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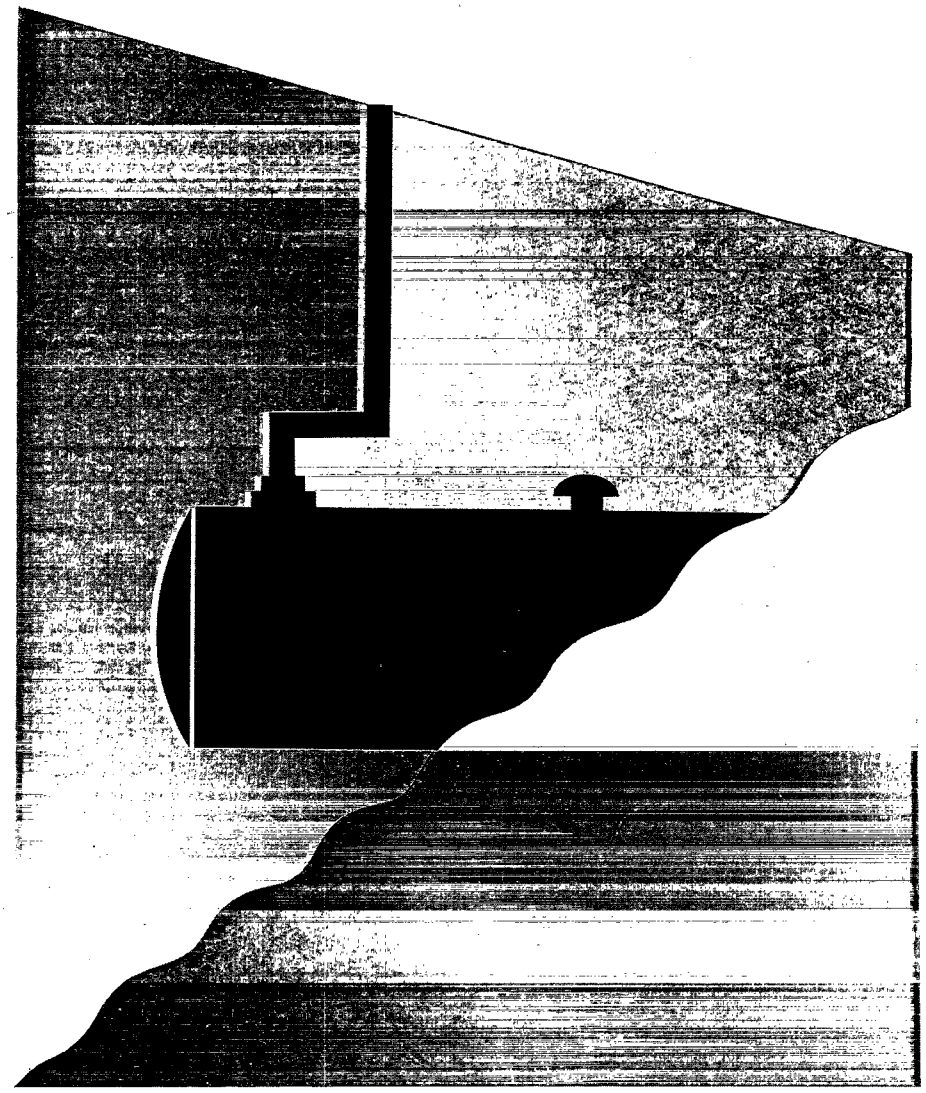
How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites

A Guide for Corrective Action Plan Reviewers



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Deborah L. Tremblay
Project Manager
October, 1994

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Chapter I

Introduction

Chapter I
Introduction

Background

As of June 1994, state and local environmental agencies across the nation have reported more than 260,000 releases from leaking underground storage tanks. Still the number of confirmed releases continues to grow, with over 1,000 new releases reported each week. This burgeoning number of releases has created a growing and, in many cases, unmanageable workload for state regulators who often must oversee 50 to 400 cleanups at a time.

To compound the problem, these cleanups are expensive. Costs of remediating sites with soil contamination generally vary between $10,000 and $125,000. Depending on the extent of contamination, costs for remediating sites with groundwater contamination can range from $100,000 to over $1 million.

A primary factor in the high cost of cleanups is the use of ineffective cleanup methods. Pump-and-treat, the most commonly used method for remediating groundwater, often results in unsuccessful cleanups. Even when properly operated, pump-and-treat systems have inherent limitations: They do not work well in complex geologic settings or heterogeneous aquifers; they often stop reducing contamination long before reaching intended cleanup levels; and they often make sites more difficult to remediate by smearing contamination across the subsurface. Landfilling, the most frequently used method for addressing contaminated soils, does not remediate soils; this method simply moves the problem from one location to another. In addition to being costly in many states, transporting contaminated soil off-site increases the risk of harming human health and the environment.

With so many sites requiring remediation at such an enormous cost, the Environmental Protection Agency (EPA) is promoting faster, more effective, and less costly alternatives to traditional cleanup methods. EPA's Office of Underground Storage Tanks (OUST) is working with state and local governments to encourage the use of cleanup technologies that are proven but are not yet widely used. These "alternative technologies" have the ability to make cleanups faster, more effective, and less costly than traditional options such as pump-and-treat or excavation and disposal in a landfill. The U.S. EPA encourages state regulators to consider alternative cleanup technologies for remedial actions at all leaking underground storage tank sites.

Purpose Of This Manual

The purpose of this manual is to provide you—state and local regulators—with guidance that will help you review corrective action plans (CAPs) that propose alternative cleanup technologies. The manual does not advocate the use of one technology over another; rather it focuses on appropriate technology use, taking into consideration site-specific conditions and the nature and extent of contamination. While the manual focuses on the remediation of leaking underground storage tank sites, some of its basic concepts can be applied at hazardous substance and hazardous waste sites as well.

The manual is designed to enable you to answer two basic questions when reviewing a CAP:

- Has an appropriate cleanup technology been proposed?
- Does the CAP provide a technically sound approach to the cleanup?

Scope And Limitations

This manual is intended to provide technical guidance to state regulators who oversee cleanups and evaluate CAPs. The document does not represent the issuance of formal policy or in any way affect the interpretation of the regulations.

