft) would allow the use of 3-hp liquid ring pumps, while multiple wells and greater depths would require higher horsepower models. For example, the NAS Fallon site with groundwater depths ranging from 1.5 to 3.7 m (8 to 12 ft) utilized 48 bioslurper wells over a 0.4 hectar (1-acre) area and required a 10-hp liquid ring vacuum pump to drive the system (Hoeppel et al. 1995).

7.2.2.3 Oil/Water Separator

Operation of a bioslurping system will result in the recovery of a mixture of groundwater, LNAPL, and soil vapor that must be separated into its individual components prior to their treatment, storage, or discharge. Because of high upflow velocities that may result from high vacuum applications and high flow rates required when groundwater depths are greater than 8 m (25 ft), stable emulsion formation and problems related to its subsequent separation can be problematic. All bioslurping systems will require, at a minimum, a gravity oil/water separator (OWS) with a 1 to 2 gpm/bioslurper well capacity. See AFCEE (1995) for recommended bioslurper system equipment.

As indicated in Figure 7.1, recovered product drains by gravity into a holding tank, while the separated groundwater drains by gravity as a subnatant into an effluent transfer tank prior to its removal. These holding and transfer tanks must be sized based on site-specific limitations that govern the frequency of product removal and the design flowrate of an aqueous treatment system if one is required.

Connolly et al. (1995) describes the effluent treatment system which uses a conventional coalescing-plate OWS for the removal of >20μm size oil droplets, followed by an additional three-layer (medium-grade chopped fiberglass matting, medium-grade steel wool, surgical cotton wool) to coalesce droplets of <20 μm in diameter. This OWS system is contained within a 200-L (52-gal) tank suspended within a 1,000 L (264 gal) holding tank. Water separated from the recovered oil is pumped into a biofilter for treatment prior to disposal. This system is designed to treat liquid from 11 recovery wells at an approximate flowrate of 5 L/min (1.3 gal/min).

7.2.2.4 Groundwater Treatment

When possible, groundwater that is recovered from a bioslurping system and which has gone through oil/water separation should be discharged directly to a local sanitary sewer. The volumetric flow rate of this recovered groundwater should be low, typically a maximum of 0.5 to 1 gpm/bioslurper well, and will contain less than 20 mg/L total petroleum hydrocarbons

(TPH) leaving the OWS. If local ordinances will allow, direct sanitary sewer discharge of this low volume, low organic loading waste stream is a cost-effective alternative to on-site groundwater treatment that should have little impact on the POTW receiving this bioslurper aqueous stream.

Where a sanitary sewer is not readily available for discharge, or where local ordinances do not allow such an untreated discharge, a variety of treatment options can be used for this aqueous stream. Aboveground bioreactors described in Section 5.4 are one option. Activated carbon can also be used, and is the method of treatment recommended in the AFCEE (1995) protocol. Additionally, both water and extracted vapor treatment can be provided in a single biofilter reactor as reported by Connolly et al. (1995) and described below.

The treated aqueous stream can typically be discharged to a sanitary sewer, or in many locations, can be discharged directly to a storm sewer or to a surface infiltration gallery.

7.2.2.5 Vapor Treatment

Bioslurper systems are similar to bioventing systems (Section 4.2) in that their cost-effectiveness depends upon specific requirements for the treatment of offgas generated in the operation of the system. A bioslurper system incorporates bioventing into the overall treatment design. However, unlike bioventing, bioslurper extraction wells are generally located within the highest areas of contamination at a site to maximize their effectiveness in recovering free product and residual-phase material. In doing so, high contaminant vapor concentrations will result, particularly during the initial phases of system operation, often requiring offgas treatment to meet strict local air quality discharge requirements. If discharge limits are based on total mass emission rates on a monthly or yearly basis, vapor treatment may not be required and should be negotiated with the local permitting authority. Provisions for temporary vapor treatment using portable treatment equipment, or operating the bioslurping system in a cyclic fashion to reduce overall vapor emissions should also be considered.

If vapor treatment is required, several practical options exist for the low volumetric flow rate (≈ 3 to 20 scfm/bioslurper well) vapor stream recovered by bioslurping systems. First, vapor reinjection and in situ bioventing of the extracted vapors may be possible if vapor reinjection is allowed by the local permitting authorities. Limitations to this option include a thin unsaturated zone, low-permeability soils within the reinjection area, local subsurface structures (i.e., basements, utility corridors, etc.) that may be adversely impacted by vapor reinjection, and regulatory opposition to reinjection of

contaminated vapors. The reader is referred to Section 4.2 for design details of bioventing systems.

Treatment of extracted vapors using vapor-phase activated carbon treatment is also a viable option for bioslurping systems. Typically, a series of two or three 91 kg (200 lb) carbon canisters are used to treat the bioslurper offgas. Flow is passed through the canisters until complete breakthrough is observed in the first canister. At this point, the first canister is removed from service and disposed or regenerated, the second canister then becomes the first canister in the treatment train, and a new, second or third canister is added to the effluent stream. In this way, maximum use is made of the sorption capacity of the carbon, and essentially complete treatment of the vapor stream is provided. Figure 7.1 shows a typically activated carbon treatment system used for bioslurper offgas treatment.

The U.S. Air Force has evaluated the use of internal combustion engines (ICEs) for the treatment of offgas from bioslurper systems (AFCEE 1995) and has found them to be efficient and cost-effective, particularly if only temporary offgas treatment (i.e., during initial operation of the bioslurping system) is required. These ICEs have special computer-controlled carburetor systems allowing them to run solely on combustible contaminant vapors when extracted concentrations are high. Natural gas or propane is used as a make-up fuel for these units during ICE startup and when concentrations fall below combustible levels in the bioslurper offgas. Trailer-mounted units from RSI, Inc. are available for bioslurper applications.

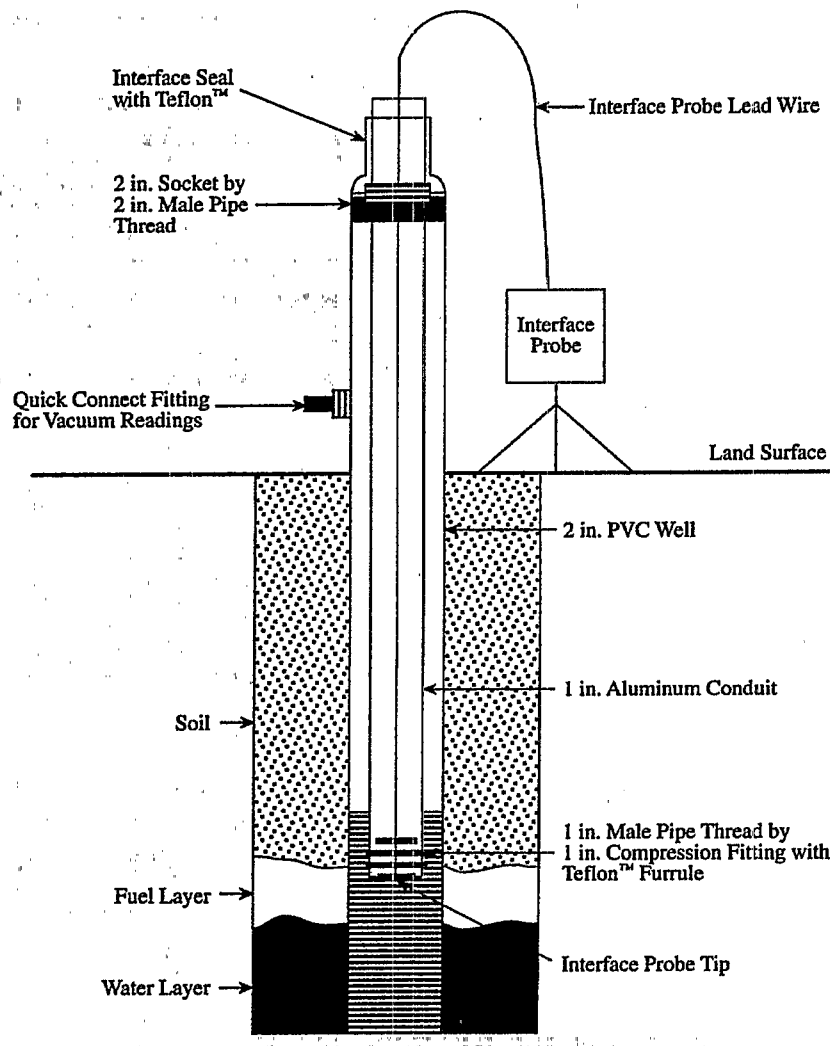
An additional vapor treatment system that has been used in bioslurper applications was described by Connolly et al. (1995) and consists of a biofilter system designed to treat both the aqueous and vapor streams recovered from a bioslurping system. Figure 7.2 shows this combined water and vapor treatment system in which vapor from a liquid/vapor separator is injected into the base of the biofilter while the aqueous effluent from an OWS was dispersed over the surface of the sand-media biofilter. The biofilter used in this application had a volume of 17 m^3 (55.8 ft^3), a depth of 1.75 m (5.74 ft), and a water contact time of approximately 60 minutes. The system operated in this mode produced non-detect levels of volatiles in the effluent vapor stream and of TPH and BTEX components in the treated liquid.

7.2.2.6 Field Instrumentation and Monitoring

Field monitoring requirements for bioslurping systems are similar to those described in Section 4.2.2 of this monograph for bioventing systems and include the use of soil vapor monitoring probes to measure of soil gas pressure, and soil gas oxygen, carbon dioxide, and contaminant

concentrations. In addition, groundwater level and LNAPL thickness measurements must be collected during bioslurper operation using an interface probe and vacuum-tight well seal as shown in Figure 7.3.

Figure 7.3
Schematic of a Vacuum-Tight Interface Probe System Used for Groundwater and LNAPL Level Measurements in Bioslurper Systems



Source: AFCEE 1995

7.2.2.7 Field-Scale Treatability Testing

Because of the significant effect subsurface site and soil conditions and the actual distribution of residual product have on the recovery of mobile free product and residual phase material, the Air Force (AFCEE 1995) developed a field-scale bioslurping treatability test protocol designed to evaluate bioslurping effectiveness and a variety of other free product recovery methods for the recovery of free product on a site-specific basis. The reader is referred to the AFCEE (1995) document for details of the testing protocol. A summary of the testing method is provided below.

As indicated in Table 7.4, the AFCEE bioslurping protocol consists of a sequence of operations with a single bioslurping well installation to evaluate the recovery potential for free product using a variety of recovery techniques ranging from simple bailing, to skimming, to drawdown pumping, and finally, to high vacuum bioslurping operation. The testing is designed to be conducted over a two-week period using portable vacuum extraction, groundwater pumping, and effluent treatment equipment. Initial activities are used to assess the "recoverability" of LNAPL at the site through an initial baildown test, and to assess the bioventing potential for degradation of contaminants in the unsaturated zone through monitoring point installation and limited soil gas sampling to collect evidence of bioactivity within the unsaturated zone, i.e., oxygen depletion and carbon dioxide production within the vadose zone.

With completion of these preliminary site assessment activities, a 10-day field bioslurper pilot test is specified which involves 2-day operation of the system in a skimming mode without vacuum (Figure 7.4), 4-day operation in the vacuum-enhanced bioslurper mode (Figure 7.5), 1-day operation in a repeat skimming mode without vacuum, and finally, a 2-day groundwater depression operating mode (Figure 7.6). Soil gas composition, free product thickness, and groundwater elevation measurements are made throughout the 10-day pilot test, as are the cumulative volumes of extracted free product, groundwater, and soil gas. The latter measurements are required to determine the overall effectiveness of each free product recovery method and the contribution to overall free product of the bioventing component of the bioslurping system.

Selection and design of a full-scale product recovery and site remediation system that is optimal for the site can be made based on the outcome of this field treatability test. From treatability test results, sites showing only marginal improvements in product recovery for bioslurping systems over simple skimming methods (i.e., Bolling AFB, DC Bldg. 41 site in Table 7.5) can be differentiated from those sites in which vacuum-assisted product recovery

Table 7.4
Schedule of Activities for a Typical Bioslurper Field Treatability Study as Recommended by AFCEE

Pilot Test Activity	Schedule
Site-Specific Test Plan Completed	14 days prior to approval
Test Plan Approval (when required)	Prior to Pilot Test
Mobilization	Days 1-2
Site Characterization	Days 2-3
Product/Groundwater Interface Monitoring	
Baildown Tests	
Monitoring Point Installation	
Soil Gas Survey	
Soil Sampling	
System Installation	Days 2-3
Test Startup and Operation	Day 4
Skimmer Test (2 days)	Days 4-5
Soil Gas Permeability Test	Day 6
Bioslurper Vacuum Extraction Test (4 days)	Days 6-10
Skimmer Test 2 (1 day)	Day 11
Drawdown Pump Test (2 days)	Days 12-13
In Situ Respiration Test (4 days)	Days 10-14
Demobilization	Days 13-15

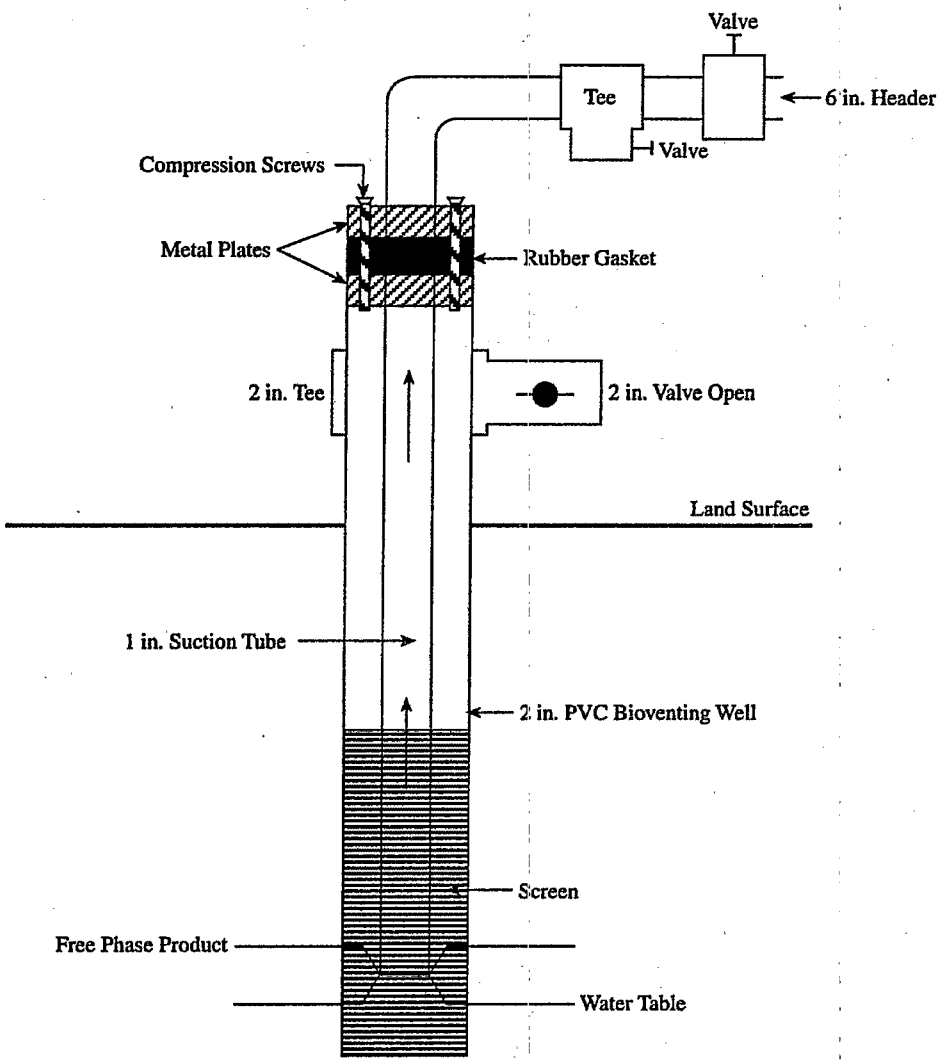
Source: AFCEE 1995

and bioventing using bioslurping technology significantly accelerates source treatment and product removal (i.e., Bolling AFB, DC Bldg. 18 and Travis AFB, CA JFSA-1 sites in Table 7.5).

7.2.3 Process Flow Diagrams

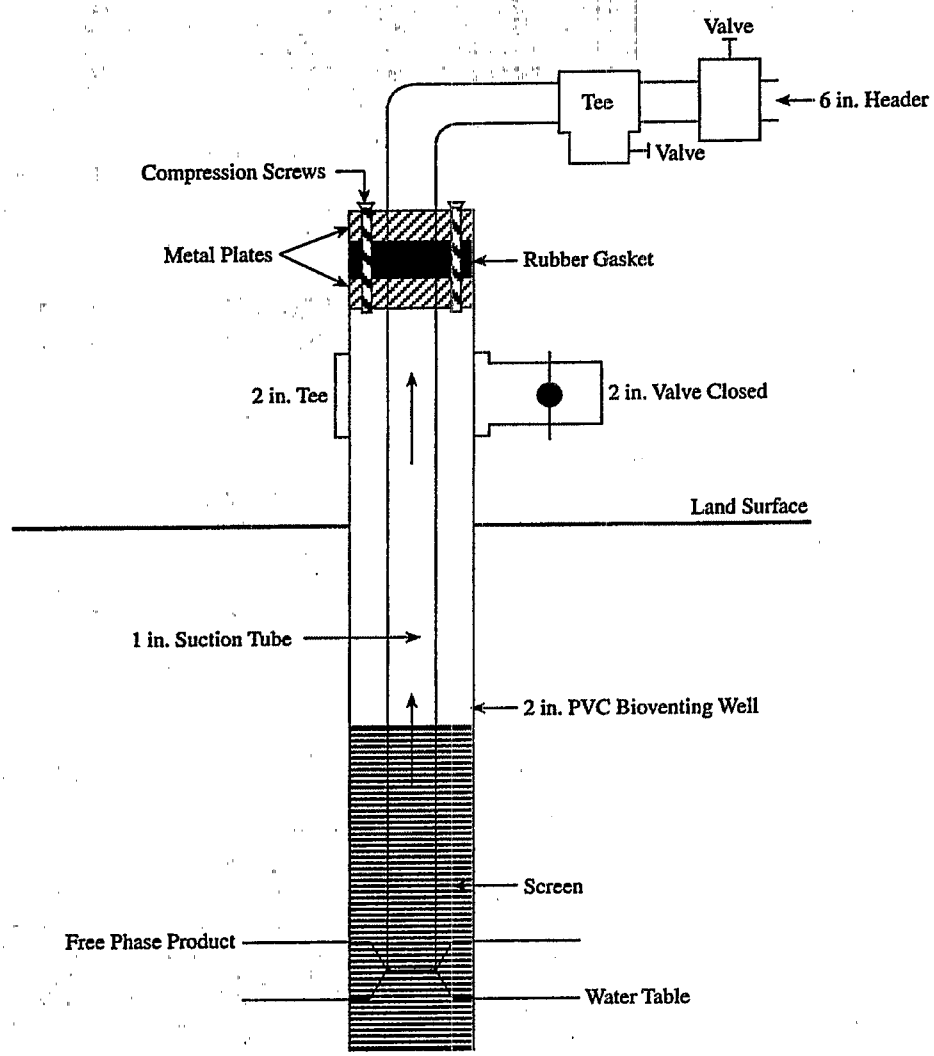
A typical bioslurper system process flow diagram has been presented in Figure 7.1. All systems will have the same general configuration, with slight variations in their layout depending upon whether vapor and liquid effluent treatment are required, and on the specific treatment option selected, if they are needed. The reader is referred to Section 4.2 for bioventing systems, 5.4 for aboveground reactors, and 6.2 for biofilter systems, all of which provide options for offgas or recovered groundwater treatment using biological treatment methods.

Figure 7.4
Schematic of a Bioslurper System Operating in a Skimmer Mode



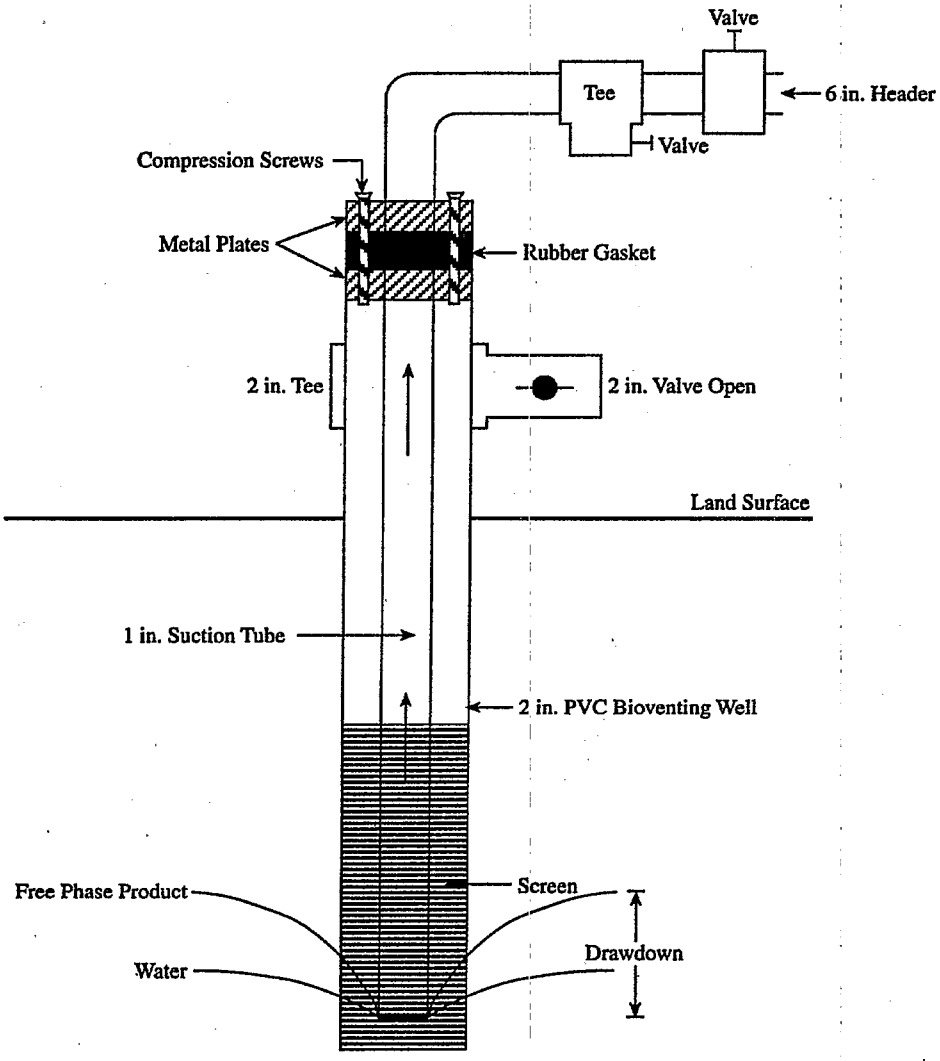
Source: AFCEE 1995

Figure 7.5
Schematic of a Bioslurper System Operating In a Vacuum-Enhanced Bioslurper Mode



Source: AFCEE 1995

Figure 7.6
Schematic of a Bioslurper System Operating in a Groundwater Drawdown Mode



Source: AFCEE 1995

Table 7.5
Summary of Bioslurper Field Treatability Performance for Selected Sites

Site Location	Depth to Water (ft)	Initial Product Thickness (ft)	Thickness After 24 hour Baildown Test (ft)	Well Diameter (in)
Boling AFB, DC, Bldg. 18	23.65	4.44	3.52	2
Boling AFB, DC, Bldg. 41	19.06	0.34	0.34	4
Travis AFB, CA, JFSA-1	8.7	Skimmer Active	Skimmer Active	6

	Average Fuel Recovery Rate (gal/d)			
Site Location	2-Day Skimmer Test	4-Day Bioslurper Test	1-Day Skimmer Test	2-Day Drawdown Test
Boling AFB, DC, Bldg. 18	16.9	59.8	8.2	31.2
Boling AFB, DC, Bldg. 41	0.86	1.14	NA	0.13
Travis AFB, CA, JFSA-1	0	3.85	0	3.76

Site Location	Soil Gas Radius of Influence (ft)	Vadose Zone Biodegradation Rate (mg/kg/d)
Boling AFB, DC, Bldg. 18	454755.3	NA
Boling AFB, DC, Bldg. 41	0.86	12.9 to 15.3
Travis AFB, CA, JFSA-1	0	61 to 82

NA = Test not performed

Source: Kittle et al. 1996

7.2.4 Process Modifications

As indicated in Figures 7.4 through 7.6, a bioslurping well can be operated in a variety of modes by changing the vacuum applied at the wellhead and by adjusting the depth of the slurper tube with respect to the LNAPL/groundwater interface. The standard mode of operation is with a high vacuum applied at the well and the slurp tube located at the static product/groundwater interface to encourage horizontal flow of product into the well as indicated in Figure 7.5. When product recovery rates fall off as recoverable product is removed from the subsurface over time, bioslurping systems

can easily be converted to combined groundwater depression and bioventing systems by operating in the groundwater depression mode as indicated in Figure 7.6. This operating mode can be highly effective in source remediation if a significant smear zone exists at a site. Groundwater depression via the bioslurping system can effectively dewater the capillary fringe allowing oxygen to be transferred to this residual saturation, stimulating its aerobic degradation via bioventing.

7.2.5 Pretreatment Processes

Since this treatment technology is designed to provide groundwater and free product recovery and biovent the associated unsaturated zone, no specific pretreatment steps are normally required this technology.

7.2.6 Posttreatment Processes

Because the bioslurping process is carried out in situ, soils are left in place following treatment, and posttreatment of soils is unnecessary. However, as indicated in Section 7.2.2.3 through 7.2.2.5, there may be significant posttreatment process requirements for the various effluent streams based on local discharge requirements. In addition, actions taken for the removal and disposal or recycling of recovered liquid product will be governed by local requirements and may vary from strict manifesting of the product as a hazardous waste to the contracting of recycling or disposal services with a local waste oil handler.

7.2.7 Process Instrumentation and Control

A typical process instrumentation used in a bioslurping system is shown in Figure 7.1. In addition to vacuum pump performance, the mass of contaminant removed in the free phase (LNAPL), aqueous phase (recovered groundwater), vapor phase, and via degradation in the vadose zone are also monitored over time. The following describes process monitoring associated with a typical bioslurping system.

7.2.7.1 Flow Measurement

Vapor flowrates from the bioslurping system are typically measured using pitot tube flow indicators. Differential pressure across a pitot tube connected to the inlet side of the liquid ring pump indicates the total flowrate through the system. Vapor flow measurements can be estimated based on subtraction of the product and liquid recovery rates, and/or by measurement of the vapor stream generated following oil and water separation.

Groundwater extraction rates are generally determined using an in-line flow totalizer on the aqueous discharge line from the OWS. Liquid product recovery rates are determined using manual or automated gauging of product levels in the product holding tank or with in-line flow totalizers on the product discharge line from the OWS.

7.2.7.2 Flow Stream Composition Monitoring

To quantify the mass of contaminant recovered as free product, dissolved or vapor phase contaminant, or through biodegradation, concentration data must be collected for contaminants of concern for each recovery pathway.

LNAPL samples should be collected for analysis during each phase of the field treatability test and routinely thereafter throughout the free product recovery phase of remediation at a site. Samples are collected using Teflon™ bailers during the baildown test or from the product holding tank when it is used, in glass vials fitted with Teflon-lined septa. Analysis of the product samples should be carried out, as appropriate, for the analytes of concern. These analyses are used to quantify the mass of specific contaminants recovered as free product and to track the "weathering" of the residual product material over time in response to bioslurper treatment. The product sampling frequency should be determined on a site-specific basis, but would typically be performed daily during the initial operating period of the bioslurper system, then reduced to weekly or bimonthly as product recovery rates decrease.

Samples for specific compound analysis in the vapor phase are recommended (AFCEE 1995) to be collected using evacuated, 1-L, stainless steel, Summa polished canisters from the vapor discharge line of the bioslurping unit. If vapor treatment is required at a specific installation, both pre- and posttreatment samples would be required. These data are used to quantify the mass of contaminant recovered in the vapor phase during bioslurper treatment and for the evaluation of offgas treatment system performance. Continuous or semi-continuous vapor monitoring using a non-specific total hydrocarbon or total halogen detector would be desirable for locations where strict vapor emission limits are placed on the system. With a non-specific field detector, a recommended non-continuous vapor phase sampling frequency would be hourly following initial system startup, every 4 hours after 4 hours of operation, every 12 hours after 12 hours of operation, then daily when system operation stabilized. Specific compound samples for fixed-base laboratory analysis would be collected to augment total contaminant level field measurements at system startup, and at 4 hours, 12 hours, 1 day, 1 week, weekly, and then monthly — once the system operation stabilized —

so that a representative estimate of specific compound recovery rates could be made.

Aqueous samples for specific constituent analysis are collected from the bioslurper OWS aqueous discharge line, and from a water treatment system effluent line, if one is required, using standard 40-ml VOA vials with Teflon-lined septa. The composition of this flow stream would be expected to change less rapidly over time than that of the vapor stream, and would be sampled at a frequency suggested above for the LNAPL product samples. These data are used to quantify the mass of contaminant recovered in the aqueous phase during bioslurper treatment, and for the evaluation of aqueous treatment system performance.

7.2.7.3 In Situ Biodegradation Rate Determinations

As indicated in Table 7.5, at some sites vadose zone biodegradation of residual contamination can be a significant contaminant reduction process. If contaminants of concern are aerobically biodegradable, quantification of this contribution to overall contaminant removal can be provided through the conduct of routine in situ respiration tests (Section 4.2.1.3) using vapor monitoring points installed for bioslurper performance monitoring. In these tests, the bioslurper system is turned off and oxygen and carbon dioxide concentrations are measured (Section 4.2.7.3) over time from soil vapor monitoring probes throughout the site. Reductions in oxygen concentrations with parallel production of carbon dioxide indicate biological consumption of oxygen during the degradation of contaminants within the soil matrix. Data reduction procedures for degradation rate estimates have been described in Section 4.2.9.1. The reader is referred to the Air Force Bioventing Protocol (Hinchee et al. 1992) for a complete description of in situ respiration rate test procedure.

Routine monitoring of the oxygen and carbon dioxide levels throughout the vadose zone and in the vapor discharge from the bioslurping system also provide quantitative estimates of the mass of contaminant "recovered" in the vapor phase due to biodegradation reactions. Oxygen concentrations in the recovered vapor below (and carbon dioxide levels above) background soil gas concentrations indicate of biological activity in the soil volume from which the gas is recovered. A quantification of the mass of oxygen depleted or mass of carbon dioxide produced in the recovered vapor can be converted to an equivalent mass of indicator contaminant that has been biodegraded using the stoichiometry for biodegradation known for this indicator compound. The reader is referred to Sections 4.2.9 and 5.5.9, and Table 5.11 for information regarding the stoichiometric conversion of oxygen use to

equivalent contaminant mass, and to Section 7.2.9 for sample calculations related to this mass degradation estimate.

7.2.8 Process and Instrumentation Diagrams

Figure 7.1 provides a process and instrumentation diagram for a typical bioslurping system.

7.2.9 Sample Calculations

Calculations routinely carried out for bioslurper systems include: cumulative contaminant recovery rates in the product, aqueous, and gaseous flow streams; contaminant recovery associated with vadose zone biodegradation; and data reduction for pneumatic pump tests conducted as part of the field treatability study.

7.2.9.1 Contaminant Recovery Rates

Contaminant recovery rates within the product are easily determined based on the volume of product recovered per unit time, the concentration of specific contaminants within the recovered product, and the measured or estimated product density using the following relationship:

$$\text{Product Mass Recovery Rate} = \frac{V\rho[\text{Contaminant}]}{t} \qquad (7.1)$$

where:

V	=	volume of product recovered per unit time t (m^3);
ρ	=	product density (kg/m^3); and
[Contaminant]	=	contaminant concentration (mg/kg).

Contaminant recovery rates in the aqueous phase are calculated in a manner similar to that in the recovered product, with slight modifications to reflect the aqueous nature of the flow stream as indicated in Equation 7.2:

$$\text{Aqueous Phase Mass Recovery Rate} = Q[\text{Contaminant}]_{aq} \qquad (7.2)$$

where:

Q	=	aqueous stream flow rate (m^3/time); and
$[\text{Contaminant}]_{aq}$	=	contaminant aqueous concentration (mg/m^3).

Finally, the contaminant recovery rate in the vapor stream is calculated using Equation 7.2, with Q being the vapor flow rate and [Contaminant] being the vapor stream concentration, both having the units as indicated above.

7.2.9.2 Contaminant Biodegradation

Contaminant biodegradation rates are normally determined from routine in situ respiration tests. These tests are conducted during periods when the bioslurping system is not operating so that the rate of oxygen consumption can be followed at specific soil gas probe locations over time. Data reduction techniques for in situ respiration tests were described in Section 4.2.9.1, along with an equation (Equation 4.1) to convert oxygen utilization rates with units of %/hour into biodegradation rates with units of mg/kg/d. Total contaminant removal due to biodegradation is determined from this method by multiplying the biodegradation rate by the soil mass on a dry weight basis for which this biodegradation rate is representative.

Additionally, contaminant biodegradation can be estimated from oxygen and carbon dioxide concentration measurements in the recovered vapor compared to concentration of these gases in uncontaminated soil gas. The reduction in oxygen concentration below or the increase in carbon dioxide levels above background levels times the vapor flow rate times the stoichiometric relationship between oxygen use or carbon dioxide production (with proper unit conversions) allows the determination of equivalent contaminant mass that is being degraded within the unsaturated zone affected by the bioslurper. Assuming an estimate based on equivalent hexane mass biodegradation, the following stoichiometric equation allows the determination of the oxygen requirement to degrade 1 gmol of hexane:

$$C_6H_{14} + 19/2\ O_2 \rightarrow 6CO_2 + 7H_2O \qquad (7.3)$$

indicating that 9.5 gmol oxygen are required, or 6 gmol of carbon dioxide are generated when 1 gmol or 86 g of hexane are completely degraded.

Using this relationship, the following expression allows the determination of the mass of hexane equivalent recovered from the system in the form of depleted soil gas oxygen or elevated carbon dioxide levels:

$$\text{Hexane Equivalent Degraded} = \left[\frac{Q\ (\Delta\%O_2)}{(22.4\ L/gmol)} \bullet \frac{(1\ gmol\ hexane)}{(9.5\ gmol\ O_2)}\right](MW_{hexane}) \qquad (7.4)$$

$$\text{Hexane Equivalent Degraded} = \left[\frac{Q\,(\Delta\%CO_2)}{(22.4\ L/gmol)} \bullet \frac{(1\ gmol\ hexane)}{(6\ gmol\ CO_2)}\right](MW_{hexane}) \tag{7.5}$$

where:

$\Delta\%O_2$ = change in oxygen concentration compared to background (%);

$\Delta\%CO_2$ = change in carbon dioxide concentration compared to background (%); and

MW_{hexane} = molecular weight of hexane = 86 g/gmol.

7.2.9.3 Pneumatic Pump Test Data

During bioslurper system field treatability testing, in situ air permeability measurements are collected at several locations throughout the site to evaluate vapor flow and soil conductivity, along with the radius of influence provided by each bioslurping well. One approach that has become a recommended standard for in situ soil air permeability measurements was described by Johnson et al. (1990) and is based on Darcy's Law and equations for steady-state radial flow at a vent well. The method entails the use of a single vent well with soil vapor probes placed radially and vertically away from it to monitor soil gas vacuum throughout the field site when air is extracted at a constant rate at the wellhead.

The governing equation for such a system, assuming one-dimensional radial flow from the extraction well, is shown in Equation 7.6:

$$P' = \frac{Q}{4\,\pi\,m\left(\frac{k}{\mu}\right)}\left[-0.5772 - \ln\left(\frac{r^2\varepsilon\mu}{4\,k\,P_{atm}}\right) + \ln(t)\right] \tag{7.6}$$

where:

P' = "gauge" pressure (g/cm-sec^2) measured at the vapor probes some radial distance r (cm) from the vent well at time t (sec);

m = vent well screen interval (cm);

k = soil gas permeability (cm^2);

μ = air viscosity ($1.8 \bullet 10^{-4}$ g/cm-sec @ 18°C);

ε = soil air filled porosity (decimal %);
Q = volumetric air flow rate at the vent well (cm^3/sec); and
P_{atm} = atmospheric pressure (1 atm = 1.013×10^6 g/cm-sec^2).

Soil gas pressure or vacuum data collected over time at various vapor probe locations following initiation of vent well pumping allow the determination of in situ soil gas permeability and its variability throughout the site. Vapor probe readings are plotted as a function of the natural log of time, generating a straight line with a slope equal to Equation 7.7:

$$\text{Slope} = \frac{Q}{4\pi m\left(\frac{k}{\mu}\right)} \tag{7.7}$$

Rearrangement of this equation allows the determination of k directly as:

$$k = \frac{Q\mu}{4 \text{ Slope } \pi \text{ m}} \tag{7.8}$$

This approach to data reduction will not be possible if the assumption of radial flow is not maintained at the field site. Radial flow will not occur if a significant vertical air velocity component exists due to shallow contamination and subsequently a small well screen interval (<10 ft), and if the soil is coarse grained. Under these conditions, vacuum measured in the vapor sampling points will reach constant values very quickly, requiring that the data be reduced using Equation 7.9:

$$k = \frac{Q\,\mu\,\ln\left(\frac{R_w}{R_I}\right)}{H\pi P_w\left[1-\left(\frac{P_{atm}}{P_w}\right)^2\right]} \tag{7.9}$$

where:

R_w = the radius of the vent well (cm);
H = the depth to the top of the well screen (cm);
R_I = the minimum radius of vent well influence under steady-state flow conditions (cm); and
P_w = the absolute pressure at the well head (g/cm-sec^2)

R_I can be estimated from inspection of field data, or by extrapolating the relationship of vapor probe vacuum versus log(r) to a 0 vacuum value.

7.2.10 Safety Requirements

Safety requirements for a bioslurping system are similar to those specified for bioventing systems (Section 4.2.10) and biosparging systems (Section 5.5.10), and involve: (1) safeguards for electrical equipment to prevent explosions, (2) prevention of uncontrolled subsurface vapor migration into confined spaces, and (3) precautions that must be taken when operating equipment at high vacuum. In addition, the free product recovery aspect of bioslurping requires that adequate precautions be taken to prevent exposure of site personnel to this material. Precautions include the use of personal protective clothing (safety goggles, disposable gloves, coveralls, disposable boot covers, and appropriate respirator) by site personnel when they are sampling or handling free product material. AFCEE (1995) has developed a general site Health and Safety Plan for bioslurping field treatability studies that is useful in developing site safety plans for full-scale bioslurper operations.

7.2.11 Specifications Development

Specifications for vent wells and monitoring points will generally follow state-specific drillers' standards for monitoring well installations. General specifications for size and materials of construction for bioslurper wells and monitoring points are shown in Figures 7.1 and 4.4, respectively.

Bioslurping system piping is generally constructed of PVC, with Schedule 80 PVC generally preferred for shallow burial applications and for connections to individual bioslurper wells. To improve system durability, galvanized piping and valves can be used for connections entering and exiting the blower and for all aboveground piping. ASTM standards should be consulted for general specifications for high-vacuum piping and valves used in a bioslurping applications.

Motors and blowers should conform to ASME standard PTC-9 and the National Electric Code. For operation in potentially explosive atmospheres, NEC Sections 500-505 also apply.

7.2.12 Cost Data

Only limited data are available describing the cost of bioslurping systems for the recovery of free product and contaminated groundwater and bioventing of vadose zone contamination under full-scale field conditions.

The only study to date reporting cost for field-scale bioslurping systems is that of Connolly et al. (1995) which described the recovery of gasoline and diesel fuel from a site with fractured rock with a water table depth of approximately 4.9 m (16 ft). The system used eleven 2-inch bioslurper wells with both offgas and groundwater treatment provided by a biofilter using the system. With this system, 3,900 L (1,030 gal) of product have been recovered for a total design and installation cost of $80,000, and annual operating costs of $40,000. This product volume does not include vapor phase product recovery nor product destruction provided by in situ biodegradation in the vadose zone, so it is a conservative estimate of bioslurper performance at this site. With a reported liquid volume recovery of 15% to 25% of the estimated total release volume, the unit costs for this bioslurper system were: $20.50/L ($77.67/gal) design and capital costs, and $10.25/L ($38.83/gal) in annual O&M costs. Due to the general lack of cost data for this technology, more data are required to improve these cost figures beyond the preliminary values presented here.

7.2.13 Design Validation

As with any engineering design, bioslurper design should be subject to peer reviews of all assumptions and design calculations. The applicability of a bioslurping system at a given site should be based on field treatability testing results generated using procedures suggested by AFCEE (1995). Selection of a specific operating mode for product recovery and/or bioventing at a site should be made based on these field treatability data, and further system design and operating refinements should be made based on results of ongoing monitoring of liquid and vapor streams generated by the bioslurper unit, and from soil gas and groundwater and product level data collected during system operation. Decisions regarding the need for additional bioslurping wells based on actual field determinations versus estimated liquid and vapor phase radii of influence should be made as field performance data are collected and evaluated. Additional system design modification or operating mode changes should be implemented as necessary in response to changing product, groundwater, and vadose zone conditions that develop as product removal and contaminant degradation proceed at a site.

7.2.14 Permitting Requirements

Permit requirements for this technology, as with others, can vary significantly from state to state. In general, the construction of the bioslurper well will require a standard well permit. Some states also require a standard well permit for vapor monitoring probe installations. In some states, disposal of

drill cuttings that may contain RCRA-listed wastes can be an expensive and time consuming byproduct of bioslurping field work.

Discharge permit considerations for this technology include both air (Section 6.2.14) and water (Section 5.4.14) discharges, and requirements for the proper handling and disposition of free product recovered during bioslurping. The appropriate permitting authorities should be consulted regarding local restrictions on liquid and vapor discharges, and on acceptable handling and permitting methods for recovered free product.

7.2.15 Design Checklist

Table 7.6 provides a list of items that need to be considered in the design and implementation of the bioslurping process for product recovery and source remediation at a given site.

7.2.16 Implementation

It is recommended that implementation of a bioslurping system begin with a field-scale treatability assessment of product recovery techniques as described by AFCEE (1995). The primary requirements of the field treatability study are the proper drilling, sampling, installation, and completion of the bioslurper well and associated system monitoring points. Next, electrical service, equipment support pads, storage buildings, security, fencing, lighting, access roads, etc., should be provided as necessary to support short-term field testing that is to take place. A system shakedown consisting of a brief start-up test should be conducted to ensure that all system components are operating properly. A system checklist should include: the liquid ring pump; aqueous effluent treatment pump; OWS; vapor, fuel, and water flowmeters; emergency shutoff float valve on the effluent transfer tank; and all analytical equipment. Finally, all appropriate local agencies should be notified of planned field activities.

7.2.17 Start-up Procedures

Bioslurper system start-up procedures should be initiated through a field-scale bioslurping treatability study as described by AFCEE (1995). This field treatability test consists of three distinct product recovery tests and leads to the selection of the optimal operating mode for a given site. A description of each phase in the treatability testing effort are described below.

Table 7.6
Bioslurper Process Design Checklist

Site Characterization	Type and distribution of contaminants and free product
	Soil characterization
	Delineate contaminated soil, groundwater, and product volume
	Aquifer characteristics
Site Features	Property lines
	Nearest power source
	Building/confined spaces locations
	Underground utilities
	Concrete/asphalt surfaces
	Normal use and traffic patterns
Field Treatability Test Results	Adequate production rate of free product
	Adequate vacuum enhancement to product recovery
	Adequate vadose zone conductivity
	Appropriate microbial activity in vadose zone
	Product recovery rate adequate
Well Design	Screened intervals
	Well locations
	Completion methods
	Slurper tube location (operating mode)
Effluent Treatment	All regulated compounds treated
	Precipitation potential addressed
	Sufficient capacity
	Residuals addressed
	Discharge stream quality acceptance
Free Product Handling	Permitting acquired as necessary
	Storage and handling procedures adequate
	Storage volume adequate
	Containment adequate
	Personal protection and monitoring adequate
Fluid Transfer System	Lines deep enough to avoid freezing/heat traced
	Check valves, flow meters, control valves
	Surge tank controls
	In line filters
	All prime movers explosion proof
	Adequate compatibility with product being recovered

7.2.17.1 Initial Skimming Test

The first product recovery test recommended in the bioslurper treatability test is a 48-hour skimming test. In this test, the slurper tube is set at the product/groundwater interface with atmospheric pressure maintained on the wellhead by leaving open the wellhead ball valve (Figure 7.4). Prior to starting the pump test, the bioslurper pump and OWS are primed with diesel fuel, and the flow totalizers for the product and aqueous effluent streams are zeroed.

The liquid ring pump is started and free product and groundwater extraction rates are monitored on an as-needed basis throughout the test. Product/groundwater levels are monitored periodically (every 1/2 hour for 2 hours and on an as-needed basis from that point on) over the 48-hour duration of the test. Final product and groundwater extraction rates and product/groundwater levels are made at the end of this portion of the field test.

7.2.17.2 Bioslurper Test

When the initial skimming test is complete, the ball valve on the extraction wellhead is closed so that vacuum levels sufficient to provide bioslurping in the well can develop (Figure 7.5). The vacuum-enhanced bioslurper test continues for 96 hours, during which time system performance variables (product, groundwater, vapor flow rates; contaminant concentrations; product depth; etc.) are monitored.

As part of the bioslurper test, a pneumatic pump test should also be conducted. Here, soil gas probe vacuum monitoring is carried out from throughout the site at a high frequency during the first 20 minutes of bioslurper operation, then less frequently after that point to monitor vacuum development produced by the bioslurper well. As indicated in Section 7.3.9, reduction of this pressure versus time data allows the estimation of gas permeability at each of the sampling locations where data are collected. Soil gas oxygen and carbon dioxide concentrations and total or specific contaminant concentrations are also monitored at soil gas probe locations to evaluate the radius of influence of the bioslurping well in terms of oxygen transfer, and to aid in the evaluation of the distribution of biological activity taking place throughout the site.