The text focuses on engineering-related considerations for evaluating each technology. It does not provide instruction on the design and construction of remedial systems and should not be used for designing CAPs. Nor should it be used to provide guidance on regulatory issues such as securing permits and establishing cleanup standards, health and safety issues, state-specific requirements, or cleanup costs.

This document is not intended to be used as the sole reference for CAP review. Rather, it is intended to be used along with published references, guidance from others more experienced with alternative technologies, information from training courses, and current journals.

The material presented is based on available technical data and information and the knowledge and experience of the authors and the peer reviewers.

How To Use This Manual

We encourage you to use this manual at your desk as you review CAPs. We have designed the manual so that you can tailor it to meet your state's or your own needs. The three-ring binder allows you to insert additional material and remove certain tools (e.g., flow charts, checklists) for photocopying. Add your own notes or information to the margins provided.

The manual contains discussions of eight different alternative cleanup technologies. Tabs signal the beginning of each chapter (including the Introduction and Abbreviations And Definitions) so you can flip quickly to the appropriate section. We have included a table of contents in each chapter to help you locate the information you need.

Each technology chapter contains the following tools which can help expedite and/or improve the review process:

- An evaluation process flow chart, the third exhibit in each chapter, can help you understand the overall review process for each technology. This flow chart serves as a "road map" for the chapter and for the decisions you will make during the evaluation process.

- A checklist, located at the end of each chapter, can help you determine whether or not the CAP contains all of the necessary information. The checklist lists the most important factors to evaluate for the successful implementation of each technology.

- A list of current references, located near the end of each chapter, provides sources of additional information.

- In addition, each chapter has a number of charts that display advantages and disadvantages of each technology, initial screening criteria, and other data specific to each technology.

Please note the evaluation form located at the end of the manual. We are very interested in your comments on the usefulness of this document. OUST relies on your feedback to improve our products. Please fill out the form and return it to us.

How to Obtain Additional Copies of the Manual

OUST plans to make this manual available through the Government Printing Office. To obtain the information you will need to order copies, please call EPA's RCRA/Superfund Hotline. The Hotline is open Monday through Friday from 8:30 to 7:30 p.m. EST. The toll-free number is 800 424-9346; for the hearing impaired, the number is TDD 800 553-7672.

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Soil Vapor Extraction

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Chapter II
Soil Vapor Extraction

Overview

Soil vapor extraction (SVE), also known as soil venting or vacuum extraction, is an *in situ* remedial technology that reduces concentrations of volatile constituents in petroleum products adsorbed to soils in the unsaturated (vadose) zone. In this technology, a vacuum is applied to the soil matrix to create a negative pressure gradient that causes movement of vapors toward extraction wells. Volatile constituents are readily removed from the subsurface through the extraction wells. The extracted vapors are then treated, as necessary, and discharged to the atmosphere or reinjected to the subsurface (where permissible).

This technology has been proven effective in reducing concentrations of volatile organic compounds (VOCs) and certain semi-volatile organic compounds (SVOCs) found in petroleum products at underground storage tank (UST) sites. SVE is generally more successful when applied to the lighter (more volatile) petroleum products such as gasoline. Diesel fuel, heating oils, and kerosene, which are less volatile than gasoline, are not readily treated by SVE but may be suitable for removal by bioventing (see Chapter III). SVE is generally not successful when applied to lubricating oils, which are non-volatile, but these oils may be suitable for removal by bioventing. A typical SVE system is shown in Exhibit II-1. A summary of the advantages and disadvantages of SVE is shown in Exhibit II-2.

This chapter will assist you in evaluating a corrective action plan (CAP) which proposes SVE as a remedy for petroleum-contaminated soil. The evaluation process, which is summarized in a flow diagram shown in Exhibit II-3, will serve as a roadmap for the decisions you will make during your evaluation. A checklist has also been provided at the end of this chapter to be used as a tool to evaluate the completeness of the CAP and to help focus attention on areas where additional information may be needed. The evaluation process can be divided into the following steps.

- **Step 1: *An initial screening of SVE effectiveness***, which will allow you to quickly gauge whether SVE is likely to be effective, moderately effective, or ineffective.

Exhibit II-1
Typical SVE System

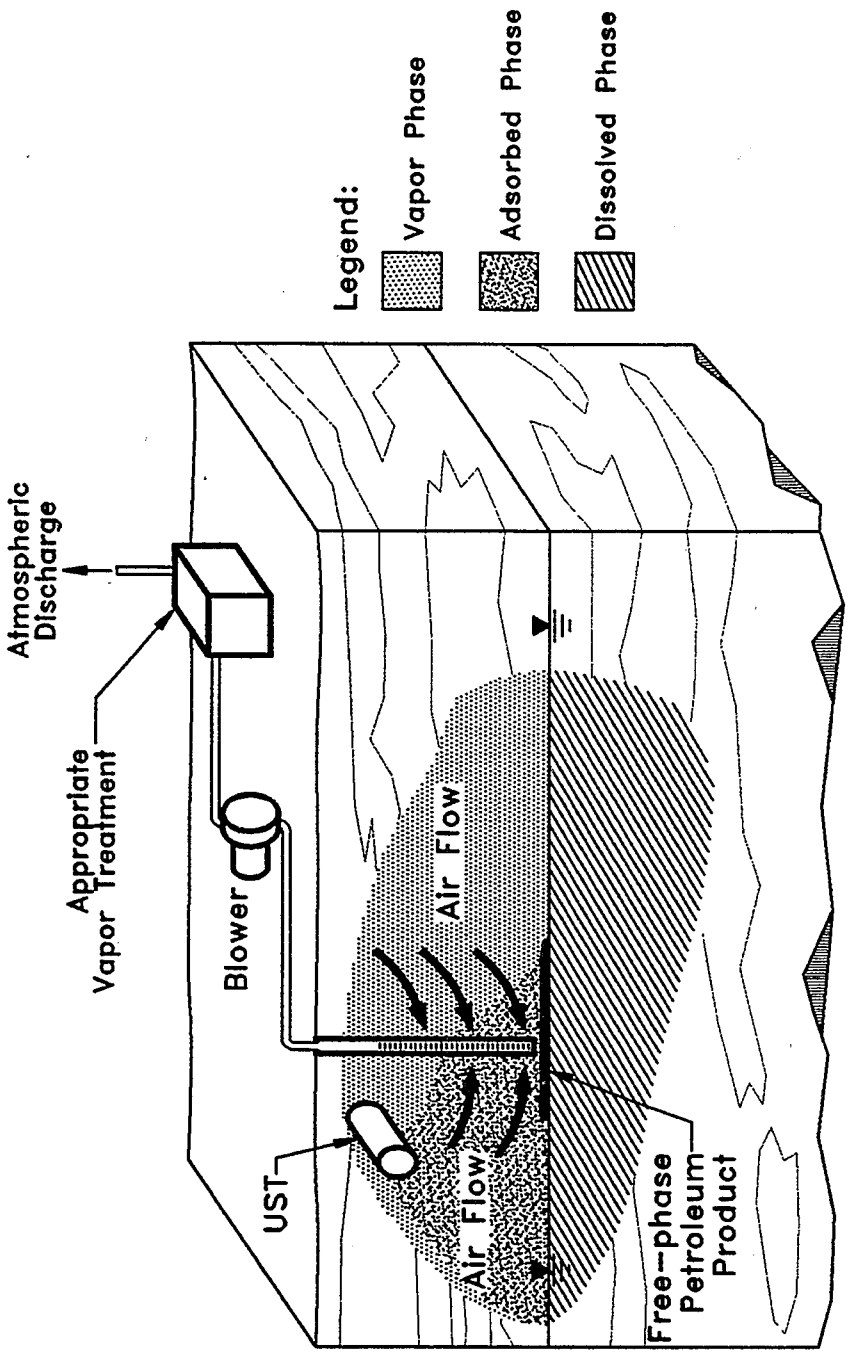


Exhibit II-2
Advantages And Disadvantages Of SVE

Advantages	Disadvantages
○ Proven performance; readily available equipment; easy installation.	○ Concentration reductions greater than about 90% are difficult to achieve.
○ Minimal disturbance to site operations.	○ Effectiveness less certain when applied to sites with low-permeability soil or stratified soils.
○ Short treatment times: usually 6 months to 2 years under optimal conditions.	○ May require costly treatment for atmospheric discharge of extracted vapors.
○ Cost competitive: $20-50/ton of contaminated soil.	○ Air emission permits generally required.
○ Easily combined with other technologies (e.g., air sparging, bioremediation, and vacuum-enhanced dual-phase extraction).	○ Only treats unsaturated-zone soils; other methods may also be needed to treat saturated-zone soils and groundwater.
○ Can be used under buildings and other locations that cannot be excavated.	

- **Step 2:** ***A detailed evaluation of SVE effectiveness***, which provides further screening criteria to confirm whether SVE is likely to be effective. To complete the detailed evaluation, you will need to find specific soil and constituent characteristics and properties, compare them to ranges where SVE is effective, decide whether pilot studies are necessary to determine effectiveness, and conclude whether SVE is likely to work at a site.

- **Step 3:** ***An evaluation of the SVE system design***, which will allow you to determine if the rationale for the design has been appropriately defined based on pilot study data or other studies, whether the necessary design components have been specified, and whether the construction process flow designs are consistent with standard practice.

- **Step 4:** ***An evaluation of the operation and monitoring plans***, which will allow you to determine whether start-up and long-term system operation monitoring is of sufficient scope and frequency and whether remedial progress monitoring plans are appropriate.

Initial Screening Of SVE Effectiveness

Although the theories that explain how SVE works are well-understood, determining whether SVE will work at a given site is not simple. Experience and judgement are needed to determine whether SVE will work effectively. The key parameters that should be used to decide whether SVE will be a viable remedy for a particular site are:

- *Permeability* of the petroleum-contaminated soils. Permeability of the soil determines the rate at which soil vapors can be extracted.

- *Volatility* of the petroleum constituents. Volatility determines the rate (and degree) at which petroleum constituents will vaporize from the soil-adsorbed state to the soil vapor state.

In general, the type of soil (e.g., clay, silt, sand) will determine its *permeability*. Fine-grained soils (e.g., clays and silts) have lower permeability than coarse-grained soils (e.g., sands and gravels). The *volatility* of a petroleum product or its constituents is a measure of its ability to vaporize. Because petroleum products are highly complex mixtures of chemical constituents, the volatility of the product can be roughly approximated by its boiling point range.

Exhibit II-4 is an initial screening tool that you can use to help assess the potential effectiveness of SVE for a given site. This exhibit provides a range of soil permeabilities for typical soil types as well as ranges of volatility (based on boiling point range) for typical petroleum products. Use this screening tool to make an initial assessment of the potential effectiveness of SVE. To use this tool, you should scan the CAP to determine the soil type present and the type of petroleum product released at the site.

Information provided in the following section will allow a more thorough effectiveness evaluation and will identify areas that could require special design considerations.