7.2.17.3 Secondary Skimming Test

Following the 96-hour bioslurping test, a second skimming test is carried out to provide additional data regarding sustained product recovery using conventional techniques versus vacuum-assisted bioslurping. This test is run for a 24-hour period with the wellhead valve open to maintain atmospheric

pressure in the bioslurper well and the slurp tube maintained at the static product/water interface.

7.2.17.4. Dual-Pump/Drawdown Test

This final product recovery test is designed to assess the effect of product drawdown on its rate of recovery in the bioslurping well. Groundwater and product drawdown are produced by lowering the slurp tube to below the static water table level. The depth below the water table to which the slurp tube is lowered is recommended to be equivalent to the vacuum produced at the wellhead during the bioslurping portion of the field treatability test. In case of extremely high or low vacuum readings observed at a site, default values of a maximum drawdown of 3 ft and a minimum drawdown of 1 ft are recommended by AFCEE (1995). This dual-pump test (Figure 7.6) is carried out for a 24-hour period during which time the following process variables are monitored: product, groundwater, and vapor flow; groundwater and product elevations; and contaminant concentrations.

7.2.17.5 In Situ Respiration Tests

In situ respiration testing should take place following oxygenation of the unsaturated zone below the site in the bioslurper test portion of the field treatability study. AFCEE (1995) recommend that the test be initiated concurrently with the second skimming test using procedures described above in Section 7.2.7.3 to evaluate the contribution to overall contaminant recovery at a site that can be attributed to aerobic biological degradation.

7.2.18 Performance Evaluation

7.2.18.1 Operations Practices

Operation of a bioslurper system is mechanically simple, and requires only adjustments of vacuum produced by the liquid ring pump, and of bioslurper tube depth during each phase of field treatability testing. In addition, groundwater and product elevations; product, groundwater, and vapor flowrates; and contaminant composition data must be collected over time. Once an optimal operating mode is selected at a given site based on field treatability test results, operating requirements primarily consist of checking and adjusting operating vacuums and system flow rates, managing product storage requirements, checking and adjusting effluent treatment systems, and collecting flow stream data for performance evaluation and regulatory compliance monitoring.

7.2.18.2 Operations Monitoring

As indicated in Section 7.2.2.6, operations monitoring requirements for bioslurping systems are similar to those of bioventing systems, with the additional monitoring necessary for the product/liquid stream generated in the bioslurping process. Liquid and vapor contaminant recovery rates and contaminant in situ biodegradation rates are important process performance variables that determine which operating mode is best suited for optimizing remediation of a given site. Quantification of the contaminant removal rates in each of these pathways is crucial in selecting an operating mode for long-term use at a site. Likewise, once a specific operating mode is selected, the long-term performance of the bioslurping system must be based on data collected to describe a mass balance for product recovery by a bioslurping system.

Long-term operation monitoring must include:

- free product, groundwater, and vapor phase recovery rates;
- free product, groundwater, and vapor phase contaminant concentration data;
- free product and groundwater elevation data from throughout the site; and
- contaminant removal provided by in situ biodegradation estimated ideally by both in situ respiration measurements and oxygen and carbon dioxide concentration measurements in the extracted vapor stream.

Collection of these data over time allows an ongoing assessment of the effectiveness of a bioslurper system for the recovery of product, extraction of dissolved contaminant mass, and destruction of residual contaminant mass in the unsaturated zone. These data also enable a periodic modification of field operating procedures to provide continuous process improvement as site and contaminant conditions change.

7.2.18.3 Quality Assurance/Quality Control

A Quality Assurance/Quality Control (QA/QC) plan should contain the practices to be used during bioslurper operation to ensure the accuracy, precision, completeness, representativeness, and comparability of all collected data as described in *Test Methods for Evaluating Solid Waste, SW 846* (US EPA 1986c, 1986d) and the *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans* (US EPA 1980). The reader is referred to a general outline for such a quality assurance plan presented in Table 5.15. QA/QC practices applicable to the bioslurping process include

practices common to other bioremediation technologies (i.e., the use of blanks, blind duplicates, and spiked samples for laboratory and field measurements). In addition, engineering practices to ensure data quality and QC should include:

- an ongoing review of health and safety practices;
- review of sampling and analysis procedures;
- ongoing training of new field personnel;
- routine maintenance of all field process equipment; and
- routine maintenance and calibration of all field monitoring and sampling equipment.

8

CASE STUDIES

8.1 Biofilter Vapor Treatment

The development, pilot testing, and implementation of a soil bioreactor for the treatment of vapors from the S.C. Johnson Wax Facility in Racine, Wisconsin are described. This project was conducted jointly by the US EPA Laboratory in Ada, Oklahoma, (Robert S. Kerr Laboratory) and S.C. Johnson & Sons, Inc. of Racine, Wisconsin. S.C. Johnson Wax (Johnson Wax) implemented an in-ground soil reactor based on the results of US EPA and their own testing. The soil reactor was, initially, successful in treating the vapors, but then failed in cold weather and was eventually replaced with a more traditional gas treatment method.

8.1.1 Site Description

Johnson Wax operates a manufacturing facility in Racine, Wisconsin, where a variety of consumer products are produced, some of which are packaged in aerosol cans. During the filling process, some of the propellant is released. The propellant consists of a mixture of light hydrocarbons, primarily propane, n-butane, and isobutane. In 1986, the filling losses were collected and vented directly to the atmosphere, the common industrial practice at that time. Although a reasonably available control technology (RACT) standard had not been developed as of 1986, Johnson Wax anticipated that the state of Wisconsin would soon develop RACT regulations that would require an 85% reduction in industrial emissions, such as those from their aerosol can filling process.

8.1.2 Technology Selection

It had long been known that indigenous soil microorganisms could degrade a wide range of organic compounds, including the hydrocarbons present in the propellant. Studies in the Netherlands had shown that as much as 5 mg of methane/kg of soil/hour could be degraded in a soil biofilter after a suitable acclimation period. Based on this and other experience, largely in Europe, Johnson Wax and the US EPA researchers decided that biological vapor treatment using soil as the filter-bed matrix was a viable option for treating the propellant-laden gases.

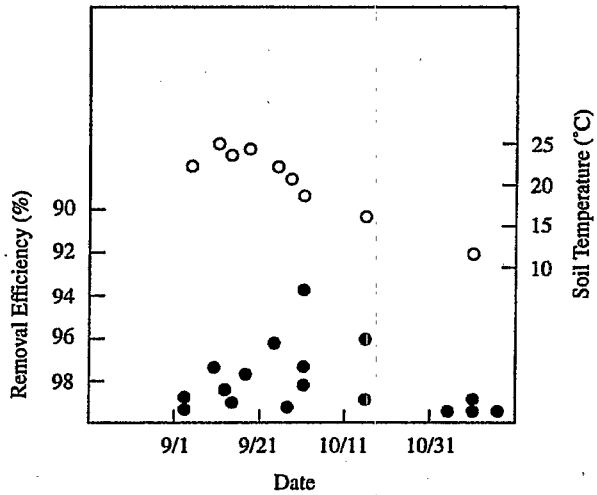
8.1.3 Technology Evaluation

Laboratory tests were conducted at the Robert S. Kerr Laboratory in Ada, Oklahoma, to evaluate biofilter biodegradation potential. These tests were conducted in serum microcosms using site soil maintained at 30% moisture content and 22 to 24°C. Propellant gases consisting of 29 mol% isobutane, 44 mol% n-butane, and 27 mol% propane were used in these laboratory studies. Further laboratory tests were conducted by the Ada laboratory to evaluate biofilter acclimation and to generate laboratory degradation kinetic parameters. Propellant gas mixtures were introduced into the bottles with approximately 60 times greater volume of air than the air-filled pore spaces of the prototype biofilter. Aliquots of gas were periodically removed and analyzed by gas chromatography with a detection limit of approximately 20 to 50 ppmv. Tests were conducted in duplicate or triplicate, and data were analyzed for fit by regression analysis.

Evaluation of the laboratory test results led to a prediction of between 90% and 95% removal efficiency in the bioreactor at a soil temperature of 24°C. Figure 8.1 presents the hydrocarbon removal rates achieved in the prototype reactor which corresponded well with the laboratory test results. Acclimation in the laboratory tests was slow, with little increase in degradation rates over several weeks. Johnson Wax experienced acclimation times of approximately 20 days in the field unit. Following acclimation, degradation rates increased by approximately a factor of 100 over the initial rates as observed in the biofilter.

As shown in Figure 8.2, disappearance of the three hydrocarbons was rapid and extensive. Hydrocarbon disappearance could have been due to a variety of mechanisms: sorption to soil components; abiotic transformations; or physical loses through adsorption to glass or leakage from the serum microcosms. However, leakage from the microcosms was not observed.

Figure 8.1
Hydrocarbon Removal/Degradation in Prototype Reactor



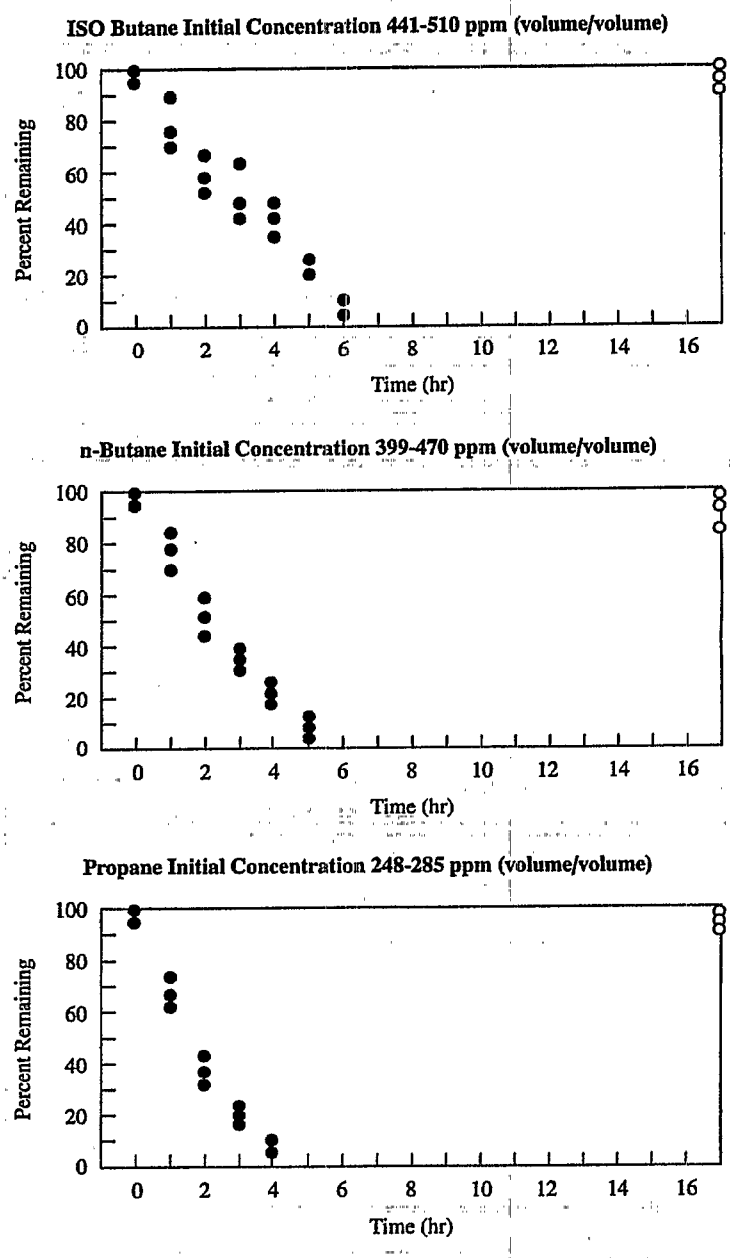
● Percent of Injected Hydrocarbon Degraded
○ Soil Temperature at Depth of Injection

Source: Kampbell et al. 1987. Used with permission.

Preliminary laboratory investigations indicated that biodegradation might be able to satisfy regulatory requirements for the reduction in volatile organic compound (VOC) emissions from aerosol can filling operations. To verify the preliminary laboratory VOC destruction efficiencies and determine cold weather effects, Johnson Wax planned the construction of a prototype soil bioreactor. After discussions with the Wisconsin Department of Natural Resources (WDNR) to ensure acceptability of the data obtained from the pilot operation, the bed was constructed. Initial startup occurred in May 1984.

At the request of WDNR, the prototype soil bioreactor (Figure 8.3) was lined with an 0.8-mm reinforced polyvinyl chloride (PVC) liner to prevent groundwater contamination. The air pipes (10-cm [4-in.]) Schedule-40 PVC pipe perforated with 3-mm holes) were installed above the liner and buried in Rollin muck soil. This soil contained 6.5% organic matter and 45% clay and had a pH of approximately 7.4. The surface area of the bed was 190 m^2 (2,040 ft^2), and the soil depth was 90 cm (3 ft). The bottom of the bed was

Figure 8.2
Removal/Degradation of Hydrocarbons in Initial Laboratory Experiments

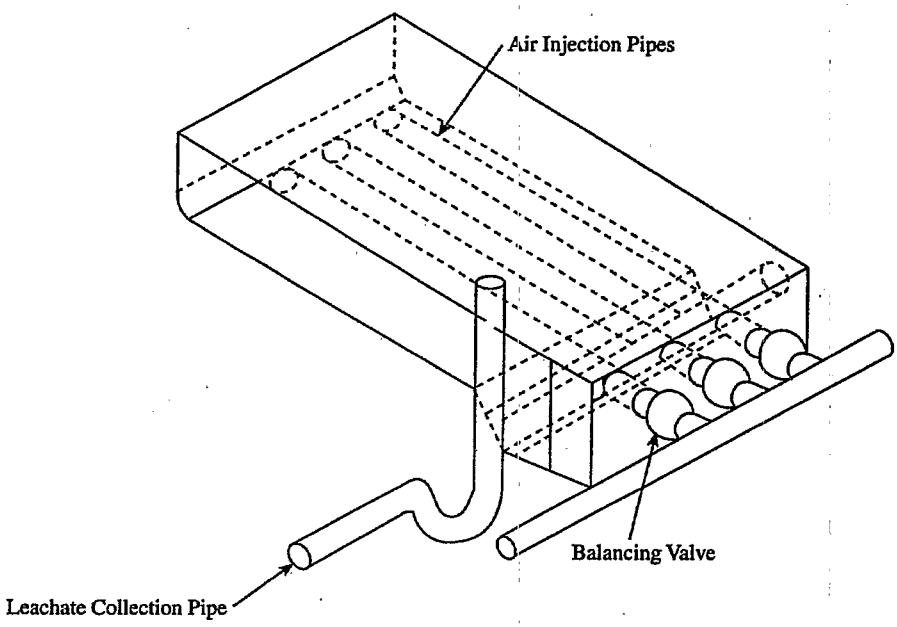


● Soil from a Depth of 90 cm/Acclimated
○ Control Soil not Previously Acclimated

Source: Kampbell et al. 1987. Used with permission.

sloped 0.75% to carry leachate to a sump. The injected air contained approximately 2,000 ppm (v/v) total hydrocarbons. The intended flow rate was 3.0 cm^3 air/cm^2 of surface area/minute, making the residence time nearly 15 minutes. The pressure drop across the bed was approximately 85 cm (33 in.) of water.

Figure 8.3
Schematic of Prototype Vapor Treatment System



Source: Kampbell et al. 1987. Used with permission.

To monitor bed performance, offgases were collected in a modified 55-gallon drum. The drum was open at the bottom, had opposing baffles at the rolling hoops, and had a small vent hole in the top. It was positioned on the soil bed at random, and allowed to come to equilibrium before sampling. Offgases in the bottom third of the barrel were withdrawn directly into a portable organic vapor analyzer (OVA) (Foxboro Century OVA Model 128) with a flame ionization detector (FID). The influent gas was sampled through a valve on the distribution pipe. The soil temperature was monitored with a thermocouple buried 75 cm (30 in.) in the soil bed.

It was anticipated that prior exposure of soils to hydrocarbon vapors would elevate the microbial density, particularly of those microorganisms able to utilize the hydrocarbons being tested. Based on a comparison with control reactors, it was concluded that biodegradation was occurring and was the primary mechanism for disappearance of the three hydrocarbons.

No lag periods were observed, and the disappearance of hydrocarbons was proportional to their inlet concentrations, although at higher concentrations it appeared that the biodegradation rate was limited by the microbial capacity to metabolize the organic compounds. For the most part, degradation followed first-order degradation rates described by:

$$1/V = 1/V_{max}(1 + K_m/S) \tag{8.1}$$

where:

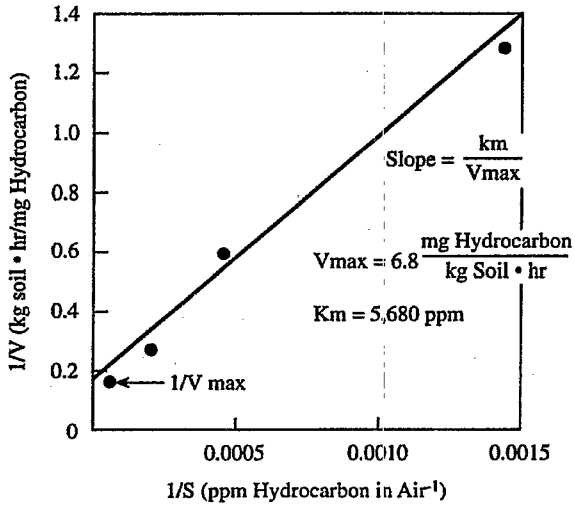
V = the biodegradation rate;
V_{max} = the maximum possible biodegradation rate;
K_m = an empirical constant representing the concentration where biodegradation shifts from first-order to zero-order kinetics (commonly called the half-saturation constant); and
S = the concentration of the organic compound in air.

The removal rate of hydrocarbons was examined at 700, 6,000, and 20,000 ppm (v/v) to cover the transition from first- to zero-order kinetics. Figure 8.4 is a graphical representation of the prototype bioreactor test results. This plot indicates that the hydrocarbon degradation followed hyperbolic kinetics. The slope determines the half-saturation constant, K_m, (5,680 ppmv). The intercept of the y-axis indicates the maximum biodegradation rate for the system, which was 6.8 mg propellant/kg of soil/hour. Hydrocarbon degradation rates should be first-order for vapor concentrations of less than 500 ppmv.

The biodegradation rates for the three hydrocarbons were similar, varying only by a factor of 3. As might be expected, the branched hydrocarbon, isobutane, was the slowest to degrade in the pilot biofilter.

It was anticipated that degradation would be fastest within the deepest portion of the prototype soil bed. However, the opposite was occurred. The primary reason for this apparent anomaly may have been that the higher moisture content within this interval restricted movement of hydrocarbon vapors through these soils. The moisture content was elevated in this interval because of the liner that prevented adequate drainage from the biofilter.

Figure 8.4
Hydrocarbon Removal/Degradation Kinetics in Prototype Reactor



Source: Kampbell et al. 1987. Used with permission.

The probable byproducts of alkane biodegradation are alcohols and ketones. Both classes of compounds are biodegradable so disappearance of the alkanes should not be accompanied by the production of stable intermediates, particularly since the feed gas contained oxygen far in excess of the amount required for biodegradation of the hydrocarbons. Consistent with these observations, no hydrocarbon or intermediate byproducts were observed in the biofilter leachate.

Concern over performance during the cold winters in Wisconsin led to tests that evaluated degradation rates at 12 and 24°C. As shown in Figure 8.1, the test results indicated that performance would not be significantly impacted over the temperature range tested. The effects of temperatures below 12°C were not investigated, so it was not possible to know the lowest temperature at which satisfactory performance could be expected.

8.1.4 Implementation

Subsequent to the laboratory and prototype reactor tests, Johnson Wax constructed and field tested a full-scale soil injection bed (SIB). The bed

was approximately 57 by 49 m (185 by 160 ft). The active treatment zone consisted of 1 m (3 ft) of soil underlain by slotted PVC pipe that introduced air into the soil from a manifold that delivered aerosol-laden air from the aerosol production line gas house. The PVC pipe was contained within 0.3 m (1 ft) of gravel overlaid by 0.7 m (2 ft) of soil. Beneath this soil was a leachate collection system consisting of slotted sewer drain pipe that transferred leachate to the process sewer.

Because the SIB was a nonstandard air pollution control device, demonstration of performance was required. Influent air flow velocity and constituent levels were easily measured using standard methods. Because the effluent from the SIB discharged over a large surface area at very low flow rates, compliance demonstration required methods specific to the design of the system. Effluent gas was collected using a special hood which was placed on a portion of the SIB. The hood collected effluent gas from a bed surface area of approximately 10 m^2 (110 ft^2). The discharged effluent was directed through a 5-cm (2-in.) diameter Schedule-40 FVE open-ended discharge pipe. A calibrated Kurts Model 505-9B-00 Mass Flow Meter was used to measure the discharge rate which was recorded on a strip chart recorder. Samples of influent and effluent gas were collected and measured on a gas chromatograph fitted with an FID.

The hood was moved around the bed to numerous locations where flow rates and effluent quality were measured. Statistical methods and correction loss factors for air flow rate loss within the hood and discharge pipe were applied to calculate total bed flow rate and percent conversion of the three hydrocarbons within the active biofilter.

Analysis of flow revealed a fairly complex pattern. Further, a good deal of the effluent air was unaccounted for. Sheet piling was installed on three sides of the bed along with a clay barrier on the fourth side to minimize lateral air losses.

Further investigation using the hood identified several high flow zones. To correct this problem, the bed was tilled to yield a more uniform air flow. Regrading of the bed eliminated a swale that had been engineered into the original design to facilitate runoff control. Even after these modifications, only 40% of the air flow was accounted for.

Additional testing indicated very little leakage to the sides of the bed where the sheet piling had been placed. However, the side with the clay barrier indicated air leakage that extended a substantial distance outside the formal limits of the SIB. This increased the volume of the soil bed and, fortunately, the degree of treatment provided to the waste stream gases.

The percent destruction and removal efficiency (DRE) decreased dramatically when the air flow through the filter bed exceeded approximately $0.015 m^3/sec/100 m^2$ (3 cfm/100 ft^2). Had the actual bed volume not been larger than the design volume, adequate treatment would not have been achieved. The measured DRE for the three areas ranged from 85% to 95%. However, because not all of the air flow could be accounted for, even including areas outside the SID, the official reported overall treatment efficiency was 60%; just over half of the reduction was attributed to the designed reactor bed volume.

The regulatory requirement for treatment was 52% DRE so the reported system performance was adequate. Had all of the air flow been accounted for, the actual DRE probably would have been significantly higher than 60%, possibly close to the 88.5% DRE achieved for that portion of the air flow that was accounted for.

Although Johnson Wax demonstrated compliance with the required 52% DRE, performance problems during cold weather resulted in Johnson Wax's decision to replace the SIB.

8.1.5 Conclusions

Johnson Wax achieved 85% to 90% DRE of hydrocarbons contained in an aerosol-laden air using the SIB. They were able to identify air flow losses and take appropriate actions to contain some of the lost air flow through their biofilter. Treatment met regulatory requirements during warm weather. However, year-round use of the SIB was terminated because of decreased performance during winter months. Reduced performance levels during winter, combined with the need to report lower performance values than actually achieved because it was not possible to account for all of the air flow, meant that the reported efficiencies were not satisfactory year round.

This case history demonstrates that despite pilot tests, which incorporated both the filter bed matrix that was used at full-scale and the specific gas compositions to be treated, problems can still arise. These problems can relate to control and measurement of air flow, uniformity of the filter bed with respect to air flow velocities, and achievable degradation capacity at full-scale. The need to account for nearly all of the effluent volume can be critical when attempting to validate process performance in biofilter systems.

8.2 Biosparging

This case study outlines design and implementation of an integrated sparging and vapor extraction system to achieve site closure (numerical standards) at an industrial facility in the eastern United States.

8.2.1 Site History

The site is a former manufacturing facility that operated from the 1940s to 1988. No operations have been conducted at the facility since 1988. A site plan of the facility is presented in Figure 8.5.

The background information collected during hydrogeologic investigations identified nonaqueous-phase liquids (NAPLs) and elevated concentrations (several hundred ppm) of VOCs in the unsaturated and saturated zone soils . The highest observed concentrations of VOCs in the subsurface soils were between 1.5 to 2.5 m (5 to 8 ft) below ground surface; the average depth to groundwater at the site was 1.25 to 2 m (4 to 6 ft). VOC concentrations in the groundwater up to mg/L were also identified. The primary VOC detected was toluene.

The source of the VOCs is believed to be several solvent transfer lines that ran in an underground trench from the aboveground storage tank located at the west end of the site. The transfer lines and the aboveground tanks were removed from the site in 1989. The site investigation data suggested that approximately 4,500 kg (10,000 lb) of toluene were present in site soils.

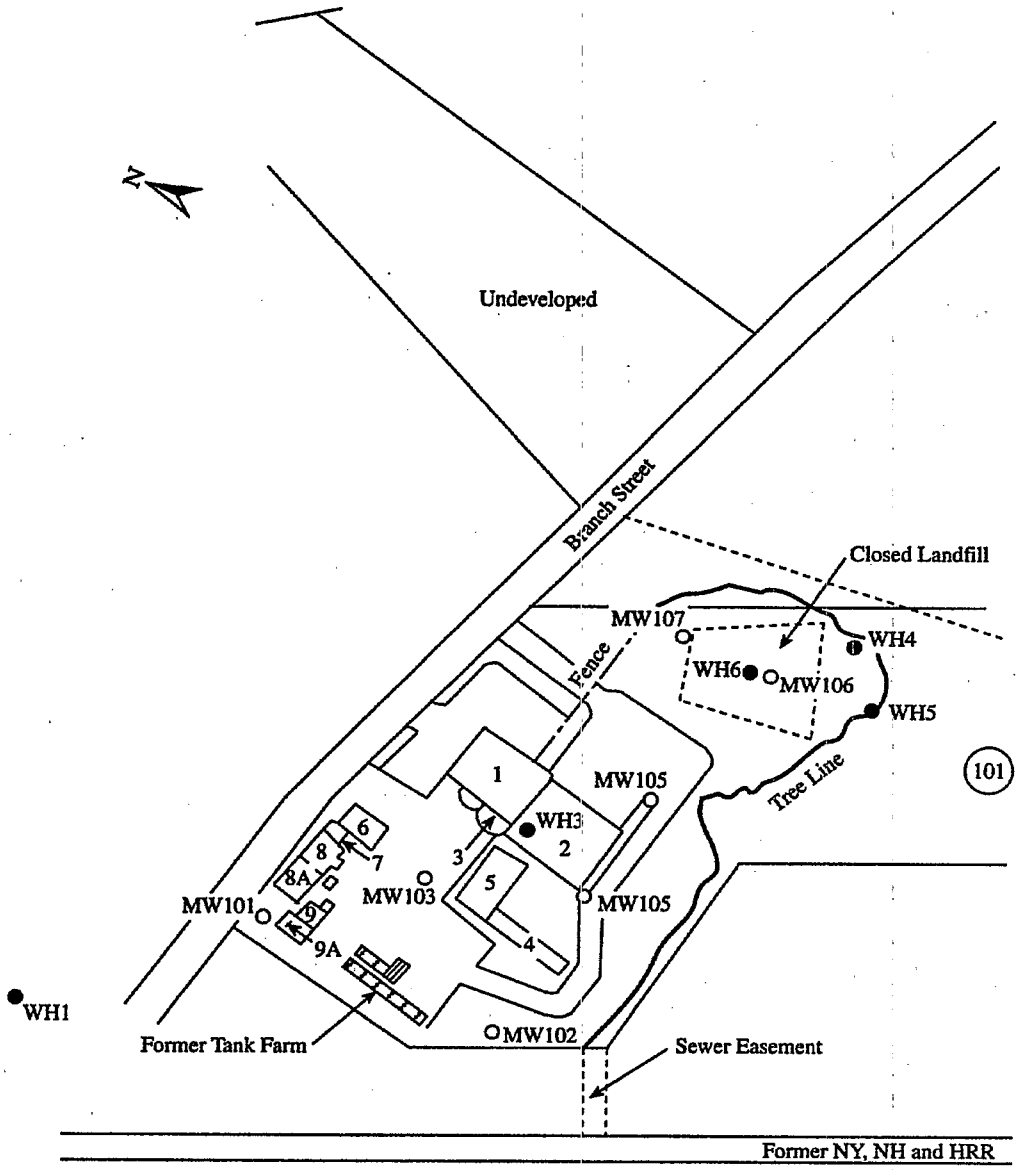
The geologic materials are relatively consistent across the site. Fine to medium sands and silts are present from 0 to 0.6 m (0 to 2 ft) below grade and is underlain by medium to coarse sands and gravel to a depth of at least 5.2 m (17 ft).

The site investigation results dictated implementation of an interim remedy. Based on the contaminant mass and its volatility and biodegradability, the approved interim remedy included the implementation of a full-scale in situ soil vapor extraction (SVE) and air sparging (AS) system.

8.2.2 System Design and Implementation

A pilot study design was developed following a review of pertinent soil sampling and analysis data. This design called for the installation of two SVE and AS test well networks, each consisting of one vapor extraction well, one air sparging well, four shallow vapor probes, and two sets of nested piezometers. Each test well network was used to evaluate the critical

Figure 8.5
Site Plan
(not to scale)



parameters used in the design of the SVE and AS systems. The test areas were chosen to provide an evaluation of the design parameters over the variable site conditions that were expected during operation of the full-scale system. One test area, which was paved, had elevated VOC concentrations

in unsaturated and saturated zone soils and groundwater and displayed the presence of NAPLs. The second area was unpaved and had lower levels of unsaturated soil and groundwater contamination (Figure 8.6).

A series of short-term pilot tests were performed to obtain the data necessary to determine the feasibility of using SVE and AS technologies at the site and the related design parameters. The tests were performed at SVE wells using a 34-m^3/hr (20-scfm) 1.5 hp rotary-vane pump. The pump was manifolded to the wells using 38-mm (1 1/2-in.) flexible pipe. SVE system offgases were passed through two 91-kg (200-lb) vapor-phase carbon canisters arranged in series for treatment. Air flow rates from each test well were regulated by an in-line gate valve. SVE wells were tested at two flow rates (primary and secondary) to allow for air-flow model calibration and verification during the data analysis process.

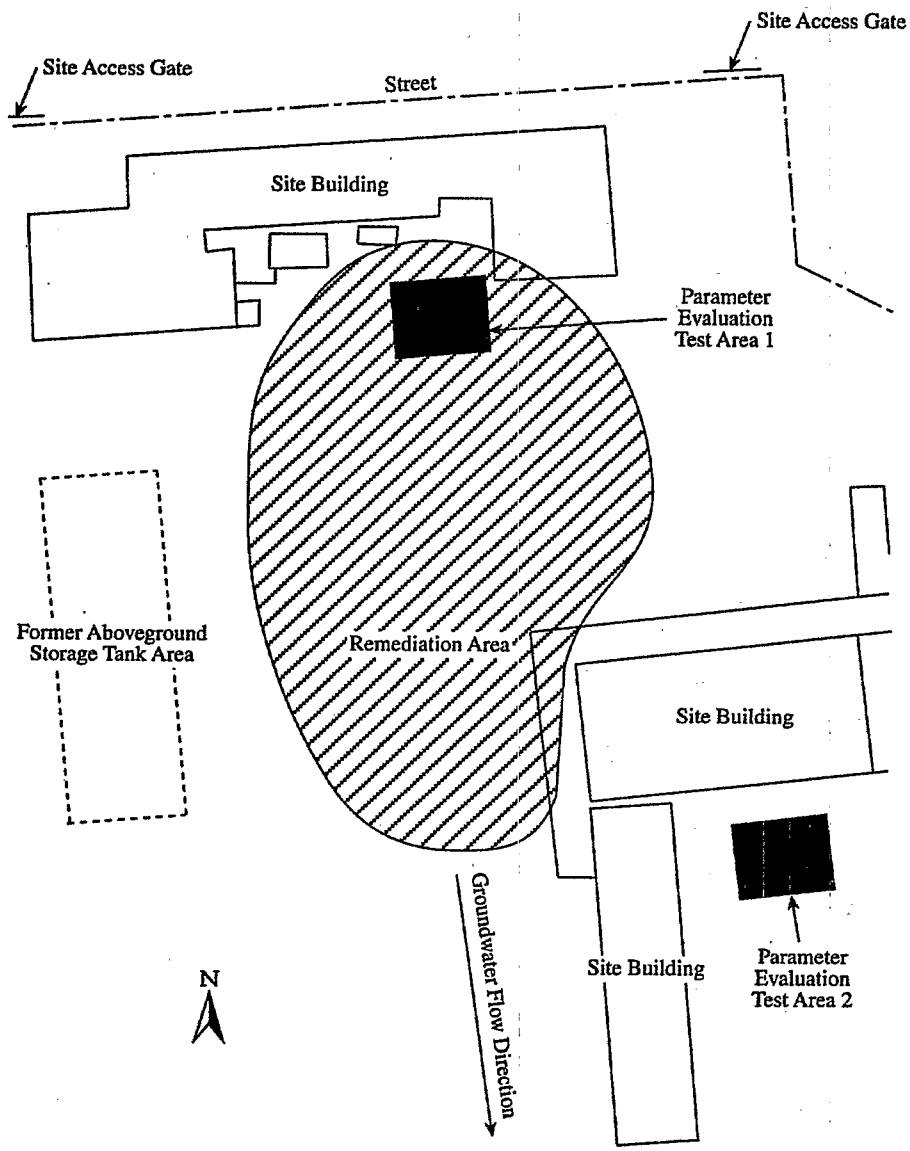
Vacuum pressure distribution was recorded at the vacuum wellhead and at the local soil gas monitoring points during each test using a set of differential pressure gauges. The vacuum distribution was measured periodically until vacuum pressures stabilized. Air flow rates were also measured periodically during each test using an in-line 0- to 34-m^3/hr (0- to 20-cfm) orifice plate air flow meter. During each test, SVE system discharge samples were collected and analyzed for total hydrocarbon concentration using an OVA equipped with a FID. One discharge vapor sample was collected from each test area for certified laboratory analysis. Several discharge vapor samples were also collected from each test area and analyzed in the field using a GC equipped with FID/photoionization detectors (PIDs).

AS parameter evaluation tests were performed at AS wells using a 2.5 hp oil-less air compressor. The air compressor was manifolded to the wells using 10-mm (3/8-in.) high-pressure rubber air hose. Air flow rates and air pressure to each test well were regulated by an in-line pressure regulator. The duration of each test varied up to 8 hours. Vacuum and pressure distribution were recorded at the wellhead, local piezometers, vapor probes, and existing monitoring wells during each test using a set of differential pressure gauges. Sparging air flow rates were measured during each test using a 0- to 17-m^3/hr (0- to 10-cfm) orifice plate air flow meter.

To evaluate potential groundwater mounding effects from air sparging, water levels and free product thickness were also measured periodically in local piezometers and wells using an interface probe. Pre- and post-AS test groundwater dissolved oxygen (DO) concentrations were also measured in nearby monitoring wells and piezometers using a DO meter. Local piezometers and monitoring wells were adapted so that saturated zone pressures could be monitored during the AS testing.

Pre- and post-AS test soil gas and helium tracer concentrations were measured in all local vapor probes for each AS test. Soil vapor discharge samples were collected from the SVE system periodically and analyzed for total hydrocarbon concentration using the OVA and field GC.

Figure 8.6
Remediation Area
(not to scale)



The results of the SVE field testing and subsequent air flow modeling indicated that the physical characteristics of soils (i.e., the permeabilities of the soil strata and air flow potential) across the site were within the range considered optimal for the application of SVE technology. Data analyses indicated the effective radius of vacuum influence (based on radially- dependent pore volume exchange rates) of a vapor extraction well in the unsaturated zone in unpaved areas to be approximately 3 to 8 m (10 to 26 ft) at an air flow rate of approximately 8 to 17 m^3/hr (5 to 10 scfm). (A *pore volume exchange* is defined as a volume of clean air which moves through a unit volume of contaminated soil. Pore volume exchange rates are essential to determine of an SVE well radius of influence for the remediation of VOCs. Observed vacuum alone does not indicate pore volume exchange rates).

Discharge VOC concentrations during SVE tests indicated that the highest VOC levels were observed in the northern area of the site where vadose zone soils contained VOCs as a residual and/or nonaqueous phase. Lower levels of VOCs detected in the southern area of the site indicated lower levels of groundwater and soil contamination.

Several short-term AS tests were conducted to evaluate the feasibility of using air sparging technology to remediate VOC-contaminated saturated zone soils at the site and to develop a conceptual full-scale design. The results of the field testing indicated that the physical characteristics of soils (i.e., the permeabilities of the soil strata and air flow potential) across the site were within the range considered optimal for the application of AS technology. Data analysis, computer modeling, and previous experience at similar sites indicated an effective radius of influence of 3 to 8 m (10 to 26 ft) at an air injection flow rate of 7 m^3/hr (4 scfm). Due to the estimated mass of VOCs present, the design radius was selected to ensure rapid mass removal via volatilization with system polishing through biodegradation.

8.2.3 Full-Scale Design and Installation

8.2.3.1 Full-Scale Design

The conceptual, full-scale SVE/AS design was developed under the assumption that the goal for the site was to reduce the VOC sources contributing to groundwater contamination to state-mandated standards (maximum contaminant levels [MCLs]) in 18 to 24 months of system operation.

The full-scale SVE system design was developed to remove vadose zone soil VOCs and to capture AS vapors across the delineated remediation area. The full-scale AS design was developed to remove VOCs from saturated

zone soils and groundwater to a depth of 2.5 m (8 ft) below grade across the delineated remediation area.

Injection of air into saturated zone soils displaces groundwater and forms a random distribution of air channels in the vicinity of an AS well. At this site, plume migration due to water displacement was expected to be minimal, based on the observed low air entry pressures, minimal groundwater mounding during the pilot testing, and the proposed pulsed-mode of system operation. However, to control the minimal displacement and natural migration of contaminated groundwater, a series of defensive AS wells (a sparging curtain) was designed around the eastern, western, and southern portions of the remediation area.

Based on a review of site conditions, pilot test results, and contaminant distribution, it was determined that approximately 67 SVE/AS well pairs and three single SVE wells were required to remediate the target area. Design vapor extraction well (VEW) flow rates were in the range of 8 to 17 m^3/hr (5 to 10 scfm) at 50 to 75 mm (2 to 3 in.) of water vacuum. Design air sparging flow rates per air sparging well (ASW) were in the range of 5 to 7 m^3/hr (3 to 4 cfm) at 35 to 55 kPa (5 to 8 psi) pressure.

8.2.3.2 Full-Scale Installation

The 67 SVE/AS well pairs and three single VEWs were installed in spring 1993. All borings were completed using standard rotary auger techniques. Auger cuttings were visually classified for soil type and screened for VOCs in the field with a portable OVA. Site soils were visually classified as medium to coarse sand and gravel.

The ASWs were constructed of steel well points with 0.6 m (2 ft) screens attached to steel rises. The installation of the well points consisted of first advancing a 160-mm (6.25-in.) inside-diameter hollow stem auger to approximately 3 m (10 ft) below grade. The well points were then driven to a depth of approximately 5.2 m (17 ft) below grade using a 140-kg (300-lb) drop hammer. The open borehole was then backfilled with bentonite from approximately 3 m (10 ft) below grade to approximately 2 m (6.5 ft) below grade. For this particular site, driving ASWs proved to be cost-effective compared to installation by standard hollow-stem auger techniques, but this ASW installation technique may not be applicable to all sites. All ASWs were finished with 15 to 30 cm (0.5 to 1 ft) of riser above grade to allow manifold connections to be made at a later date.

The VEWs were installed by standard hollow-stem auger or wash-and-drive techniques and were constructed of 50-mm (2-in.)

Schedule-40 PVC well screen with 0.5-mm (0.02-in.) slots and a 50-mm (2-in.) Schedule-40 PVC riser. Screen lengths for each well were 1.2 to 1.5 m (4 to 5 ft). The borehole was then backfilled with silica sand to the top of the well screen. A 0.6-m (2-ft) thick bentonite seal was placed above the silica sand. The VEWs were finished with 15 to 30 cm (0.5 to 1 ft) of riser above grade to allow manifold connections to be made at a later date. The SVE and AS well layouts are presented in Figures 8.7 and 8.8, respectively.

Following installation of the SVE and AS wells, manifold piping and equipment required to complete the full-scale SVE/AS system were installed. Approximately 1,500 m (5,000 ft) of 50- and 75-mm (2- and 3-in.) Schedule-40 PVC manifold line were installed aboveground from the SVE and AS wells to the equipment staging area. All manifold lines were directed into the 4-m by 4.8-m (12-ft by 16-ft) equipment building where the connections were made to their respective blowers or compressors.

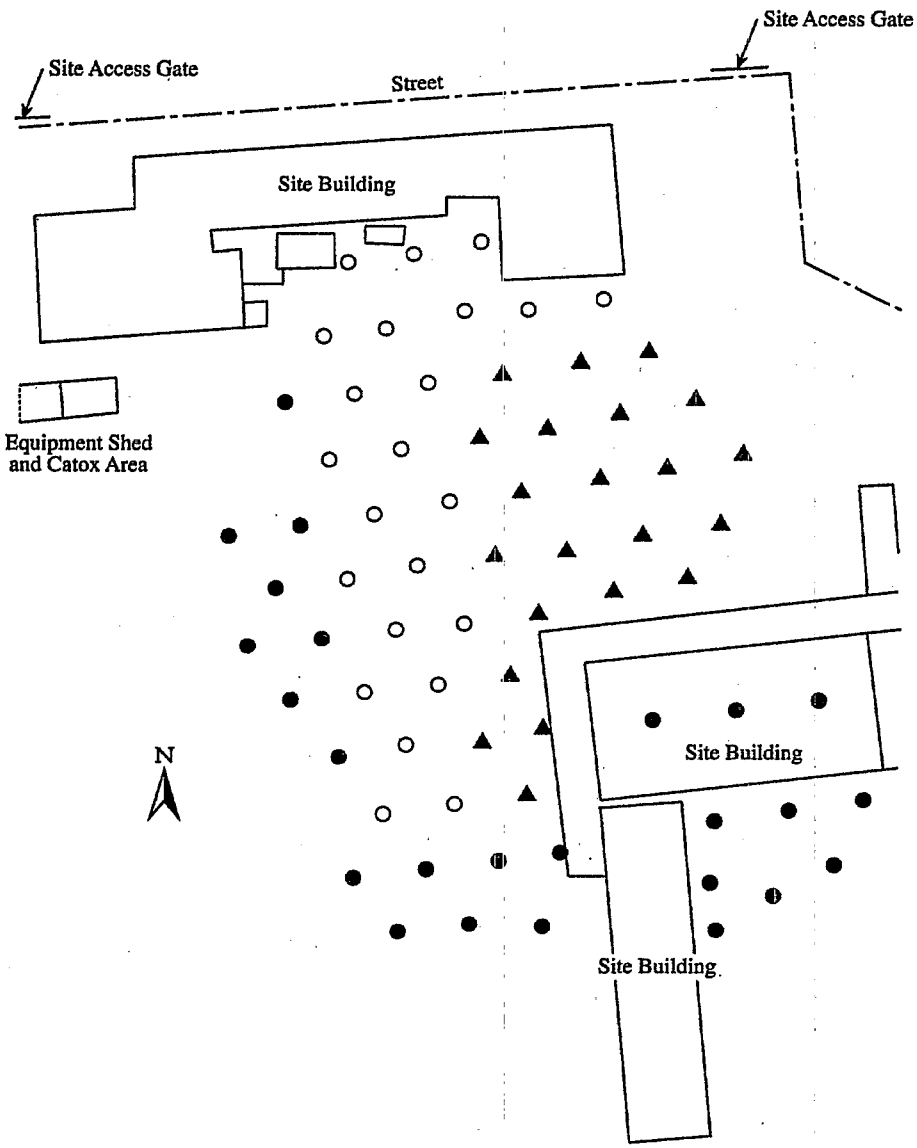
Three 204-m^3/hr (120-scfm) explosion-proof SVE blowers were installed. Each blower was fitted with an air/water separator with a high-water-level shut-off switch, an in-line particulate filter, and an adjustable vacuum relief valve. Each of the SVE systems was manifolded to separate sections of SVE wells. Systems 1 and 2 were manifolded to extract vapors from interior SVE wells; System 3 was manifolded to extract vapors from the perimeter SVE wells (refer to Figure 8.7).

Also installed at the site were one 170-m^3/hr (100-cfm) and one 85-m^3/hr (50-cfm) AS compressors. Each AS compressor was fitted with intake and exhaust silencers and an adjustable pressure relief valve. The AS systems were configured to direct the air flow from the 170-m^3/hr (100-cfm) AS compressor to the perimeter AS wells, and to direct the air flow from the 85-m^3/hr (50-cfm) AS compressor to a valve bank where it could be distributed to any one of three groups of interior AS wells. The AS valves in the valve bank were electrically actuated and controlled by a timer to allow automatic operation (i.e., cycling of AS well groups). The 170-m^3/hr (100-cfm) compressor was also connected to a timer to allow it to be automatically cycled. Refer to Figure 8.8 for AS well groupings.