Exhibit II-3
SVE Evaluation Process Flow Chart

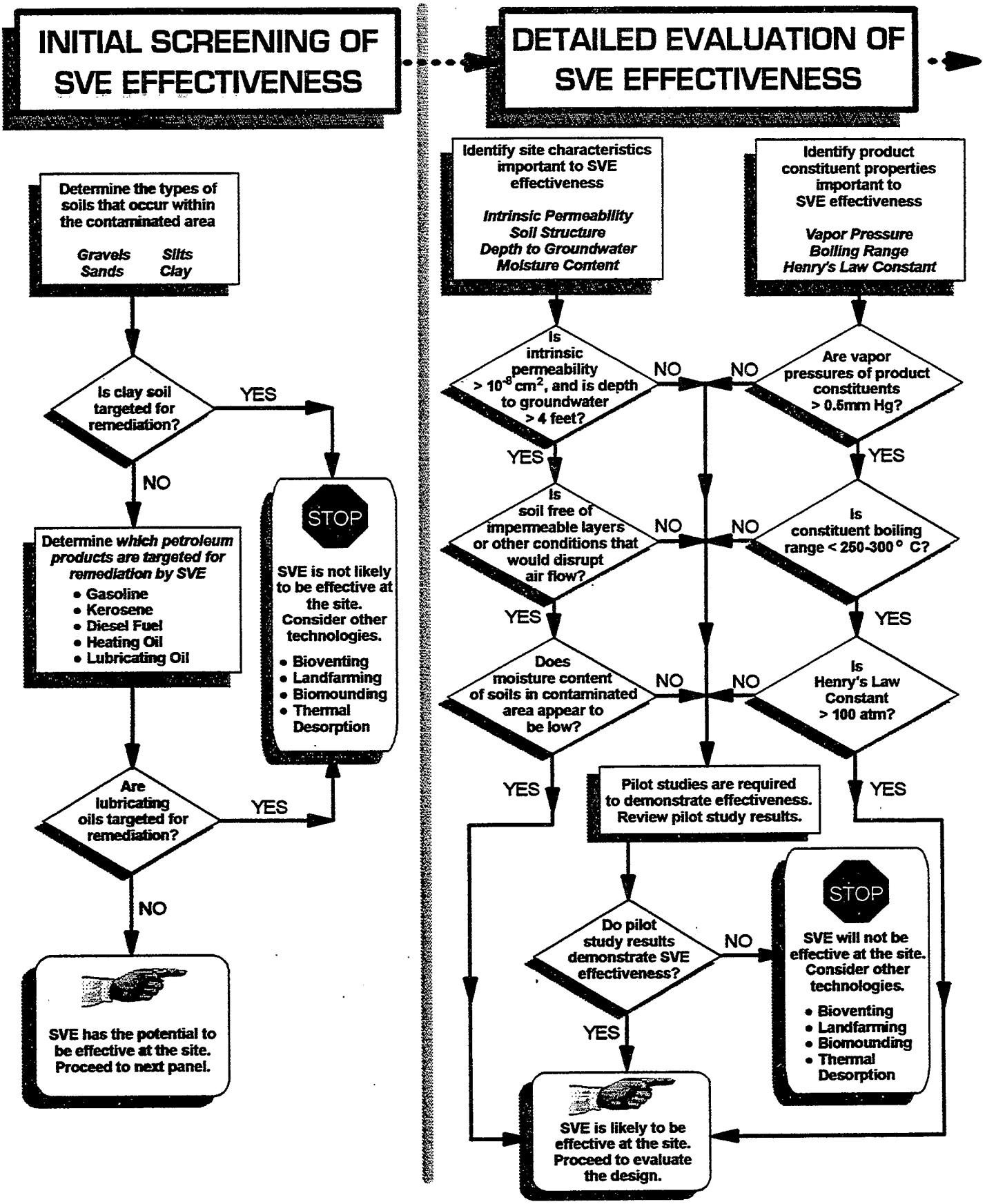


Exhibit II-3
SVE Evaluation Process Flow Chart

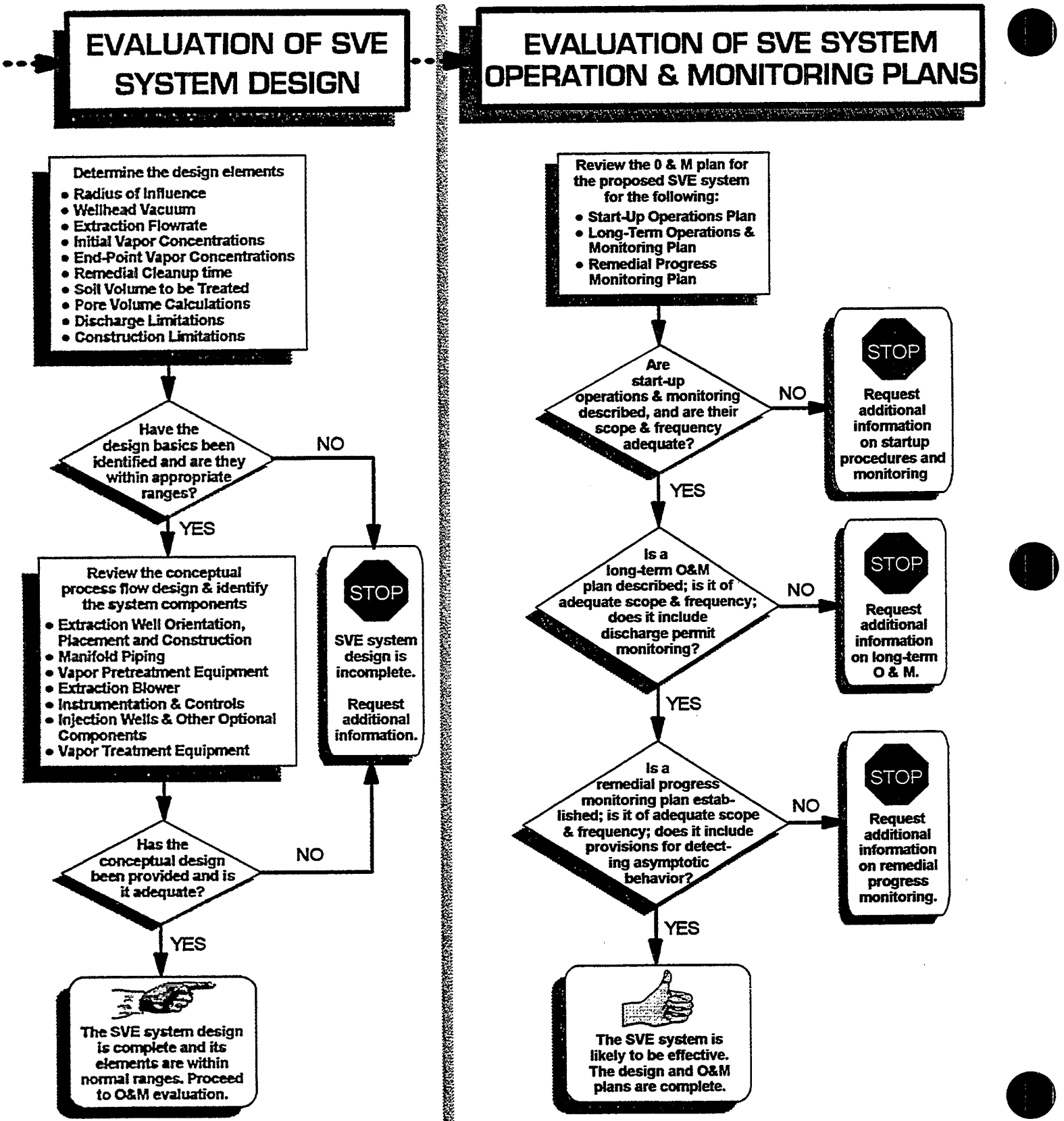
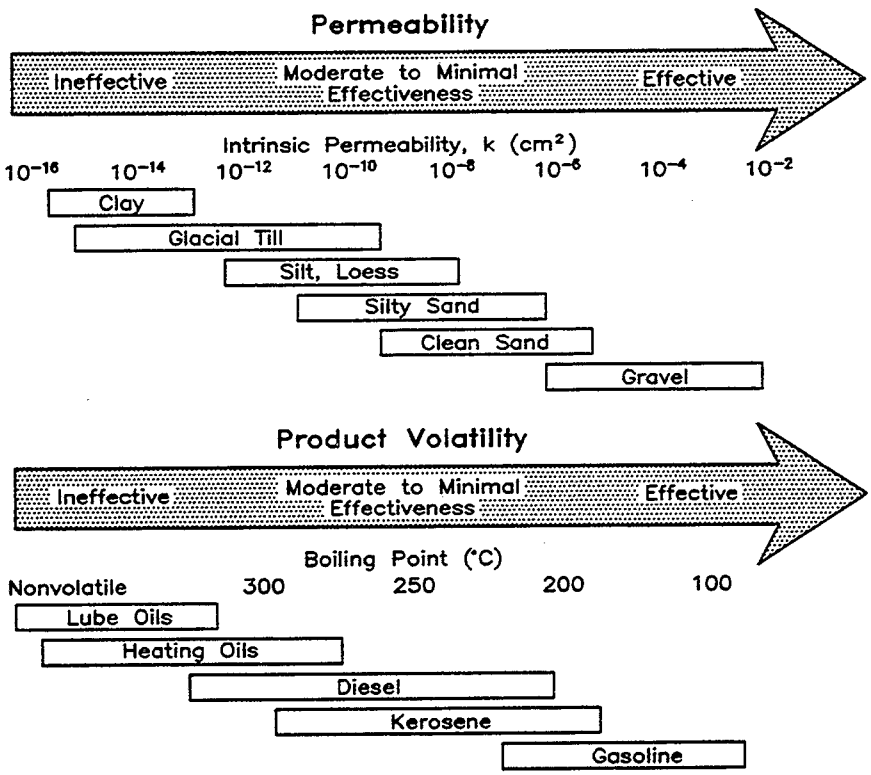