Three 170-m^3/hr (100-scfm) catalytic oxidation units (CATOX) were installed to control the VOC emissions from the SVE system discharge. The CATOX units were installed adjacent to the equipment building in a 4-m by 6-m (12-ft by 20-ft) fenced area with a locking gate. The CATOX units discharged treated air to the atmosphere through a 150-mm (6-in.) diameter stack at a height approximately 4 m (12 ft) above grade. The CATOX control units were connected to a phone modem that was programmed to notify operations personnel if any of the systems shut down. The CATOX control

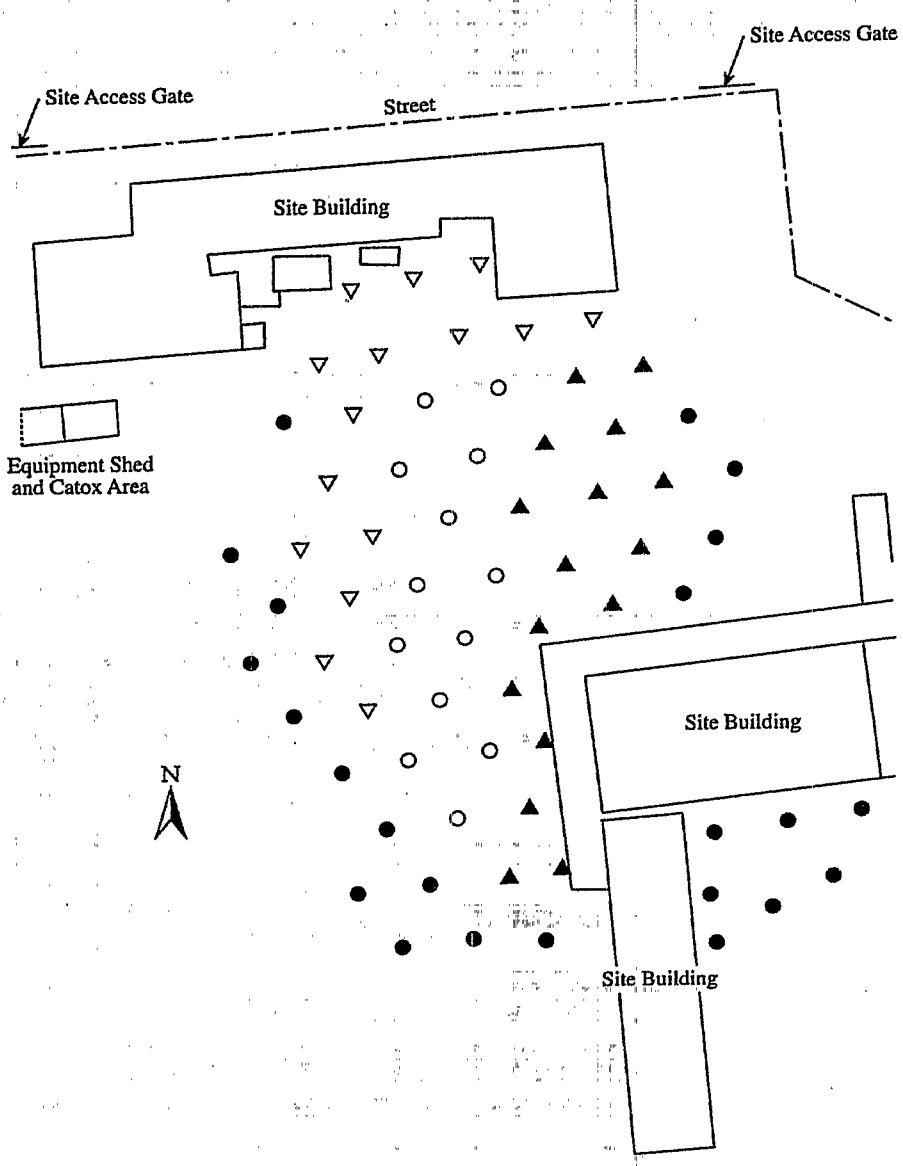
units were also tied into the SVE systems and the AS compressors. When any of the CATOX units shut down, the associated blower and both AS compressors were also automatically stopped.

Figure 8.7
SVE Well Layout
(not to scale)



▲ SVE Well Group 1
○ SVE Well Group 2
● SVE Well Group 3 (Perimeter)

Figure 8.8
AS Well Layout
(not to scale)



● Perimeter AS Group
▽ AS Well Group 1
○ AS Well Group 2
▲ AS Well Group 3

8.2.4 System Operation

8.2.4.1 Year 1

A properly designed and implemented SVE/AS system provides flexibility of operation so that system operators can adapt the SVE/AS systems to maximize VOC removal at a given site. At this site, valves were used to allow control of the air flow through SVE and AS system manifolding and at individual SVE and AS wellheads. Additionally, timers were installed to automate cyclical operation of the AS wells. Data obtained during routine system site checks allowed system optimization on an ongoing basis.

In late spring 1993, SVE Systems 1, 2, and 3 were activated and initial VOC concentrations prior to treatment by the CATOX units were 1,250, 1,100, and 50 parts per million on a volume basis (ppmv), respectively. During subsequent site checks and SVE system optimization, SVE System 1 and 2 VOC discharge concentrations exceeded 2,000 ppmv, and SVE System 3 concentrations exceeded 100 ppmv. (SVE/AS systems installed in the presence of NAPL normally commence with SVE operation only. Once the VOCs in the SVE discharge and the potential for NAPL migration has been sufficiently reduced, the AS system is started. This operation allows efficient offgas treatment selection based on the life-cycle of the SVE/AS system.)

Initial estimates of SVE-only operation at the site were 1 to 2 months. During summer 1993, historically low groundwater table elevations were recorded at the site. This low water table condition exposed more VOCs (i.e., a "smear zone") to the influence of the SVE system. VOC mass removal is more efficient through SVE than by AS since SVE will normally provide more effective contact between the air and contaminant than AS. Therefore, to maximize VOC removal, SVE-only operation was implemented to take advantage of the low water table.

After two months of SVE-only operation, the perimeter AS system was activated and operated in a pulsed mode. Pulsing AS systems are more efficient for a number of reasons. First, the capital and operation costs are reduced because less total system air flow is required and smaller compressors can be used. Second, as discrete AS channels are formed during steady-state operation, continuous injection will generally impact water, primarily in the vicinity of these channels. Pulsing mixes the groundwater, thereby enhancing air/water contact. Third, through pulsing, spatial changes in channel formation have been observed (on a site-specific basis). This spatial variability in channels also enhances mixing of contaminated groundwater in the vicinity of the AS wells, thereby enhancing contact of contaminated groundwater with AS channels over time.

The duration of the perimeter AS well cycle times was determined from pilot test data. Because the perimeter AS wells were designed to prevent downgradient migration of dissolved-phase VOCs, frequent AS cycling times (i.e., 2 hours on and 3 hours off) were used.

The interior AS systems were activated in fall 1993. SVE-only VOC discharge concentrations had dropped to concentrations of less than 1,000 ppmv that permitted the activation of the interior AS systems. To determine optimal initial AS cycling times for the interior wells, the system was optimized to maximize VOC removal while remaining within the operating constraints of SVE offgas treatment (i.e., the CATOX units). An increase in SVE VOC levels due to AS activities in the source area leveled off after approximately 3 hours of air injection at concentrations exceeding 2,000 ppmv. However, after approximately 1 to 2 days of source area sparging (i.e., operating each AS well group for 3 hours twice a day), the CATOX units shut down due to exceedance of catalyst temperatures. It was determined that the SVE system could not sufficiently purge the VOC-laden vapors released by the AS system between cycles. This created a buildup of VOC levels in the SVE systems that could not be handled by the CATOX units. Therefore, AS cycle time was reduced to 2 hours twice daily.

During AS system operation in the winter 1993/1994, the interior AS wells had to be deactivated for short periods (i.e., less than 7 days) to prevent water uptake by the SVE system due to high groundwater table elevations and groundwater mounding by AS operation. Although groundwater mounding was negligible for a single AS well, the combined effects of multiple active AS wells created a temporary mound in the groundwater. Although the groundwater mounding was temporary (dissipated in 2 to 3 hours), the temporal change in depth to groundwater did cause unplanned SVE system shutdowns due to water uptake.

In addition to recording historically low groundwater table elevations at the site during summer 1993, historically high groundwater table elevations of 0.6 m (2 ft) below ground surface were recorded during spring 1994. This abnormally high water table elevation prevented SVE/AS system operation in March 1994. During this period of high water table elevation, the state agency was petitioned to allow operation of the perimeter AS system without the SVE system. Supporting documentation of estimated VOC discharge to the atmosphere during perimeter AS operation (0.07 kg [0.15 lb] to 0.23 kg [0.5 lb] per day) was presented to and approved by the agency. Based on this approval, the perimeter AS system was activated without SVE. Site groundwater table elevations receded by late spring 1994, after which the SVE system was reactivated.

Figure 8.9
VOC Plume — May, 1993 (Units of mg/L)
(not to scale)

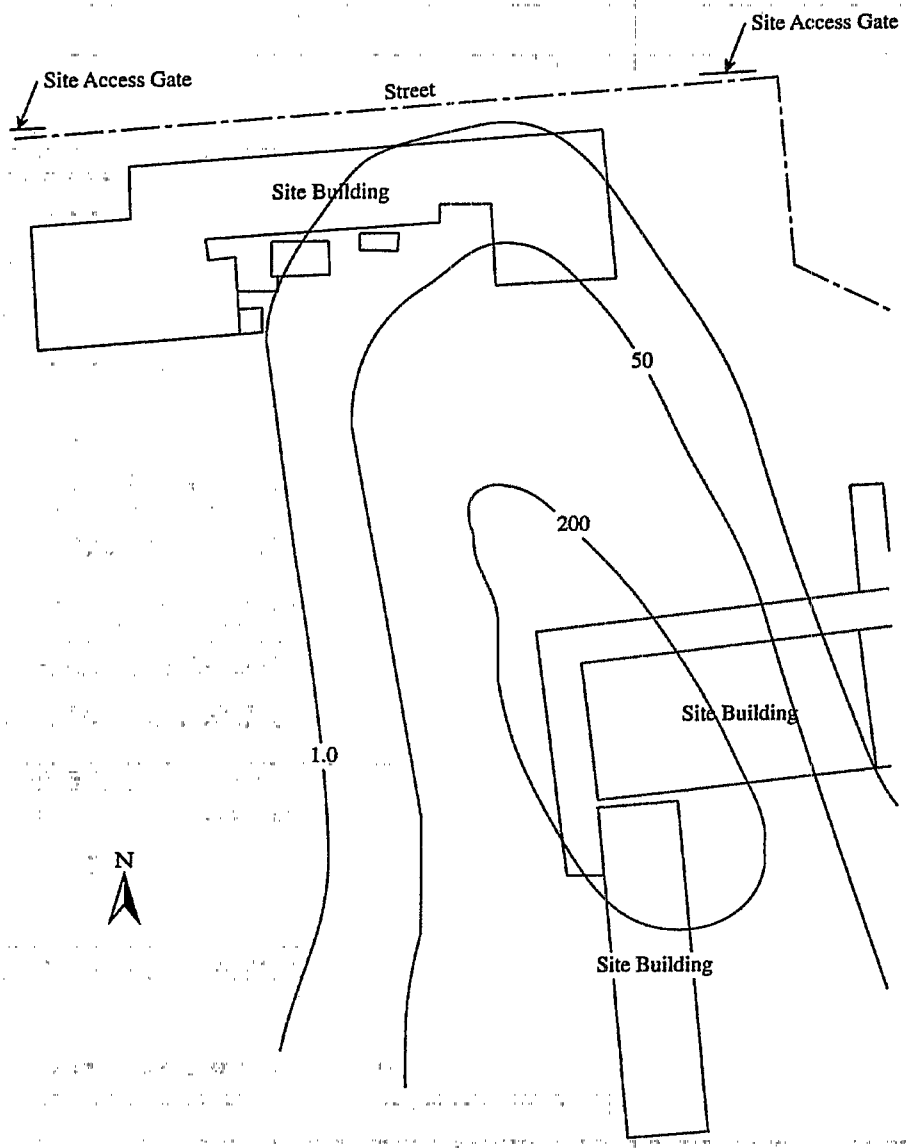
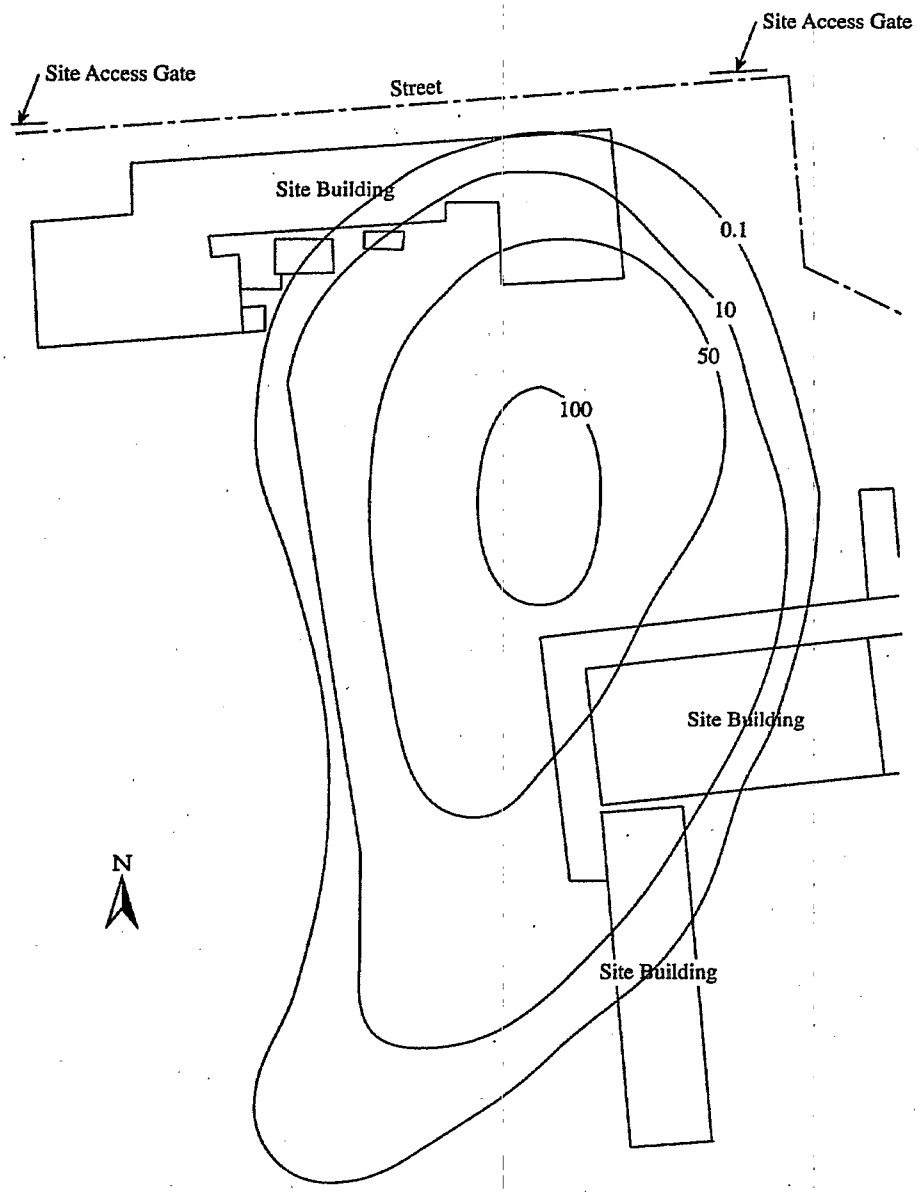


Figure 8.10
VOC Plume — April, 1994 (Units of mg/L)
(not to scale)



Approximately 60 soil samples were collected for analysis from within the remediation area approximately half each from the vadose zone and half from the saturated/smear zone. A subsample of the soils was sent for confirmatory laboratory analyses for VOCs. The laboratory results indicated that the levels of VOCs in the soils had been reduced from residual levels to nondetectable levels (less than 100 ppb) in all areas except the limited nonaccessable area under the corner of a building. This area was subsequently remediated within 1 to 2 months after the system was expanded to encompass that location.

8.2.6 Conclusions

A closely-spaced AS/SVE system was successful in the remediation (to MCLs) of impacted soils and groundwater at a manufacturing facility in the eastern United States based on posttreatment soil and groundwater data collected from throughout the site. The AS/SVE system operated, as designed, to remove approximately 10,000 kg (22,000 lb) of VOCs over a 2-year period. The problems encountered were mostly associated with the physical plant and with fluctuating water table levels impacting SVE system performance. The role of biodegradation increased significantly over the duration of the project.

8.3 Bioventing

During early February 1990, a ruptured pipe at a Burlington Northern Railroad (BNRR) fueling pumphouse in Alliance, Nebraska, resulted in over 230 m^3 (60,000 gal) of #2 diesel fuel being released onto the surrounding soil. Several months later, a subsurface investigation indicated that soils were contaminated to a depth of over 20 m (65 ft) below ground surface (bgs) and could impact groundwater which was observed at approximately 22 m (70 ft) bgs. State regulatory agencies requested that BNRR develop and implement a remedial action plan to treat these diesel-contaminated soils and protect local groundwater. This case study summarizes activities carried out by Parsons Engineering Science, Inc. (Parsons ES) to evaluate a variety of remediation technologies, and highlights the soil bioventing system used to remove volatile BTEX compounds and provide long-term biodegradation of all fuel residuals.

Bioventing pilot testing was used to determine soil properties, such as air permeability, and assess the potential for both volatilization and long-term biodegradation of diesel fuel residuals at the site. Pilot-test results confirmed that bioventing was feasible for the remediation of this site, so a full-scale bioventing system was installed in September 1991. This system operated continuously for over four years. System performance and a review of site characterization test results is summarized below.

8.3.1 Site Description

The site is located south of a diesel fuel pumphouse, where the pipe rupture occurred (Figure 8.11). An estimated 13,000 m^3 (15,000 yd^3) of soil was contaminated to a depth of approximately 22 m (70 ft) bgs. In preparation for the pilot test, a single 10-cm (4-in.) diameter vent well (VW) and six 5-cm (2-in.) diameter vapor monitoring points (VMPs) were installed. The results of the pilot test and a more detailed description of the methods used to conduct the test were reported by Parsons Engineering Science (1991).

8.3.1.1 Groundwater Conditions

Groundwater was observed at depths of 21.5 to 22 m (68 to 70 ft) bgs. Dilute levels of BTEX compounds were detected in groundwater beneath the site; however, only benzene and total petroleum hydrocarbon (TPH) concentrations exceeded their clean-up levels of 5 µg/L and 2 mg/L, respectively. Due to the large vadose zone above the water table, the vast majority of the diesel fuel spill was adsorbed and occluded in these unsaturated soils. Without soil treatment, soluble BTEX compounds could continue to percolate downward toward the groundwater, creating a larger and more concentrated plume of hydrocarbon contamination than existed at the time.

8.3.1.2 Soil Conditions

Soils at this site were characterized during the construction of the VMPs and the VW in April 1991. The general lithology in this area, shown in Figure 8.12, consists of fine- to medium-grained silty sands from the ground surface to approximately 9.5 to 11 m (30 to 35 ft) bgs (upper sand zone), interbedded sand and silt/clay lenses that extend from 11 to 16 m (35 to 50 ft) bgs (interbedded zone), and another layer of fine- to medium-grained silty sand that extends to a depth of 22 to 24 m (70 to 75 ft) bgs (intermediate sand zone). Soil moisture varied from 2% in the intermediate sand to 11% in the interbedded silts and clays.

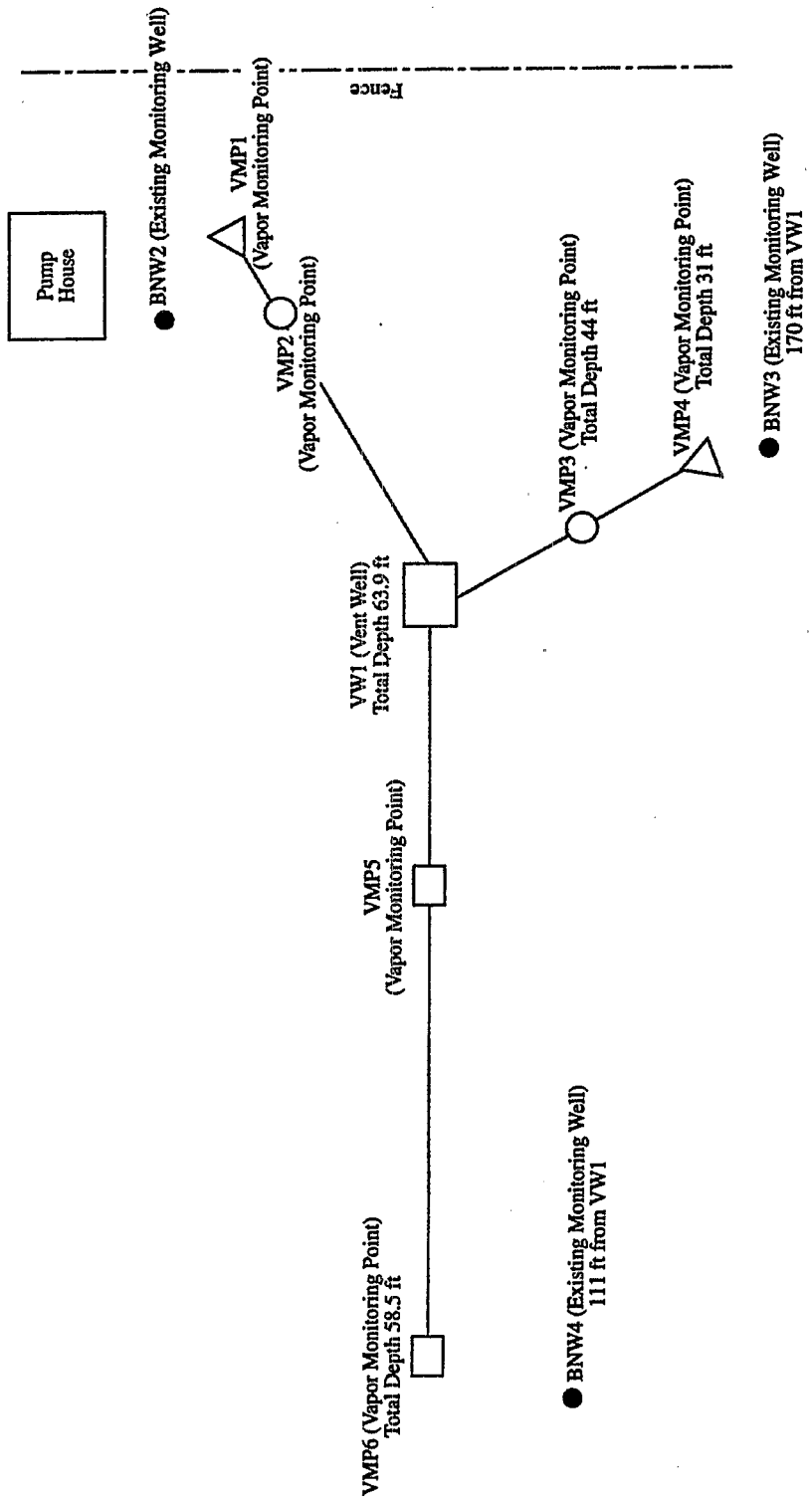
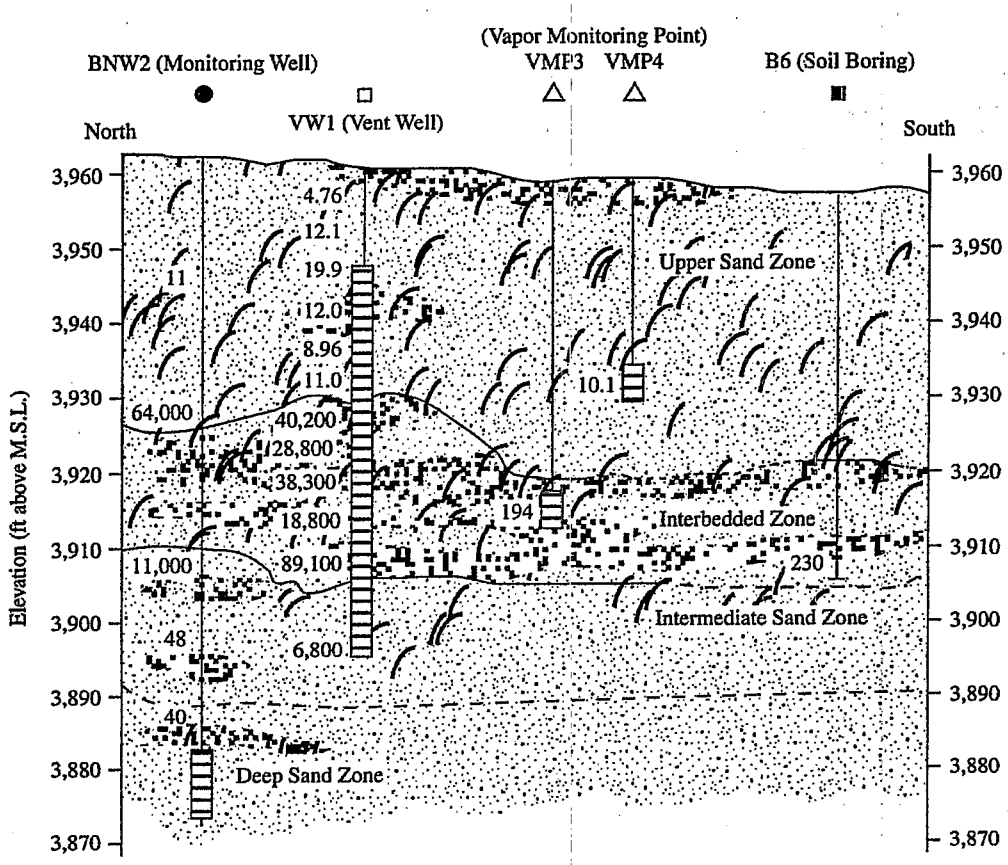


Figure 8.11
Site Plan — Full-Scale Bioventing Demonstration Pumphouse Spill Site, Alliance, Nebraska
(not to scale)

Reproduced courtesy of Parsons Engineering Science (1991)

Figure 8.12
Geologic Section — Full-Scale Bioventing Demonstration
Pumphouse Spill Site, Alliance, Nebraska
(not to scale)



Clay
Silt
Clayey Sand
Silty Sand
38,300 Initial Soil TRPH Concentration (mg/kg)(Samples collected in April 1991)
---- Groundwater Elevation
— — Geologic Contact, Dashed where Inferred
Screened Interval and Total Depth of Well

Reproduced courtesy of Parsons Engineering Science (1991)

Soil gas permeability was quantified through vacuum response tests conducted as part of the pilot test in April 1991. Vacuum response and oxygen concentrations were measured at the VMPs and nearby groundwater monitoring wells (Figure 8.12) while soil gas was being extracted from the VW

using a 10-hp vacuum blower. The soil responded rapidly to the vapor extraction system, with measurable vacuum response and increases in oxygen concentrations occurring in all soil zones, including the interbedded silt/clay zone. Using test methods described by Hinchee et al. (1992), the average soil gas permeability was estimated at 5 Darcys. Because the contaminated soil zone was entirely oxygenated using only the pilot-scale VW, no additional VWs were required for the full-scale system.

8.3.2 Initial Soil Contamination and Nutrient Availability

The diesel fuel contamination in the soil appeared to be localized within a 19-m (60-ft) radius of the pumphouse (Figure 8.11). Initial total recoverable petroleum hydrocarbon (TRPH) concentrations are plotted on the geologic section shown in Figure 8.12. Based on initial soil analyses and observations made during drilling, it appeared that diesel fuel migrated rapidly downward at the spill site until it encountered the interbedded sand and silt/clay zone at approximately 9.5 to 11 m (30 to 35 ft). At this depth, the fuel spread laterally and continued its downward movement through more permeable sand lenses in the interbedded layer.

Initial soil samples collected from the screened intervals of VMP4 and VMP5 were analyzed for ammonia- and nitrate-nitrogen, total Kjeldahl nitrogen (TKN), and water-soluble phosphates. These analyses were performed to determine the concentrations of naturally-occurring nutrients available in the soils. Ammonia-nitrogen was found at concentrations of 204 mg/kg in the upper sand zone (VMP4) and 4.2 mg/kg in the intermediate sand zone (VMP5), while nitrate-nitrogen levels ranged from 4 mg/kg in the upper sands to 11 mg/kg in the intermediate sand zone. TKN levels were found to be 4 mg/kg in both sand zones. Water-soluble phosphate concentrations ranged from 177 mg/kg in the upper sands to nearly 6,000 mg/kg in the intermediate sands. The relatively low nitrogen concentrations found in these soils may have been limiting biodegradation rates. To determine if nitrogen addition could improve natural biodegradation rates, an ammonium-nitrate solution was added to several VMPs after several months of bioventing. However, the addition of the nutrient solution did not significantly accelerate fuel consumption rates.

8.3.3 Remedial Goals

The objective of this remediation project was to reduce the potential impact of soluble diesel components on local groundwater by removing BTEX from the soil through a combination of short-term SVE and continuous

bioventing. A secondary objective was to remediate this large site without disruption to existing rail lines or the fuel pumphouse where the spill occurred and to obtain regulatory closure for the lowest possible cost.

8.3.4 Full-Scale System Design and Operation

Based on the air permeability and oxygen influence observed during the pilot test, an extraction rate of 3.2 m^3/min (100 scfm) was selected for full-scale bioventing operations. A 7-hp regenerative blower system capable of producing this design flow rate was installed at the site, plumbed to the existing VW; operation began in September 1991. Soil gas extraction was selected over air injection due to the immediate need to remove volatile and soluble BTEX compounds from the soil before further groundwater contamination occurred. In December 1994, the system was switched to injection mode, and the flow rate was decreased to 2 m^3/min (60 scfm). This modification was made because much of the soluble BTEX had already been removed/biodegraded, and because bioventing systems require much less maintenance when operated in an air-injection mode. The six VMPs installed during the pilot test were used to monitor pressure response and ensure that aerobic conditions were maintained throughout the contaminated soil volume.

The full-scale bioventing system operated continuously for over 4 years with minimum maintenance downtime. The monthly electrical cost for the system was estimated at approximately $280. BNRR personnel were responsible for weekly system checks and monthly blower filter changes.

8.3.5 Long-Term Performance Monitoring

The fuel-consuming capability of native soil bacteria was examined during seven in situ respiration tests conducted by Parsons ES over the four-year operation period. Emissions of volatile hydrocarbons to the atmosphere were monitored to ensure regulatory compliance and estimate the amount of hydrocarbons physically removed from the soil. Three soil sampling events, including the initial sampling event in April 1991, were conducted to document the removal/biodegradation of petroleum hydrocarbons at the site.

8.3.5.1 In Situ Respiration Testing

Continuous air injection into contaminated soil zones provides the necessary oxygen for aerobic biodegradation. When the blower is turned off, oxygen is no longer delivered and soil bacteria consume the available oxygen. Oxygen consumption and carbon dioxide production were moni-

tored at each VMP using a portable O_2/CO_2 gas analyzer. The rate at which soil bacteria consumed oxygen was an important indicator of the viability of the fuel-degrading organisms in soils near each VMP. Uncontaminated background VMPs were also monitored during the initial respiration test. Oxygen levels at these background VMPs remained relatively constant at approximately 18% by volume, indicating that biological oxygen consumption of natural (nonfuel) organic carbon and abiotic oxygen consumption were not significant in these uncontaminated soils.

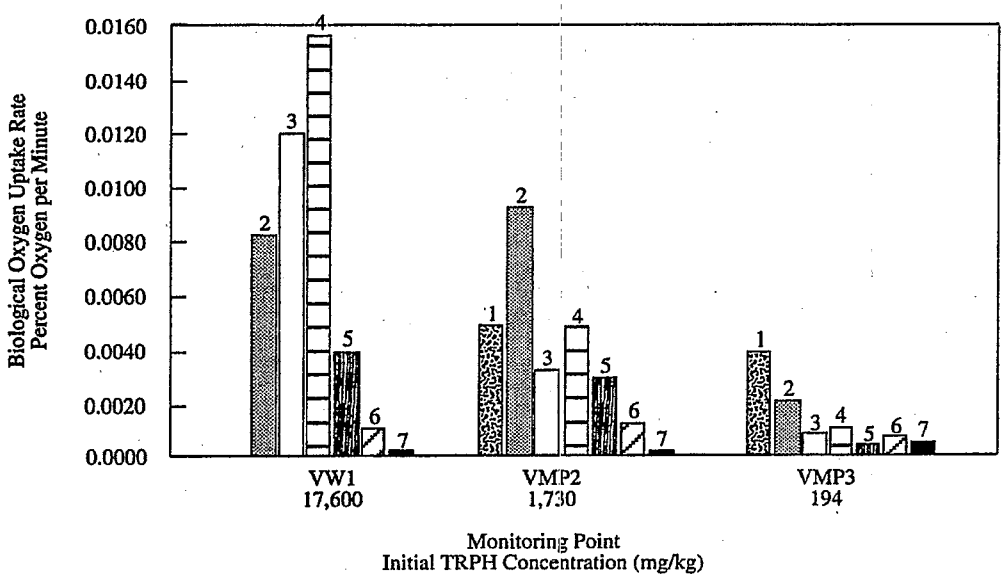
The results of respiration tests at the VW and VMPs 2 and 3 are shown in Figure 8.13 and indicate that the apparent rates of oxygen utilization decreased significantly over time. Very low rates of respiration (<0.001% by volume oxygen/min) were measured in VMP3 during the last three tests, indicating that little fuel remained for biodegradation near this monitoring point. Soil sampling at VMP3 in September 1995 confirmed that TRPH levels were reduced from 194 mg/kg to less than 3.3 mg/kg over four years of system operation. Respiration rates also decreased significantly at VW1 and VMP2. Although TRPH concentrations were still somewhat high at fuel-impacted depths at these locations, respiration rates were minimal. Low respiration rates at VW1 and VMP2 indicate that the majority of the readily-biodegradable fraction of the diesel fuel had been eliminated. The remaining TRPH in site soils is likely high-molecular weight material, with corresponding low water solubilities, low bioavailability, and low biodegradation rates.

Using a conservative ratio of 3.5 kg of oxygen per 1 kg of hydrocarbon consumed, the fuel biodegradation rates were estimated for soils immediately surrounding VW1 and each VMP. Using this estimation method, the average biodegradation rate at the center of the spill (near the VW) was approximately 3,400 mg of TRPH degraded/kg of soil/year during the first two years of system operation (September 1991 to November 1993). During the final respiration testing event in September 1995, the average fuel hydrocarbon consumption rate was estimated to be 130 mg of TRPH degraded/kg of soil/year. This represents an order of magnitude decrease in the rate of fuel consumption and indicates that the bioventing system successfully accomplished its objective.

8.3.5.2 Volatilization

The removal of volatile and water-soluble compounds, such as BTEX, from this large diesel fuel spill was also a key objective of this remediation project. Regular sampling of extracted soil gas indicated that approximately 0.3 kg (0.66 lb) of BTEX and 14.7 kg (32 lb) of diesel vapors were removed

Figure 8.13
Biological Oxygen Uptake During Respiration Tests —
Full-Scale Bioventing Demonstration Pumphouse
Spill Site, Alliance, Nebraska



Respiration Test 1 (Nov 91)
Respiration Test 2 (Dec 91)
Respiration Test 3 (April 92)
Respiration Test 4 (April 93)
Respiration Test 5 (Nov 93)
Respiration Test 6 (Dec 94)
Respiration Test 7 (Sept 95)

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per day of bioventing operation while the system operated in extraction mode (September 1991 through December 1994). During this time, an estimated 21,400 kg (47,000 lb) of total volatile hydrocarbons were removed via extraction by the bioventing system. This mass of hydrocarbon removal could account for approximately 10,000 mg/kg reduction in soil TRPH.

8.3.5.3 Soil Sampling

To more accurately assess remediation progress, soil sampling programs were conducted in November 1993 and September 1995. In each sampling event, soil samples were collected from a number of boreholes located within a 6.5-m (20-ft) radius of VW1. This area was selected for sampling

because it represented the most contaminated portion of the site based on initial soil sampling. Sampling depths matched those of the initial site characterization in April 1991. A total of 18 samples were collected from four boreholes in September 1993, and 19 samples were collected from five boreholes in September 1995. All soil samples were analyzed for TRPH by US EPA Method 418.1, and six soil samples from each sampling event were also analyzed for BTEX by Method 8020 (US EPA 1986d). The samples analyzed for BTEX compounds were chosen based on elevated field hydrocarbon analyzer readings.

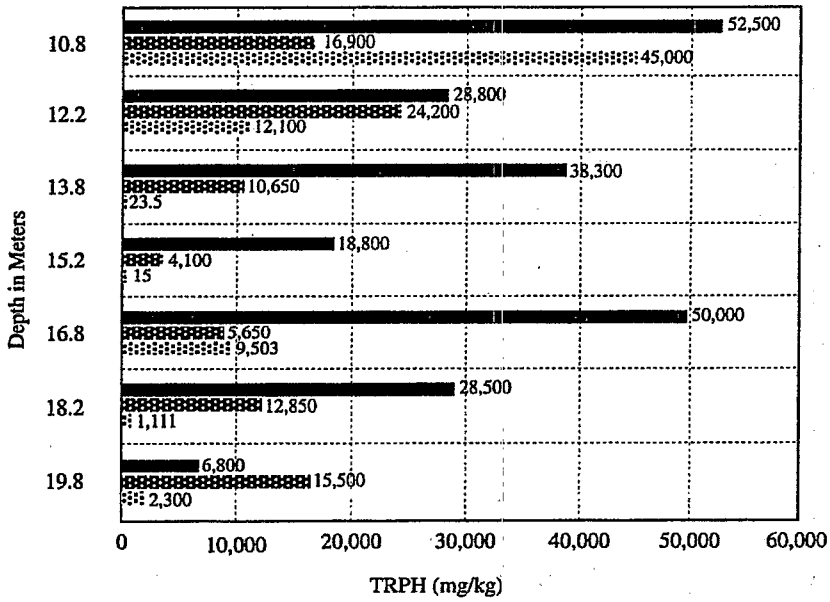
Figure 8.14 illustrates the general reduction in diesel fuel concentrations from initial April 1991 levels. These soil sampling results indicate that an overall TRPH reduction of 75% occurred over the four years of bioventing. Only the 11-m (35-ft) depth interval showed a significant increase in fuel concentrations from the 2-year to 4-year sampling event, likely caused by the nonuniform distribution of hydrocarbon contamination in the interbedded zone at this depth. Concentrations of fuel contamination are likely to be greater in clay lenses in the zone because of higher capillary retention of liquids, and because oxygen is more difficult to deliver in these soils. The soil sample collected during the September 1995 event could easily have contained a higher percentage of fine-grained soils than the sample collected during the November 1993 event, thereby yielding a higher fuel concentration.

The overall TRPH reduction observed during the first four years of system operation was approximately 75%. Fifty-five percent of the TRPH was removed in the first two years of system operation, with an additional 20% removal between November 1993 and September 1995. These results indicate that the rate of TRPH removal is slowing and the benefits of continued system operation are decreasing over time.

Figure 8.15 illustrates the reduction in BTEX concentrations achieved during the last two years of system operation (from November 1993 to September 1995), and Table 8.1 summarizes the results of BTEX analyses for the September 1995 sampling event. Total BTEX concentrations were reduced substantially at all depths, and overall BTEX concentrations were reduced 75% between November 1993 and September 1995.

An estimated 4,320 kg (9,500 lb) of BTEX were spilled at the Alliance site in 1990. In November 1993, an estimated 740 kg (1,630 lb) of BTEX remained in contaminated soil zones. As of September 1995, only 173 kg (380 pounds) of BTEX were estimated to be present in site soils. This remaining BTEX represents only 4% of the 4,320 kg (9,500 lb) of BTEX initially released. Be-

Figure 8.14
Four-Year Petroleum Hydrocarbon Reduction — Full-Scale Bioventing Demonstration Pumphouse Spill Site, Alliance, Nebraska



All 2-year samples represent an average of two or more sample locations per depth.

Initial (April 1991)
2-Year (November 1993)
4-Year (September 1995)

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cause 96% of the risk-driving BTEX compounds were removed/biodegraded, the health risk at this site has been substantially reduced.

8.3.6 Conclusions

Full-scale bioventing at this large diesel fuel spill site produced encouraging results during the four years of operation. Remediation took place throughout a 22-m (70-ft) soil profile with no disruption to railroad operations or facilities. Specific indicators of progress include:

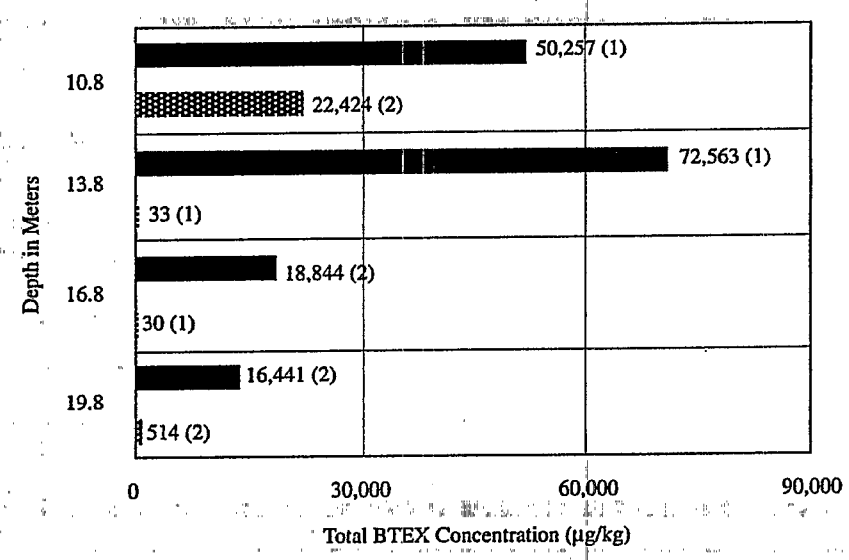
- a 75% decrease in TRPH in the most contaminated portion of the site during the four-year demonstration (based on soil sampling

results). Also, a 75% reduction in soil BTEX concentrations occurred in the last two years of system operation (between November 1993 and September 1995). The low levels of remaining BTEX should pose little or no risk to the local groundwater or to workers during any potential soil excavation at the site; and

- significant decreases in respiration rates across the site. These reductions in respiration rates indicate a significant reduction in the concentration of readily-biodegradable, low- to medium-molecular-weight petroleum hydrocarbons in the fuel-impacted soils.

Figure 8.15

Total BTEX Reduction in the Last Two Years of System Operation — Full-Scale Bioventing Demonstration Pumphouse Spill Site, Alliance, Nebraska



Number of samples indicated in parentheses.

2 Year (November 1993)
4 Year (September 1995)

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Table 8.1
BTEX Concentrations in Soil Samples Taken Within 6 m (20 ft) of the Vent Well -- September, 1995

Sample I.D.	Depth m (ft)	Concentrations in µg/kg			
		Benzene	Toluene	Ethylbenzene	Xylenes
BN-AL-SB8-65	19.8 (65)	ND	ND	ND	ND
BN-AL-SB8-35	10.8 (35)	140J	300J	550J	27,000
BN-AL-SB7-65	19.8 (65)	ND	ND	2.3J	4.8J
BN-AL-SB7-55	16.8 (55)	6.3J	2.8J	ND	ND
BN-AL-SB7-45	13.8 (45)	2.6J	ND	ND	ND
BN-AL-SB7-35	10.8 (35)	88J	270J	1,500	15,000

J-Detected, but value is estimated because it is below the practical quantitation limit.
ND - Not detected.

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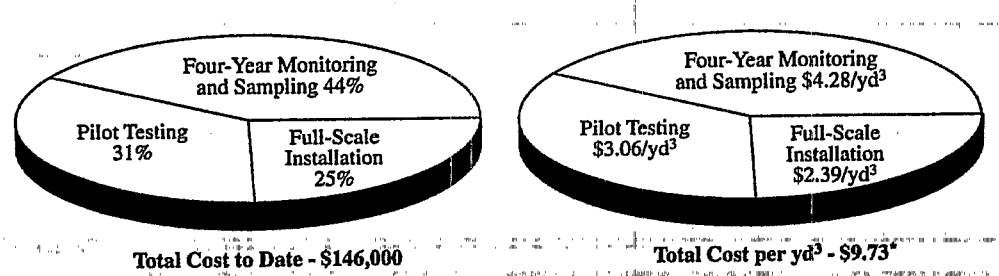
8.3.7 Cost Summary

The total cost to date of bioventing at this site including pilot testing, full-scale installation, and four years of operation and maintenance is approximately $146,000. Figure 8.16 provides a breakdown of total cost and a cost per volume of soil based on an estimated contaminated soil volume of 13,000 m^3 (15,000 yd^3). These totals include all project administration and reporting costs, but do not include electrical costs or BNRR labor costs for system checks.

Because the majority of the volatile and water-soluble contaminants (i.e., BTEX compounds) have been volatilized and biodegraded, and because the high-molecular weight compounds remaining in the soil are not expected to cause further deterioration of groundwater quality, it was recommended that a risk-based closure of vadose zone soils be pursued at this site. Early in 1996, the state of Nebraska reviewed soil data from the site and agreed that the site could be closed based on the significant risk reduction that was achieved using bioventing technology.

Figure 8.16
Cost Summary — Full-Scale Bioventing Demonstration
Pumphouse Spill Site, Alliance, Nebraska



*Based on an estimated 15,000 yd³

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8.4 Raymond Process

This case study describes successful application of enhanced bioremediation of an aquifer at the French Limited Superfund Site in Crosby, Texas (Adapted from Dey et al. 1993; O'Hayre et al. 1993; Thomson et al. 1995; and Biotreatment News 1993,1994). Specifically, the study of this complex site illustrates the following:

- observational approach to achieving an effective remedial system;
- use of more than one type of electron acceptor;
- incorporation of an alternate water supply;
- integration of bioremediation with the use of a barrier and an in situ slurry reactor;
- use of intrinsic remediation as a polishing step to achieve a shorter active treatment period; and
- planning and budgeting for significant system modifications that require capital expenditures.

The approach described in this case study reduced the time of remediation, perhaps by as much as 50%, without having to over-design the system.

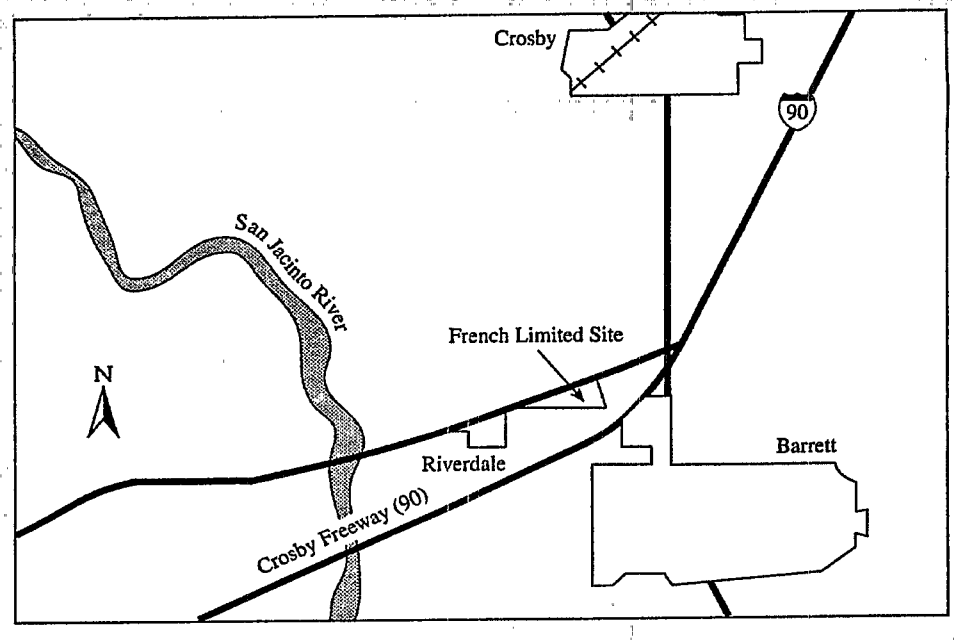
8.4.1 Site Description

The French Limited Superfund Site is located within the flood plain of the San Jacinto River as shown in Figure 8.17. For many years, the site and another nearby Superfund site (Sikes) were used as sand pits. Both sites were converted for use as disposal lagoons for liquid chemical waste. At the French Limited site, this practice continued from 1967 through 1972. Residues from the waste materials formed a sludge at the bottom of the lagoon. This material, which contained elevated levels of organic constituents and metals, infiltrated the soils adjacent to and beneath the lagoon. Dissolved-phase liquids and NAPLs migrated into the underlying aquifer and impacted soil and the shallow alluvial groundwater beneath and downgradient of the lagoon.

In 1982, the site was placed on the National Priorities List and was designated for remediation under the CERCLA. The potentially responsible parties (PRPs) formed the French Limited Task Group (FLTG) to manage all activities at the site, including the remedial investigation (RI); feasibility study (FS); remedial action plan (RAP); and engineering design, construction, and operation. FLTG maintained control over the site and provided the primary contact with US EPA. Several contractors and consultants were employed on the site; Applied Hydrology Associates (AHA) provided the primary consulting services related to aquifer remediation.

The unique site geology determined the design features of the aquifer bioremediation system. Shallow alluvial deposits extend to a depth of about 17 m (55 ft) and consist of sands, silts, and clays. This interval contains four units whose properties dictated the well configurations discussed below. These units, from the surface downward, are an unconsolidated zone (UNC), a sandy zone (S1), a discontinuous clay layer (C1), and an interbedded silt zone (INT). The shallow alluvial deposits are underlain by a second, thicker clay unit (C2) which averages 20 m (70 ft) and contains minor sand and silt lenses. A silty sand unit (S2) is found below the C2 unit and averages 7 m (20 ft) in thickness. The UNC unit consists of clay, silt, and sand over an interval of 0 to 3 m (0 to 9.5 ft). The S1 unit extends from 3 to 9 m (9.5 to 28.5 ft) and consists of coarse-grained sand with occasional gravel layers. The C1 unit ranges from 0 to 3 m (0 to 9.5 ft) in thickness and serves to separate the S1 unit from the INT unit where it exceeds 1 m (3 ft) in thickness. The INT unit consists of interbedded silty sand and silt with variable clay over a vertical interval of 5 to 8 m (16 to 25 ft) beginning at 9 to 12 m (28 to 38 ft) below the groundwater surface. Groundwater is first encountered within the UNC zone as depicted in Figure 8.18.

Figure 8.17
French Limited Site Location Map
(not to scale)

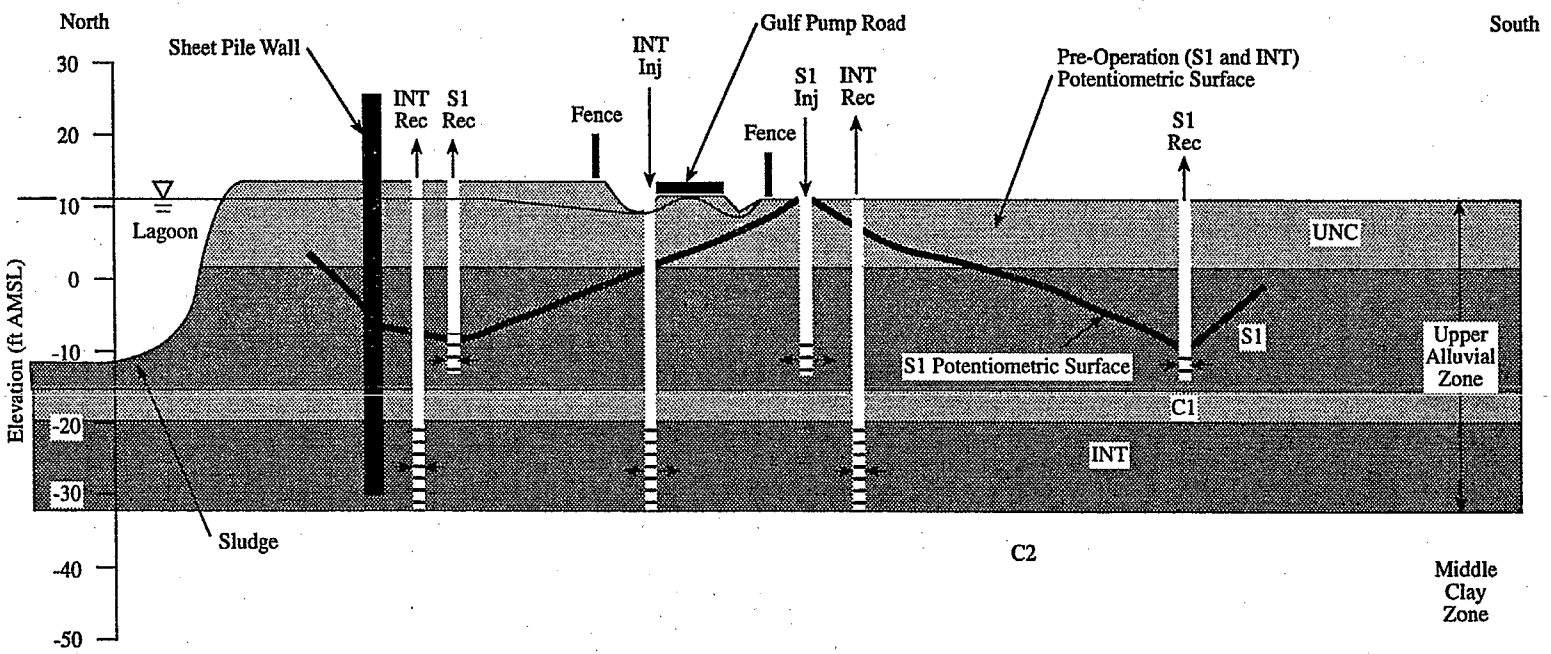


Source: O'Hayre, Day, and Thomson 1993. Used with permission.

The lagoon was excavated to the base of the S1 unit. The contamination subsequently addressed by the remediation was largely contained within the S1 and INT units. The S1 unit is significantly more permeable ($k = 10^{-3}$ cm/sec) than the INT unit ($k = 10^{-4}$ cm/sec). The INT unit is underlain by the Beaumont clay aquitard (C2) whose permeability ($k = 10^{-7}$ cm/sec) and thickness has served to prevent migration of dense nonaqueous-phase liquids (DNAPLs) and dissolved phase contaminants to the deeper sandy unit (S2).

The principal constituents found in the soils and groundwater on which the groundwater clean-up criteria (Federal MCLs) were based were monoaromatic hydrocarbons and chlorinated ethenes and ethanes. Concentrations of benzene, toluene, 1,1-dichloroethane (1,1-DCA), 1,2-dichloroethane (1,2-DCA), and vinyl chloride, as well as total organic carbon (TOC) were used to track remediation progress. Benzene, 1,2-DCA, and vinyl chloride concentrations were of particular interest because: (1) the health-based clean-up criteria associated with these compounds was low, (2) they were the most widespread at the

Figure 8.18
French Limited Project Geologic Cross-Section



Source: O'Hayre, Day, and Thomson 1993. Used with permission.

site, and (3) all three compounds are particularly mobile. These compounds were also the only VOCs that exceeded their MCLs outside the property boundary within the INT unit at the time intrinsic remediation was implemented.

DNAPL residuals, including DNAPL pools, were present at the site. DNAPL was found in both the S1 and INT units, mostly within the steel sheet-pile wall. The sheet-pile wall was driven through the shallow alluvial sediments into the underlying clay unit, C2, as a barrier to subsurface groundwater flow, containing the lagoon source area. A few smaller occurrences of DNAPL were observed south of the eastern end of the lagoon between the sheet-pile wall and Gulf Pump Road. DNAPL samples collected from these areas contained up to 44% VOCs, which, by weight, consisted mainly of higher chlorinated VOCs such as chloroform, carbon tetrachloride, perchloroethene (PCE), and trichloroethene (TCE).

The dissolved-phase plumes within the S1 and INT units extended downgradient of the lagoon south and southwest across Gulf Pump Road. Prior to implementation of in situ bioremediation, the plume covered an area of approximately 60,000 m^2 (15 acres). Concentrations of 1,2-DCA in groundwater were as high as 860,000 µg/L near DNAPL sources and much higher in soils (380,000 mg/kg), soil leachate (2,900,000 µg/L), and recovered DNAPL (14% by weight). Similar high concentrations existed for carbon tetrachloride and chloroform. Very significant levels of vinyl chloride and benzene were also detected. The highest concentrations of 1,2-DCA and the other halogenated VOCs were detected immediately downgradient of the lagoon. In addition to the VOCs, other major contaminants, including polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs) and heavy metals, were present in the chemical-rich sludge located at the bottom of the lagoon. Leaching of the lagoon sludges and dissolution from DNAPL-impacted soils were identified as the sources of the dissolved-phase plume and, along with the properties of the contaminants, explains the distribution and composition of the dissolved-phase plume throughout the site.

8.4.2 Regulatory Considerations

Pilot tests of bioremediation of the lagoon sludges and subsoils (effectively, a large in situ slurry reactor) were conducted in 1987 as part of the FS. Based on the success of these tests, US EPA granted approval of in situ bioremediation as the preferred remedial action for the lagoon sludges. This remedy was incorporated into the Record of Decision (ROD) in 1988. The ROD also specified a pump-and-treat remedial action for the contaminated groundwater and associated subsoils surrounding the lagoon.

The alluvial deposits are considered to be a drinking water aquifer and thus were required by the ROD to be in compliance with federal drinking water standards. The compliance boundary was defined in the ROD as the site boundary, approximately 32 m (100 ft) to the south of the lagoon.

8.4.3 Design Approach

The remedial program for groundwater and subsoils at the French Limited site had two major objectives: (1) isolate contaminant source areas, such as DNAPL zones, so that they could not provide a continuing supply of dissolved constituents to groundwater; and (2) remove or degrade dissolved and adsorbed contaminants in the affected groundwater and subsoils outside the source areas.

The sheet-pile wall completely surrounded the lagoon disposal area and was keyed into the underlying clay unit, providing containment of DNAPL-impacted subsoils in the lagoon source area. In addition, the well pumping and injection network was operated so that hydraulic containment of the source area was maintained. One isolated DNAPL zone was identified outside the sheet-pile wall on the basis of direct investigation and indirect groundwater quality data. This zone was hydraulically contained under the groundwater operating scheme and was eventually permanently isolated by an extension of the lagoon sheet-pile wall.

The focus of the groundwater and subsoil in situ bioremediation program at the French Limited site was placed on the affected aquifer units outside the known DNAPL source areas. Enhancement of pump-and-treat systems was considered because of the well-documented failure of such systems to remediate soils and groundwater in all but the most ideal conditions. Pump-and-treat systems fail as remedial technologies because most contaminants have limited solubility and are easily adsorbed by soils, and effective groundwater/contaminated soil contact is rarely possible under field conditions.

As contaminated groundwater passes through the pore space of the aquifer soils, dissolved contaminant constituents are transferred to the soil matrix by the processes of adsorption and diffusion. In most cases, the mass of a contaminant constituent adsorbed onto soil particles or diffused into low-permeability lenses far exceeds that dissolved in the groundwater. Slow desorption and diffusion from soils into groundwater can act as a continuing, long-term secondary source of groundwater contamination. Similarly, zones of DNAPLs can compromise remedial activities because they also provide a continuing source of pollutants to groundwater unless they can be removed or isolated from active groundwater flow.

The existence of soil contamination and/or DNAPL zones limits the ability of pump-and-treat remedial schemes to achieve stringent remedial criteria. One of the advantages of in situ bioremediation, as discussed in Section 5.2, is that contaminants adsorbed onto the aquifer matrix are directly addressed. Direct bioremediation of DNAPL zones has not been demonstrated because, in part, the very high concentrations of organics in DNAPL are likely to be toxic to microorganisms.

8.4.4 In Situ Bioremediation Design Basis

Considerable information was gathered during the lagoon pilot studies in 1987 to verify that aerobic bioremediation would be effective in meeting remedial action criteria for chlorinated and nonchlorinated volatile organics in the lagoon sludges and subsoils. As might be expected, the more mobile organic constituents found in lagoon sludges were also found in the groundwater outside the lagoon "source" area. Unlike the lagoon, however, aggressive mixing and blending of contaminated aquifer solids with biologically-stimulating ingredients was not feasible. The challenge was to establish subsurface conditions conducive to stimulating bioremediation by injection and distribution of appropriate electron acceptors and nutrients (i.e., to implement the Raymond Process).

The in situ bioremediation system at the French Limited site incorporated the addition of both oxygen and nitrate as electron acceptors. Historically, oxygen has been the most widely used electron acceptor for in situ bioremediation programs. Nitrate was included as an alternate electron acceptor because oxygen has limited solubility in water and would be rapidly consumed by the high concentrations of TOC in the alluvial soils and groundwater. Nitrate is more soluble than oxygen and, therefore, can be distributed more widely within the aquifer system. Stimulation of different consortia of microbial populations under aerobic and denitrifying conditions would result in direct oxidation of monoaromatic hydrocarbons (with the exception of benzene), under denitrifying conditions and promote co-metabolic biodegradation of some chlorinated compounds. This is believed to be the primary mechanism for biodegradation of chlorinated organic constituents under these conditions. Reductive dechlorination of the chlorinated compounds would be anticipated in the absence of nitrate and oxygen and in the presence of sulfate and areas of methanogenic activity.

In the presence of nitrate or oxygen, degradation processes involving other electron acceptors would be inhibited. Nitrate was added to the injection water stream, initially in the form of concentrated aqueous solution of ammonium nitrate. Its addition was controlled so that the concentration of

nitrate in the receiving water would not exceed the drinking water standard of 10 mg/L as nitrogen. Ammonium nitrate is also a source of nitrogen nutrient. During the course of the remediation, the nitrogen source was changed to potassium nitrate based on concerns that ammonium could be exerting an oxygen demand in the aquifer during nitrification.

Oxygen was added to the injection water stream by direct injection of gaseous oxygen. The oxygen was stored on-site in liquid form and converted to gaseous form in vaporizer units. Liquid oxygen was particularly attractive because it was already being used on-site for lagoon bioremediation in much larger quantities than would be required for the aquifer remediation.

Phosphate addition (as potassium tripolyphosphate [KTPP]) was evaluated through a series of precipitation tests using site water from several wells. The tests indicated that precipitation could lead to plugging of the injection wells and the adjacent formation if KTPP were used to amend recycled groundwater. The recycling of treated groundwater was a concern with respect to potential precipitation of calcium, magnesium, and iron if phosphate were added and possible precipitation of iron oxy-hydroxides following injection of oxygen-rich water. The solution to this potential problem was to discharge treated water to the lagoon and the San Jacinto River and use low total dissolved solids water from a deeper aquifer for injection purposes.

Four test areas, two in each of the S1 and INT units, were constructed to establish operational parameters for the in situ bioremediation system before going full-scale. The major purpose of the test areas was to confirm that addition of chemicals and oxygen would not have detrimental effects on the aquifer system. Injection water was amended in phases. First, water with no nutrient or oxygen amendments was injected. This "clean water" front had the effect of flushing groundwater containing relatively high concentrations of iron and other cations away from the injection well screens. The second phase of injection involved amendment of injection water with ammonium nitrate and KTPP. The last phase of injection included the addition of oxygen.

Despite a thorough hydrogeologic investigation, it was not possible to locate all injection and extraction wells in the optimum locations. Therefore, an inherently flexible approach to well placement was adopted. Injection and extraction wells were initially placed in fairly regular patterns similar to a five-spot array. Because of the order-of-magnitude difference in hydraulic conductivity between the S1 and INT units and the semicontinuous C1 clay layer that separated the two units, separate injection well/recovery well systems were designed for each unit. The spacing between wells was larger for the more permeable S1 unit than for the C1 layer. After the system was operated for a sufficient length of time to assess performance with respect to

the time needed to remediate individual areas, additional wells were added to accelerate remediation of "hot spots" and/or areas of relatively low hydraulic conductivity. This empirical/observational approach allowed for the placement of some wells based on aquifer response and for flushing and electron acceptor delivery to those portions of the aquifer that would otherwise require longer times for remediation.

The design called for a phased sequence of injection water amendments to be applied to the entire injection well field. The sequence of amendments, which took into account the higher mobility of nitrate compared with oxygen in the subsurface, was designed so that three zones of subsurface activity would be developed. The leading zone, developed farthest away from the injection well, was a zone where flushing enhanced conditions for in situ bioremediation by reduction of high concentrations of organic and inorganic constituents. This zone was followed by an anaerobic denitrifying zone where nitrate in the injection water was the primary electron acceptor. Closest to the injection well was the aerobic zone. Rapid utilization of nitrate and especially oxygen, retarded penetration of the electron acceptors relative to the clean water front.

The injection of clean water, combined with groundwater recovery, served to flush soluble organic compounds (to remove contaminated mass) and inorganic ions (iron, calcium, magnesium, etc.) from the aquifer to reduce complications (i.e., reduced permeability) from nutrient and oxygen addition. Removal of unidentified organic compounds was not only beneficial because of the reduced TOC levels, but also because removal of such mass could reduce the demand for electron acceptors.

The in situ bioremediation sequence of flushing, denitrifying conditions, and finally aerobic conditions was designed to take advantage of the naturally different rates of metabolism occuring under different electron acceptor conditions and to stimulate different consortia of microorganisms at different times within the aquifer. The strategy was to establish beneficial co-metabolic biodegradation processes and to maximize the biodegradation of the wide variety of chlorinated and nonchlorinated organic constituents found at the site.

Recovered groundwater was pumped to an equalization tank and then treated in an aboveground biological reactor. The reactor also treated water pumped from the lagoon to maintain water levels in the lagoon. Microbial cultures obtained from the lagoon were maintained for periodic addition to the reactor. The discharge from the bioreactor was polished using carbon adsorption, discharged to the San Jacinto River and, when necessary, recycled to the lagoon.

Initially, groundwater was recovered from 49 S1 wells and 33 INT wells and amended water was injected through 11 S1 wells and 13 INT wells. As a result, 700 m^3 (200,000 gal) of groundwater containing approximately 400 mg/L of TOC as well as VOCs and metals were being removed from the aquifer and treated on a daily basis. This corresponded to the removal of approximately 300 kg (670 lb) of TOC per day.

During operations, groundwater samples were analyzed for TOC, VOCs, pH, nitrate, dissolved oxygen, ammonium, ortho and total phosphate, and other inorganic parameters.

8.4.5 Remedial Progress

Remedial progress at the site was primarily gauged on the basis of changes in dissolved constituent concentrations in groundwater over time as measured by periodic sampling of monitoring wells in both S1 and INT units. The primary VOCs used to determine remedial progress were benzene, 1,2-DCA, and vinyl chloride.

1,2-DCA was representative of the chlorinated solvent compounds found in the DNAPL in the source areas. Dissolved concentrations of 1,2-DCA up to 800,000 µg/L were observed near DNAPL source areas, and benzene exceeded 1,000 µg/L throughout most of the area immediately downgradient from the lagoon. The concentration range of these compounds in the INT groundwater unit before remediation was similar but slightly less widespread.

After 15 months of system operation, monitoring indicated reduction in the dissolved concentration of all chlorinated organic compounds in the S1 groundwater to below the 5 µg/L detection limit, except in the immediate vicinity of known DNAPL areas. Continued monitoring confirmed that these reductions continued through December 1994. During the same period, significant reductions in benzene concentrations were observed. By January 1994, benzene was the only VOC in S1 groundwater that exceeded its drinking water clean-up criteria at the point of compliance. The reduction in constituent concentrations in S1 groundwater through time is illustrated by the results from monitoring well S1-106. Denitrifying conditions have prevailed in the vicinity of this well throughout most of this time period. This was indicated by relatively low concentrations of nitrate in the groundwater compared with ammonium and potassium, which were injected with the nitrate.

A significant portion of the reduction in dissolved VOC concentration observed in the S1 groundwater can be attributed to flushing by injection water. However, it is not possible to explain the reduction entirely by this mechanism. Indirect evidence indicates that biological degradation under

denitrifying conditions played a significant role in the reduction of the chlorinated solvent constituents. Numerous studies have indicated that benzene does not readily degrade under denitrifying conditions, hence it can be used as a conservative indicator of flushing effectiveness when denitrifying conditions prevail. Given appropriate adjustments for different sorptive characteristics of the compounds of interest, the projected change in concentration of a constituent due to flushing only can be estimated on the basis of observed reductions in benzene concentrations at a monitoring well. Flushing is unlikely to have been the only mechanism that reduced VOC concentrations in the S1 groundwater in the vicinity of well S1-106.

The reduction of benzene concentrations by in situ biological mechanisms is not likely to occur under denitrifying conditions. DO monitoring indicated that oxygen in the injection water was rapidly consumed within a fairly short distance of the injection wells. Oxygen utilization probably occurred during both biological and chemical subsurface reactions. As a result, the migration rate of the aerobic injection water "front" was between 0.45 and 1.2 m (1.5 and 4 ft) per month compared with a fluid migration rate of up to 30 m (100 ft) per month. Aerobic bioremediation became more efficient as flushing and denitrifying bioremediation continued to decrease the total organic carbon concentration in the aquifer ahead of the aerobic front.

The extent of oxygenated groundwater (arbitrarily set at greater than 5 mg/L) steadily increased in both the S1 and INT units over the course of remedial operations. Reductions in benzene and vinyl chloride concentrations in groundwater to below analytical detection limits coincided with the "breakthrough" of oxygenated conditions. This indicated that bioremediation was a major process influencing the breakdown of these organic constituents in the subsurface.

The reduction of VOC concentrations in S1 groundwater to below the cleanup criteria over some areas of the site allowed certain parts of the active remedial system to be turned off in September 1993. These areas were monitored to evaluate the potential for rebound of groundwater concentrations that might result from slow desorption or diffusion of contaminants from soils into groundwater. More than a year after shut-off, there was no indication of constituent concentration increases in monitoring wells. Slight increases in VOC concentrations at pumping wells were attributed to the small volume of dewatered S1 unit in the immediate vicinity of the well that was less effectively remediated under continuous pumping conditions. These increases were addressed by the initiation of a "pulsed" pumping program over a few months. This program was successful in achieving remedial objectives at the wells, and the pumps were eventually turned off in March 1994.

Predictably, remedial progress in the lower permeability INT unit was less rapid than in the S1 unit. As with the S1 unit, affected areas outside of known DNAPL zones showed significant reductions in constituent concentrations as a result of the in situ bioremediation system operation, but attainment of clean-up criteria took considerably longer than in the S1.

To avoid continuing remediation activities for an extended period in areas where achievement of remedial goals was slower due to either higher contaminant levels or lower permeability, additional INT wells were installed. A total of 66 additional INT injection and production wells were added during the course of active operations. Installation and use of these wells corresponded with removal of some S1 and later INT wells from the active system, and thus, the pretreatment and posttreatment requirements remained relatively constant over most of the operating period.

An important aspect of the project was the removal of a large portion of the organic mass (TOC) through groundwater recovery. This greatly reduced the demand on electron acceptors, allowing electron acceptor consumption to be more beneficially and cost-effectively applied to VOC biodegradation. During the project, approximately 182,000 kg (200 tons) of TOC were removed from the aquifer via groundwater recovery.

8.4.6 Intrinsic Remediation

The ROD for the site stated that groundwater recovery and treatment was to continue until modeling showed that the concentration of volatile organics would be reduced to a level consistent with the 10^{-6} human health criteria through natural attenuation in 10 years or less. This allowed FLTG to integrate intrinsic remediation at the end of the process as a polishing step. This approach also provided the potential to meet the human health and environment protection objectives in a manner consistent with the ROD, while reducing overall project costs by eliminating a significant portion of the long-term O&M costs.

8.4.6.1 Intrinsic Remediation Modeling

The basis for determining if intrinsic remediation was viable was the use of modeling techniques to simulate future groundwater quality at the French Limited Superfund Site 10 years after shutting off the active remediation system. To achieve agency approval to terminate active remediation, it was necessary to demonstrate that continued degradation/attenuation would result in site clean-up criteria being met at and beyond the compliance boundary within 10 years.

As discussed in Section 5.3 of this monograph, the modeling of intrinsic remediation is based on a combination of transport mechanisms, advection and dispersion, retardation (adsorption/desorption of the contaminants by the aquifer matrix), and degradation (biodegradation and, potentially, chemical reactions). To the extent possible, site-specific data should provide values for the parameters used in the model.

Where practical, numerical models are preferred over analytical models for evaluation of complex sites. In this case, visual MODFLOW© was selected from among several well-established codes to simulate post-remediation groundwater flow. The effects of hydrodynamic dispersion, retardation, and biodegradation (natural attenuation) were superimposed on the visual MODFLOW© output using BioTrans©. BioTrans© was selected because it simulates oxygen- (or oxygen equivalent-) limited degradation of multiple chemical species.

For this site, a large volume of data was available with respect to groundwater quality and aquifer characteristics. Groundwater quality, nitrate, and DO data were obtained from the results of the November 1995 sampling event and were supplemented with data from earlier sampling events where necessary. The data were assigned to a grid and contoured using SURFER®, with appropriate controls for peripheral areas.

Individual contour maps were prepared for benzene, 1,2-DCA, and vinyl chloride. As previously discussed, these compounds were selected as indicator parameters because they had the lowest health-based clean-up criteria of the VOCs present in the aquifer, are the most mobile of the VOCs, and were the only VOCs exceeding their MCLs outside the property boundary. Other VOCs were present in very limited areas and thus were not included in the modeling process. Individual contours were also generated for TOC and for total electron acceptors; a concept comprising a combination of DO and nitrate concentrations, the parameter "DO+," was derived as follows (Borden, Gomey, and Becker 1995):

$$DO+ = DO + 2.5(NO_3 - N) \tag{8.2}$$

All three types of contour maps were prepared for both the S1 and INT units.

Visual MODFLOW© was used to model the regional San Jacinto basin shallow alluvial aquifer to produce long-term, steady-state, hydraulic gradients and flow velocities. Upgradient and downgradient boundaries were fixed-head boundaries based on long-term hydraulic gradients measured at the site before active remediation commenced. Crossgradient boundaries were based on mapped geological contacts with the underlying and adjacent

Beaumont Clay aquitard which were modeled as impermeable barriers. It was assumed that long-term vertical groundwater migration between the upper S1 and lower INT shallow alluvial aquifer units would be insignificant. The steel sheet-pile flood wall was also treated as an impermeable barrier. The aquifer properties in Table 8.2 were used.

Table 8.2
Properties Used in Aquifer Modeling

Unit	Top Contact m (ft) MSL	Thickness m (ft)	Horizontal Permeability m/d (ft/day)	Storage Coefficient Type	Storage Coefficient
UNC	4.6 (15.0)	3 (10.0)	0.3 (1.0)	specific yield	0.1
S1	1.5 (5.0)	6 (20.0)	6 (20.0)	specific storage	0.00003/m (0.00001/ft)
C1	-4.6 (-15.0)	1.5 (5.0)	0.3 (1.0)	specific storage	0.00003/m (0.00001/ft)
INT	-6 (-20.0)	6 (20.0)	1.5 (5.0)	specific storage	0.00003/m (0.00001/ft)
C2	-12 (-40)	modeled as impermeable base			

Source: O'Hayre, Day, and Thomson 1993. Used with permission.

Groundwater elevation measurements collected as part of the long-term monitoring program for the site were used to provide ongoing flow model calibration. Groundwater flow models of four subareas selected for natural attenuation modeling were developed using the head (groundwater elevation) data generated by the regional San Jacinto shallow alluvial aquifer model. Each model covered one area that did not meet compliance criteria based on VOC plume results.

8.4.6.2 Model Input and Results

The model input parameters are shown in Table 8.3. The soil bulk-density, 1.7 g/cc, and grid spacing were kept constant. However, grid spacing varied among the four areas modeled. The other parameters were varied over the ranges shown in Table 8.3 to determine model sensitivity to parameter variability.

Table 8.3
Model Input Parameters

Input Parameter	Unit	Base Case	Uncertainty/Sensitivity Range
Grid spacing	ft	5/15	-
Time step	day	50	0.1 - 800
Half life[a]	day	60	30 - 90
Initial DO/nitrate (as equivalent "DO or DO+")[b]			
Dispersivity			
f_{oc}[c]			
Effective porosity	-	0.2	0.1 - 0.3
Nondegradable TOC	ppm	200	West area: 20 - 1000 Wall area: 20 - 200

[a]Determined from site data.
[b]Data obtained in September 1995 were used for DO and nitrate levels.
[c]Measured values.

Source: O'Hayre, Day, and Thomson 1993. Used with permission.

Transport related properties obtained from the literature were used to calculate Kd values for use in the model. The calculated Kds for TOC and the primary VOCs at three f_{oc} levels are shown in Table 8.4.

The output parameters generated for each of the four areas include: (1) the percentage reduction in both maximum concentrations and mass for TOC and the three indicator VOCs and (2) the maximum distance (to the furthest point beyond the compliance boundary) where MCLs would be exceeded based on the simulations.

Model parameters, dispersivity, grid spacing, and time-step were adjusted based on published techniques to optimize model stability. Sensitivity analyses were also performed. The relative sensitivity of the model to all variable parameters was determined for each of the four areas. Based on this analysis, a range of input parameter values was used to simulate groundwater quality to determine if intrinsic remediation was reasonably certain of meeting the criteria contained in the ROD.

The main changes from the sensitivity analysis base case were dispersivity and *nondegradable TOC*. The longitudinal dispersivity value

initially used for the base case, 1.5 m (5 ft), was not well supported, whereas the values of 5.3 m (17.5 ft) (INT unit) and 19 m (61 ft) (S1 unit), obtained from applying the 1/10th rule are strongly defensible.

Table 8.4
Transport-Related Constituent Parameters

Chemical	K_{oc}	Kd at f_{oc} = 0.12 %	Kd at f_{oc} = 0.15 %	Kd at f_{oc} = 0.18 %	Source
Benzene	83	0.0996	0.1245	0.1494	Howard
1,2-DCA	33	0.0396	0.0495	0.0594	Howard
Vinyl chloride	2.5	0.0030	0.0038	0.0045	M & W
TOC	$1.25 \cdot 10^6$	1,500	1,875	2,250	ES&T

Source: O'Hayre, Day, and Thomson 1993. Used with permission.

Consideration of nondegradable TOC did not support the use of a single value for the entire site; further evaluation of the French Limited on-site bioreactor studies strongly supported the use of 50% of the measured TOC value.

The model outcome is presented in Table 8.5. The model demonstrated that vinyl chloride, 1,2-DCA, and benzene in all simulated areas will decrease by between 96% and 100% in 10 years and that no areas of VOCs exceeding site clean-up criteria will exist at or beyond the compliance boundary within this time frame.

8.4.7 Conclusions

Based on the modeling results, it was determined that natural attenuation would meet the requirements of the ROD. As an extra measure, ONE month prior to shut-off of the active remediation systems, target S1 and INT unit zones were dosed with nitrate, dissolved oxygen, and phosphate to provide elevated levels of nutrients and electron acceptors to further facilitate degradation during the early phases of intrinsic remediation. On December 15, 1995, active remediation was terminated and intrinsic site restoration was initiated.

Table 8.5
Demonstration Runs — Input Parameters and Summary Results

Parameter	Unit	INT West	INT Central	INT Wall	S1 East
Grid spacing	m (ft)	4.6 (15)	3 (10)	1.5 (5)	3.7 (12)
Time step	day	50	50	50	50
Half life	day	60	60	60	60
Final DO/nitrate	–	9/95	9/95*	9/95	9/95
Dispersivity	m (ft)	5.3 (17.5)	5.3 (17.5)	5.3 (17.5)	19 (61)
DO stoichiometry	–	2.75	2.75	2.75	2.75
f_{oc}	%	0.15	0.15	0.15	0.15
Effective porosity	–	0.2	0.2	0.2	0.25
Nondegradable TOC	%	50	50	50	50
Benzene max. conc. % red.	%	82	55	100	98
1,2-DCA max. conc. % red.	%	99	100	100	100
Vinyl chloride max. % red.	%	95	98	100	100
TOC max. conc. % red.	%	3	40	100	79
DO+ max. conc. % red.	%	20	18	14	50
Benzene % reduction	%	91	93	100	99
1,2-DCA % reduction	%	99	100	100	100
Vinyl chloride % reduction	%	96	98	100	100
TOC % reduction	%	55	94	100	92
DO+ % reduction	%	13	2	0	25
Benzene distance	m (ft)	0	0	0	0
1,2-DCA distance	m (ft)	0	0	0	0
Vinyl chloride distance	m (ft)	0	0	0	0

*with INT-60 converted to injection (11/95).

8.5 Bioremediation of Explosives-Contaminated Soil Using Composting Technology*

This case study provides an example of the application of composting technology, a modification of soil cell treatment as discussed in Section 4.4, for the treatment of explosives-contaminated soil. The composting technique was developed by the Army Environmental Center and implemented at the Umatilla Army Depot Activity (UMDA) near Hermiston, Oregon, by Bioremediation Service, Inc., of Portland, Oregon. Agricultural waste products (or amendments) were blended with the contaminated soil during treatment. Specialized soil turning equipment mixed the compost for optimum biological action and homogeneity. Homogeneity of the compost mix ensured rapid degradation of all contaminants. Physical and chemical properties were closely monitored to ensure that thermophilic bacteria played a dominant role in the degradation process.

8.5.1 Site Description

UMDA is a nearly 8,000-hectare (20,000-acre) munitions storage facility located in northeastern Oregon. Past activities performed at UMDA included the demilitarization of conventional munitions. The facility used a pressurized hot water system to remove and recover explosives from a variety of ordnance including 227- and 340-kg (500- and 750-lb) Composition B bombs (60% royal demolition explosive [RDX] and 40% 2,4, 6-trinitrotoluene [TNT]) and 90-mm projectiles. The explosive-laden hot water was allowed to cool in various containers, and the RDX/TNT sludge, which precipitated out, was removed and reclaimed in a variety of ways.

Weekly flushing and draining of the plant's storage tanks and vats produced 567 m^3 (150,000 gal) of contaminated water that was flushed down an open trough outside the building into two evaporation lagoons covering approximately 930 m^2 (10,000 ft^2). These "washout" lagoons were used intermittently; one lagoon was filled with the week's flush of "pink water" (from its characteristic color), while the other was being emptied of its evaporation residue. These residual solids were then transported to another area of UMDA and burned.

*Adapted with permission from the paper by Emery and Faessler (1996) of Bioremediation Service, Inc., submitted to the Engineering Foundation for publication in the *Annals of the New York Academy of Sciences.*

Although this wastewater disposal technique was acceptable practice at the time the plant was in operation, the site was placed on the National Priorities List in 1987 because contamination was affecting not only the soils under the lagoons, but also the groundwater.

The soil from the munitions washout lagoons contained high concentrations of TNT and RDX, as well as lower levels of high melting explosive (HMX). Also found at the site were lower levels of tetryl-dinitrotoluene (DNT), trinitrobenzene (TNB), dinitrobenzene (DNB), and nitrobenzene (NB) contaminants as impurities or degradation products of TNT.

Of the several possible remediation techniques that could have been used to decontaminate the site, biological remediation was the method of choice. The Army Corps of Engineers, Army Environmental Center, US EPA, and Oregon Department of Environmental Quality sponsored the major innovative composting remediation project at UMDA.

As indicated in Section 4.4 of this monograph, composting is not a new technology, but if properly designed and implemented, it has been shown to produce dramatic degradation and transformation of recalcitrant contaminants, such as nitroaromatics and nitramines, in contaminated materials. The resulting treated soil is rich in organic matter and nutrients. The Army has a research program underway to evaluate possible re-use or recycling of the treated material.

8.5.2 Pilot-Scale Remediation

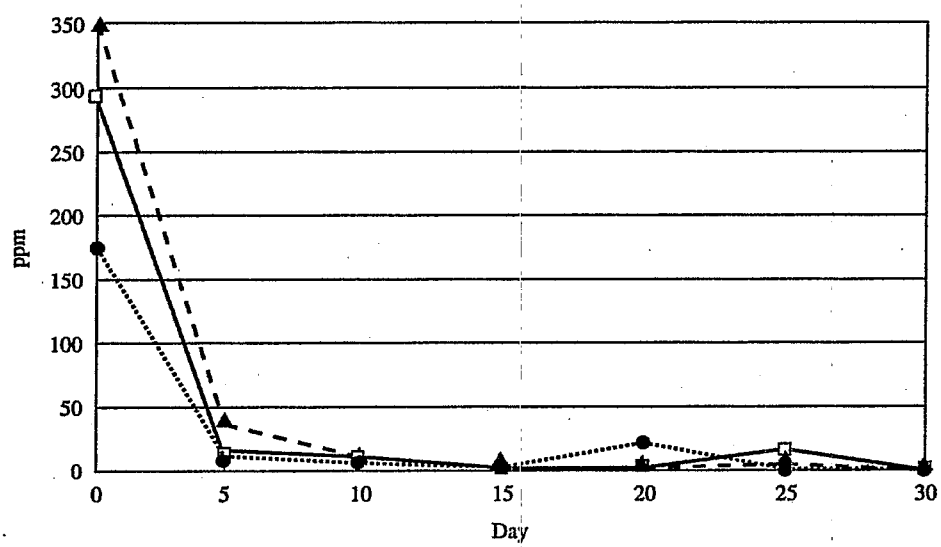
A comprehensive trial test was performed for equipment and process optimization before full-scale production was authorized. Many bench-scale and pilot-scale tests performed by various organizations preceding the trial test showed favorable results for the degradation of munitions waste compounds in contaminated soil using a compost system. The trial test contractor used this information to optimize field-scale efficiency, as well as confirm that all contaminants and contaminant byproducts were degraded to acceptable clean-up levels. Initial pilot studies demonstrated that munitions-contaminated soils could be aerobically composted in 30 to 40 days. During the comprehensive trial test at UMDA, more than 280 Method 8330 tests were performed, which demonstrated that the clean-up goal of 30 mg/kg TNT and RDX could be achieved in less than 22 days (Figures 8.21 and 8.22), while clean-up levels for HMX occurred more rapidly (Figure 8.21). Daily turning of the compost pile produced the fastest degradation results. Two degradation byproducts, 2-Am-DNT and 4-Am-DNT, temporarily accumulated (Figures 8.24 and 8.25), but were subsequently degraded

to below detection levels following further composting treatment. All other byproducts (i.e., 2,4-DNT; 2,6-DNT; 1,3-DNB; NB; 1,3,5-TNB, and methyl-2,4,6-trinitrophenylnitramine) were also shown to be below their detection levels.

8.5.3 Full-Scale Remediation

From July through December 1995, over 3,800 m^3 (5,000 yd^3) of explosives-contaminated soil were successfully treated. Analytical results for this treated soil show that 93% of all results for TNT were below the detection level of 4 mg/kg, while the RDX level in 68% of all samples were below its detection level of 2 mg/kg. All sampling points were below 30 mg/kg for both TNT and RDX. Three hundred thirty Method 8330 analyses confirmed these results.

Figure 8.19
Pilot-Scale Results of TNT Degradation in Windrow Composting Units

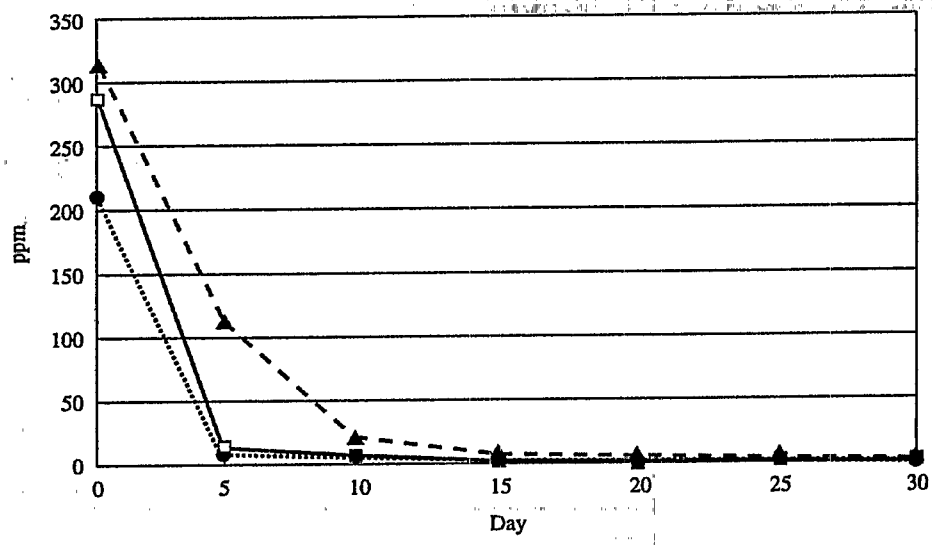


Turned Daily
Turned Tri-Daily
Turned Variable

Each data point on the average of 12 EPA Method 8330 analyses

Source: Emery and Foessler 1997. Used with permission.

Figure 8.20
Pilot-Scale Results of RDX Degradation in Windrow Composting Units



Turned Daily
Turned Tri-Daily
Turned Variable

Each data point on the average of 12 EPA Method 8330 analyses

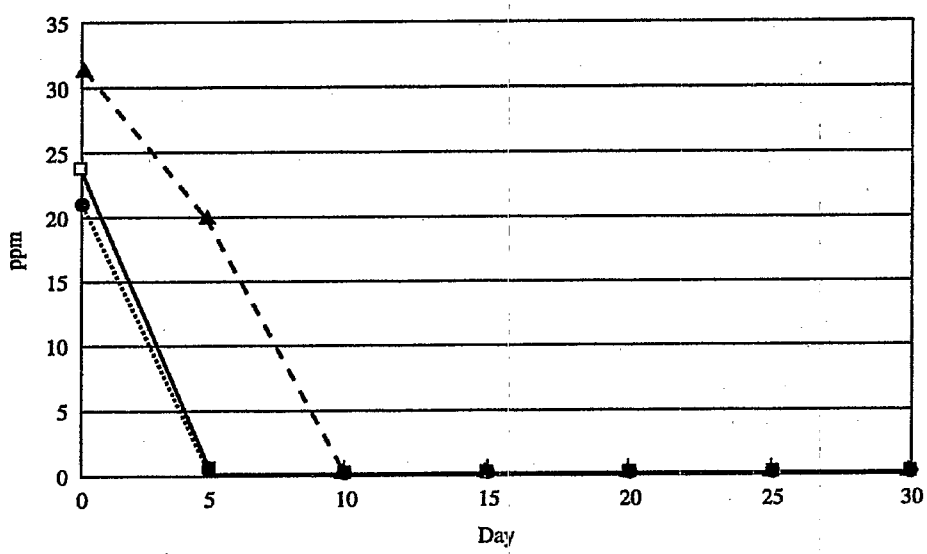
Source: Emery and Foessler 1997. Used with permission.

The rate of degradation during full-scale remediation improved by over 25% from the initial trial test. Required action levels were achieved in 12 to 15 days of treatment.

8.5.4 Composted Soil

Composted soil is very rich in humic material and is an ideal candidate for recycling and reuse. An accepted method of evaluating bioremediation treatment residue is the use of toxicity and leachability tests. This approach is consistent with the Superfund National Contingency Plan objectives of evaluating the toxicity, mobility, and volume reduction effects of innovative treatment technologies.

Figure 8.21
Pilot-Scale Results of HMX Degradation in Windrow Composting Units



Turned Daily
Turned Tri-Daily
Turned Variable

Each data point on the average of 12 EPA Method 8330 analyses

Source: Emery and Foessler 1997. Used with permission.

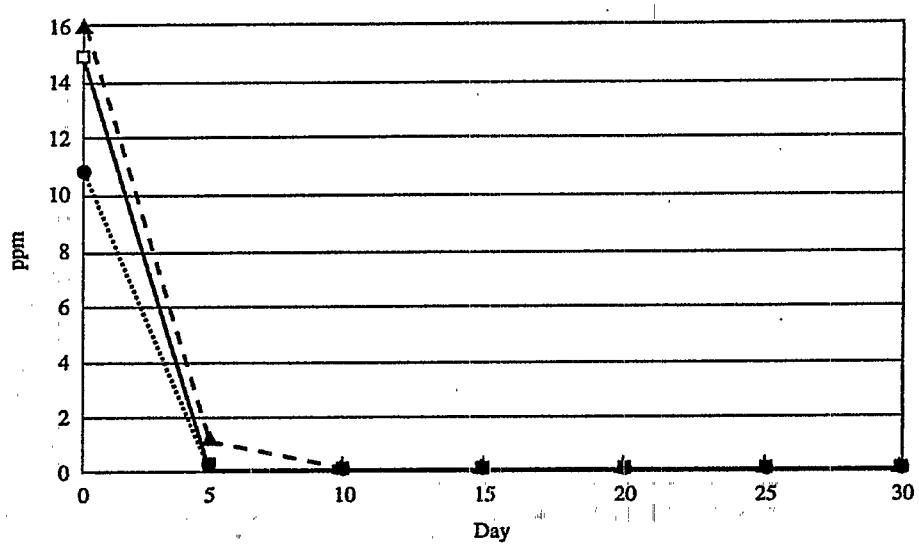
8.5.4.1 Previous Toxicity and Leachability Studies

Toxicity and leachability studies have been performed on composted soil with known TNT-biotransformation products. Results suggest that the final biotransformed product of TNT may be a polymeric species of very limited solubility.