Exhibit II-4
Initial Screening For SVE Effectiveness



Detailed Evaluation Of SVE Effectiveness

Once you have completed the initial screening and determined that SVE may have the potential to be effective for the soils and petroleum product present, further scrutinize the CAP to confirm that SVE will be effective.

Begin by reviewing the two major factors that determine the effectiveness of SVE: (1) permeability of the soil and (2) constituent volatility. The combined effect of these two factors results in the initial contaminant mass extraction rate, which will decrease during SVE operation as concentrations of volatile organics in the soil (and soil vapor) are reduced.

Many site-specific parameters can be used to determine permeability and volatility. These parameters are summarized in Exhibit II-5.

Exhibit II-5
Key Parameters Used To Evaluate Permeability Of Soil And Constituent Volatility

Permeability Of Soil	Constituent Volatility
Intrinsic permeability	Vapor pressure
Soil structure and stratification	Product composition and boiling point
Depth to groundwater	Henry's law constant
Moisture content	

The remainder of this section describes each parameter, why it is important to SVE, how it can be determined, and a range of values over which SVE is effective.

Factors That Contribute To Permeability Of Soil

Intrinsic Permeability

Intrinsic permeability is a measure of the ability of soils to transmit fluids and is the *single most important factor* in determining the effectiveness of SVE. Intrinsic permeability ranges over 12 orders of magnitude (from 10^{-16} to 10^{-3} cm^2) for the wide variety of earth materials, although a more limited range applies for common soil types (10^{-13} to 10^{-5} cm^2). Intrinsic permeability is best determined from field tests, but can be estimated within one or two orders of magnitude from soil boring logs and laboratory tests. Coarse-grained soils (e.g., sands) have greater intrinsic permeability than fine-grained soils (e.g., clays or silts). Note that the ability of a soil to transmit air, which is of prime importance to SVE, is reduced by the presence of soil water, which can block the soil pores and reduce air flow. This is especially important in fine-grained soil, which tend to retain water.

Intrinsic permeability can be determined in the field by conducting permeability tests or SVE pilot studies, or in the laboratory using soil core samples from the site. Procedures for these tests are described by EPA (1991a). Use the values presented in Exhibit II-6 to determine if intrinsic permeability is within the effectiveness range for SVE.

Exhibit II-6
Intrinsic Permeability And SVE Effectiveness

Intrinsic Permeability (k)	SVE Effectiveness
$k \geq 10^{-8}$ cm^2	Generally effective.
$10^{-8} \geq k \geq 10^{-10}$ cm^2	May be effective; needs further evaluation.
$k < 10^{-10}$ cm^2	Marginal effectiveness to ineffective.

At sites where the soils in the saturated zone are similar to those within the unsaturated zone, hydraulic conductivity of the soils may be used to estimate the permeability of the soils. Hydraulic conductivity is a measure of the ability of soils to transmit water. Hydraulic conductivity can be determined from aquifer tests, including slug tests and pumping tests. You can convert hydraulic conductivity to intrinsic permeability using the following equation:

$$k = K (\mu / \rho g)$$

where: k = intrinsic permeability (cm^2)
K = hydraulic conductivity (cm/sec)
μ = water viscosity (g/cm · sec)
ρ = water density (g/cm^3)
g = acceleration due to gravity (cm/sec^2)

At 20°C: $\mu/\rho g = 1.02 \cdot 10^{-5}$ cm/sec

To convert k from cm^2 to darcy, multiply by 10^8

Soil Structure And Stratification

Soil structure and stratification are important to SVE effectiveness because they can affect how and where soil vapors will flow within the soil matrix under extraction conditions. Structural characteristics such as microfracturing can result in higher permeabilities than expected for certain soil components (e.g., clays). However, the increased flow availability will be confined within the fractures but not in the unfractured media. This preferential flow behavior can lead to ineffective or significantly extended remedial times. Stratification of soils with different permeabilities can increase the lateral flow of soil vapors in the more permeable stratum while dramatically reducing the soil vapor flow through the less permeable stratum.