One study showed that there was practically no leachable ^{14}C activity after a simulated 1,000-year leaching test (Griest et al. 1991). Based on the 1,000-year acid rain leaching simulation, any release of transformed explosive from composted soil into the environment would not be significant.

Toxicity tests that have been used on bioremediation treatment residues include: (1) Microtox™; (2) Ames assays for mutagenicity; (3) aquatic toxicity tests on soil leachates; (4) oral rat feeding studies; and (5) earthworm toxicity tests.

Figure 8.22
Pilot-Scale Results of 2-Am-DNT Degradation in Windrow Composting Units



Turned Daily
Turned Tri-Daily
Turned Variable

Each data point on the average of 12 EPA Method 8330 analyses

Source: Emery and Foessler 1997. Used with permission.

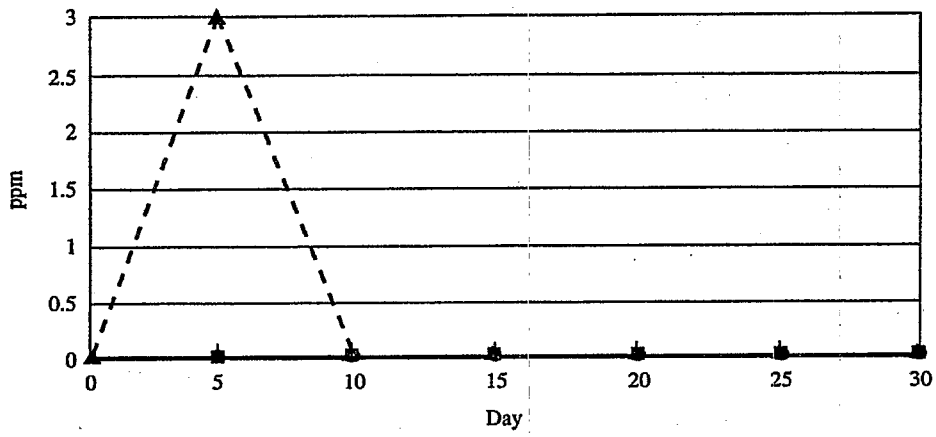
The final conclusions developed from this study on previous pilot-scale compost residues from UMDA are:

- composting is a safe and effective process for decontaminating and detoxifying explosives-contaminated soils; and
- the compost product should allow the re-establishment of plant and animal populations in land application, although some inhibitory effects were noted for some plant types.

8.5.4.2 Plant Uptake Studies in Composted Soil

The degradation results achieved during the first full-scale composting effort at UMDA were better than previous pilot-scale treatability tests. The composted soil provided an excellent opportunity to demonstrate the reuse and recycling potential of the soil.

Figure 8.23
Pilot-Scale Results of 4-Am-DNT Degradation in Windrow Composting Units



—□— Turned Daily
- ▲ - Turned Tri-Daily
···●··· Turned Variable

Each data point on the average of 12 EPA Method 8330 analyses

Source: Emery and Foessler 1997. Used with permission.

From late July through late October, several plants were successfully grown in the treated soil. Those plants included indigenous plants (sagebrush); agricultural varieties of fruits, vegetables, and grasses (statesman perennial ryegrass, chewing fescue, creeping red fescue, Kentucky bluegrass); carrots (scarlet nantes); turnip (purple top white globe); strawberry plants; as well as flowers common to landscaping (carnations, chrysanthemums, marigolds). In November, these plants were harvested and prepared for analysis. Analytical results to date for TNT, RDX, 2,4-DNT, and 2,6-DNT showed nondetectable levels in all plant varieties investigated.

8.5.4.3 Additional Testing

Studies that augment previous evaluation of the potential toxicity of composted soil were also commissioned. One involves "503 Class A" sludge pathogen testing (40 CFR 503 Standards). The Code of Federal Regulations sets standards for pathogenic bacteria present in compost. The treated soils from UMDA met or exceeded all criteria that include Helminth ova, *Salmonella sp.*, Fecal Coliform and Enteric Virus. A second

comprehensive study involving the following tests is currently underway to further define the toxicity of compost-treated munitions-contaminated soils:

- Plant Toxicity Tests:
  - Root Elongation, and
  - Early Seedling Growth;
- Earthworm Toxicity Test;
- Freshwater Elutriate Tests:
  - Algal Growth Test,
  - Invertebrate Survival and Reproduction Test, and
  - Fish Survival and Growth Test; and
- Freshwater Sediment Tests:
  - Amphipod Survival Test, and
  - Invertebrate Bioaccumulation Test.

8.5.5 Remediation Costs

Table 8.6 summarizes projected compost treatment remediation costs per ton of munitions-contaminated soils based on pilot- and full-scale remediation trials conducted at UMDA. These costs include installation and removal of the composting system components, asphalt pad construction, runoff containment, asphalt recycling, and final grading. Also included are treatment/containment tents designed to reduce volatile emissions and provide positive moisture control at the site. These costs were based on a 2-year life. It is important to note that the reported costs include mobilization, demobilization, site preparation, special facilities, trial tests, and bond insurance costs, a significant portion of which would not be necessary in future projects.

8.5.6 Conclusions

Nearly 3,800 m^3 (5,000 yd^3) of soil have been successfully treated, and more than 70% of all analyses indicate nondetectable levels of both TNT and RDX in the compost-treated soil. The U.S. Army Corps of Engineers estimates that over $2.6 million is being saved using bioremediation at UMDA. All indications are that the composted soil contains no intermediate byproducts of explosive contaminants, and the original primary contaminants have been degraded to well below the clean-up levels established in the baseline risk assessment for protection of human health and environment at

the site. Furthermore, the composted soil is suitable for recycling or reuse since it complies with the National Contingency Plan requirements as follows:

- the soil residue is nontoxic;
- the soil residue contains no leachable contaminants;
- transformation products that may exist are less toxic than TNT, and the covalent bonds that fix these metabolites to soil or compost are extremely rugged. Repetitive aqueous leaching of the composted soil and also ultraviolet light irradiation followed by leaching suggest that the product should not be released appreciably by acid rain or sunlight (Major, Bollag, and Ames 1994);
- the composted soil meets the same requirements as a Class A biosolid under US EPA 503 regulations;
- the composted soil is very rich in humic material and nutrients;
- the soil residue can support a wide variety of plant species; and
- plant species tested could not remobilize transformed compounds existing in the treated soil or uptake any residual TNT, RDX, or intermediate compounds.

Table 8.6
Composting System Remediation Costs* for Munitions-Contaminated Soils ($/ton contaminated soil)

Treatment	$150.00
Analyses:	
Method 8330	$7.73
Field screening tests	$3.21
Treatment/containment tents	
(>60,000 ft^2)	$34.00
Miscellaneous	$61.56
Total	**$256.50**

*Treatment costs are aggregated costs which include contaminated soil excavation and materials handling (screening, mixing, pile preparation, etc.) costs

8.6 Integrated Technologies

This case history demonstrates the use of laboratory- and pilot-studies and the design of a remedial system which syngeristically integrated several bioremediation technologies. The remedial system is unique in that the entire subsurface system had to be installed during construction of a retail facility with limited future access to the subsurface. The system included the Raymond method, air sparging, bioventing, LNAPL recovery, and a soil cell. A programmable logic control system provided pulsed flow of the air sparging system and coordination of bioventing and air sparging within individual areas of the site.

8.6.1 Site Description

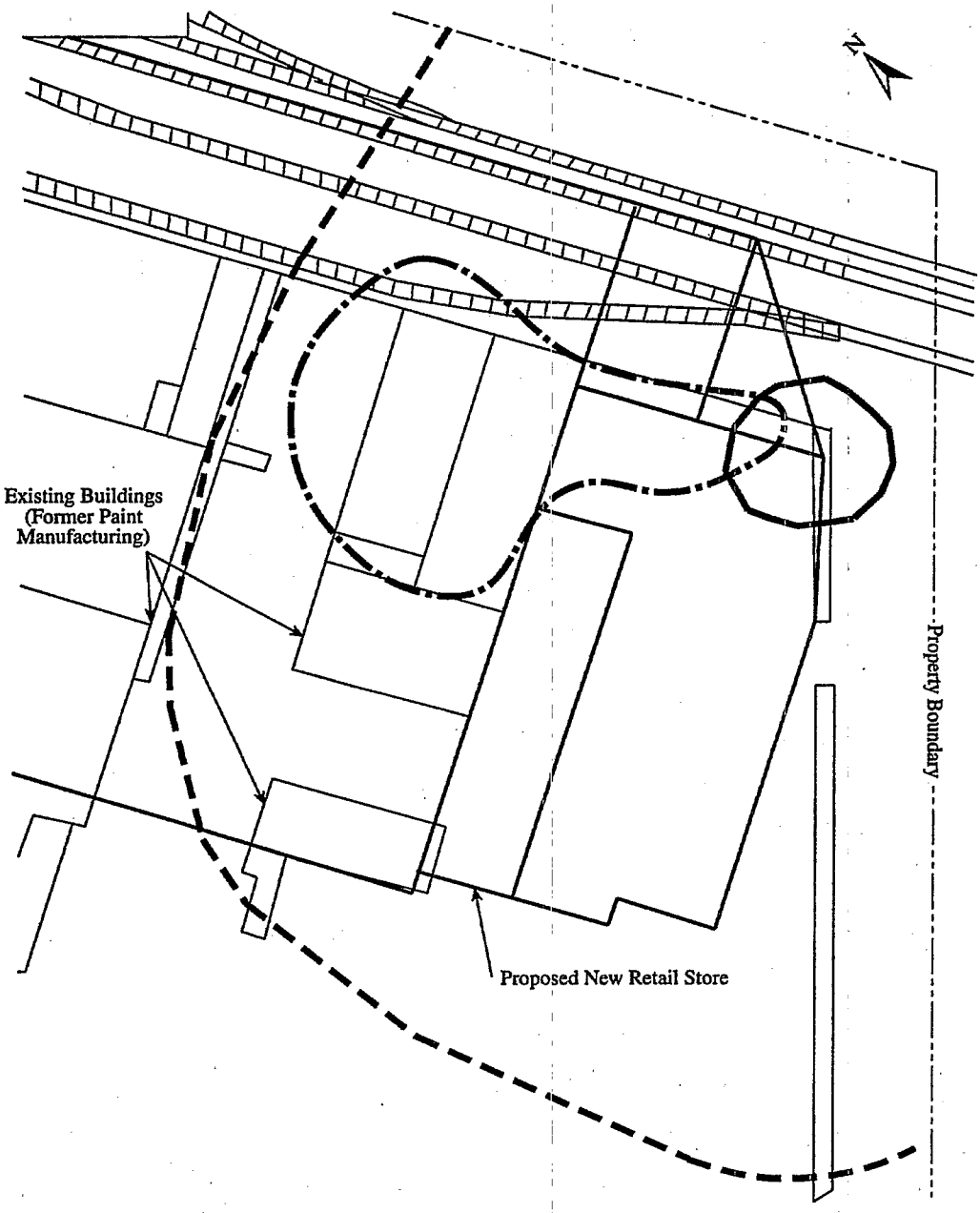
The subject property was a former paint factory that was investigated as part of a property transfer agreement. At one time, the property contained 16 underground storage tanks (USTs) used to store gasoline, heating oil, and varsol (a gasoline-like solvent). Many of these tanks had been removed in prior years as well as during the months immediately preceding the property transaction. All of the UST locations were identified as areas of environmental concern and were included as part of the initial site characterization.

The investigation revealed petroleum hydrocarbon compounds (PHCs) in the subsurface. Light nonaqueous-phase liquids (LNAPLs), varsol, gasoline, and fuel oil were found on-site as liquid-phase PHCs, dissolved-phase PHCs, and adsorbed-phase PHCs in both saturated and unsaturated soils. Fuel oil was largely present in the unsaturated soils. Varsol represented the majority of the PHCs present. (See Figure 8.24).

8.6.1.1 Geology and Hydrogeology

The site consisted of unconsolidated soils from elevation 32.3 m (106 ft) City of Philadelphia relative site datum (RSD) to approximately 28.9 m (95 ft) RSD and was comprised of varying fill material. This material is of varying permeability, but is generally characterized as being of low permeability and is underlain by gray to tan silts and clay with thin interbedded fine sand lenses. This silt and clay extends from the base of the fill material to varying elevations ranging from 28.4 to 27.4 m (93 to 90 ft) RSD. The silt and clay sediments are underlain by brown sands with little silts and gravel. This sand tends to grade into a weathered schist mix and, in some locations, is interbedded with sand. The schist becomes less weathered and more competent with depth. The weathered bedrock soil types and sand horizon are

Figure 8.24
Building Locations and Petroleum Hydrocarbon Compound Boundaries
(not to scale)



Adsorbed-Phase PHC
Dissolved-Phase PHC
Liquid-Phase PHC

Total Area of Impact = ~150,000 standard ft

considered part of the unconsolidated zone, and groundwater appears to exist in this zone under water table conditions. Although the interface between the unconsolidated material and bedrock occurs at various elevations beneath the site, the interface was assumed to exist uniformly at 9.2 m (30 ft) below ground surface or at 23.2 m (76 ft) RSD for purposes of the hydrogeologic analysis.

The shallow groundwater beneath the site exists under water table conditions within the unconsolidated silt and sandy sediments and into the weathered bedrock schist. The monitoring well measurement and liquid level gauging data indicated a groundwater flow direction to the south with an estimated average groundwater gradient *i*; of 0.004.

The aquifer was tested to assess the feasibility of in situ remediation. Testing included two aquifer pump tests, seven step-drawdown tests, and 20 slug tests. Based on evaluation of data from these tests, the following aquifer characteristics were identified:

- Transmissivity (T) = 134 m^2/day (1,444 ft^2/day); and
- Hydraulic Conductivity (K) = 29 m/day (96 ft/day).

Capture zones used in the final design with each recovery well pumping at 15.1 Lpm (4 gpm) were as follows:

- Crossgradient — 15.2 m (50 ft); and
- Downgradient — 12.2 m (40 ft).

Average groundwater flow rates were calculated as follows based on the hydraulic conductivity value presented above:

$$V_p(\text{pore velocity}) = Ki / n_e = 29(0.004) / 0.20 = 0.58\text{m / day } (1.93\text{ft / day}) \quad (8.3)$$

where:

n_e = the soil porosity (unitless) 0.20 at this rate.

The flow of groundwater is affected by hydrodynamic dispersion and the flow of dissolved-phase contaminants in the groundwater is affected by adsorption to soil as well as other attenuation factors (biological degradation and redox reactions). As an initial assessment of contaminant transport, the effective velocity for contaminant flow can be estimated. For this site, where it is assumed that soil adsorption is the only attenuation mechanism, the migration rate of benzene was calculated as follows:

$$V_e(\text{effective velocity of the contaminant}) = V_p / R = 0.58 / 2.98 = 0.2 \text{ m / day } (0.65 \text{ ft / day}) \quad (8.4)$$

where:

R = the retardation coefficient = 2.98 for benzene at this rate.

The heterogeneous nature of the subsurface stratigraphy, both laterally and vertically, and the corresponding variation in hydraulic conductivity of the various materials were considered during design and analysis of the aquifer tests and the subsequent design of remedial system components. Design of specific remediation system components using conservative input values allowed for operation of the remediation system at or above design specifications.

8.6.1.2 Contaminant Profile

Soils. PHCs were detected in the unsaturated and saturated soils beneath the site. These PHCs were identified as gasoline, varsol, and small quantities of fuel oil using modified US EPA Method 8015 (US EPA 1986d) and GC/MS analyses. The VOC, benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, and 1,2,4-trimethylbenzene, were identified as specific PHCs of concern relative to regulatory remediation guidelines.

The horizontal and vertical extent of PHCs was assessed during two phases of site characterization. The PHCs extended vertically from ground surface (elevation of about 32.3 m [106 ft] RSD), through the water table (about 27.7 m [91 ft] RSD), and to the unconsolidated zone and bedrock interface (about 23.2 m [76 ft] RSD). The concentrations of PHCs detected at the unconsolidated bedrock interface were below remediation guidelines. Based on the known lateral extent of TPH and total VOC soil contamination, the total lateral extent of the soil adsorbed-phase PHCs covered approximately 7,157 m^2 (77,000 ft^2).

Groundwater. Groundwater sampling was conducted via a series of monitoring wells that were installed during Phase 1 (MW-1 through -8) and Phase 2 (MW-9 through -17) site characterization activities. Results indicated PHCs in groundwater at concentrations ranging from 0.16 to 430 mg/L. These PHCs were identified as gasoline, varsol, and lower concentrations of fuel oil. Results also identified specific chemicals including BTEX, naphthalene, and 1,2,4-trimethylbenzene at concentrations ranging from 0.232 to 670 mg/L. BTEX compounds indicate a light petroleum distillate fraction representative of gasoline, and in this case, also of varsol.

The highest concentrations of dissolved-phase PHCs and BTEX were detected near the eastern corner of the property. Only this area consistently exhibited of liquid-phase PHCs which were identified as varsol constituents using a GC/MS "fingerprint" analysis as compared to various petroleum standards.

Monitoring wells installed during Phase 2 site characterization were used to further assess the groundwater contaminant plume, especially off-site south and west. Results indicated that the highest contaminant concentrations in groundwater were located in the southeast corner of the property. So this area became the target of remedial efforts.

The extent to which the plume extended beyond the property boundary in the south and east directions was not delineated (but is currently under investigation). The lateral extent of the on-site dissolved-phase hydrocarbon plume was approximately 13,940 m^2 (150,000 ft^2).

The presence of liquid-phase PHCs suggested that any remedial action should incorporate free-phase product recovery. The volatility of varsol and gasoline and the biodegradability of the PHCs present in the subsurface suggested that bioremediation, air sparging, and soil vapor extraction/ bioventing were also appropriate remedial technologies for this site.

8.6.2 Initial Remedial Goals

Due to the potential extent of the contamination and the planned use of the property as a retail strip mall, the property buyer was concerned about the time required to remediate the site in conjunction with plans to remove existing buildings and develop the property. To meet financial commitments as well as lease the property, the buyer required a defined course of action for site remediation.

The Commonwealth of Pennsylvania Department of Environmental Protection (PADEP) has oversight responsibility for the site. The PHCs in the subsurface were not in compliance with the Pennsylvania Clean Streams Act. PADEP agreed that the UST corrective action regulations (Corrective Action Process for Owners and Operators of Storage Tanks and Storage Tank Facilities and Other Responsible Parties, PA - Title 25, Chapter 245, Subchapter D, 245.301) would be used as a procedural guideline to bring the site into compliance. According to these laws and regulations, the responsible party conducted a site characterization which was followed by a remedial alternative analysis (feasibility study) since soils and groundwater were found to contain chemical substances in excess of regulatory limits. All remedial action plans had to be reviewed and approved by PADEP.

Based on development plans for the site, a significant portion of the contaminated soil and groundwater was directly beneath the area that was to be used as a concrete pad for one of the developer's future tenants. Due to the extent of the contamination and the time frame established by the developer/ tenant lease contract, a remedial action plan had to be put into effect quickly.

Part of the plan was to remove a limited amount of contaminated soil, but the majority of the remediation was to be accomplished via an in situ system.

Due to time limitations, the remediation plan had to be designed and approved in conjunction with plans by the developer. Buildings and foundations, as well as soils, were removed to allow for the installation of remediation system's pipes and tubing. To ensure a controlled operation, the same contractor was chosen to perform soil and macadam removal as well as trenching for the subsurface remediation system. Since the area to be remediated was directly under a planned concrete pad, scheduling of work had to be coordinated with the future tenant's contractor. To remediate the area under the planned pad and monitor the impact of the remediation process, air sparging points, water reinjection points, vapor monitoring points, and monitoring wells had to be placed within the footprint of the tenant's store.

Within 20 weeks, the system piping had been laid and covered. A 40-mil geomembrane was laid on top of the area to be remediated. The contractor was made aware of critical areas, especially those near sewer lines and utility installation points.

The imminent conversion of the impacted area to a retail facility required that any long-term remedy be unobtrusive and require minimum activity across much of the impacted area. Plus, upgrading or modifying the remediation system after installation would not be possible.

8.6.3 Design Approach

8.6.3.1 Identification of Target Elements

Prior to identification and selection of remedial technology alternatives, target elements were established. A target element was an operational zone within which a single remediation alternative could be applied to achieve remediation. The establishment of target elements was based on macroscopic properties, such as overall matrix permeability, relative humidity/moisture content, accessibility, depth below ground surface, and contaminant state and concentration.

Three target elements for the former paint manufacturing site were established, based on the following site properties:

- liquid-phase PHCs floating on or residing near the water table;
- PHCs above the water table adsorbed on soil particles, present as liquid product retained in soil interstitial spaces, present as soil vapor, and dissolved in soil moisture; and

- PHCs below the water table dissolved in groundwater, adsorbed onto soils below the water table, and present as liquid product retained in soil interstitial spaces below the water table.

The feasibility study focused on identifying and evaluating appropriate and applicable technologies, and eliminating inappropriate remedial technologies from further consideration. Remediation alternatives were generated by combining retained technologies for target elements into integrated systems. The alternatives were then subjected to screening, detailed evaluation, and selection for final remedial alternative identification.

8.6.3.2 Remedial Objectives

The remedial objectives for this project were:

- to reduce the potential risk to human health and the environment. This included the following minimum goals:
  - eliminating recoverable liquid-phase PHCs;
  - reducing hydrocarbon concentrations within the vadose zone by 95%;
  - reducing soil contaminant levels by 90%;
  - reducing groundwater contaminant levels by 90%;
  - negotiating achievable site-specific clean-up criteria acceptable to PADEP;
- to prepare the site for redevelopment operations and return the site to productive use; and
- to reduce future environmental liability associated with the site.

8.6.4 Remedial Design

8.6.4.1 Technology Selection

Selection of specific technologies for remediation of this site was dictated by the properties of the petroleum hydrocarbons, their distribution within the subsurface, and the planned use of the site. Special consideration was given to the planned imminent development of the property, including consideration of the health and safety of pedestrians following site redevelopment. Any in situ remedial system needed to account for the potential migration of PHC liquids or gases. The selected remedial system was required to achieve immediate remediation of shallow soils to accommodate site redevelopment

construction and remediation of deeper soils in a manner that did not inhibit the commercial re-use of the site.

Initially, a broad range of technologies was considered following the standard remedial investigation protocol specified by CERCLA. Remedial technologies were considered for each target element. A combination of in situ aeration and biodegradation techniques was selected as the final remedial option for the hydrocarbon-contaminated soils at the site. Additionally, recovery of liquid-phase hydrocarbons in conjunction with groundwater recovery was selected because this option was compatible with other remedial components and was the fastest and least expensive method of removing a significant portion of the hydrocarbon mass at the site.

Impacted shallow soil, which contained primarily fuel oil, was excavated for on-site treatment. This option was compatible with installation of other remedial system components, which required soil excavation anyway, and would ensure that the upper several feet of soil were clean prior to construction of new buildings.

Excavated soil was treated with a technology compatible with that used in the in situ system in aboveground treatment cells constructed on an adjacent parcel that remained under the seller's ownership. Biological soil cells were selected for treatment of excavated soil based on: (1) the biodegradability and low volatility of most of the hydrocarbon mass present in these soils; (2) the potential to use the same offgas treatment system used for the in situ treatment system; (3) the availability and proximity of a large area for construction of the cells; (4) the benefit of on-site reuse of the treated soil; and (5) the relatively low cost of this process. The soil cells were constructed and treated using methods described in Section 4.4.

The soil and groundwater at depth were largely impacted with varsol, which is both volatile and biodegradable, and is only slightly water soluble. Based on these properties, remediation through a combination of biodegradation and physical removal in the vapor phase was the most appropriate approach. Bioventing has been used successfully at numerous sites and is easily applied in sandy soils, such as those at this site. The sandy soils within the upper aquifer also made the site conducive to biosparging (air sparging to enhance biodegradation as well as physical removal of VOCs). The use of biosparging with bioventing provides much more air flow through the highly impacted capillary zone than can be provided by bioventing alone. Other positive factors for the use of bioventing at this site were that the area was to be capped and the depth to water was greater than 3 m (10 ft) belowground surface. As a result, the radius of influence of the air

capture system would be large, making bioventing a cost-effective remediation option.

Biodegradation, subsurface aeration, and aquifer performance feasibility studies were performed. The aeration, bioremediation, and aquifer pilot study tests were generally designed and performed consistent with the methods described in Section 5.5. Biodegradation was generally limited by the supply of electron acceptor (oxygen), as adequate levels of nutrients (nitrogen and phosphorous) were found throughout the site. Iron and magnesium precipitation was identified as a potential problem, as they were present at concentrations up to 100 and 37 mg/L in groundwater, respectively. Subsurface aeration provided adequate oxygen to support bioremediation via both air sparging from below the water table and through soil vapor extraction (SVE) in the unsaturated zone immediately above the water table.

8.6.4.2 System Design

The subsurface aeration system was designed to achieve the following:

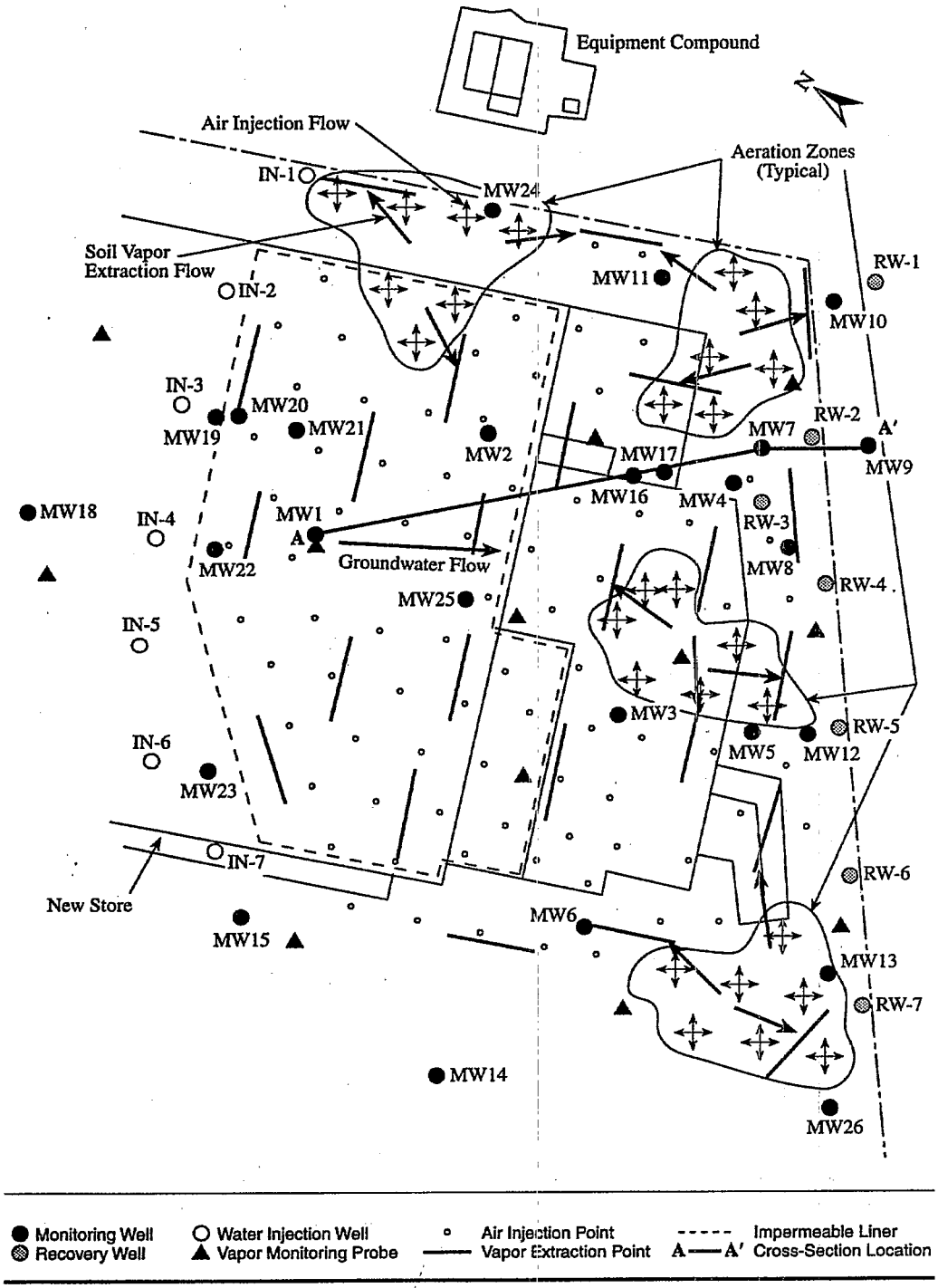
- oxygen addition to support bioremediation;
- direct soil vapor withdrawal for gross hydrocarbon removal; and
- vapor-phase process treatment prior to atmospheric discharge.

The subsurface aeration system is comprised of three subsystems including the air injection (AI) system, the SVE system, and the vapor treatment system. The AI system delivers an aggregate $1.89 \cdot 10^{-2}$ m^3/sec (40 scfm) at 138 kPa (20 psig) to the AI manifold. One hundred thirteen AI points were installed in the remediation target area, with the points operable through dedicated manual flow rate control valves and 17 automatically-controlled valves directed by the central computer for simultaneous control of groups of six to seven AI points. Figures 8.25 through 8.27 show a site plan and a cross-section diagram of the site geology and remedial system installation.

The SVE system applies an aggregate $3.7 \cdot 10^{-2}$ standard m^3/min (78 scfm) at 12.4 kPa (50 in. of water) vacuum at 25 SVE points. Vacuum is directed to each point through dedicated manual flow rate control and automatic valves. Typically, three SVE points are operated in conjunction with a set of AI points for complete capture of injected air.

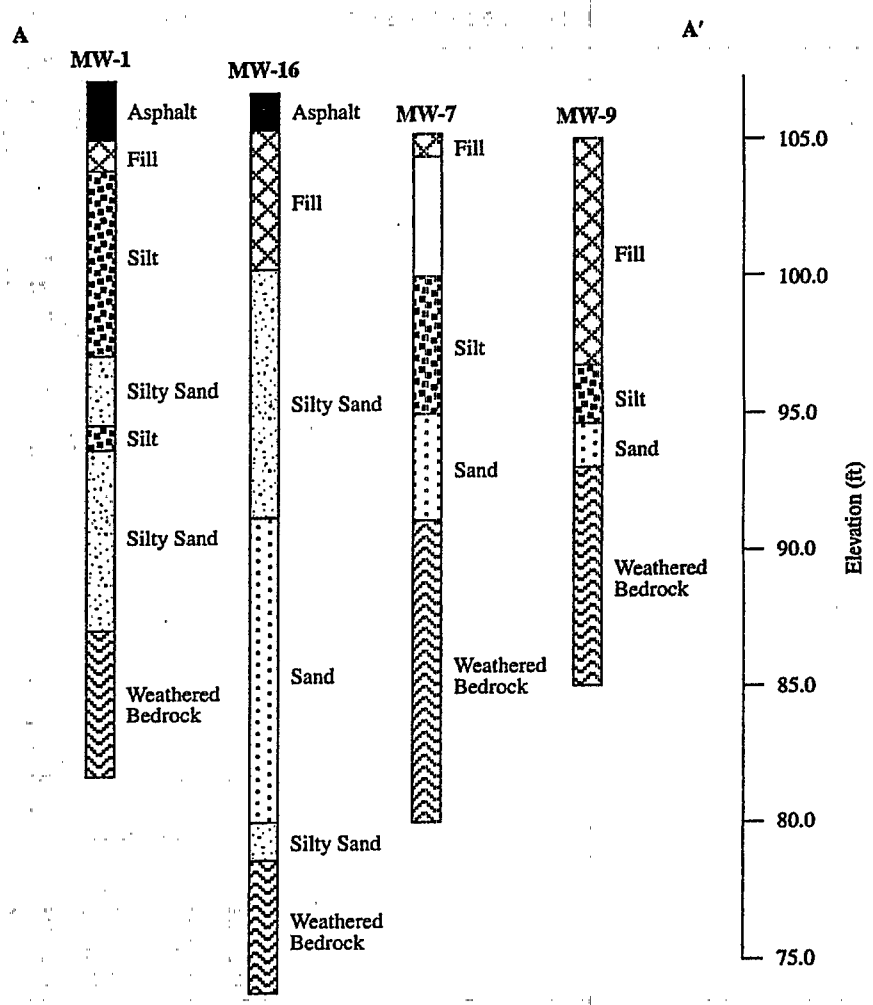
Vapor treatment included a catalytic incinerator during the initial high-VOC loading period, and vapor-phase activated carbon during subsequent lower VOC recovery periods. The vapor treatment system handles the offgas from an air stripper (a wastewater treatment system component). The

Figure 8.25
Site Plan Remediation System
(not to scale)



● Monitoring Well ○ Water Injection Well ∘ Air Injection Point ----- Impermeable Liner
⊗ Recovery Well ▲ Vapor Monitoring Probe —— Vapor Extraction Point A——A' Cross-Section Location

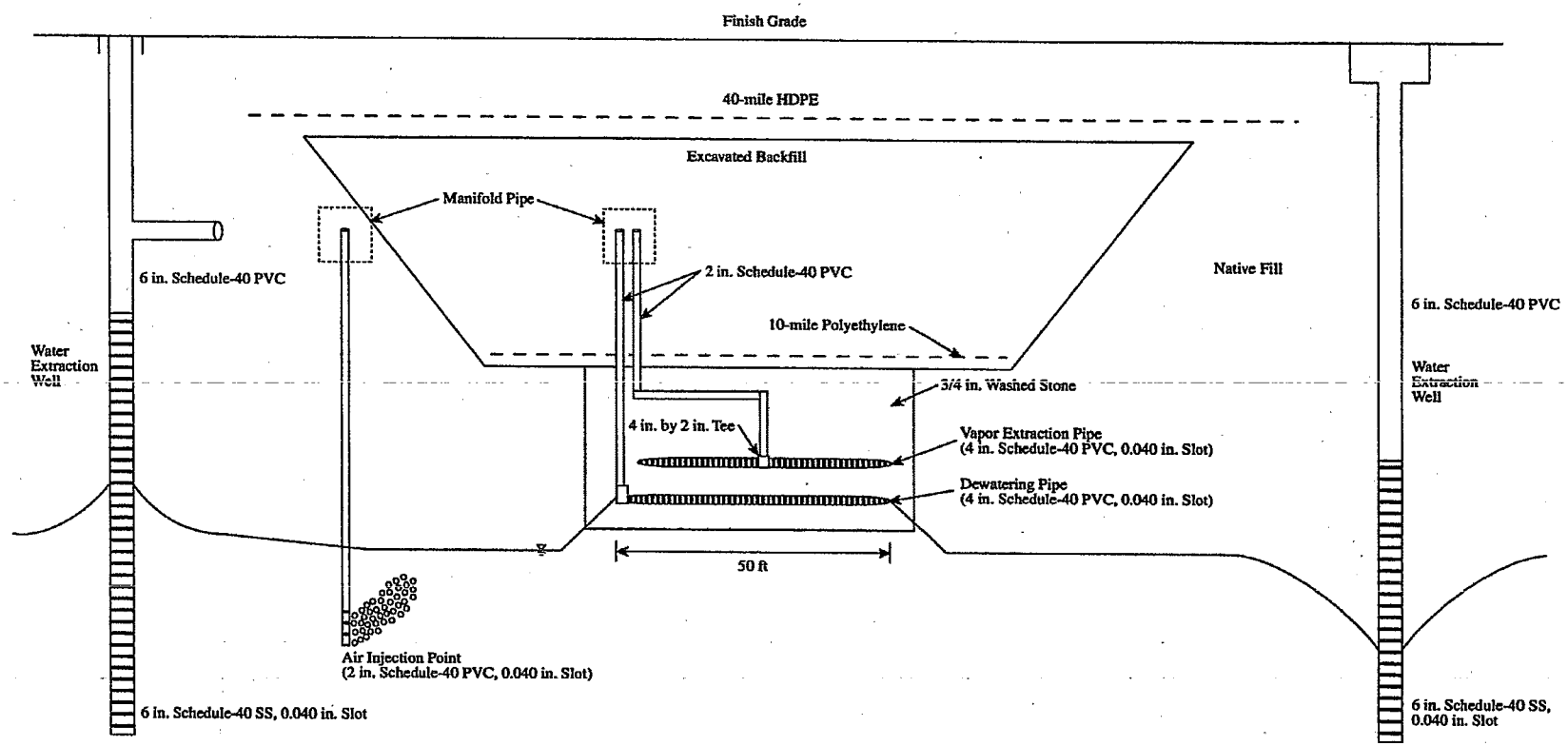
Figure 8.26
Cross-Section A-A'
(not to scale)



phased treatment design is based on a cost-effectiveness analysis indicating a "break-even" vapor-phase VOC concentration of 375 ppm.

One concern of air sparging is that the air typically moves through distinct channels. As a result, removal of dissolved-phase constituents or provision of oxygen for biodegradation requires movement of the constituents or oxygen by advection, dispersion, or diffusion. These processes can be relatively slow and can control the rate of remediation. Both pulsed-air injection and recovery and reinjection of groundwater increases the rate of advection and thus the rate of

Figure 8.27
Subsurface Aeration System Components



remediation. The relatively permeable soils within the aquifer allow for adequate groundwater recovery rates and consequently, groundwater flow rates that will significantly enhance advection between air sparging channels. Because of the need to recover liquid-phase PHCs, groundwater recovery provides the benefit of enhanced liquid-phase PHC recovery, recovery of a significant fraction of the mass for surface treatment, enhancement of air sparging, and with reinjection, the opportunity to add nutrients to ensure that nutrient levels are not rate limiting within the saturated zone.

The planned removal of soil for on-site treatment allowed horizontal vapor recovery lines to be used to provide an additional method to reinject water and nutrients, if necessary. The horizontal lines provide more efficient vapor recovery over the relatively narrow vertical interval where hydrocarbon-impacted soil remained after partial excavation.

The water management system was designed to achieve the following:

- hydraulic control of the shallow aquifer downstream of the remediation target zone via groundwater recovery through a series of recovery wells (RWs);
- direct liquid-phase PHC recovery at RWs where present;
- groundwater recovery (dewatering) in the vicinity of SVE points in dewatering wells (DWs) to prevent flooding of the SVE points;
- process water treatment prior to discharge to the city sanitary sewer or on-site reinjection; and
- water injection and distribution of nutrients required for support of the saturated zone bioremediation system.

The water management system is comprised of three subsystems, including the groundwater recovery system, the water treatment system, and the water injection system. Groundwater and liquid-phase PHCs are recovered through a series of seven RWs and 25 DW points. Pneumatic total fluid pumps are used in RWs where liquid-phase PHC recovery is necessary. Two of the RWs require electric pumps during the maximum flow rate start-up period to achieve 37.9-Lpm (10-gpm) flow rate. Other wells are expected to produce approximately 7.6- to 14.1-Lpm (2- to 4-gpm) long-term flow rates.

The water treatment system accepts groundwater and liquid-phase PHC for storage and/or treatment. Treated water may be discharged to the municipal utility or through the water injection system as needed.

The water injection system accommodates the addition of both nutrients (ammonium nitrate and/or potassium tripolyphosphate) at specified

concentrations, and the metered injection of amended water to a series of seven injection wells. Based on an aggregate long-term flow rate of 57 Lpm (15 gpm), the groundwater turnover period is approximately 1 year.

Materials management provided by the subsurface aeration and water management systems established the basis for the final remedial element: a combination of limited area air sparging and intrinsic remediation. Hydrocarbon mineralization will occur over a 2-year period at design aeration and oxygen delivery flow rates assuring a 20% utilization of injected oxygen. This time frame may be shortened based on the improved distribution created by the continuous enhanced groundwater flow through the target zone and intermittent air injection, allowing greater time for distribution through dispersion and diffusion.

The selected in situ remedial system is highly integrated, consisting of groundwater recovery with aboveground treatment, injection of treated and nutrient-amended groundwater, liquid-phase PHC recovery, biosparging, bioventing, and aboveground treatment of offgasses. The remediation components were designed to be either underground or located in a treatment facility adjacent to the tenant's building. Electronic controls located in the treatment facility along with other design features permit operation with minimal need to enter the tenant's building.

8.6.4.3 Automatic Control System

The automated control system is driven by a programmable logic controller (PLC) which provides standard relay-type operation of water level controllers and flow control valves. Air injection, vapor extraction, and dewatering system operation are controlled through the PLC timer.

The PLC is used to operate the remediation system controls and the solenoid valve primary control unit. The PLC system is comprised of hardware (physical equipment) and software (programmable features). PLC hardware includes components required for electrical connections to the power supply, connection to and control of valve solenoids, and the user interface. All hardware is housed in the water system sub-panel and is adjusted or maintained only by specialized personnel trained in the use of the PLC. PLC software includes components that are preset by the supplier and a component that allows field operator adjustment. Preset components include those to establish basic PLC configuration, parameters that may be changed by the field operator, and field operator interface format. Of these, all except those pertaining to the field operator interface can be adjusted or maintained by specialized personnel trained in the use of the PLC.

The preset software configuration is a computer program that allows the field operator to change the solenoid valve operation schedule by downloading an array template provided by a user-friendly DOS support program. In general, the DOS program allows: (1) selection of a desired number of "sequence slots," (2) assignment of a time duration for each of the sequence slots, and (3) assignment of one or multiple valves that are to be opened for each sequence slot.

Through the use of the PLC user programs, the system is configured so that each set of air injection valves opens in sequence, and the appropriate vapor extraction valves open simultaneously to allow recovery of all injected gas in the area of application. The PLC system also allows pulsing of the biosparging system. Further, dewatering points located proximally to operating vapor extraction points may be operated synchronously with the air sparging/SVE system.

Valve opening configurations may by altered either during the initial configuration or by modifying an existing configuration as indicated below:

- the number of sequence slots created (limited to a maximum of 17);
- the time duration for each sequence slot in minutes (limited to a maximum of 1,440);
- the AI set valves assigned to a sequence slot including one or multiple valves (values from 01 through 17);
- the SVE-point valves assigned to a sequence slot including one or multiple valves (values from 01 through 25); and
- the DW-point valves assigned to a sequence slot including one or multiple valves (values from 01 through 25).

8.6.5 Implementation

Expedited remedial construction was implemented through the following steps:

1. Initial excavation of shallow soils exhibiting elevated contaminant levels permitted site redevelopment construction to proceed immediately. Excavated soils were stockpiled on an adjoining parcel for treatment in a soil cell.
2. The site redevelopment contractor was selected as the remedial contractor to allow seamless transition between remedial and redevelopment civil construction. Simultaneous and optimal task sequencing was achievable without contractor conflicts.

Construction tasks, such as excavation of poor structural soils and replacement with acceptable fill, were conducted in conjunction with the excavation of contaminated shallow soils, as well as the excavation and construction of subsurface treatment system components. Developer goals and environmental work plan goals were achieved concurrently.

3. Preliminary design and construction of subsurface components were conducted prior to the completion of final mechanical plant design. This was acceptable based on the known applicability of the remedial techniques selected. Documentation and designs for groundwater recovery systems, subsurface aeration systems, and impermeable liner systems are standard in the industry. Final blower, pump, treatment, and instrumentation system selection and integrated engineering were completed during expedited subsurface system construction. The availability of off-the-shelf remediation equipment from reputable vendors for processes within previously-documented application ranges ensured that an appropriately-sized and constructed mechanical plant could be completed.

A critical aspect of the construction effort was the remote access system, which was needed due to operational constraints imposed by the use of the commercial property overlying the target zones. System construction incorporated the necessary plumbing, including 125 1.3-cm (1/2-in.) ID HDPE tubes leading from each air injection point and vapor monitoring point to the treatment facility, 74 5-cm (2-in.) diameter PVC pipes leading from water and vapor points to the treatment facility, as well as electrical and pneumatic conduit for the groundwater recovery pumps. All tube, pipe, and conduit installations were completed in the field and demarcated and stubbed while treatment facility design was completed and construction was undertaken. Incorporation into the mechanical plant then proceeded, providing point access from the central location, with limited field access available for water system components only.

Individual air injection, vapor extraction, groundwater recovery, and injection well performance tests were conducted during startup. Manual flow control valves were adjusted to achieve the desired flow rates, and secondary automatic valves were operated by the system computer based on a variable operator input program.

Operation of the in situ remediation system was divided into three phases. During Phase I of operation, the following remedial actions were implemented:

- liquid-phase PHC recovery with <0.5 m (1 ft) drawdown at recovery points;
- SVE operation at SVE-point triads in which VOC concentrations measured by field PID measurements were >100 ppmv; and
- clean water injection through injection wells, as much as possible using: (1) liquid-phase granular activated carbon treated process water, and (2) tap water.

Phase I operation will continue until liquid-phase PHC recovery decreases by at least 50%.

During Phase II operation, the following remedial actions will be implemented:

- groundwater recovery will be increased through all RWs. The pumping drawdown will be progressively increased in 1-m (3-ft) increments at a minimum of 48-hour durations followed by incremental drawdown increases when the liquid-phase PHC recovery has decreased sufficiently;
- injection of amended water into the injection wells at up to design flow rates; and
- operation of the subsurface aeration system (i.e., SVE system operation only) as a continuation of the Phase I operation.

This operational period will continue until the VOC recovery rate decreases by approximately 80%.

During Phase III operation, the following remedial actions will be implemented:

- groundwater recovery system will be continued as in Phase II operations;
- water injection system operation shall be a continued as in Phase II operations; and
- initiation of full-scale subsurface aeration including SVE and air injection in accordance with engineering specifications for automatic SVE and AI point activation.

This operational period shall continue until the following monitoring results are obtained:

- detectable liquid-phase PHC is not observed in monitoring or other wells; and

- groundwater quality compliance results indicate that hydrocarbon concentrations in groundwater have decreased to below established remediation standards.

8.6.6 Operation Results

Since startup, no LPH has been detected in site wells, and LPH has not been recovered in recovery wells. Hydrogeologic evaluations indicate that the material is most likely present in its original locale, but has become adsorbed or trapped within soil interstitial areas.

Initial testing and operation of the SVE system indicates that operation is within design parameters. The system has been recovering VOCs at a rate somewhat below its design rate. Therefore, conversion of treatment operation from the catalytic incinerator (used during high-VOC loading) to vapor-phase activated carbon (used during low-VOC loading) occurred within the first several months of operation.

Preliminary testing of the air injection system indicates that operational performance deterioration of approximately 25% is to be expected. This deterioration was adequately compensated for by performance allowances in design and conservative estimates of performance based on pilot-test results.

The first round of quarterly groundwater monitoring data were collected approximately 3 months after remedial system startup. Results have not been reported to date, but will be used during final system optimization.

8.6.7 Conclusions

The environmental project undertaken at the subject site was a cooperative effort to meet the needs of all interested parties. This cooperative climate enabled the environmental specialists and constructors to create an effective and practical remediation system within the broader scope of providing a usable commercial property in an expedited fashion.

This project also showed the value of conducting treatability and pilot tests, combined with a somewhat conservative design to allow system installation at a site where access subsequent to construction would be limited. Additionally, the design incorporated synergistic technologies that are integrated to improve performance of one technology based on the specific design of another.

8.7 Intrinsic Remediation of a Hydrocarbon-Contaminated Aquifer

This case study describes the application of intrinsic remediation for fate and transport assessment and plume management at Site 13/26 at Eielson Air Force Base (AFB), Alaska, which was contaminated with fuel hydrocarbons. This case study was developed from a 2-year field project conducted from 1993 to 1995 by the Utah Water Research Laboratory at Utah State University and funded through the U.S. Air Force Center for Environmental Excellence, Brooks AFB, San Antonio, Texas (Dupont et al. 1996). Characteristics of the intrinsic remediation methodology described in Section 5.3 of this monograph are highlighted as they apply to site assessment, contaminant fate and transport evaluation, and long-term modeling with and without implementation of source removal to develop a recommended remediation strategy for the site.

8.7.1 Site Description

Eielson AFB is located in the Tanana River Valley in Central Alaska, approximately 200 km (124 mi) south of the Arctic Circle. Most of the base is constructed on fill material underlain by an unconfined aquifer consisting of 60 to 90 m (200 to 300 ft) of alluvial sands and gravels overlying a low-permeability bedrock formation (USAF 1994). The aquifer system below the base is bounded to the northeast by the Yukon-Tanana uplands and is approximately 70 to 80 km (43 to 50 mi) wide in the area of the base (CH2M Hill 1982). The direction of groundwater flow throughout the base is generally to the north, with groundwater encountered at 2.5 to 3.5 m (8 to 12 ft) below ground surface at various times of the year.

The actual source(s) of contamination at Site 13/26 and the exact mass of contaminant released to the environment are unknown. The release of product from several JP-4 and diesel fuel storage tanks near the southeast end of the main taxi-way and fuel bladder filling operations are believed to have contributed to groundwater contamination in this portion of the site. Leakage of a large aboveground JP-4 storage tank and its associated piping is also known to have occurred.

Figure 8.28 is a conceptual model of pure product, residual saturation, and dissolved hydrocarbon plume distribution throughout Site 13/26 based on groundwater and free product samples collected from November 1993 to July 1995. It is noted that it was originally thought that one large (>600-m

[>1,875-ft] long) hydrocarbon contaminant plume existed at the site moving north from the area near Tank 300. This conceptual model was based on 15 relatively widely-spaced, large-diameter groundwater monitoring wells. As indicated in Section 5.3, finely-spaced monitoring points are essential if the boundaries of contaminant plumes are to be accurately delineated in the intrinsic remediation plume management approach. This guidance is highlighted in Figure 8.28. Based on the improved site characterization possible from the 45 closely-spaced monitoring points placed throughout Site 13/26, four distinct contaminant plumes were identified, each much smaller than the originally-defined plume. The length of groundwater plumes has a significant impact on the outcome of an intrinsic remediation evaluation in terms of verifying degradation rates and in modeling long-term plume behavior; it is critical to properly identify unique contaminant plumes before further evaluation.

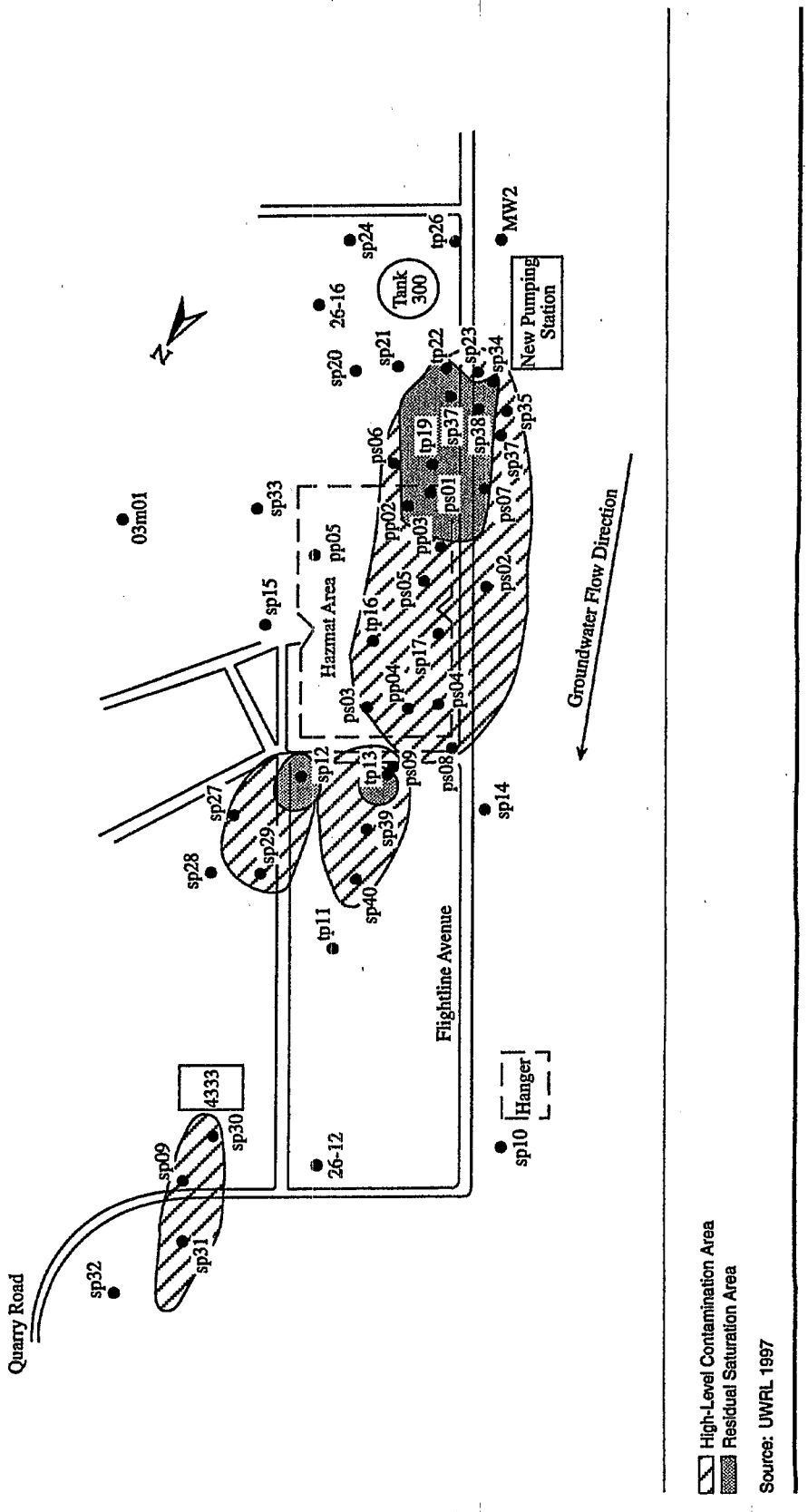
8.7.2 Implementation of Intrinsic Remediation Plume Management Approach

The intrinsic remediation plume management approach focuses on evaluation of the potential or real risk posed by contamination at a given site. This evaluation is made using the protocol presented in Section 5.3 and involves the following:

- determining whether the plume is stable under existing site conditions;
- verifying that contaminant attenuation is mediated through biological action;
- quantifying the contaminant degradation rates taking place under site conditions;
- evaluating the long-term behavior of the plume with and without active source removal; and
- making decisions regarding implementation of long-term monitoring and/or source removal based on: (1) regulatory and public acceptance of intrinsic remediation, and (2) the technical feasibility and cost-effectiveness of source removal actions at the site.

This general approach was implemented at Site 13/26. Details of the intrinsic remediation management efforts at this site are given in the following sections.

Figure 8.28
Conceptual Model of Free Product and Residual Saturation Within Source Areas — July, 1995
(not to scale)



Source: UWRL 1997

8.7.2.1 Assessment of Steady-State Conditions

Steady-state conditions were assessed at Site 13/26 by inspection of plume centerline concentrations over time and analysis of integrated plume mass data for the site. Steady-state conditions were evident from centerline concentration data as indicated by TPH results shown in Figure 8.29. Center of Mass data also indicated a stable, continuous source of hydrocarbon contamination at Site 13/26.

8.7.2.2 Estimation of Contaminant Degradation Rates

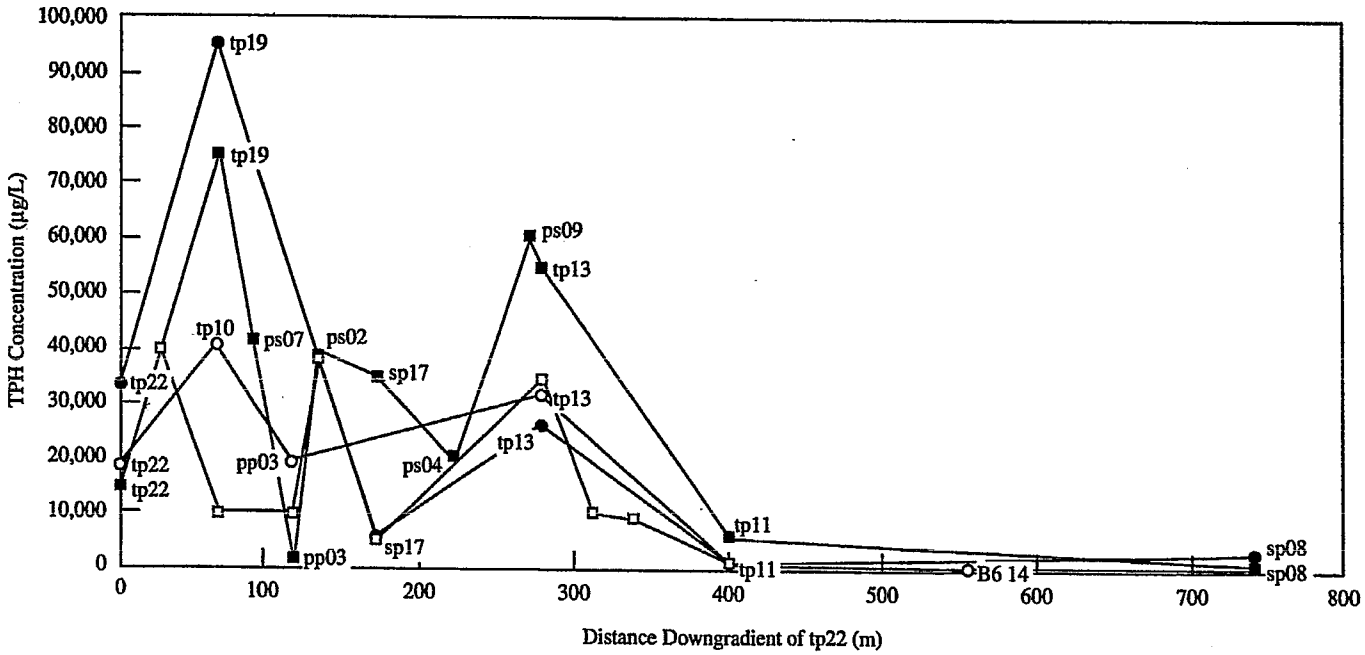
Biological contaminant removal at Site 13/26 was verified through an analysis of the concentration distribution of nondegradable plume-resident tracer compounds (PRTs) in the plume relative to that of the more degradable BTEX components. As indicated in Section 5.3, accelerated loss of BTEX compounds relative to the PRTs provides evidence of biodegradation within a contaminant plume. Figure 8.30 shows the normalized concentration profile for BTEX and four tracer compounds (1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and 2,4-dimethylpentane) that were identified throughout the plume at Site 13/26. As indicated in Figure 8.30, as the plume moves downgradient away from the source area at TP19 toward PS05 (see Figure 8.28 for sampling point locations), even the groundwater in equilibrium with residual-phase material becomes significantly depleted in BTEX components and is highly enriched in the less degradable tracer compounds, confirming a biologically-mediated pathway for BTEX removal.

Due to the extent of groundwater data available, the estimation of contaminant degradation rates for Site 13/26 was possible using the Domenico (1987) model mentioned in Section 5.3 and described in detail by Gorder et al. (1996).

A distinct free product phase was observed in the source area at Site 13/26 at various times throughout the study. The actual extent of mobile, free-phase liquid was dependent on groundwater depths; product was observed when the groundwater table was low, but not when high groundwater levels submerged and occluded product below the groundwater table.

Figure 8.28 shows residual- and dissolved-phase contamination identified from groundwater samples collected from the site in July 1995. The distribution of free-phase product and residual saturation throughout a site must be delineated to identify the point at which a true dissolved-phase plume begins because fate and transport models provide estimates for degradation rates only in the dissolved plume. At Site 13/26, the edge of residual-phase

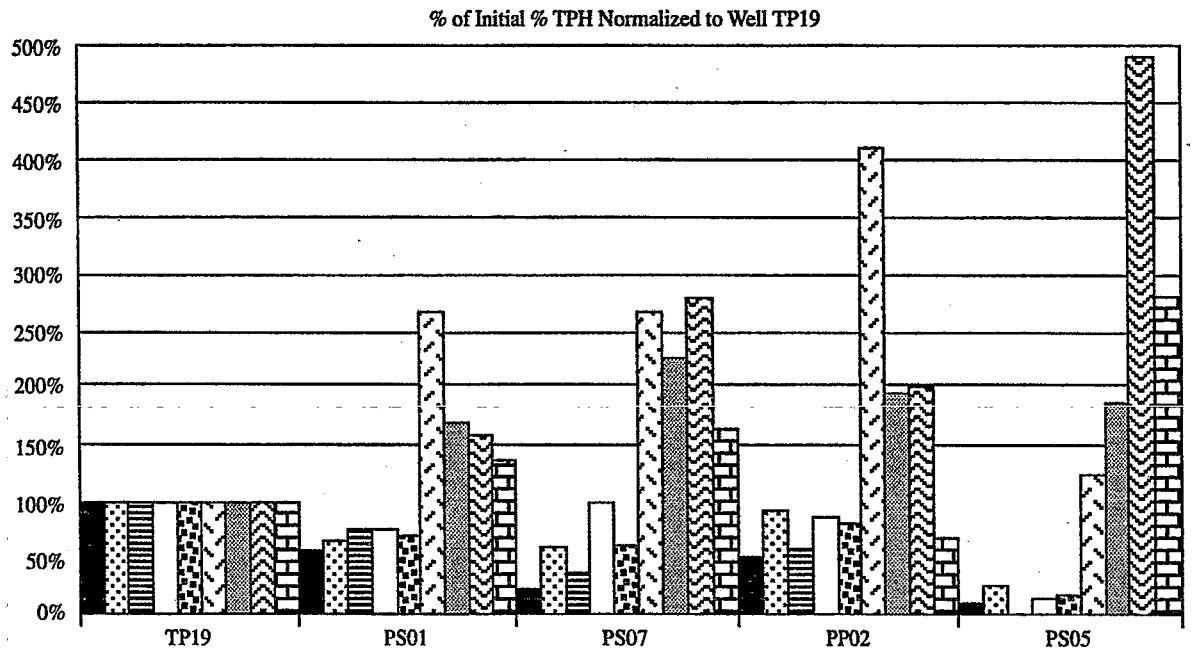
Figure 8.29
Centerline Groundwater TPH Concentration Data Over Time



● November 1993
○ May 1994
■ September 1994
□ July 1995

Source: UWRL 1997

Figure 8.30
Compound Concentration Data for BTEX and PRTs Normalized to Values in TP19 — July, 1995



Groundwater movement is from left to right in this figure.

Benzene
Toluene
E-Benzene
p-Xylene
BTEX
1,2,3-TMB
1,2,4-TMB
1,3,5-TMB
2,4-DMP

Source: UWRL 1997

contamination downgradient of the source area was identified based on the known composition of product from the site and a comparison of individual compound concentrations measured in the groundwater to those expected in equilibrium with the product material based on Raoult's Law. The Raoult's Law concentration ($C_{equilib}$) is based on the mole fraction X_A, of a specific contaminant in the product material as indicated in Equation 8.5:

$$C_{equilib} = X_A S_A \tag{8.5}$$

where:

S_A = the pure compound solubility of Compound A in the aqueous phase.

If the measured concentration of Compound A in the groundwater is equal to or greater than $C_{equilib,}$ the groundwater can be considered to be in equilibrium with mobile free product or residual-phase NAPL within the soil pore space. Modeling of dissolved-phase contaminant migration must begin at points downgradient from the identified residual material if degradation rates are to be representative of field conditions observed at the site.

Once the edge of a plume was identified, PRTs were used in this modeling approach to develop "dilution-corrected" degradation rates for the reactive BTEX components of the groundwater plume. These tracer compounds were used to provide flow calibration for the Domenico fate and transport model. The model was calibrated by setting the groundwater velocity, source configuration, and simulation time input data to values shown in Table 8.7. Estimated retardation coefficient values, R, and measured dissolved plume source area concentrations, C_o, for these compounds were then used to fit the model to measured centerline concentration values. PRT degradation rates and aquifer dispersion values were adjusted until maximum model fit (minimum mean square error [MSE]) to measured field data was achieved. With the low degradation rates observed for these compounds, aquifer dispersion properties had the greatest impact on model-fitting results, facilitating model calibration to field-estimated aquifer dispersion values.

This calibration effort resulted in the mean dispersion properties listed as final model calibration values in Table 8.7, which were used to estimate the degradation rates of the more reactive BTEX components. BTEX degradation rates were estimated by minimizing the MSE of the Domenico model fit to measured plume centerline groundwater data by adjusting their biodegradation rates. Final model calibration results for two of the PRTs and benzene are shown in Figure 8.31, and contaminant degradation rates estimated for all compounds of interest using this modeling approach are listed in Table 8.8.

Table 8.7
Final Calibration Results Using Plume-Resident Tracers Identified Throughout the Plume — July, 1995

Parameter	1,2,3-TMB	1,2,4-TMB	1,3,5-TMB	2,3 DMP	Final Model Calibration Value
Longitudinal Dispersion (m)	1.9	1.5	1.9	2.1	1.85
Tangential Dispersion (m)	0.095	0.075	0.095	0.105	0.092
Vertical Dispersion (m)	0.001	0.001	0.001	0.001	0.001
Degradation Rate (l/d)	0.00052	0.0002	0.0003	0.0002	*
R	7.3	11.6	6.1	3.8	**
Groundwater Velocity (m/d)	0.069	0.069	0.069	0.069	0.069
Simulation Time (d)	4,650	4,650	4,650	4,650	4,650
Co (mg/L)	0.17	0.38	0.34	0.26	**
Source Width (m)	50	50	50	50	50
Source Thickness (m)	2	2	2	2	2

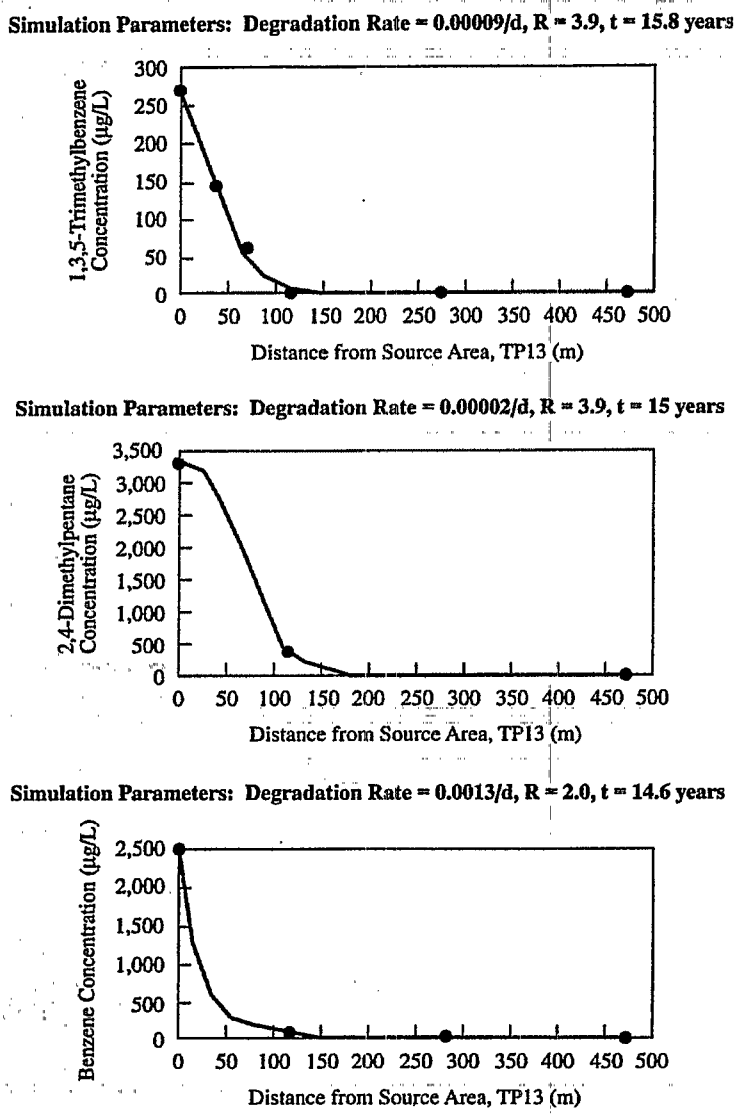
* Parameter varied to obtain the minimum MSE value in BTEX calibration.
** Specific to each compound.

8.7.2.3 Estimation of Source Mass

The multiple source areas and individual contaminant plumes shown in Figure 8.28 were delineated based on: (1) free product observed at the site during field sampling, and (2) dissolved BTEX concentrations above equilibrium values based on free product composition results. The residual saturation areas included groundwater samples where BTEX levels equal to or higher than those in equilibrium with pure product were measured, indicating that a nondissolved, residual product material remained trapped in the soil matrix in those areas. The areas delineated as high-level contamination areas in Figure 8.28 included sampling locations where BTEX and TPH levels were below the levels indicative of equilibrium with residual saturation, but that were above regulatory limits. Using these data, the amount of residual mass at Site 13/26 was estimated assuming a residual saturation, S_r, of 25% of the pore volume based on the sandy soil texture of the site (Mobil Oil Corporation 1995). The results of the contaminant mass estimation are

summarized in Table 8.9 and suggest that more than 760,000 kg (1,672,000 lb) of JP-4 equivalent product remained in the site soil and groundwater.

Figure 8.31
Domenico Model Calibration to Groundwater Plume Centerline Data for Two PRTs and Benzene — July, 1995



— Predicted
● Observed: 5/94

Source: UWRL 1997

Table 8.8
Contaminant Degradation Rates Estimated from Model Calibration to Field Data

Compound	Degradation rate (l/d)
Benzene	-0.00145
Toluene	-0.00149
Ethylbenzene	-0.00087
p-Xylene	-0.00036
2,4-Dimethylpentane	-0.00042
1,3,5-Trimethylbenzene	-0.00012
1,2,4-Trimethylbenzene	-0.00015
1,2,3-Trimethylbenzene	-0.00021

Table 8.9
Estimated Source Area Mass and Lifetime

Soil Porosity (n)	0.3
Residual Saturation, Sr (%n)	25
Product Density	801 kg/m^3 (49.9 lb/ft^3)
Residual-Phase Product Area	
Width	50 m (164 ft)
Length	100 m (328 ft)
Depth	2 m (6.6 ft)
Total Volume	10,000 m^3 (352,876 ft^3)
Residual-Phase Product Volume	949 m^3 (33,523 ft^3) (250,681 gal)
Residual-Phase Product Mass (g)	759,758,497
Source Lifetime Estimation	
Measured Mass Flux From Source Area	99,492 mg/ft/d 1,242 g/d
Estimated Years to Deplete Source Based on Flux Rate	1,676

8.7.2.4 Estimation of Source Lifetime

The required time for source area depletion for a steady-state plume can be estimated based on the integrated mass removal rate of contaminant within the plume. This integrated degradation rate can be equated to the mass flux of contaminant from the source area into the plume for a plume that has reached steady-state. The flux rate of mass into the plume was calculated using Equation 8.6.

$$\text{Mass Flux} = v\theta AC_o \tag{8.4}$$

where:

v	=	pore water velocity (m/d);
θ	=	aquifer total porosity (decimal);
A	=	source cross-sectional area perpendicular to groundwater flow (m^2); and
C_o	=	source area concentration (g/m^3).

This flux rate was then used as the value of k_o in Equation 5.28 to estimate a source lifetime without remediation as shown in Table 8.9 of more than 1,600 years.

8.7.2.5 Prediction of Long-Term Plume Behavior

Consideration of long-term plume behavior involves an evaluation of the plume footprint over time with and without source removal implemented at a site. If the plume under consideration is at steady-state, its plume footprint should remain constant in position over time until the source of contamination is depleted or physically removed. Following source depletion or removal, the dissolved plume will begin to contract as the assimilation of contaminants in the aquifer exceeds their release rate from the source area. The impact of source removal can be modeled using the approach described by Gorder et al. (1996) which entails superimposing a plume with a source area concentration, $-C_o$, at the time of source removal and modeling the combined plume for time intervals t + T, where t = cumulative time from the beginning of the release to when source removal occurred, and T = time since source removal occurred. This procedure allows the prediction of the time required for the dissolved plume to degrade below the level of regulatory concern following source removal. Based on this information, a decision can be made regarding the expected benefit from source removal in terms of reducing the time required for management of the site to ensure long-term risk reduction.

This analysis was conducted for Site 13/26 where the source term was projected to have an extensive lifetime. Results for benzene plume centerline concentration predictions are shown in Figure 8.32. As indicated in this figure, due to the rapid degradation rate observed for benzene at this site, plume concentrations are projected to be below regulatory limits of 5 mg/L within 7 years following source removal. While 100% source removal is probably impossible, results of this analysis indicate that source removal is important at the site due to the large mass of residual-phase material that serves as a continuous, long-term source of groundwater contamination and the rapid assimilation of this plume once the flux of contaminant into the aquifer is halted.

8.7.3 Results of Intrinsic Remediation Assessment

8.7.3.1 Selection of Intrinsic Remediation Plume Management Approach

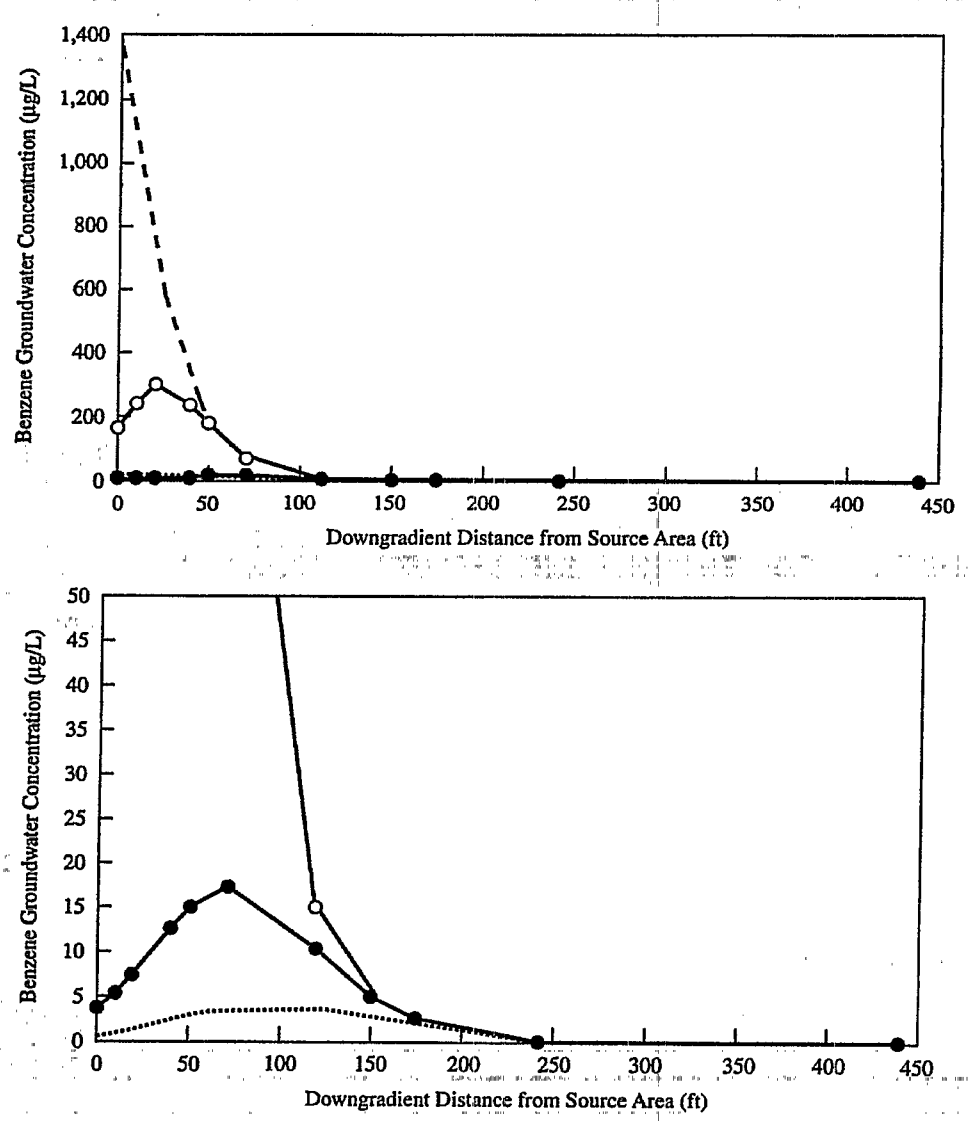
Based on decision logic presented in Figure 5.15, selection of intrinsic remediation depends on the acceptability of the expected life of the plume, which would be long at Site 13/26 without some source removal. An evaluation of the assimilative capacity of the TEA pool existing at Site 13/26 using the stoichiometry presented in Table 5.11 is summarized in Table 8.10. These calculations suggest that marginal levels of TEAs exist to metabolize the dissolved BTEX components found at Site 13/26 and that nitrate and sulfate are the two primary active TEAs there.

Based on: (1) the result of the source mass and source lifetime calculations previously presented, (2) the prediction of a short plume lifetime with source removal at the site, and (3) the finding that an insufficient supply of TEAs exists throughout the site to provide continual attenuation of the hydrocarbon plume without source treatment, the final recommendation for Site 13/26 was implementation of intrinsic remediation for dissolved plume management, with active source removal to reduce the source and plume lifetime and contaminant flux into the plume to acceptable levels.

8.7.3.2 Long-Term Monitoring Plan

With implementation of intrinsic remediation, a long-term monitoring network is required. For this network to serve multiple purposes, a combination of upgradient, downgradient, and within-plume monitoring locations is necessary. The recommended monitoring network for Site 13/26 is shown in Figure 8.33.

Figure 8.32
Benzene Centerline Concentrations Predicted
1, 5, and 7 Years Following 100% Source Removal



Predicted Steady-State Plume with No Source Removal
Predicted @ t = 1 yr after 100% Source Removal
Predicted @ t = 5 yr after 100% Source Removal
Predicted @ t = 7 yr after 100% Source Removal

Simulation Parameters: Degradation Rate = 0.00145/d, R = 2.0, Steady-State Plume

Source: UWRL 1997

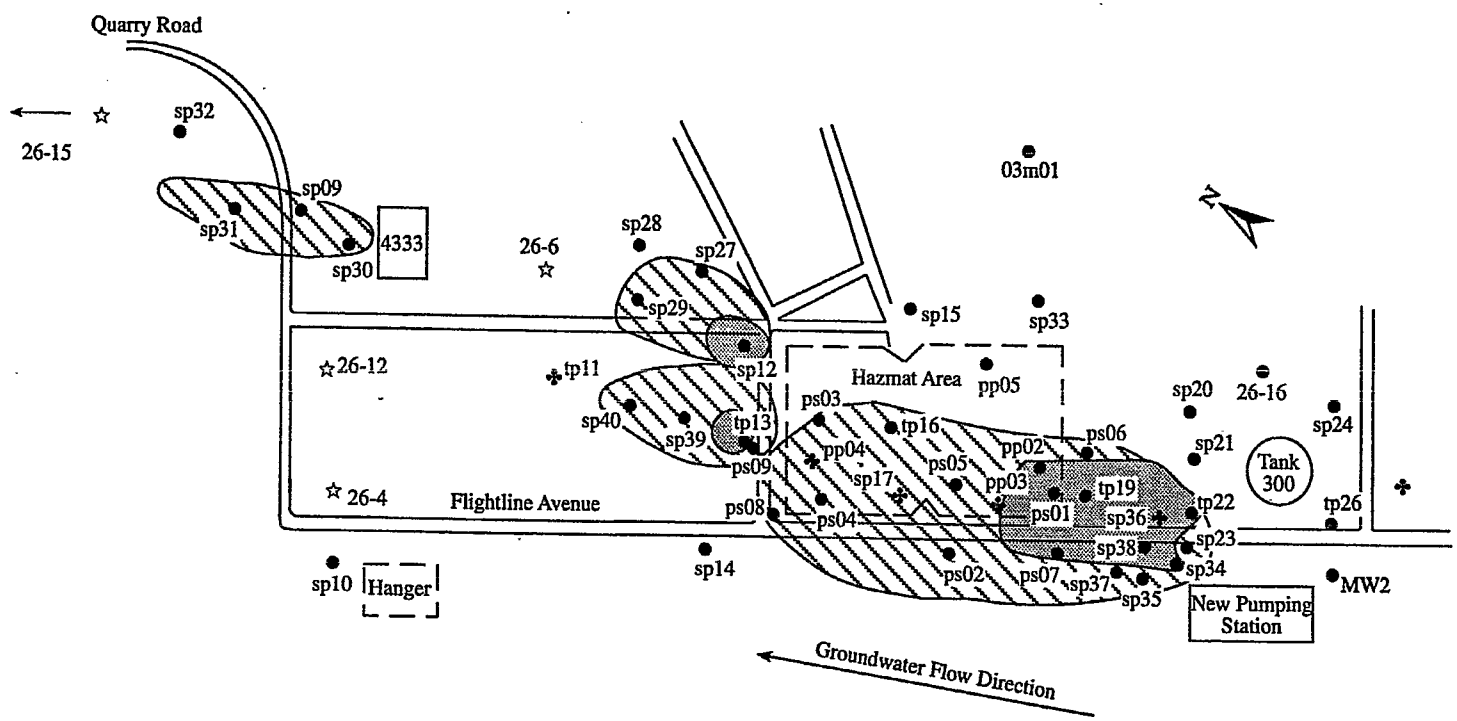
Table 8.10
Expressed Assimilative Capacity of the Aquifer System—July 1995

Electron Acceptor/Process	(µg BTEX or TPH/L)
Dissolved oxygen	1,030
Nitrate-N	9,350
Iron/manganese reduction	4,360
Sulfate	10,100
Methanogenesis	485
Total Assimilative Capacity	25,325
Highest Observed Dissolved BTEX	26,702
Highest Observed Dissolved TPH	60,468

Two sets of wells are used at Site 13/26 as part of the long-term monitoring strategy. The first set, the long-term monitoring wells, consists of a transect of plume centerline wells composed of one existing well located upgradient of the JP-4 source area (Monitoring Well 13-1) and six additional wells located within the observed hydrocarbon plume area. These wells are used to verify the intrinsic remediation process and allow the conceptual model to be updated for plume and source area configuration over time. The second set of monitoring wells consists of a transect of three existing wells (26-4, 26-12, 26-6) generally perpendicular to the direction of plume migration (approximately 100 m [305 ft]) downgradient from monitoring point TP11) and an existing well, 26-15, approximately 100 m (305 ft) downgradient of sampling point Sp32 to establish the point-of-compliance (POC) for this site. The purpose of the POC wells is to verify that no BTEX exceeding the federal MCL (5 µg/L) migrates beyond the area under institutional control.

A three- to five-year sampling frequency was recommended for the site due to the projected lifetime of the source area and dissolved plume with complete source removal. This interval provides sufficient data over time to verify plume stability and source area depletion at a reasonable frequency based on cost considerations, without compromising human health or environmental quality. Samples should be collected at the same time of the year to ensure comparable groundwater table elevations at each sampling event so that true changes in groundwater concentrations can be identified from historical data.

Figure 8.33
Long-Term Monitoring Network Proposed for Validation of Intrinsic Remediation Plume Management — July, 1995
(not to scale)



High-Level Contamination Area
Residual Saturation Area
Proposed Long-Term Monitoring Wells
Proposed Point-of-Compliance Wells

Source: UWRL 1997

8.7.3.3 Costs

The field intrinsic remediation study conducted at this site cost approximately $450,000 over the 2 1/2-year project life. Initial feasibility study documentation (U.S. Air Force 1993) identified three treatment schemes for remediation of petroleum hydrocarbon contamination at Site 13/26. These included: (1) a bioventing alternative with capping, bioventing, passive product skimming, and hydraulic containment of the groundwater plume; (2) an SVE alternative with soil excavation, SVE, active skimming, and groundwater extraction and treatment; and (3) an extraction alternative that included soil excavation and groundwater extraction and treatment. Total remediation costs for each alternative are summarized in Table 8.11 (U.S. Air Force 1993), while the estimated costs for an intrinsic remediation management alternative with long-term monitoring and source control at the site are shown in Table 8.12. As indicated in the tables, intrinsic remediation which does not require soil or groundwater removal and treatment reduces the estimated cost of site remediation from $16,000,000 to $39,000,000 to less than $6,500,000 while achieving the same remedial goals which are protective of public health and the environment.

8.7.4 Summary and Conclusions

This case study highlights the intrinsic remediation process described in detail in Section 5.3. This process involves: (1) the assessment of steady-state plume conditions, (2) determination of degradation rates, (3) estimation of the source quantity, (4) estimation of the source lifetime, (5) prediction of the long-term behavior of the plume with and without source removal, (6) assessment of aquifer assimilative capacity and the desirability of source removal at the site, and (7) development of a long-term monitoring strategy for verification of intrinsic remediation process performance and regulatory compliance purposes. These procedures were successfully applied at a hydrocarbon-contaminated site at Eielson AFB, Alaska.

Approximately 950 m^3 (250,000 gal) of fuel were thought to remain as residual saturation in the source area of the largest plume found at this site. With an assessment of the impact of source removal on the lifetime of the dissolved plume, it was recommended that some active source removal take place to reduce the baseline source lifetime estimate (>1500 years) to a more acceptable level. Long-term monitoring with upgradient, in-plume, and downgradient POC wells was prescribed for the site at a sampling frequency of once every three to five years to monitor the progress of intrinsic remediation and allow for the continual refinement of the conceptual model of fate and transport of hydrocarbon contaminants at the site.

Table 8.11
Summary of Estimated Present-Worth Costs of Proposed Remedial Action Alternatives*

Alternative	Bioventing	SVE	Extract
Capital Costs			
Soil Remediation	$980,500	$2,250,000	$16,540,300
SVE/Bioventing	$558,500	$1,666,875	
Passive Skimming	$115,000		
Groundwater Extraction	$40,000	$153,000	$185,000
Groundwater Monitoring	$5,000	$5,000	$5,000
Groundwater Treatment	$429,000	$434,000	$434,000
Mobilization	$319,200	$676,300	$3,432,800
O&M Costs			
Soil Remediation	$913,000	$173,000	
SVE/Bioventing	$440,000	$342,000	
Passive Skimming	$100,000		
Groundwater Extraction	$1,826,000	$1,742,000	$1,246,000
Groundwater Monitoring	$4,458,000	$2,278,000	$186,000
Groundwater Treatment	$3,943,000	$4,166,000	$504,000
Contingencies, Administrative, Engineering	**$1,942,400**	**$4,114,825**	**$16,352,900**
TOTAL	**$16,070,000**	**$18,001,000**	**$38,886,000**

* Unit costs and present-worth calculation used in this cost estimate were taken from those presented in US EPA 1993. Present-worth calculations are made assuming an interest rate of 5% for an operating period of 50 years for bioventing, 30 years for SVE, and 20 years for the Extract alternative.

Implementation of the intrinsic remediation plume management approach at this hydrocarbon-contaminated site appears to be an effective alternative to conventional remedial options involving pump-and-treat, SVE, and excavation and off-site treatment of the contaminated soil because it provides equivalent protection of public health and environmental quality at a significantly lower cost. This is particularly true if the plume lifetime can be reduced to 50 years or less with some form of active remediation within the source area at the site.

Table 8.12
Summary of Estimated Present-Worth Costs for Proposed Intrinsic Remediation with Limited Source Removal*

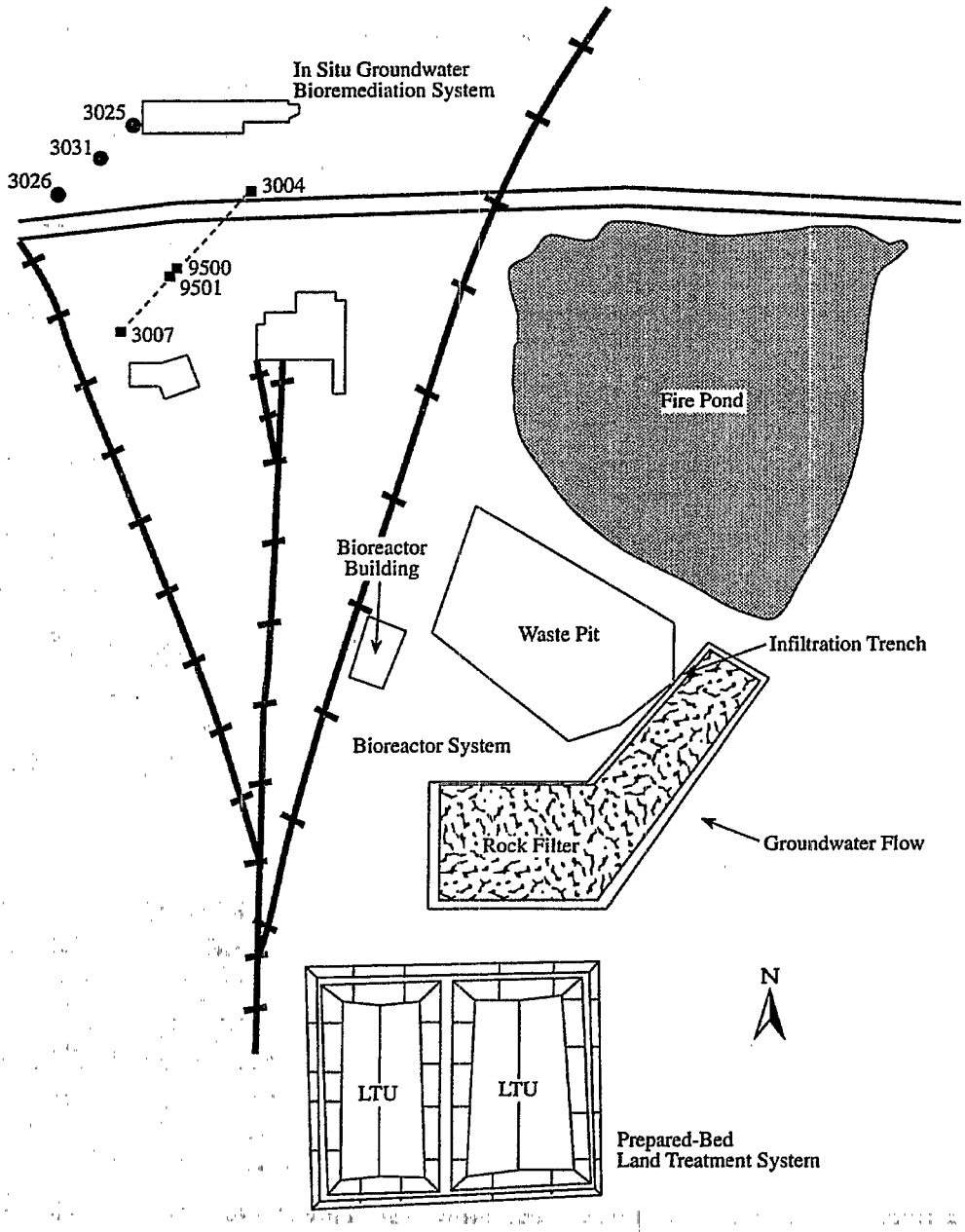
Capital Costs	
Soil Remediation	$230,700
SVE/Bioventing	$314,700
Passive Skimming	$115,000
Groundwater Extraction	
Groundwater Monitoring	$5,000
Groundwater Treatment	$10,000
Mobilization	$101,310
O&M Costs	
Soil Remediation	$55,000
SVE/Bioventing	$402,000
Passive Skimming	$100,000
Groundwater Extraction	
Groundwater Monitoring	$4,458,000
Groundwater Treatment	
Contingencies, Administrative, Engineering	**$616,708**
TOTAL PRESENT WORTH	**$6,408,418**

*Unit costs and present-worth calculation used in this cost estimate were taken from those presented in US EPA 1993. Present-worth calculations are made assuming an interest rate of 5% for an operating period of 30 years.

8.8 Land Treatment

An integrated bioremediation program has been implemented at the Champion International Superfund Site (Libby Site), a former wood-preserving facility in Libby, Montana. The design consists of a land treatment system to remediate contaminated soils, a groundwater extraction and aboveground treatment system to treat heavily-contaminated groundwater, and an oxygen injection system for in situ treatment of the contaminated aquifer (Figure 8.34). The land treatment system consists of two 4,050-m^2 (1-acre) prepared-bed land treatment units (LTUs), which have been operating since 1989. This case study details the design and analysis of pilot-scale and full-scale LTUs that have led to the successful biological treatment of wood-preserving waste-contaminated soils at this Superfund site.