You can determine the intergranular structure and stratification of the soil by reviewing soil boring logs for wells or borings and by examining geologic cross-sections. You should verify that soil types have been identified, that visual observations of soil structure have been documented, and that sampling intervals are of sufficient frequency to define any soil stratification. Stratified soils may require special consideration in design to ensure less-permeable stratum are addressed.

Depth To Groundwater

Fluctuations in the groundwater table should also be considered when reviewing a CAP. Significant seasonal or daily (tidal or precipitation-related) fluctuations may, at times, submerge some of the contaminated soil or a portion of the extraction well screen, making it unavailable for air flow. This is most important for horizontal extraction wells, where the screen is parallel to the water table surface.

SVE is generally not appropriate for sites with a groundwater table located less than 3 feet below the land surface. Special considerations must be taken for sites with a groundwater table located less than 10 feet below the land surface because groundwater upwelling can occur within SVE wells under vacuum pressures, potentially occluding well screens and reducing or eliminating vacuum-induced soil vapor flow. Use Exhibit II-7 to determine whether the water-table depth is of potential concern for SVE effectiveness.

Moisture Content

High moisture content in soils can reduce soil permeability and thereafter, the effectiveness of SVE by restricting the flow of air through soil pores. Airflow is particularly important for soils within the capillary fringe where, oftentimes, a significant portion of the constituents can accumulate. Fine-grained soils create a thicker capillary fringe than coarse-grained soils. The thickness of the capillary fringe can usually be determined from soil boring logs (i.e., in the capillary fringe, soils are usually described as moist or wet). The capillary fringe usually extends from inches to several feet above the groundwater table elevation. SVE is not generally effective in removing contaminants from the capillary fringe. When combined with other technologies (e.g., pump-and-treat to lower the water table or air sparging to strip contaminants from the capillary fringe) the performance of SVE-based systems is considerably increased.

Exhibit II-7
Depth To Groundwater And SVE Effectiveness

Depth To Groundwater	SVE Effectiveness
> 10 feet	Effective
3 feet < depth < 10 feet	Need special controls (e.g., horizontal wells or groundwater pumping)
< 3 feet	Not generally effective

Moist soils can also occur from stormwater infiltration in unpaved areas without sufficient drainage. This moisture may be a persistent problem for fine-grained soils with slow infiltration rates. SVE does dehydrate moist soils to some extent, but the dehydration process may hinder SVE performance and extend operational time.

Factors That Contribute To Constituent Volatility

Vapor Pressure

Vapor pressure is the *most important constituent characteristic* in evaluating the applicability and potential effectiveness of an SVE system. The vapor pressure of a constituent is a measure of its tendency to evaporate. More precisely, it is the pressure that a vapor exerts when in equilibrium with its pure liquid or solid form. Constituents with higher vapor pressures are more easily extracted by SVE systems. Those with vapor pressures higher than 0.5 mm Hg are generally considered amenable for extraction by SVE.

As previously discussed, gasoline, diesel fuel, and kerosene are each composed of over a hundred different chemical constituents. Each constituent will be extracted at a different rate by an SVE system, generally according to its vapor pressure. Exhibit II-8 lists vapor pressures of selected petroleum constituents.

Exhibit II-8
Vapor Pressures Of Common Petroleum Constituents

Constituent	Vapor Pressure (mm Hg at 20°C)
Methyl t-butyl ether	245
Benzene	76
Toluene	22
Ethylene dibromide	11
Ethylbenzene	7
Xylenes	6
Naphthalene	0.5
Tetraethyl lead	0.2

Product Composition And Boiling Point

The most commonly encountered petroleum products from UST releases are gasoline, diesel fuel, kerosene, heating oils, and lubricating oils. Because of their complex constituent composition, petroleum products are often classified by their boiling point range. Because the boiling point of a compound is a measure of its volatility, the applicability of SVE to a petroleum product can be estimated from its boiling point range. The boiling point ranges for common petroleum products are shown in Exhibit II-9.

Exhibit II-9
Petroleum Product Boiling Point Ranges

Product	Boiling Point Range (°C)
Gasoline	40 to 225
Kerosene	180 to 300
Diesel fuel	200 to 338
Heating oil	>275
Lubricating oils	Nonvolatile

In general, constituents in petroleum products with boiling points less than 250° to 300°C are sufficiently volatile to be amenable to removal by SVE. Therefore, SVE can remove nearly all gasoline constituents, a portion of kerosene and diesel fuel constituents, and a lesser portion of heating oil constituents. SVE cannot remove lubricating oils. Most petroleum constituents are biodegradable, however, and might be

amenable to removal by bioventing. (See Chapter III for information about Bioventing.) Injection of heated air also can be used to enhance the volatility of these products because vapor pressure generally increases with temperature. However, energy requirements for volatility enhancement are so large as to be economically prohibitive.

Henry's Law Constant

Another indicator of the volatility of a constituent is by noting its Henry's law constant. Henry's law constant is the partitioning coefficient that relates the concentration of a constituent dissolved in water to its partial pressure in the vapor phase under equilibrium conditions. In other words, it describes the relative tendency for a dissolved constituent to partition between the vapor phase and the dissolved phase. Therefore, the Henry's law constant is a measure of the degree to which constituents that are dissolved in soil moisture (or groundwater) will volatilize for removal by the SVE system. Henry's law constants for several common constituents found in petroleum products are shown in Exhibit II-10. Constituents with Henry's law constants of greater than 100 atmospheres are generally considered amenable to removal by SVE.