Figure 8.34
Bioremediation Process Technologies Used at the Libby Site
(not to scale)



● Monitoring Wells
■ Injection Wells

Source: Sims et al. 1995a

8.8.1 Site Description

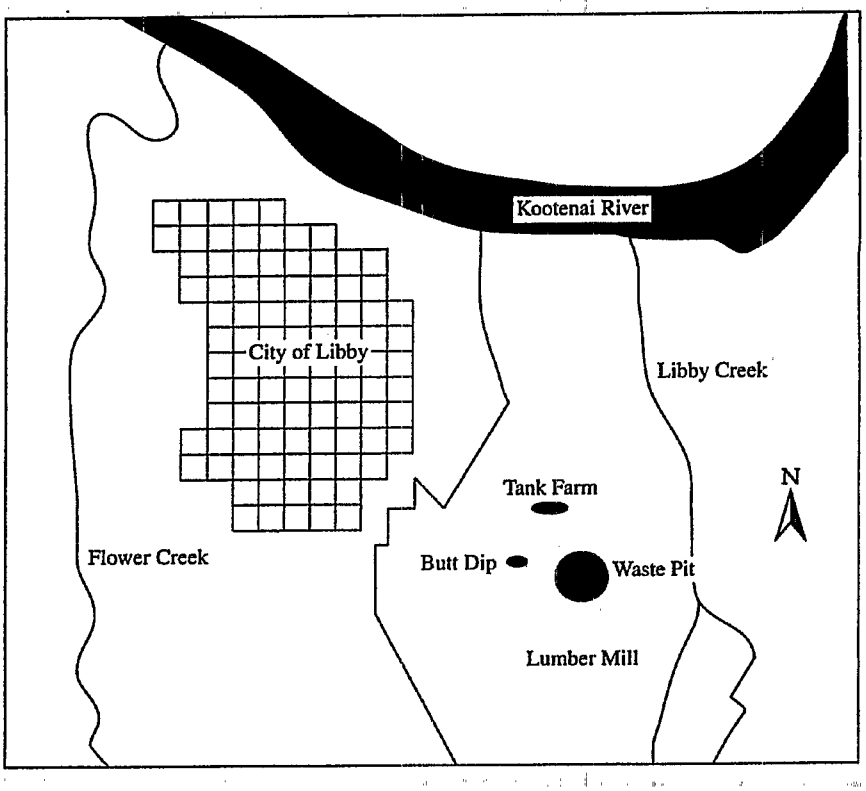
The Libby Site is an active lumber and plywood mill located southeast of the town of Libby in northwestern Montana. Contamination of soils at the Libby Site resulted from wood-preserving operations conducted from 1946 to 1969. Disposal of chemical wastes used in the wood-treating processes contaminated the soils around the mill and the underlying groundwater. Residual contamination consists primarily of creosote and pentachlorophenol (PCP) wood preservatives. Specific contaminants of most concern in soils at the site include:

- polycyclic aromatic hydrocarbons (PAH compounds), which are the primary components of creosote. PAH compounds are associated primarily with the soil solid phase by adsorption;
- PCP which is somewhat volatile and, in the ionized form, soluble in water; and
- dioxins, an impure component in technical-grade PCP. Dioxins are nonvolatile, highly insoluble in water, and closely associated with the soil solid phase.

Contaminated soils were located in three primary source areas at the Libby Site: (1) an unlined waste pit, where wastewater and sludges had been discharged during the operation of the pole-treating retort facility; (2) an unlined pole butt-dip area, where treating fluids had been spilled during operations; and (3) a former tank farm storage area, where treating fluids were accidentally spilled into the surrounding bermed area (Figure 8.35). In 1989, contaminated soils from these three areas (approximately 57,400 m^3 [75,000 yd^3] of materials) were excavated down to the water table. Before the tank farm and butt-dip areas were filled with clean soil, samples were collected and analyzed to verify that contamination had been removed.

Because the major contaminants of concern were expected to be associated with finer-grained materials, the soils excavated from the tank farm and butt-dip areas and the contaminated materials excavated from the waste pit area (a total of approximately 57,400 m^3 [75,000 yd^3] of soil and rock materials) were physically screened to remove rocks larger than 2.54 cm (1 in.) in diameter (referred to as de-rocking). The screened soils from all three areas (approximately 34,400 m^3 [45,000 yd^3] were placed in the excavated waste pit area. The separated rocks were placed upgradient to the waste pit area to construct sub-grade infiltration galleries. This rock percolation bed is used for biological treatment of the contaminated rocks using effluent from the above-grade, fixed-film bioreactor that is used to treat contaminated groundwater at the site.

Figure 8.35
Contamination Source Areas at the Libby Site
(not to scale)



Source: Sims et al. 1995a

Initial soil concentrations of contaminants of concern, expressed as a geometric mean, in the contaminated soils from all three areas were determined as follows:

- 189 mg/kg total carcinogenic PAH compounds;
- 29 mg/kg PCP; and
- 0.9×10^{-3} mg/kg tetrachloro-dibenzo-p-dioxin (2,3,7,8-TCDD) equivalency.

However, the concentrations of contaminants in the soils varied from sample to sample; the maximum concentrations for individual carcinogenic PAH compounds, PCP, and 2,3,7,8-TCDD equivalency were greater by factors from 6 to 90 than the geometric mean concentrations.

8.8.2 Initial Remedial Goals/Regulatory Environment

The contaminated surface soils at the Libby Site presented a potential public health threat via direct contact and ingestion. They were also of concern because they served as source materials for ongoing releases of contaminants to the groundwater. In 1979, Libby residents living near the mill began drilling wells for lawn irrigation after the public utility increased their water rates. Residents adjacent to the mill discovered creosote and PCP chemicals that discolored and caused odor in the water from their newly drilled wells.

In 1983, the US EPA placed the Libby Site on the National Priorities List as a result of the residents' concerns and initial investigations. In 1985, Champion International provided an alternative water supply to people whose wells were contaminated and conducted studies of the contamination problems, which included pilot-scale testing of remedial technologies. The City of Libby enacted a well permitting ordinance that prohibited new wells in the areas of contamination.

In 1988, a pilot-scale land treatment demonstration unit (LTDU), 24 m by 12 m (80 ft by 40 ft), was constructed with berms adjacent to the waste pit area (Piotrowski 1991). Baseline sampling of PAH and PCP concentrations in the soil layers below the LTDU was conducted. Approximately 46 m^3 (60 yd^3) of screened contaminated soil was placed on the unit and spread to a uniform depth of 15 cm (6 in.). Initial PAH and PCP concentrations were determined in this soil lift. The soil was periodically tilled and irrigated with a nutrient/microbial solution. Nutrients consisted of a dilute solution of inorganic nitrogen and phosphorus. The microorganisms used in the mix were isolated from the soils at the site and were grown as a mixed culture in 26.5-m^3 (7,000-gal) batches, with molasses as the organic growth substrate. Individual microbial species within the innoculum were not identified.

During the treatment period, soil pH and moisture content were monitored. Moisture adjustments were made as required; no pH adjustments were required. Triplicate, composited soil samples were collected monthly for three months to determine changes in contaminant levels in the soil lift during treatment. At the end of the study, soil layers below the LTDU were analyzed for PAH and PCP. Results were compared to the baseline data collected before a lift was placed on the LTDU to evaluate contaminant migration into the underlying soil during lift treatment.

After 100 days of treatment, large reductions in contaminant concentrations were achieved (Table 8.13). In addition, little vertical migration was observed below the LTDU, indicating that the contaminant reductions had been primarily the result of biodegradation. Monthly results showed that most of the biodegradation had occurred during the first 48 days of treatment.

Table 8.13
Summary of LTDU Results for Contaminant Concentrations in Treated Soil Over Time — 1988

Date	Concentrations[1] (mg/kg) PCP	Total PAH Compounds[2]	Carcinogenic PAH Compounds[3]
July 1	750 ± 292	785.6 ± 133.9	237.6 ± 47.8
August 17	90 ± 13	171.2 ± 15.4	137.1 ± 15.7
September 12	24 ± 8	96.0 ± 5.2	68.9 ± 6.9
October 10	22 ± 0	73.6 ± 1.9	62.8 ± 1.8
Percent Reduction (Overall)	97	91	74

1 Concentrations expressed as mean ± standard error of analytical results from three composite replicates collected on each date.
2 Total PAH compounds = Sum of concentrations of 16 priority pollutant PAH compounds.
3 Carcinogenic PAH compounds = Sum of concentrations of 12 of the 16 priority pollutant PAH compounds that are considered to be or are potentially carcinogenic.

Source: Woodward and Clyde 1990

Based on the results of the pilot-scale studies, in December 1988, the US EPA and the Montana Department of Health and Environmental Sciences signed a Record of Decision (ROD) that designated biological treatment as the remedial method for both soil and groundwater remediation. Target remediation levels (clean-up goals) for the contaminated soils (on a dry-weight basis), as specified in the ROD (US EPA 1988c), were:

- 88 mg/kg total carcinogenic PAHs [sum of fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene];
- 8 mg/kg naphthalene;
- 8 mg/kg phenanthrene;
- 7.3 mg/kg pyrene;
- 37 mg/kg PCP; and
- <0.001 mg/kg dioxin equivalency (sum of 2,3,7,8-TCDD-equivalent concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans).

During the summer of 1989, a full-scale land treatment demonstration was conducted to collect information on contaminant degradation rates, evaluate the potential for contaminants to migrate downward during treatment, and demonstrate that biodegradation was the major mechanism of contaminant loss. The first of two 4,050-m^2 (1-acre) LTUs was constructed (see Section 8.8.3, Design Approach). The 1989 demonstration involved sequential application and treatment of two 30.5-cm (12-in.) thick lifts of contaminated screened soil to the LTU (Piotrowski 1991; Woodward-Clyde Consultants 1989c). Each lift contained approximately 600 m^3 (800 yd^3) of soil.

The first lift had been biologically pretreated with periodic tilling and irrigation during storage in the former waste pit area before it was applied to the LTU. Results from treatment of this lift were anticipated to be representative of LTU performance under typical operating conditions. The second lift was freshly excavated and contained recognizable fragments of pure naphthalene crystals. Results from treatment of this lift were expected to be representative of LTU performance under "worst-case" conditions (Piotrowski 1991).

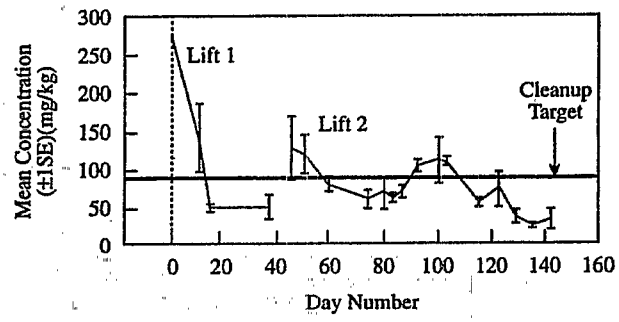
The first lift was applied in July 1989. The lift was periodically tilled and irrigated as necessary. No microbial solution was added. Composite soil samples were collected from four quadrants in the LTU every other week, and the samples were analyzed for PAH compounds and PCP. Leachate samples were also collected and analyzed when sufficient leachate accumulated. Groundwater samples were periodically collected from monitoring wells located up and downgradient from the LTU and analyzed for PAH compounds and PCP. Treatment of the first lift was continued for approximately 1 month, when analytical results indicated that target remediation levels had been achieved for all contaminants except pyrene (Figures 8.36 and 8.37).

The second lift was applied in August 1989. Treatment continued until early November (three months). Higher initial contaminant concentrations and cooler ambient fall temperatures may have increased the time required for treatment of the second lift over that required for the first lift (Figures 8.37 and 8.38).

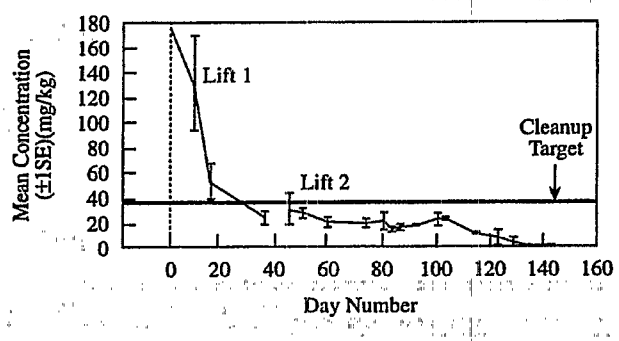
Leachate and groundwater analyses indicated that little contamination was migrating downward during land treatment. Similarly, qualitative investigations indicated that little contamination was volatilizing during tilling operations. In addition, appreciable numbers of total and viable microorganisms were counted in soil samples.

Figure 8.36
Mean Concentrations of Target Contaminants in Soils Treated in the LTU — 1989

A. Total Carcinogenic PAHs (Target remediation level: 88 mg/kg)



B. Pentachlorophenol (Target remediation level: 37 mg/kg)



Day Number 0 = June 21st
Day Number 50 = August 8th
Day Number 150 = November 10th

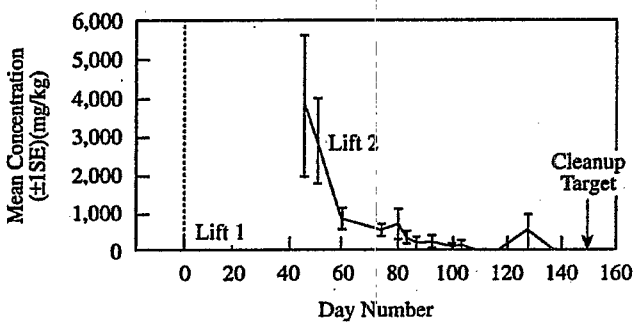
Error bar = ±1 standard error

Source: Piotrowski 1991

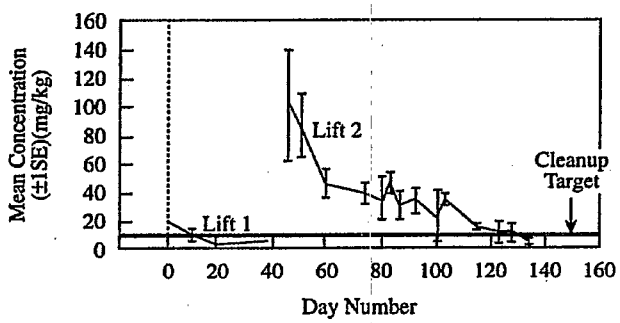
During operation of the LTU, researchers from Texas A&M University evaluated toxicity of the treated soils using the *Salmonella*/microsome bioassay (Ames test) (Donnelly et al. 1992). Soil samples from two lifts in Cell 1 and background samples from the surrounding areas were screened. One lift had undergone land treatment for three months and contaminant concentrations had reached remedial goals. The second lift had been treated for five weeks, but concentrations had not yet reached remedial goals. Results indicated that toxicity levels of the fully-treated lift samples were within the range of the values for the Libby background soil samples, while the toxicity

Figure 8.37
Mean Concentrations of Target Contaminants in Soils Treated in the LTU — 1989

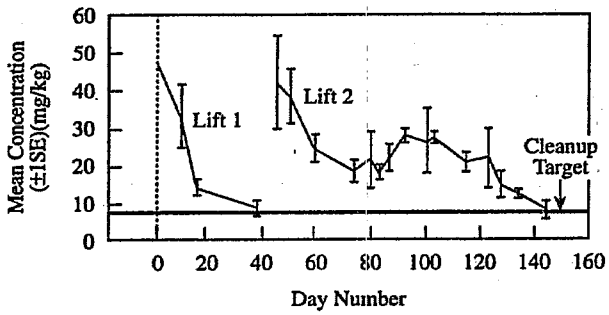
A. Naphthalene (Target remediation level: 8 mg/kg)



B. Phenanthrene (Target remediation level: 8 mg/kg)



C. Pyrene (Target remediation level: 7.3 mg/kg)

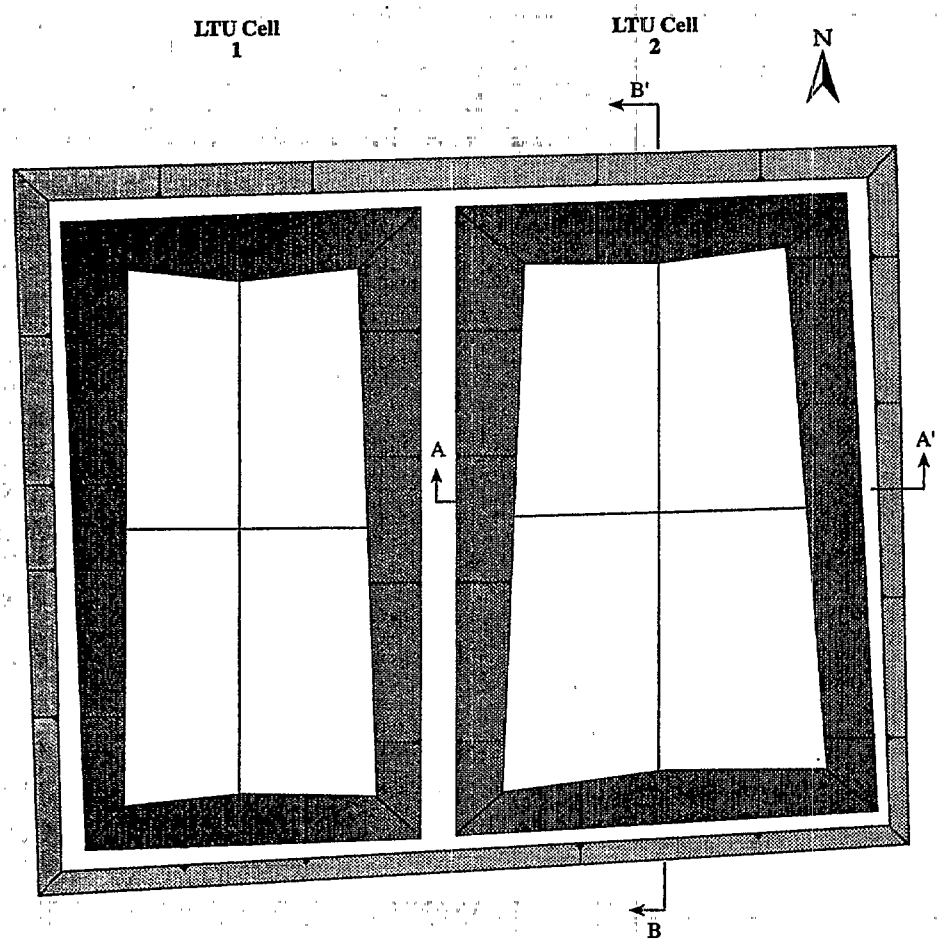


Day Number 0 = June 21st
Day Number 50 = August 8th
Day Number 150 = November 10th

Error bar = ±1 standard error

Source: Piotrowski 1991

Figure 8.38
Configuration of Treatment Cells Used in the LTU at the Libby Site



Source: Sims et al. 1995a

levels of the partially-treated lift samples were twice as high as background toxicity levels. The toxicity levels of the untreated waste pit soil samples were one to two orders of magnitude higher than toxicity levels in the treated soils. Therefore, biological treatment of the soil did not form intermediate breakdown products that were more toxic than the parent organic contaminants (Piotrowski et al. 1994).

Based on the results of the demonstration, a consent decree that required Champion International to use bioremediation as the selected remedial

technology was entered in federal district court in October 1989. Although US EPA had formally approved the plan, land disposal restrictions promulgated under the RCRA restricted application of the soils to land after August 8, 1990. Therefore, a "No-Migration Petition" (Woodward-Clyde Consultants 1989d, 1990) was filed with US EPA in February 1990, which included data from the demonstration conducted in 1989 that showed that no migration of contaminants would occur during treatment. The US EPA formally approved the petition in October 1990, and full-scale soil remedial activities commenced at the site in 1991.

8.8.3 Design Approach

The soil remediation program was designed to reduce organic contaminant concentrations to target levels that had been defined as acceptable from a regulatory perspective and to minimize risks to public health and the environment.

The location for construction of the two 4,050-m^2 (1-acre) LTU cells was selected based on previously existing site factors as well as possible future influences resulting from operation of the facility. Previously existing site factors that influenced selection of the LTU location included: (1) proximity to the contaminated soils to be treated; (2) company on-site operational constraints; and (3) soil and water quality analyses that indicated low level contamination of surface soil and subsurface environments.

Contaminated soils are treated in lifts (approximately 15 to 30 cm [6 to 12 in.] in thickness) in the designated LTU cell until target soil contaminant levels are achieved for a given lift. Degradation rates, amount (volume) of soil to be treated, initial contaminant concentration, duration of summer operational period, and LTU size determine the time required to remediate a given lift of contaminated soil. Based on an estimated 45-day time frame for remediation of each applied lift of contaminated soil to acceptable contaminant levels, an estimated volume of 34,400 m^3 (45,000 yd^3) of contaminated soil requiring remediation, and a 8,100-m^2 (2-acre) total LTU surface area, the time for completion of soil remediation was initially estimated to be 8 to 10 years.

Design criteria for each LTU cell include provisions for total containment of contaminated soils, water, and leachate, with ultimate treatment and disposal of all contaminated soils within the LTU.

8.8.3.1 Size

The lined, prepared-bed LTU is composed of two cells with a final surface area of 4,050m^2 (1 acre) each (Figures 8.38 and 8.39). The first cell was completed in 1989, while the second cell was constructed in 1991. The

surface area required was based on the estimated total quantity of material excavated from the source areas minus the quantity of materials greater than 2.54 cm (1 in.) in diameter removed during de-rocking since contaminants were expected to be associated with finer soil materials.

Each LTU cell is surrounded by a berm constructed with low-permeability soils that were compacted with a dozer. Incremental berm construction design allows modification of the LTU height to increase storage capacity as needed. At least 0.6 m (2 ft) of elevation difference is maintained between the top of the treatment zone and the top of the berms. The use of berms allows for containment, treatment, and ultimate disposal of additional contaminated soils if required. The berm was designed to control run-on and runoff associated with a 25-year, 24-hour storm event.

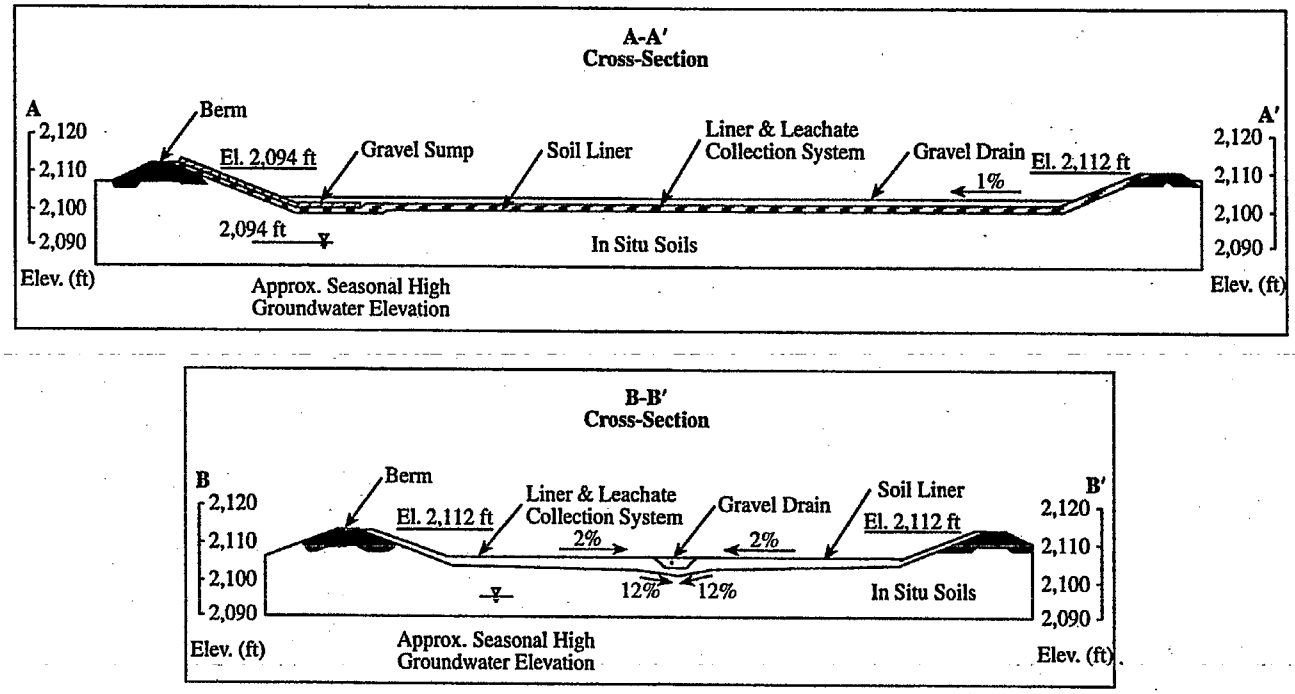
The LTU cells are each sloped to a central gravel drain (2% slope) to control water within the unit. The gravel drain also is sloped to a gravel sump (1% slope).

8.8.3.2 Treatment Zone

The treatment zone (i.e., the zone in which the contaminated soil is tilled and treated with moisture and nutrients) consists of a lower layer of sandy material (46 cm [18 in.]) supporting a top layer (30.5 cm [12 in.]) of silty material. The sandy material was collected on-site and consists of uncontaminated material meeting the Unified Soil Classification System (USCS) definition of SP-SM (poorly graded sands or gravelly sands and silty sands) or SM (silty sands). Maximum size is 1.3 cm (1/2 in.). The silty material consists of silts and/or clays collected from an on-site area and meets the USCS definition of ML (silts and very fine sands, silty or clayey fine sands, or clayey silts of low plasticity), ML-CL (silts and very fine sands, silty or clayey fine sands, or clayey silts of low plasticity with clays of low to medium plasticity or gravelly, sandy, or silty clays) or CL-ML (clays of low to medium plasticity or gravelly, sandy, or silty clays with silts and very fine sands, silty or clayey fine sands, or clayey silts of low plasticity). Standard filter criteria were used for material sizing between the treatment zone silty layer and sandy layer to reduce clogging potential.

The contaminated soil is placed on top of the sandy/silty layer and is actively treated through management activities. After reaching target remediation levels, additional lifts of contaminated soil are placed on previously-treated soils in the treatment zone.

Figure 8.39
Cross-Section of Treatment Cells Used in the LTU at the Libby Site
(not to scale)



Source: Sims et al. 1995a

8.8.3.3 Liner System

A liner system was designed to minimize migration of leachate that may be generated from treatment operations and that might otherwise continue downward through unsaturated zone soils into groundwater.

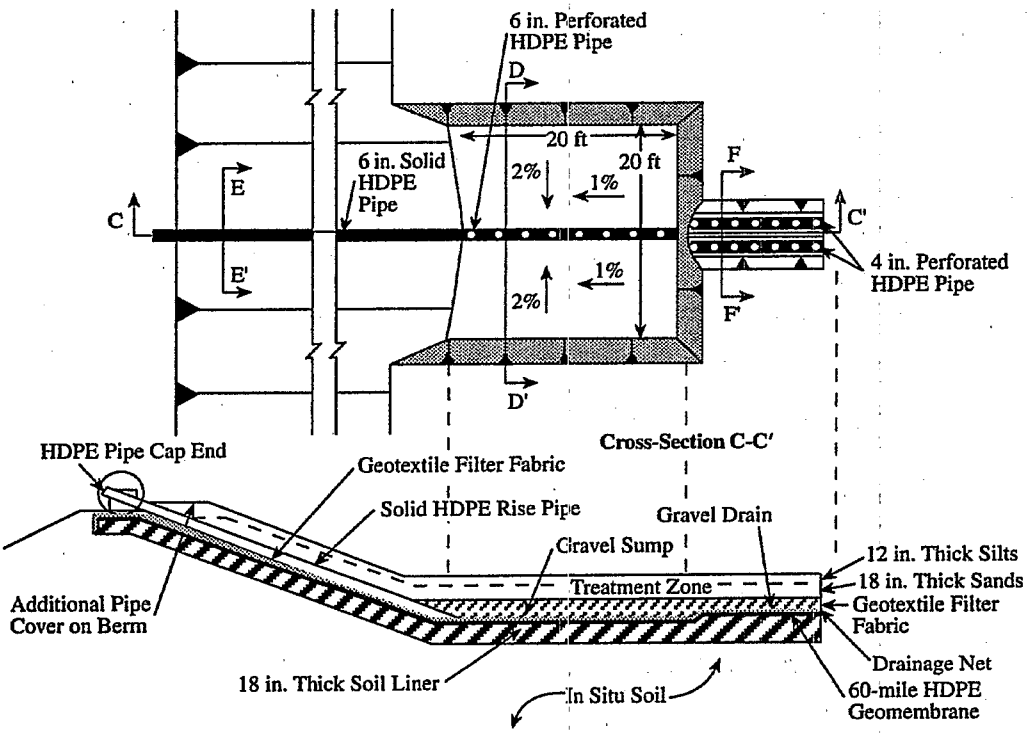
The underlying liner system for each LTU cell consists of a 60-mil synthetic flexible geomembrane liner placed on top of a compacted soil liner (46 cm [18 in.] thick) constructed from low-permeability ($5 \cdot 10^{-5}$ cm/sec) soils (glacial lake sediments) collected on-site. The compacted soil beneath the high density polyethylene (HDPE) liner was compacted to accomplish a maximum permeability of $5 \cdot 10^{-7}$ cm/sec. HDPE was chosen for the geomembrane liner due to its documented compatibility with most common wastes and waste byproducts. Leakage testing of the geomembrane liner was performed using electrical resistivity. This method involves flooding the lined facility and installing an electrical source in the water within the contained area and an electrode outside the unit to complete the electrical circuit. The intact geomembrane liner acts as a resistance to the imposed current, and any leaks can be detected using voltmeters to locate areas of high-current flows. Additional analysis of leakage through the liner under different scenarios of liner rupture was accomplished using the Hydrological Evaluation of Leachate Performance (HELP) model.

8.8.3.4 Leachate Collection System

The purpose of the leachate collection system is to prevent leachate from accumulating within the LTU and to monitor contaminant concentrations. The leachate collection system, including surface water pumping, subsurface drainage net, gravel drains, and collection pipes, is designed to collect leachate generated from two sources of water: (1) water applied during operation of the LTU, and (2) water from precipitation events. Leachate collected in the bottom of each cell is removed to minimize buildup of leachate (hydraulic head) on the liner system, thus reducing potential for leakage, and to prevent free water buildup in the LTU that could eventually lead to horizontal migration if the water levels were to exceed the top of the flexible membrane liner.

A drainage net (Tensar DN-3) covered by a geotextile filter fabric (Typar 3601) was placed over the geomembrane/soil liner system (Figures 8.40 and 8.41). Water filtration criteria were used to select the geotextile filter fabric in order to minimize migration of treatment zone sands from above into the drainage net, which could clog the leachate collection system.

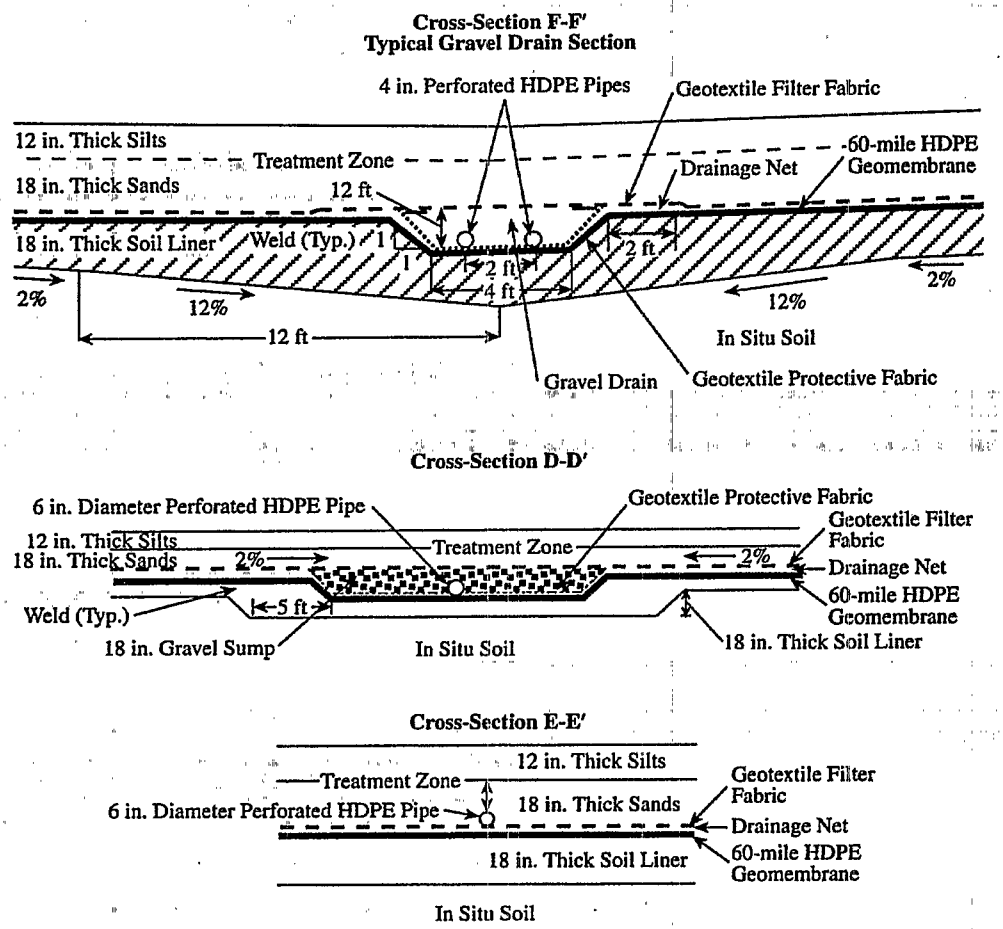
Figure 8.40
Geomembrane/Soil Liner System Used for Leachate Collection in the LTU at the Libby Site
(not to scale)



Source: Sims et al. 1995a

A gravel drain (30.5-cm [12-in.] thickness) was constructed along the entire length of the floor in each LTU cell. River gravels, which contain non-angular materials, were used in the drainage system to reduce puncture potential and to maintain liner integrity. A collection sump and sloping riser were constructed at the lowest point of the gravel drain (at the north end of each LTU cell, centered in the east-west direction). Two 10-cm (4-in.) diameter slotted HDPE pipes were wrapped in geotextile filter fabric and placed in the gravel drain which was sloped to the collection sump. The drain and sump were backfilled with gravel and completely enclosed in geotextile filter fabric. A single slotted 15-cm (6-in.) diameter pipe was located along the base of each sump and was connected to a solid 15-cm (6-in.) diameter HDPE pipe that rises upward along the interior slope of the north berm of each cell. This pipe provides access to the sump area for leachate removal.

Figure 8.41
Cross-Sections of Leachate Collection System Used in the LTU at the Libby Site (not to scale)



Source: Sims et al. 1995a

Leachate is removed from the leachate collection system sump area using an automated leachate collection pump and piping system (which can be overridden for manual control). The automated system ensures that a significant level of water will not collect in the sump area. Self-priming pumps located in a heated pump house are used for leachate removal. High- and low-level automatic pump activation switches were installed near the base of the HDPE pipe located in the sump for each cell. The level controls are

usually set so that 1 to 2 m^3 (300 to 600 gal) are pumped when the system is activated. The flow rate that is achieved is monitored using a flow meter located within the pump house. Discharge pipes installed below the frost depth carry leachate to two 190-m^3 (50,000-gal) storage tanks or to the bioreactor. These pipes are insulated and heat-taped where exposed.

Daily inspections of the pump removal system are made on regular work days. If failure should occur in the pumps or piping system, the system is repaired within one week to ensure continued removal of leachate from the LTU.

Surface water is managed by daily monitoring of the LTU during regular work days to see if significant amounts of water have collected on the surface of the LTU. The surfaces of the LTU cells are sloped so that surface water collects at the low point of the cells above the leachate collection sumps. If water collects to a sufficient depth to be pumped by a submersible pump, the water is promptly removed until the submersible pump is unable to continue pumping.

The recovered water is sprayed directly on the rock pad or injected into closed or open trenches. These disposal areas were selected because they should be able to handle the maximum design storm event, which is the 24-hour, 25-year storm of 6 cm (2.4 in.). This maximum design storm event could result in approximately 570 m^3 (150,000 gal.) over the 24-hour event being recovered from the 8,100-m^2 (2-acre) LTUs and associated haul roads. The trenches were tested at a 15.8-Lps (250-gpm) injection rate and were able to handle water discharged at this rate. The leachate collection pumps have a pumping rate of only 3 Lps (50 gpm), so the infiltration trenches should be able to handle the water being recovered from the LTU at this lower rate.

8.8.3.5 Leachate Storage Unit

Effluent in the two 190 m^3 (50,000 gal) storage tanks can be directed to: (1) the LTU cells for irrigation in the summer months; (2) the infiltration galleries/infiltration trench, where it can be amended with nutrients for use in the in situ aquifer bioremediation system; (3) to the rock pad; or (4) to open trenches. To prevent freezing of collected liquids in the storage tanks, the design incorporates a combination of electric immersion heating and sparging with warm, compressed air. In addition, all exposed piping is insulated.

8.8.3.6 Passive Moisture Control System

A passive moisture control system is installed within the LTU adjacent to the incremental berms to minimize the potential for soils to become

saturated in this area. The system consists of interconnected perforated HDPE pipes, wrapped in filter fabric and placed around the perimeter of the LTU. This drainage system drains water from areas adjacent to the berms and carries it to the treatment zone above the LTU sump where it is removed by the leachate collection system when it accumulates in excessive amounts.

8.8.4 Operations Description

The screened contaminated soils from the site that are stored in the waste pit area undergo a two-step enhanced biodegradation treatment process. The first step involves stimulation of biodegradation within the waste pit area by: (1) adding nutrients (approximately five times during a summer operational season); (2) tilling twice weekly; and (3) adding bioreactor effluent, fire pond water, or LTU leachate periodically to maintain a soil moisture level in the tilling zone of 8.5% by weight. This pretreatment is used to reduce initial contaminant levels for subsequent treatment in the prepared-bed, lined LTU. Soil samples are collected and analyzed periodically to monitor moisture levels in the waste pit area and to estimate moisture requirements for the LTU. No formal monitoring program is conducted to evaluate the effect of the pretreatment process on contaminant biodegradation rates in the soils in the waste pit area (Piotrowski et al. 1994).

The second step in the treatment process involves placement and management of the soils from the waste pit area in the two LTU treatment cells, which also serve as the final disposal location for the soils. Contaminated soils are placed in the LTU cells in 15- to 30-cm (6- to 12-in.) lifts for treatment during the summer. Moisture is applied to the LTU to maintain adequate moisture levels (approximately 40% to 70% of field capacity) in the treatment zone as well as for dust control. Additional lifts are placed on the LTUs when the total carcinogenic PAH and PCP concentrations in the treatment zone for the preceding lift are at or below target remediation levels.

Field capacity is measured in the field at least once per lift to assess the moisture-holding capacity of the soils and to define the target moisture levels corresponding to the desired 40% to 70% field capacity range. Field capacity is determined by wetting a small area (approximately 1.5 m by 1.5 m (5 ft by 5 ft) with fire pond water, covering the area with a plastic sheet, and waiting 48 hours before a sample is collected. For example, if the capacity as measured in the field is approximately 13% by weight, the soil moisture content in the LTU should be maintained at approximately 5% to 9% by weight. Weekly laboratory moisture measurements are made to calculate the amount of water to be applied to the LTU to reach the target level. To estimate moisture needs between weekly laboratory measurements, field

observations are made consisting of: (1) daily visual observations of the moisture content of the surface soils; (2) the soil moisture profile with depth; and (3) the amount of dust generated from the LTU operations. Additional moisture applied to the LTU is usually added immediately prior to tilling to control the generation of dust during tilling. The LTU cells are actively managed from approximately March to October each year.

Water sources for irrigation include the fire pond, bioreactor effluent, and LTU sump leachate. The water is applied manually to the LTU using a fire hose connected to irrigation piping that is located around the perimeter of the LTU. The application of water to the LTU depends on soil moisture levels in the treatment zone. Water application is limited during high moisture periods to minimize the volume of leachate produced in the LTU sump.

Nutrients (inorganic forms of nitrogen and phosphorus, usually ammonium sulfate and ammonium phosphate) are added to the LTU by dissolving them in water applied to the LTU or by fertilizers applied directly to the LTU. The amounts of nutrients added depends on nutrient requirements for optimizing biodegradation and the amount of total organic carbon (TOC), nitrogen, and phosphorus already existing in the soil. The nutrient requirement used for bioremediation optimization was selected as a carbon:nitrogen ratio in the soils of approximately 12-30:1 and a nitrogen:phosphorus ratio of approximately 10:1. The soil in the treatment zone is monitored periodically for TOC, total Kjeldahl nitrogen (TKN), and total phosphorus to estimate concentrations already existing in the soils. The amount of nitrogen and phosphorus to be added is estimated by subtracting the amounts of nitrogen and phosphorus existing in the soil from the nutrient requirement, and multiplying the remaining concentration by the estimated weight of the lift being treated. Because a significant percent of carbon measured by the TOC analysis may exist as ash or other unavailable forms of carbon, the use of TOC to estimate the amount of carbon in the soil should result in a larger amount of nutrients being applied to the LTU than that needed to enhance degradation. Nutrients are added as frequently as every other day depending on soil moisture and nutrient needs.

To enhance microbial activity by oxygenating the soils, the entire LTU is tilled frequently (at least weekly, if possible, but dependent on weather conditions) using a tractor-mounted rototiller or similar-type equipment. If the LTU contains ponded water after storms, tilling is suspended until the soil dries sufficiently for tilling. Deep tilling to promote biodegradation is used occasionally in the LTU if deeper soils with contaminant concentrations above the target remediation levels are detected. Deep tilling is continued until the lower zone has contaminant levels at or below the target

remediation levels specified in the ROD. If contaminants consistently migrate into underlying lifts, operation procedures can be modified by: (1) applying smaller lifts; (2) increasing tilling frequency; or (3) reducing moisture application.

Operation of the LTU, including the application of soil lifts, is discontinued during winter months. New lifts are not loaded near the end of the treatment year if contaminant levels are not expected to decrease substantially before the operation of the LTU is discontinued for the winter.

After all contaminated soils have been treated in the LTU, a protective cover will be installed and maintained over the total 8,100-m^2 (2-acre) treatment unit to minimize surface infiltration, erosion, and direct contact.

8.8.5 Routine Process Monitoring Procedures

The US EPA-mandated monitoring program involves periodic collection and analyses of leachate, soil, groundwater, and air samples both outside and within the treatment cells during operation and closure periods (Woodward-Clyde Consultants 1992). Post-closure care will include monitoring and inspection following placement of the cap at the end of the closure period.

8.8.5.1 Monitoring Outside the LTU

Monitoring systems in the vicinity of the LTU include groundwater and air sample collection systems. Background samples were collected before operation of the system began and analyzed to establish a baseline for evaluating data collected during LTU operation.

The groundwater monitoring system includes six wells (three downgradient, two upgradient, and one midway between the LTU and the waste pit area). The groundwater wells around the LTU are monitored semi-annually. Samples are analyzed at an off-site laboratory.

Periodic ambient air monitoring is conducted to: (1) characterize emissions that may be released to the atmosphere from operations at the unit; and (2) quantify ambient concentrations of the compounds to protect the health of the workers at the LTU. Dust is expected to be the principal contaminant of concern for the workers at the LTU. Dust is controlled primarily by applying moisture to the LTU before tilling. If, during tilling operations, dust generation becomes visible, additional moisture is applied to the LTU to suppress the dust and/or tilling operations are discontinued until weather conditions change such that dust generation is reduced.

Air quality parameters measured include gaseous and particulate PAH and PCP constituents. Air monitoring is performed shortly after loading during the day that initial tilling occurs. This initial sampling event for a lift provides worst-case data for emissions from the LTU because the highest concentrations should be present in the soils at that time. Two air samples are collected at 1.5 m (5 ft) above ground level on the berms adjacent to the LTU to monitor for contaminant migration. One sample station is placed directly upwind of the LTU, and a second sample station is placed directly downwind of the LTU so that both downwind and upwind air quality data are obtained. To place the samplers at the appropriate locations, the prevailing wind direction is monitored at an on-site meteorological monitoring station every two hours during the sampling period. If the wind direction changes during any of the 2-hour periods, the sampling stations are rotated so that they continue to monitor the upwind and downwind air quality of the LTU. The total sampling time of each collection period is approximately 6 hours. One sample is collected for PAH and PCP analysis at two locations (upwind and downwind) around the LTU to provide four samples (two PAH and two PCP) per collection period. A duplicate sample for PAH and PCP is collected from the berm expected to be the downgradient berm prior to tilling. This duplicate sample and one field blank, as well as the air samples collected from the monitors during tilling, are analyzed by an off-site laboratory for PAH compounds and PCP. Concurrent with ambient air sampling, 1-hour values for wind speed, wind direction, sigma θ (standard deviation of wind direction), and temperature are recorded at the on-site meteorological monitoring station. These data are used to evaluate air dispersion characteristics (i.e., atmospheric stability) during air monitoring.

Concentrations of PAH compounds and PCP measured in the air samples are compared to concentrations used for modeling in the No-Migration Petition (Woodward-Clyde Consultants 1989d) to determine if acceptable concentrations are present. More frequent samples are collected if the concentrations are unexpectedly high. If, after several years of monitoring, consistently low concentrations of PCP and PAH compounds are measured from the LTU, air monitoring will be discontinued upon approval by the regulatory agencies.

8.8.5.2 Monitoring Within the LTU

Monitoring systems within the LTU include systems to collect soil and leachate samples. Soil monitoring involves collecting, compositing, and analyzing of soil samples. Three types of soil samples are periodically collected from the LTU: (1) operational, (2) confirmation, and (3) compliance.

Operational samples are collected periodically to monitor the degradation of PCP and PAH compounds in the soils during the treatment of each contaminated soil lift. These samples are analyzed by the on-site laboratory and are used primarily for making operational decisions for the LTU. The samples consist of composite samples from each quadrant of the two LTU cells. Each sample is composited from four randomly-selected individual samples from within each quadrant. After the initial tilling of a newly-placed lift of contaminated soil in the LTU cells and application of soil moisture, composited soil samples from the uppermost lift of contaminated soil are collected from the four quadrants of each cell representing the lift and are analyzed for PCP and PAH compounds. Results from this sampling are used to characterize baseline contaminant levels and identify degradation rates in the LTU cells. After initial placement of a lift, samples are usually collected every two to five weeks. The sampling frequency is increased (up to one sample per week or less) when the soil concentrations in the treatment zone are near target remediation levels. Sample collection and analyses continue until samples from each quadrant are at or below the target remediation levels. After target levels are reached, a new lift may be loaded on the LTU.