Exhibit II-10
Henry's Law Constant Of Common Petroleum Constituents

Constituent	Henry's Law Constant (atm)
Tetraethyl lead	4700
Ethylbenzene	359
Xylenes	266
Benzene	230
Toluene	217
Naphthalene	72
Ethylene dibromide	34
Methyl t-butyl ether	27

Other Considerations

There are other site-specific aspects to consider when evaluating the potential effectiveness of an SVE system. For example, it may be anticipated that SVE would be only marginally effective at a site as the result of low permeability of the soil or low vapor pressure of the constituents. In this case, bioventing may be the best available alternative for locations such as under a building or other inaccessible area.

SVE may also be appropriate near a building foundation to prevent vapor migration into the building. Here, the primary goal may be to control vapor migration and not necessarily to remediate soil.

Pilot Scale Studies

At this stage, you will be in a position to decide if SVE is likely to be highly effective, somewhat effective, or ineffective. If it appears that SVE will be only marginally to moderately effective at a particular site, make sure that SVE pilot studies have been completed at the site and that they demonstrate SVE effectiveness. Pilot studies are an extremely important part of the design phase. Data provided by pilot studies is necessary to properly design the full-scale SVE system. Pilot studies also provide information on the concentration of volatile organic compounds (VOCs) that are likely to be extracted during the early stages of operation of the SVE system.

While pilot studies are important and recommended for evaluating SVE effectiveness and design parameters for any site, they are particularly useful at sites where SVE is expected to be only marginally to moderately effective. Pilot studies typically include short-term (1 to 30 days) extraction of soil vapors from a single extraction well, which may be an existing monitoring well at the site. However, longer pilot studies (up to 6 months) which utilize more than one extraction well may be appropriate for larger sites. Different extraction rates and wellhead vacuums are applied to the extraction wells to determine the optimal operating conditions. The vacuum influence at increasing distances from the vapor extraction well is measured using vapor probes or existing wells to establish the pressure field induced in the subsurface by operation of the vapor extraction system. The pressure field measurements can be used to define the design radius of influence for SVE. Vapor concentrations are also measured at two or more intervals during the pilot study to estimate initial vapor concentrations of a full-scale system. The vapor concentration, vapor extraction rate and vacuum data are also used in the design process to select extraction and treatment equipment.

In some instances, it may be appropriate to evaluate the potential of SVE effectiveness using a screening model such as HyperVentilate (EPA, 1993). HyperVentilate can be used to identify required site date, decide if SVE is appropriate at a site, evaluate air permeability tests, and estimate the minimum number of wells needed. It is not intended to be a detailed SVE predictive modeling or design tool.

Evaluation Of The SVE System Design

Once you have verified that SVE is applicable, you can scrutinize the design of the system. A pilot study that provides data used to design the full-scale SVE system is highly recommended. The CAP should include a discussion of the rationale for the design and presentation of the conceptual engineering design. Detailed engineering design documents might also be included, depending on state requirements. Further detail about information to look for in the discussion of the design is provided below.

Rationale For The Design

Consider the following factors as you evaluate the design of the SVE system in the CAP.

- *Design Radius of Influence (ROI)* is the most important parameter to be considered in the design of an SVE system. The ROI is defined as the greatest distance from an extraction well at which a sufficient vacuum and vapor flow can be induced to adequately enhance volatilization and extraction of the contaminants in the soil. As a rule-of-thumb, the ROI is often considered to be the distance from the extraction well at which a vacuum of at least 0.1 inches of water is observed.

  The ROI depends on many factors including: lateral and vertical permeability; depth to the groundwater table; the presence or absence of a surface seal; the use of injection wells; and the extent of soil heterogeneity. Generally, the design ROI can range from 5 feet (for fine grained soils) to 100 feet (for coarse grained soils). For sites with stratified geology, design ROI should be defined for each soil type. The ROI is important for determining the appropriate number and spacing of extraction wells. The ROI should be determined based on the results of pilot study testing; however, at sites where pilot tests can not be performed, the ROI can be estimated using air flow modelling or other empirical methods.

- *Wellhead Vacuum* is the vacuum pressure that is required at the top of the extraction well to produce the desired vapor extraction flow rate from the extraction well. Although wellhead vacuum is usually determined through pilot studies, it can be estimated and typically ranges from 3 to 100 inches of water vacuum. Less permeable soils generally require higher wellhead vacuum pressures to produce a reasonable

radius of influence. It should be noted, however, that high vacuum pressures (e.g., greater than 100 inches of water) can cause upwelling of the water table and occlusion of the extraction well screens.

- *Vapor Extraction Flow Rate* is the volumetric flow rate of soil vapor that will be extracted from each vapor extraction well. Vapor extraction flow rate, radius of influence, and wellhead vacuum are interdependent (e.g., a change in the extraction rate will cause a change in the wellhead vacuum and radius of influence). Vapor extraction flow rate should be determined from pilot studies but may be calculated using mathematical or physical models (EPA 1993). The flow rate will contribute to the operational time requirements of the SVE system. Typical extraction rates can range from 10 to 100 cubic feet per minute (cfm) per well.

- *Initial Constituent Vapor Concentrations* can be measured during pilot studies or estimated from soil gas samples or soil samples. They are used to estimate constituent mass removal rate and SVE operational time requirements and to determine whether treatment of extracted vapors will be required prior to atmospheric discharge or reinjection.

  The initial vapor concentration is typically orders of magnitude higher than the sustained vapor extraction concentration and can be expected to last only a few hours to a day before dropping off significantly. Vapor treatment is especially important during this early phase of remediation.

- *Required Final Constituent Concentrations* in soils or vapors are either defined by state regulations as "remedial action levels," or determined on a site-specific basis using fate and transport modeling and risk assessment. They will determine what areas of the site require treatment and when SVE operation can be terminated.

- *Required Remedial Cleanup Time* may also influence the design of the system. The designer may reduce the spacing of the extraction wells to increase the rate of remediation to meet cleanup deadlines or client preferences, as required.

- *Soil Volume To Be Treated* is determined by state action levels or a site-specific risk assessment using site characterization data for the soils.

- *Pore Volume Calculations* are used along with extraction flow rate to determine the pore volume exchange rate. The exchange rate is calculated by dividing the soil pore space within the treatment zone by the design vapor extraction rate. The pore space within the treatment zone is calculated by multiplying the soil porosity by the

volume of soil to be treated. Some literature suggests that one pore volume of soil vapor should be extracted at least daily for effective remedial progress.