After target remediation levels are achieved in the uppermost lift, an additional sample is collected in the next lowest lift to evaluate the potential for vertical migration of contaminants during treatment. The sample is collected under the quadrant of the uppermost lift that contained the highest level of contamination during treatment. The sample consists of a four-point composite sample, collected in the same manner as the other operational samples. The sample is analyzed for PCP and PAH compounds by the on-site laboratory. If PCP and PAH compounds exceed the target remediation levels, deep tilling of the two top lifts is performed until target remediation levels are achieved.

Other operational samples collected and analyzed include: (1) composited soil samples from the four soil quadrants to measure of TOC, TKN, and total phosphorus immediately after the placement of a lift to assess nutrient requirements; and (2) weekly soil moisture measurements to determine water application rates.

After the results of the operational samples have indicated that target contaminant remediation levels have been reached, a confirmation sample is collected from each quadrant from each lift treated and submitted to an off-site laboratory for confirmation analyses. These samples may be split samples from the last operational sample analyzed or collected separately. Each confirmation sample is a composite sample. Confirmation sampling

results are used to demonstrate that target remediation levels have been achieved and to establish the validity of operational sampling data. These sampling data are provided to the regulatory agency after receipt from the off-site laboratory.

Compliance samples are used to demonstrate that target remediation levels have been met. These samples consist of previously-collected confirmation samples (if the concentrations are at or below target remediation levels), or additional samples may be collected, if required. There are two types of compliance samples. The first type is a single-lift compliance sample. A minimum of four single-lift compliance samples (one from each quadrant) is obtained from each treated soil lift to demonstrate that target remediation levels established in the ROD for PCP, carcinogenic PAH compounds, naphthalene, phenanthrene, and pyrene have been met. Typically, these samples consist of previously-collected confirmation samples. The second type of compliance sample is a 3-lift sample for dioxin analysis. Four 3-lift dioxin compliance samples are collected from each LTU cell, one from each quadrant. The samples consist of soils collected from the full vertical interval of the three lifts applied during that treatment interval. For quality assurance/quality control (QA/QC) purposes, one duplicate split sample is collected for every four samples collected. The dioxin analysis is performed by an off-site laboratory. If dioxin is detected above the target remediation level in the three-lift compliance samples, an evaluation will be made to determine how to best address remedial goals. The results of the evaluation will be presented to the regulatory agency for approval.

The compliance samples analyzed by the off-site laboratory that meet the quality requirements outlined in the Quality Assurance Project Plan (QAPP) (Woodward-Clyde Consultants 1989a) are used to evaluate whether target remediation levels are achieved. Contaminant concentrations measured in each of the four samples (one from each quadrant) for each lift are compared to the target remediation levels specified in the ROD. Only when the contaminant concentrations for all four samples (not just the mean of the four samples) are at or below the target remediation levels for total carcinogenic PAH compounds, naphthalene, phenanthrene, pyrene, and PCP is that lift considered remediated.

At the end of each treatment year, additional composite samples from each lift placed in the unit during that year are collected and analyzed. If target contamination remediation levels are not met by the end of a given year for the composite samples of all lifts placed in an LTU cell that year, LTU operations are continued in the spring of the next year. No additional lifts are placed in that LTU cell until such levels are achieved.

Leachate monitoring involves collection of samples from LTU sumps on a quarterly basis and whenever leachate is produced during rainfall events. Samples are analyzed for PCP and PAH compounds by the on-site laboratory. If a visible oil phase is present in the sample, the sample is sent to an off-site laboratory for dioxin analysis. One duplicate sample is sent to the off-site laboratory annually for PAH and PCP analyses as a QA/QC measure for the on-site laboratory. If contaminant concentrations in the leachate are below US EPA detection limits for a period of 1 year, leachate monitoring will be reduced to twice annually. Sump sampling may not be possible if little or no leachate is recovered from the sump during a quarter. The sumps (one from each cell) are monitored each work day during operation of the LTU to evaluate if the leachate collection system is operating properly.

A quality assurance program, QAPP (Woodward-Clyde Consultants 1989a), was developed and is used to ensure appropriate analytical evaluation of soil, leachate, groundwater, and air samples.

8.8.6 Results of Monitoring Activities

Results of the US EPA-mandated monitoring program conducted by the site operators have shown that lift treatment times vary. Through 1992, the time required for active treatment of the soil contaminants to reach target remediation levels ranged from 32 to 163 days. The time requirement for a specific lift depended on initial concentrations of the contaminants in the lift, the time of year lift treatment was begun, rates of biodegradation achievable for the organic contaminants of concern, and climatic characteristics (temperature and precipitation) during lift treatment (Piotrowski et al. 1994).

The length of the time required for active treatment has generally been determined by the biodegradation rate of pyrene. Pyrene has been the most recalcitrant of the target contaminants with respect to reaching its remedial goal of 7.3 mg/kg as defined in the ROD. In 1991, pyrene levels in both LTU cells had not reached target levels before the onset of winter, so treatment had to be continued during spring 1992 before additional lifts could be added. From 1989 to 1992, pyrene required an average of 92 days of active treatment (i.e., periods when tilling and irrigation are performed, but not including periods when active treatment is suspended for the winter) to reach target remediation levels; carcinogenic PAH compounds required an average of 50 days; and PCP required an average of 43 days. Due to these longer-than-expected times required for active treatment, only one to two lifts per year have been added to the LTU cells rather than one lift every 45 days as designed. Originally predicted to require 8 to 10 years for cleanup,

treatment of the total volume of contaminated soil may require as long as 30 to 40 years at the current rate of application (Hurst 1996).

In cooperation with the US EPA Robert S. Kerr Environmental Research Center and Champion International, Utah State University (USU) conducted a comprehensive field evaluation of the prepared-bed land treatment system at the Libby Site as part of the US EPA Bioremediation Field Initiative (BFI) (Sims et al. 1993; Sims et al. 1994; Huling et al. 1995a, 1995b; Sims et al. 1995a, 1995b, 1995c). The BFI was established by the US EPA in 1990 to aid in the development of bioremediation as an effective remediation technology. An objective of the BFI was to obtain and disseminate field-based data and information from field experiences concerning the implementation and performance of bioremediation techniques.

Results of the USU study indicated that statistically significant decreases (α=0.05) in PCP and PAH compounds occurred at field scale as determined by both composite (routinely used for compliance monitoring) and discrete (used in the field performance evaluation) soil sampling (Sims et al. 1995a, 1995b, 1995c; Huling et al. 1995a, 1995b). Detoxification of the contaminated soil, as measured by the Microtox™ assay, also occurred in the same time frame as the degradation of the contaminants. No increase in toxicity in lower lifts was observed when highly-contaminated soil was applied over lifts that had previously undergone active treatment. This indicated that any vertical migration of water-soluble contaminants from the contaminated lifts had no negative effect on microbial activity in the underlying treated soil.

Additional studies at USU investigated potential design and management criteria to accomplish faster remediation of the contaminated soils in the prepared-bed land treatment system (Hurst et al. 1995a; Hurst 1996). The studies focused on management of oxygen at depth in the LTU. If an oxygen concentration of 2% by volume could be maintained in the soil atmosphere, biodegradation of PAH compounds and PCP was shown to continue. Therefore, continued treatment of soils in buried lifts at oxygen levels above 2% by volume may permit an increase in frequency of lift placement. With adequate oxygen, a new lift of contaminated soil could be placed in the prepared bed before concentrations of PAH compounds and PCP in the previous lift reached target remediation levels. Methods to maintain adequate oxygen levels in the lower layers require additional investigation.

8.8.7 Future Closure and Post-Closure Activities

Closure of the LTU cells will commence following treatment of all the contaminated soil stored in the waste pit area and completion of standard

LTU operations for both cells. Closure activities will be designed to provide long-term containment of disposed materials and protection of the environment. The LTU will be closed in a manner that: (1) minimizes the need for further maintenance and (2) controls, minimizes and eliminates, to the extent necessary to protect human health and the environment, the post-closure escape of hazardous waste, hazardous waste constituents, leachate, contaminated runoff, or waste decomposition products to the groundwater, the surface water, or the atmosphere. The closed facility will be monitored to detect any contaminant releases.

Criteria that will be used to initiate closure activities include: (1) little or no evidence of movement of organics beneath the treatment zone, (2) achievement of soil target remediation levels for all constituents, and (3) no detection of regulated contaminants in leachate samples for at least the last 2 years of facility operation. A regular program for tilling, watering, and maintaining the land treatment area will be conducted until the above criteria are met.

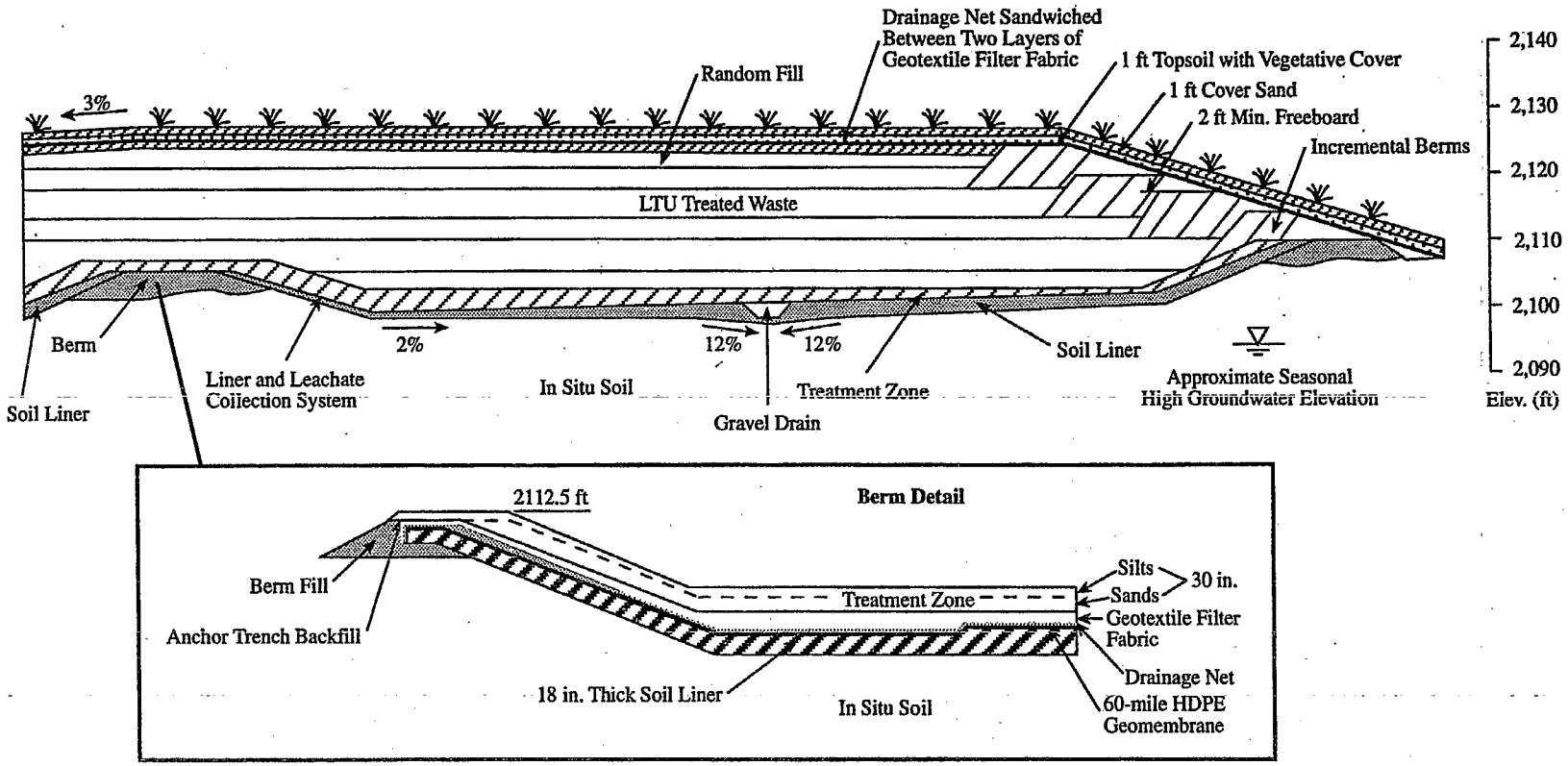
Groundwater monitoring will be continued through the closure period. Upgradient wells (two wells) and downgradient wells (four wells) will be sampled semi-annually for target constituents.

Random fill will be placed over the treated soil to prepare a minimum 3% grade from the crown of the LTU to the exterior berms (Figure 8.42). A 30-cm (12-in.) thick compacted soil layer will be placed above the random fill. A 30-mil HDPE geomembrane liner will be placed over the soil layer, and a 30-cm (12-in.) thick layer of cover sand in a single lift will be added to protect the geomembrane. A 30-cm (12-in.) thick layer of topsoil will be placed above the cover sand. The topsoil will be used to establish a vegetative cover of native plants to prevent erosion of the cover system.

The side-slope of the cover system will consist of a drainage net (Tensar DN-3 geonet) between two Typar 3601 filter fabrics placed above the exterior of the incremental and LTU-containment berm graded to a 3:1 (horizontal to vertical) slope. A 30-cm (12-in.) thick layer of cover sand will be placed above the drainage net and filter fabrics; a 30-cm (12-in.) thick layer of topsoil will be placed above the cover sand. A vegetative cover will be planted in the topsoil layer.

It has been proposed that if Criterion (3) above is met at the end of the LTU operational period, the following actions will be taken: (1) the cover system will be redesigned to exclude the flexible geomembrane and drainage net; and (2) the HDPE liner at the bottom of the LTU cells will be punctured in the sump areas, allowing the leachate to gravity drain to avoid any "bathtub" water accumulation in the system.

Figure 8.42
LTU Waste Placement and Final Cover Designs Used at the Libby Site
(not to scale)



Source: Sims et al. 1995a

Final grading of the facility will maintain the berms surrounding the LTU at a sufficient height to control run-on, runoff, and wind dispersal. The berm will be raised with uncontaminated fill to contain the 25-year, 24-hour storm event.

Post-closure care will continue for at least 5 years, to be terminated after the fifth year if target constituents in the soils, groundwater, and leachate are not detected above target remediation levels. The post-closure care period may be extended to 30 years if significant concentrations of target constituents are detected.

Primary post-closure activities include continued inspection and maintenance of the facility. The vegetative cover, run-on/runoff control system, and LTU sumps will be inspected on a monthly basis or after any major storm. The vegetative cover will be selected to adapt to the climate at the site; therefore, after the first post-closure year, irrigation will be discontinued. Access to the facility will be restricted by the company security system and fencing around the site.

8.8.8 Costs

Construction of the two LTUs at the Libby Site cost approximately $400,000. In 1992, the annual operation and maintenance costs of the land treatment system were estimated to be $117,000.

8.8.9 Lessons Learned

The remedial action design at the Libby Site was based on known biological principles and was demonstrated at the site to be effective in permanently destroying the contaminants of concern. The technology was proven during a pilot study conducted at the site prior to completion of the feasibility study. The success of the pilot study, conducted prior to the ROD (US EPA 1988c) provided federal and state regulators with the confidence needed to approve the use of bioremediation. Full-scale facilities were constructed and operated as LTDUs during the first 2 years after the ROD. The demonstration provided information required to develop reliable and cost-effective remedial designs.

A

CONTAMINANTS COMMONLY FOUND AT SUPERFUND SITES

A.1 List of Contaminants
A.2 Property Ratings of Chemical Classes
A.3 Properties

Table A.1
Contaminants Commonly Found at Superfund Sites

Halogenated Volatile Organics	Non-Halogenated Volatile Organics	Halogenated Semivolatile Organics	Non-Halogenated Semivolatile Organics	Inorganics
Liquid Solvents	***Ketones/Furans***	***PCBs*** (b)	***PAHs*** (e)	Arsenic (As)
Carbon Tetrachloride	Methyl Ethyl Ketone	Aroclor 1242	Acenaphthene	Cadmium (Cd)
Chlorobenzene	4-Methyl-2-Pentanone	Aroclor 1254	Anthracene	Chromium (Cr)
Chloroform	Tetrahydrofuran	Aroclor 1260	Benzo(a)anthracene	Cyanide (CN)
Cis-1,2-dichloroethylene (d)	***Aromatics***		Benzo(a)pyrene	Lead (Pb)
1,1-Dichloroethane (a)	Benzene (g)	***Pesticides***	Benzo(b)fluoranthene	Mercury (Hg)
1,2-Dichloroethane	Ethyl Benzene (g)	Chlordane	Benzo(ghi)perylene	Selenium (Se)
1,1-Dichloroethylene	Styrene	DDD	Benzo(k)fluoranthene	Iron (Fe) ‡
1,2-Dichloropropane (a)	Toluene (g)	DDE	Chrysene	
Ethylene Dibromide (g)	m-Xylene (g)	DDT	Dibenz(a,h)anthracene	
Methylene Chloride	o-Xylene (g)	Dieldrin	Fluoranthene	
1,1,2,2-Tetrachloroethane	p-Xylene (g)		Fluorene	
Tetrachloroethylene		***Chlorinated Benzenes***	Indeno(1,2,3-cd)pyrene	
Trans-1,2-dichloroethylene (d)		1,2-Dichlorobenzene	2-Methyl naphthalene	
1,1,1-Trichloroethane		1,4-Dichlorobenzene	Naphthalene	

1,1,2-Trichloroethane

Trichloroethylene

Gases

Chloroethane

Vinyl Chloride

Chlorinated Phenols

Pentachlorophenol (w)

2,3,4,6-Tetrachlorophenol

Phenanthrene

Pyrene

Non-Chlorinated Phenols

m-Cresol (e)

o-Cresol (e)

p-Cresol (e)

2,4-Dimethylphenol (e)

2,4-Dinitrophenol

Phenol

(a) = may be component of antiknock fluids added to fuel oils
(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
NOTE: Some contaminants listed may be present in subsurface as biological or chemical degradation products of others
‡ = Although not normally 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.

Table A.2
Property Ratings of Chemical Classes Commonly Found at Superfund Sites (from Table A.1)

Chemical Class	Melting Point	Water Solubility	Vapor Pressure	Henry's Law Constant	Density	Dynamic Viscosity	Kinematic Viscosity	Log K_{ow}	Log K_{oc}	Aerobic Biodegrad-ability	Potential Subsurface Mobility
Halogenated Volatile Organics											
Liquid Solvents*	low	moderate/ high	high	moderate/ high	high	†	†	low/ moderate	low/ moderate	†	moderate/ high
Gases	low	high	high	high	low	NA	NA	low	low	ND	high
Nonhalogenated Volatile Organics											
Ketones/furans	low	high	high	moderate	low	low	moderate	low	low	ND	high
Aromatics	low	moderate/ high	high	high	low	moderate	moderate/ high	moderate	moderate	high	moderate
Halogenated Semivolatile Organics*											
PCBs	low	low	low	moderate	high	ND	ND	high	high	low	low
Pesticides	high	moderate	low	low/ moderate	low/ high	NA	NA	high	high	low	low
Chlorinated Benzenes	low/ moderate	moderate	moderate	high	high	high	high	moderate	moderate	high	moderate
Chlorinated Phenols	moderate/ high	moderate	low[P]	low[P]	high	NA	NA	high	high[P]	high[P]	low
Non-Halogenated Semivolatile Organics											
PAHs	moderate/ high	low/ moderate	moderate/ low	†	high	NA	NA	high	high	moderate	low
Non-Chlorinated Phenols	moderate	high	moderate/ low	low/ moderate	high	high/ NA	high/ NA	low	low	high	high
Inorganics											
Se, As, CN Cr (VI)											high**
For detailed information on subsurface transport and fate behavior for these chemicals, see Table A.3.											
Hg, Pb, Cd, Cr (III)											low**

Qualitative Rating Key

Rating	Melting Point (°C)	Water Solubility (mg/L)	Vapor Pressure (mm Hg)	Henry's Law Constant (atm-m³/mol)	Density (g/cc)	Dynamic Viscosity (centi-poise)	Kinematic Viscosity (centi-stokes)	Log K_{ow}	Log K_{oc}	Aerobic Biodegrad-ability	Potential Subsurface Mobility¥
Low	≤13.00	≤1.00 E+00	≤1.00 E-03	≤1.00 E-05	<1#	<0.6	<0.4	<2.5	≤2.2	very slow or negligible	log K_{oc}>3.2
Moderate	>13.00	>1.00 E+00	>1.00 E-03	>1.00 E-05	=1	≥0.6	≥0.4	≥2.5	>2.2	moderate	2.2 < log K_{oc}≤3.2
	≤100.00	<1.00 E+03	≤1.00 E+00	≤1.00 E-03		≤1.0	≤0.8	≤3.5	≤3.2		
High	>100.00	≥1.00 E+03	>1.00 E+00	>1.00 E-03	>1*	>1.0	>0.8	>3.5	>3.2	rapid	log K_{oc}≤2.2

‡ = This key applies only to the list of chemicals given in Table A.1 and rated in Table A.2
¥ = Applies to organic compounds only
Moderate/high = Indicates that most compounds within the chemical class have a high rating for the given property but that a few have a moderate rating; see Table A.3 for compound specific values
Moderate/high = Indicates that some compounds within the chemical class have a high rating and some have a moderate rating for the given property; see Table A.3 for compound specific values
NA = Not applicable because compounds in chemical class are not liquids at room temperature
ND = No data found or available
p = Applies to pentachlorophenol only
# = Compounds within chemical class may be present in subsurface as light non-aqueous phase liquid (LNAPL), often floating on the water table
* = Compounds within chemical class may be present in subsurface as dense non-aqueous phase liquid (DNAPL); recovery of DNAPL from the saturated zone will be difficult if the DNAPL is spatially discontinuous within the aquifer
** = Se, As, Hg, Pb, and CN may be present in volatile forms which enhance their mobility; see Table A.3 for additional information
† = See Table A.3

Table A.3
Properties of Contaminants Commonly Found at Superfund Sites

Chemical	Melting Point (°C)	Water† Solubility (mg/L)	Vapor† Pressure (mm Hg)	Henry's Law† Constant (atm-m^3/mol)	Density† (g/cc)	Dynamic† Viscosity (cp)	Kine-matic† Viscosity (cs)	Log K_{ow}	Log K_{oc}	Aerobic Biodegrad-ability	MCL[17] (µg/L)
Halogenated Volatile Organics											
Liquid Solvents											
Carbon Tetrachloride	-23[7]	8 E+02[1]	9.13 E+01[1]	2 E-02[1]	1.5947[1]	0.965[1]	0.605(c)	2.83[1]	2.64[1]	D[2]	5(f)
Chlorobenzene	-45[7]	4.9 E+02[1]	8.8 E+00[1]	3.46 E-03*[1]	1.106[1]	0.756[1]	0.683(c)	2.84[1]	2.2[1]	D5,A10[2]	100(p)
Chloroform	-64[7]	8.22 E+03[1]	1.6 E+02[1]	3.75 E-03*[1]	1.485[1]	0.563[1]	0.379(c)	1.97[1]	1.64[1]	A[2]	nd
Cis-1,2-dichloroethylene(d)	-81[7]	3.5 E+03[1]	2 E+02*[7]	7.5 E-03*[1]	1.284[1]	0.467[1]	0.364(c)	1.86[1]	1.5[1]	B[2]	70(p)
1,1-Dichloroethane(a)	-97.4[7]	5.5 E+03[1]	1.82 E+02[1]	5.7 E-03*[1]	1.175[1]	0.377[1]	0.321(c)	1.79[1]	1.48[1]	A[2]	nd
1,2-Dichloroethane	-35.4[7]	8.69 E+03[1]	6.37 E+01[1]	1.1 E-03*[1]	1.253[1]	0.84[1]	0.67(c)	1.48[1]	1.15[1]	B[2]	5(f)
1,1-Dichloroethylene	-122.5[7]	4 E+02[1]	5 E+02[1]	1.54 E-01*[1]	1.214[1]	0.33[1]	0.27(c)	2.13[1]	1.81[1]	A[2]	7(f)
1,2-Dichloropropane(a)	-90[7]	2.7 E+03[1]	3.95 E+01[1]	3.6 E-03*[1]	1.158[1]	0.84[1]	0.72(c)	2.02[1]	1.71[1]	A[2]	5(p)
Ethylene Dibromide(g)	9.97[7]	3.4 E+03[1]	1.1 E+01[1]	3.18 E-04[1]	2.172[1]	1.676[21C][1]	0.79[3]	1.76[1]	1.45[1]	nd	0.05(p)
Methylene Chloride	-97[7]	1.32 E+04[1]	3.5 E+02[1]	2.57 E-03*[1]	1.325[1]	0.43[1]	0.324(c)	1.25[1]	0.94[1]	D[2]	5(f)

1,1,2,2-Tetrachloroethane	-43 [7]	2.9 E+03 [1]	4.9 E+00 [1]	5 E-04 * [1]	1.600 [1]	1.77 [1]	1.10 (c)	2.39 [1]	2.34 [1]	N [2]	nd
Tetrachloroethylene	-22.7 [7]	1.5 E+02 [1]	1.4 E+01 [1]	2.27 E-02 * [1]	1.625 [1]	0.89 [1]	0.54 (c)	3.14 [1]	2.82 [1]	A [2]	5 (p)
Trans-1,2-dichloroethylene (d)	-50 [7]	6.3 E+03 [1]	2.65 E+02 [3]	6.6 E-03 * [1]	1.257 [1]	0.404 [1]	0.321 (c)	2.09 [1]	1.77 [1]	B [2]	70 (p)
1,1,1-Trichloroethane	-32 [7]	9.5 E+02 [1]	1 E+02 [1]	2.76 E-03 * [1]	1.325 [1]	0.858 [1]	0.647 (c)	2.49 [1]	2.18 [1]	C [2]	200 (f)
1,1,2-Trichloroethane	-36 [7]	4.5 E+03 [7]	1.88 E+01 [3]	1.17 E-03 ‡ [11]	1.4436 [5]	0.119 [3]	0.824 (c)	2.17 [4]	1.75 [13]	C [2]	nd
Trichloroethylene	-87 [7]	1 E+03 [1]	5.87 E+01 [1]	8.92 E-03 * [1]	1.462 [1]	0.570 [1]	0.390 (c)	2.42 [1]	2.10 [1]	A [2]	5 (f)
Gases											
Chloroethane (b.p. 12.5 C)	-138.3 [7]	5.7 E+03 [1]	1 E+03 [1]	1.1 E-02 [1]	0.9414 0C [1]	na	na	1.43 [1]	1.17 [1]	nd	nd
Vinyl Chloride (b.p. -13.9 C)	-157 [7]	1.1 E+03 [1]	2.3 E+03 [1]	6.95 E-01 [1]	0.9121 15C [3]	na	na	0.60 [4]	0.91 [1]	nd	2 (f)
Non-Halogenated Volatile Organics											
Ketones/furans											
Methyl Ethyl Ketone	- 86.4 [7]	2.68 E+05 [11]	7.12 E+01 [3]	2.74 E-05 ‡ [11]	0.805 [5]	0.40 [3]	0.497 (c)	0.29 [17]	0.65 [11]	nd	nd
4-Methyl-2-Pentanone	- 83 [7]	1.9 E+04 [3]	1.6 E+01 [3]	1.55 E-04 ‡ [13]	0.8017 [7]	0.5848 [3]	0.729 (c)	1.25	1.38 [15]	nd	nd

Table A.3 (cont.)
Properties of Contaminants Commonly Found at Superfund Sites

Chemical	Melting Point (°C)	Water† Solubility (mg/L)	Vapor† Pressure (mm Hg)	Henry's Law† Constant (atm-m³/mol)	Density† (g/cc)	Dynamic† Viscosity (cp)	Kinematic† Viscosity (cs)	Log K_{ow}	Log K_{oc}	Aerobic Biodegradability	MCL[17] (µg/L)
Tetrahydrofuran	-108.5 [7]	3 E+05 * [6]	4.56 E+01 ‡[4]	1.1 E-04 ‡[14]	0.8892 [6]	0.55 [13]	0.618 (c)	0.46 [14]	nd	nd	nd
Aromatics											
Benzene (g)	5.5 [7]	1.78 E+03 [1]	7.6 E+01 [1]	5.43 E-03 *[13]	0.8765 [1]	0.6468 [1]	0.7379 (c)	2.13 [1]	1.81 [1]	D[2]	5(f)
Ethyl Benzene (g)	-94.97 [7]	1.52 E+02 [1]	7 E+00 [1]	7.9 E-03 * [1]	0.867 [7]	0.678 [3]	0.782 (c)	3.15 [1]	2.83 [1]	D5,A10 [2]	700 (p)
Styrene	-30.6 [7]	3 E+02 [7]	5 E+00 [7]	2.28 E-03 [7]	0.9060 [13]	0.751 [13]	0.829 (c)	3.16 [14]	nd	nd	nd
Toluene (g)	-95.1 [7]	5.15 E+02 [1]	2.2 E+01 [1]	6.61 E-03 *[13]	0.8669 [1]	0.58 [1]	0.669 (c)	2.73 [1]	2.41 [1]	D[2]	2000 (p)
m-Xylene (g)	-50 [7]	2 E+02 [3]	9 E+00 [1]	6.91 E-03 *[1]	0.8642 * [1]	0.608 [1]	0.717 [3]	3.20 [1]	2.84 [1]	nd	10000 (p)
o-Xylene (g)	-25 [7]	1.7 E+02 [3]	7 E+00 [1]	4.94 E-03 *[1]	0.880 *[1]	0.802 [1]	0.932 [3]	3.12 [1]	2.84 [1]	nd	10000 (p)
p-Xylene (g)	13 [7]	1.98 E+02 *[3]	9 E+00 [1]	7.01 E-03 *[1]	0.8610 * [1]	0.635 [1]	0.753 [3]	3.15 [1]	2.84 [1]	nd	10000 (p)
Halogenated Semivolatile Organics											
PCBs (b)											
Aroclor 1242	-19 [1]	4.5 E-01 * [1]	4.06 E-04 *[9]	3.4 E-04 [1]	1.385 [1]	nd	nd	5.58 [9]	5 [1]	N[2]	nd

Aroclor 1254	10 [1]	1.2 E-02 [1]	7.71 E-05*[9]	2.8 E-04 [1]	1.538‡[9]	nd	nd	6.03 [9]	nd	N[2]	nd
Aroclor 1260	nd	2.7 E-03 [1]	4.05 E-05*[9]	3.4 E-04 [1]	1.44 30C[1]	nd	nd	7.15 [9]	nd	N[2]	nd
Pesticides											
Chlordane	106 [1]	5.6 E-02 *[1]	1 E-05 [1]	2.2 E-04 *[1]	1.6*[1]	1.104 [3]	0.69 (c)	5.48 [1]	4.58 [1]	N[2]	2(p)
DDD	112 [7]	1.60 E-01 24C[7]	1 E-06 30C[17]	7.96 E-06‡[11]	1.385 [17]	na	na	5.56 [1]	5.38 [1]	M [2]	nd
DDE	88.4 [1]	4.0 E-02 [7]	6.40 E-06 [1]	1.9 E-04 *[1]	nd	na	na	5.69 [1]	5.41 [1]	M [2]	nd
DDT	108 [7]	3.1 E-03 [1]	1.5 E-07 [1]	2.8 E-05 *[1]	0.985 [1]	na	na	6.36 [1]	5.48 [1]	M [2]	nd
Dieldrin	176.5 [7]	1.86 E-01‡[4]	1.78 E-07 [3]	9.7 E-06 *[8]	1.75 [3]	na	na	5.34 [4]	3.23 [14]	N[2]	nd
Chlorinated Benzenes											
1,2-Dichlorobenzene	-17 [7]	1 E+02 [1]	9.6 E-01 [1]	1.88 E-03*[1]	1.306 [1]	1.302 [1]	0.997(c)	3.38 [1]	3.06 [1]	T [2]	600(p)
1,4-Dichlorobenzene	53 [7]	8 E+01 [1]	6 E-01 [1]	1.58 E-03*[1]	1.2475 [1]	1.258 [1]	1.008(c)	3.39 [1]	3.07 [1]	T [2]	750(c)

Table A.3 (cont.)
Properties of Contaminants Commonly Found at Superfund Sites

Chemical	Melting Point (°C)	Water† Solubility (mg/L)	Vapor† Pressure (mm Hg)	Henry's Law† Constant (atm-m³/mol)	Density† (g/cc)	Dynamic† Viscosity (cp)	Kine-matic† Viscosity (cs)	Log K_{ow}	Log K_{oc}	Aerobic Biodegrad-ability	MCL[17] (µg/L)
Chlorinated Phenols											
Pentachlorophenol[w]	190[7]	1.4 E+01[1]	1.1 E-04[1]	2.8 E-06[1]	1.978[1]	na	na	5.12[1]	4.80[1]	A[2]	nd
2,3,4,6-Tetrachlorophenol	69.5[7]	1.00 E+03‡[11]	nd	nd	1.839*[5]	na	na	4.1[11]	2.0[11]	nd	nd
Non-Halogenated Semivolatile Organics											
PAHs[e]											
Acenaphthene	92.5[7]	3.88 E+00*[8]	2.31 E-02*[8]	1.20 E-03*[c]	1.225[12]	na	na	3.92[12]	3.7[11]	D[2]	nd
Anthracene	216.3[7]	7.5 E-02*[8]	1.08 E-05*[8]	3.38 E-05*[c]	1.25[12]	na	na	4.45[12]	4.1[11]	A[2]	nd
Benzo (a)anthracene	167[4]	1.4 E-02*[12]	1.16 E-09‡[11]	4.5 E-06[12]	1.174[12]	na	na	5.61[12]	6.14[11]	N[2]	nd
Benzo (a)pyrene	179[7]	3.8 E-03‡[12]	5.49 E-09*[18]	1.8 E-05‡[12]	nd	na	na	6.06[11]	6.74[11]	nd	0.2[t]
Benzo(b)fluoranthene	167[4]	1.4 E-02‡[11]	5.00 E-07‡[12]	1.19 E-05‡[11]	nd	na	na	6.57[12]	5.74[11]	nd	nd
Benzo(ghi)perylene	278[12]	2.6 E-04*[7]	1 E-10[14]	5.34 E-08‡[11]	nd	na	na	6.51[11]	6.2[11]	nd	nd
Benzo(k)fluoranthene	217[12]	4.30 E-03‡[11]	9.59 E-11[14]	3.94 E-05‡[11]	nd	na	na	6.06[11]	5.74[11]	nd	nd

Chrysene	254 [7]	6 E-03 * [7]	6.3 E-09* [14]	1.05 E-06* [14]	1.274 [7]	na	na	5.61 [11]	5.3 [11]	A5,N10 [2]	nd
Dibenz(a,h)anthracene	266.5 [7]	2.5 E-03 ‡[12]	1 E-10 ‡[12]	7.33 E-08‡[11]	1.252 [12]	na	na	6.80 [11]	6.52 [11]	nd	nd
Fluoranthene	107 [7]	2.65 E-01 *[7]	E-02 [10] E-06 [12]	6.5 E-06 *[14]	1.252 [12]	na	na	4.90 [12]	4.58 [11]	A5,N10 [2]	nd
Fluorene	116.7 [12]	1.90 E+00 *[8]	6.67 E-04 *[8]	7.65 E-05 *[c]	1.203 [12]	na	na	4.18 [12]	3.9 [11]	A [2]	nd
Indeno(1,2,3-cd)pyrene	163 [12]	5.30 E-04‡[11]	1 E-10 ‡[11]	6.95 E-08 *[14]	nd	na	na	6.5 [11]	6.2 [11]	nd	nd
2-Methyl naphthalene	34.58 [7]	2.54 E+01 *[8]	6.80 E-02 *[8]	5.06 E-02 *[c]	1.0058 [12]	na	na	3.86 [12]	3.93 [14]	nd	nd
Naphthalene	80.2 [4]	3.1 E+01 *[12]	2.336 E-01 *[12]	1.27 E-03 *[c]	1.162 [12]	na	na	3.30 [12]	3.11 [14]	D [2]	nd
Phenanthrene	100 [7]	1.18 E+00 *[8]	2.01 E-04 *[8]	3.98 E-05 *[c]	0.9800 [12]	na	na	4.46 [12]	4.1 [11]	D [2]	nd
Pyrene	150 [7]	1.48 E-01 *[8]	6.67 E-06 *[8]	1.20 E-05 *[c]	1.271 [12]	na	na	4.88 [12]	4.58 [11]	D5,N10 [2]	nd

Table A.3 (cont.)
Properties of Contaminants Commonly Found at Superfund Sites

Chemical	Melting Point (°C)	Water† Solubility (mg/L)	Vapor† Pressure (mm Hg)	Henry's Law† Constant (atm-m^3/mol)	Density† (g/cc)	Dynamic† Viscosity (cp)	Kine-matic† Viscosity (cs)	Log K_{ow}	Log K_{oc}	Aerobic Biodegrad-ability	MCL[17] (µg/L)
Non-Chlorinated Phenols											
Phenol	41 [7]	8.4 E+04 [1]	5.293 E-01 [1]	7.80 E-07 [c]	1.0576 41C[1]	3.02 50C[1]	3.87 46C	1.46 [1]	1.15 [11]	D[2]	nd
2,4-Dimethylphenol(e)	26 [7]	6.2 E+03* [3]	9.8 E-02* [3]	2.5 E-06 * [c]	1.036 [7]	na	na	2.50 [4]	2.35 [14]	D[2]	nd
2,4-Dinitrophenol	112 [7]	6 E+03* [3]	1.49 E-05‡[11]	6.45 E-10 [11]	1.68 [3]	na	na	1.54 [3]	1.22 [11]	D[2]	nd
m-Cresol (e)	12 [7]	2.35 E+04 [7]	1.53 E-01 *[12]	3.8 E-05‡[12]	1.038 [7]	21 [12]	20 (c)	1.96 [12]	1.43 [15]	nd	nd
o-Cresol(e)	31 [7]	3.1 E+04 40C[7]	2.45 E-01 *[12]	4.7 E-05‡[12]	1.0273 [12]	na	na	1.95 [12]	1,23 [15]	nd	nd
p-Cresol(e)	34.8 [7]	2.40 E+04 40C[7]	1.08 E-01 *[12]	3.5 E-04‡[12]	1.0347 [7]	na	na	1.94 [7]	1.28 [15]	nd	nd

CHEMICAL		MCL
Inorganics		
arsenic (As)	May occur in more than one oxidation state in subsurface. Arsenate form (AsO_4^{3-}) will dominate under oxidizing conditions. More toxic and mobile arsenite form (AsO_3^-) may dominate under increasingly reducing and acidic conditions. **Volatile alkylated-As compounds may form** under reducing conditions. **Volatile arsine (AsH_3) may form** under highly reducing conditions. Adsorption of arsenate and arsenite forms will generally increase with decreasing pH.	nd
cadmium (Cd)	Occurs only in divalent form in aqueous solutions (e.g., Cd^{2+}, $CdCl^+$, $CdSO_4^o$). Cd^{2+} tends to be dominant species. Adsorption behavior correlates with cation exchange capacity (CEC) of soil and aquifer material. Adsorption/precipitation increases with increasing pH with most Cd precipitating out at pH>6.	5(p)
chromium (Cr)	May occur in more than one oxidation state in subsurface. Trivalent form (Cr III) is dominant under pH and redox conditions generally present in subsurface. Cr III may be converted to highly mobile and toxic hexavalent form (Cr VI) under oxidizing conditions. Cr III is readily adsorbed in the subsurface while Cr VI is not.	100(p)
cyanide (CN)	Cyanide ion (CN^-) predominates in aqueous solution only at pH>9. Hydrogen cyanide (HCN) predominates at pH<9. **HCN is volatile** (v.p. 741 mm Hg at 25C) and toxic. CN^- behaves similar to halide ions and tends to complex with iron. Undissolved cyanide salts may be present in vadose zone.	200(t)
iron (Fe)	May occur in more than one oxidation state in the subsurface. Ferrous form (Fe^{2+}) is most soluble and mobile, and dominates under reducing conditions. Under oxidizing conditions, ferrous form is converted to ferric form (Fe^{3+}). Ferric form is less soluble, less mobile, and will tend to precipitate. Compounds and metals complexed to iron may be removed from solution through the precipitation process. Conversely, compounds and metals adsorbed to iron in the subsurface may be increasingly mobilized under increasingly reduced conditions. Precipitated iron may hinder treatment processes such as in-situ bioremediation and air stripping.	300(f)
lead (Pb)	Dominant species in aqueous solution are Pb^{2+} under acidic conditions and Pb^{2+}- carbonate complexes under alkaline conditions. Adsorption behavior correlates with cation exchange capacity (CEC) of soil and aquifer material. Adsorption/precipitation increases with increasing pH with most Pb precipitating out at pH>6. **Volatile alkylated-Pb compounds may be present** or may form under reducing conditions.	5(p)
mercury (Hg)	May occur in more than one oxidation state. May occur in subsurface in mercuric form (Hg^{2+}), mercurous form (Hg_2^{2+}), elemental form (Hg^o), and in alkylated form (e.g., methyl and ethyl mercury). Hg_2^{2+} and Hg^{2+} are more stable under oxidizing conditions and are strongly adsorbed by soils. Hg^o and alkylated forms are more stable under reducing conditions. Conversion to alkylated forms may occur under reducing conditions. **Hg^o and alkylated-Hg forms are volatile**, toxic, and may not be as strongly adsorbed by soils.	2(p)
selenium (Se)	May occur in more than one oxidation state in subsurface. Selenate form (SeO_4^{2-}) will dominate under oxidizing conditions. Selenite form (SeO_3^2) will dominate under increasingly reducing conditions. Selenide form (Se^{2-}) may dominate under highly reducing conditions. Selenate and selenite are more soluble and mobile forms. Adsorption of selenate and selenite will generally increase with decreasing pH. **Volatile alkylated-Se compounds may form** under reducing conditions.	50(p)

Table A.3 (cont.)
Properties of Contaminants Commonly Found at Superfund Sites

A = significant degradation with gradual adaption
B = slow to moderate activity, concomitant with significant rate of volatilization
C = very slow biodegradative activity, with long adaption period needed
D = significant degradation with rapid adaption
M = not significantly degraded under the conditions of the test method
N = not significantly degraded under the conditions of test method and/or precluded by extensive rate of volatilization
T = significant degradation with gradual adaption followed by deadaptive process in subsequent subcultures (toxicity)

(a) = may be component of antiknock fluids added to fuel oils; remedial treatment may require consideration of constituent in oil phase
(b) = constituent in some oils, greases, dielectric liquids, and thermostatic fluids; remedial treatment may require consideration of constituent in oil phase
(c) = calculated
(d) = may be present in dye or lacquer solutions; remedial treatment may require consideration of constituent in oil phase
(e) = constituent of crude oil fractions (including fuel oils and motor oils) and/or coal tar fractions (including creosote); creosote may be present as DNAPL; remedial treatment may require consideration of constituent in oil phase
(f) = final MCL
(g) = constituent in fuel oils (e.g. gasoline); remedial treatment may require consideration of constituent in oil phase
(p) = proposed MCL
(t) = tentative MCL
(w) = combined with fuel oil #2 or kerosene when used as wood preservative; remedial treatment may require consideration of constituent in oil phase

na = not applicable
nd = no data found

[ ] Reference

† = Values are given at 20°C unless otherwise specified
* = Value is at 25°C
‡ = Value is at unknown temperature but is assumed to be at 20-30°C

B

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LIST OF ACRONYMS

AAEE	American Academy of Environmental Engineers
ATP	Adenosine Triphosphate
B(a)P	Benzo(a)pyrene
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
BOD	Biological Oxygen Demand
CEC	Cation Exchange Capacity
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COD	Chemical Oxygen Demand
CoM	Center of Mass
DCA	Dichloroethane
DCE	Dichloroethene (Dichloroethylene)
DNAPL	Dense Nonaqueous-Phase Liquid
DO	Dissolved Oxygen
DRE	Degradation/Removal Efficiency
DRO	Diesel Range Organics
FAME	Fatty Acid Methyl Ester
FID	Flame Ionization Detector
FLTG	French Limited Task Group
FS	Feasibility Study
GC	Gas Chromatograph(y)
GRO	Gasoline Range Organics
HDPE	High-Density Polyethylene
HMX	High Melting Explosive
HPLC	High-Performance Liquid Chromatography
HSP	Health and Safety Plan
HSWA	Hazardous and Solid Waste Amendments
IAS	In Situ Air Sparging
KTPP	Potassium Tripolyphosphate
LEL	Lower Explosion Limit
LNAPL	Light Nonaqueous-Phase Liquid
LTU	Land Treatment Unit
MMO	Methane Monooxygenase
MPN	Most Probable Number
MS	Mass Spectrometry
MSE	Mean Square Error
NAPL	Nonaqueous-Phase Liquid
ORC	Oxygen Release Compound
PAH	Polycyclic Aromatic Hydrocarbon

PCB	Polychlorinated Biphenyl
PCE	Perchloroethene (Perchloroethylene or Tetrachloroethylene)
PCP	Pentachlorophenol
PCR	Polymerase Chain Reaction
PID	Photoionization Detector
PLC	Process Logic Control(ler)
POC	Point of Compliance
PRP	Potentially Responsible Party
PRTs	Plume Resident Tracers
PVC	Poly Vinyl Chloride
RAP	Remedial Action Plan
RCRA	Resource Conservation and Recovery Act
RDX	Royal Demolition Explosive
RI	Remedial Investigation
RITZ	Regulatory and Interactive Treatment Zone (Model)
ROD	Record of Decision
ROI	Radius of Influence
SARA	Superfund Amendments and Reauthorization Act
SIB	Soil Injection Bed
STF	Soil Transport and Fate (Database)
SVE	Soil Vapor Extraction
TCE	Trichloroethene (Trichloroethylene)
TEA	Terminal Electron Acceptor
TKN	Total Kjeldahl Nitrogen
TNT	Trinitrotoluene
TOC	Total Organic Carbon
TCPAH	Total Carcinogenic PAH
TPH	Total Petroleum Hydrocarbon
US EPA	U.S. Environmental Protection Agency
VC	Vinyl Chloride
VOC	Volatile Organic Compound

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