You can calculate the time required to exchange one pore volume of soil vapor using the following equation:

$$E = \frac{(m^3 \text{ vapor} / m^3 \text{ soil}) \cdot (m^3 \text{ soil})}{(m^3 \text{ vapor} / \text{hr})} = \text{hr}$$

where: E = pore volume exchange time (hr)
ε = soil porosity (m^3 vapor/m^3 soil)
V = volume of soil to be treated (m^3 soil)
Q = total vapor extraction flowrate (m^3 vapor/hr)

$$E = \frac{\varepsilon V}{Q}$$

- *Discharge Limitations And Monitoring Requirements* are usually established by state regulations but must be considered by designers of an SVE system to ensure that monitoring ports are included in the system hardware. Discharge limitations imposed by state air quality regulations will determine whether offgas treatment is required.

- *Site Construction Limitations* such as building locations, utilities, buried objects, residences, and the like must be identified and considered in the design process.

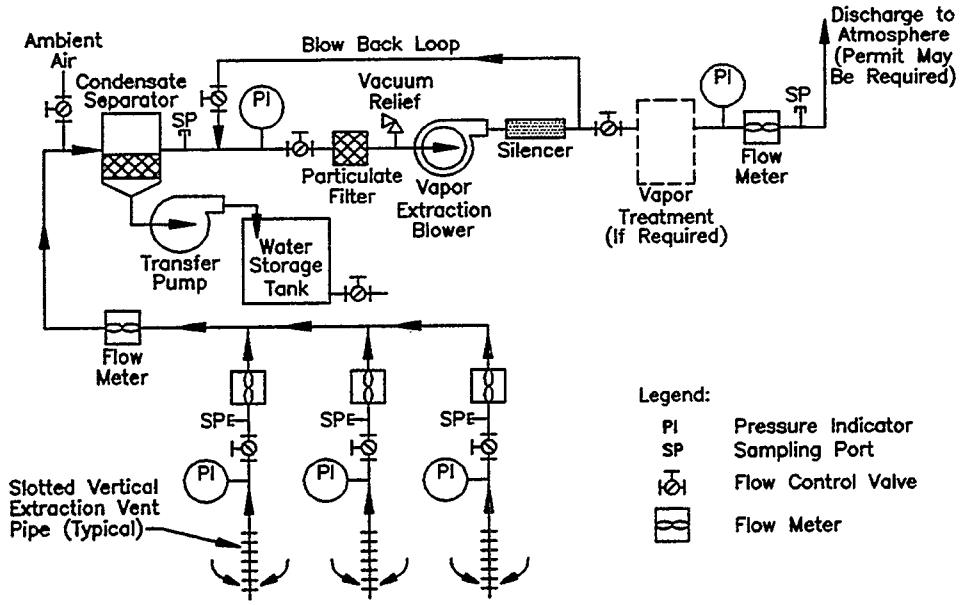
Components Of An SVE System

Once the rationale for the design is defined, the actual design of the SVE system can be developed. A typical SVE system design will include the following components and information:

- Extraction wells
- Well orientation, placement, and construction details
- Manifold piping
- Vapor pretreatment design
- Blower selection
- Instrumentation and control design
- Optional SVE components
  - -- Injection wells
  - -- Surface seals
  - -- Groundwater depression pumps
  - -- Vapor treatment systems

Exhibit II-11 is a schematic diagram of an SVE system.

Exhibit II-11
Schematic Of A Soil Vapor Extraction System



The following subsections provide guidance for reviewing the system configuration, standard system components, and additional system components.

Extraction Wells

Well Orientation. An SVE system can use either vertical or horizontal extraction wells. Orientation of the wells should be based on site-specific needs and conditions. Exhibit II-12 lists site conditions and the corresponding appropriate well orientation.

Well Placement And Number Of Wells. Determine the number and location of extraction wells by using several methods. In the first method, you divide the area of the site requiring treatment by the area of influence for a single well to obtain the total number of wells needed. Then, space the wells evenly within the treatment area to provide areal coverage so that the areas of influence cover the entire area of contamination.

$$\text{Area of influence for a single well} = \pi \cdot (\text{ROI})^2$$

$$\text{Number of wells needed} = \frac{\text{Treatment area } (m^2)}{\text{Area of influence for single extraction well } (m^2/\text{well})}$$

Exhibit II-12
Well Orientation And Site Conditions

Well Orientation	Site Conditions
Vertical extraction well	○ Shallow to deep contamination (5 to 100+ feet). ○ Depth to groundwater > 10 feet.
Horizontal extraction well	○ Shallow contamination (< 25 feet). More effective than vertical wells at depths < 10 feet. Construction difficult at depths > 25 feet. ○ Zone of contamination confined to a specific stratigraphic unit.

In the second method, determine the total extraction flow rate needed to exchange the soil pore volume within the treatment area in a reasonable amount of time (8 to 24 hours). Determine the number of wells required by dividing the total extraction flow rate needed by the flow rate achievable with a single well.

$$\text{Number of wells needed} = \frac{\varepsilon V / t}{q}$$

where:
ε = soil porosity (m^3 vapor / m^3 soil)
V = volume of soil in treatment area (m^3 soil)
q = vapor extraction rate from single extraction well (m^3 vapor/hr).
t = pore volume exchange time (hours)

In the example below, an 8-hour exchange time is used.

$$\text{Number of wells needed} = \frac{\left(\frac{m^3 \text{ vapor}}{m^3 \text{ soil}}\right) \cdot \left(\frac{(m^3 \text{ soil})}{8 \text{ hrs}}\right)}{\frac{m^3 \text{ vapor}}{hr}}$$

Consider the following additional factors in determining well spacing.

○ Use closer well spacing in areas of high contaminant concentrations to increase mass removal rates.

- If a surface seal exists or is planned for the design, space the wells slightly farther apart because air is drawn from a greater lateral distance and not directly from the surface. However, be aware that this increases the need for air injection wells.

- At sites with stratified soils, wells that are screened in strata with low intrinsic permeabilities should be spaced more closely than wells that are screened in strata with higher intrinsic permeabilities.

Well Construction. *Vertical Well Construction.* Vertical extraction wells are similar in construction to groundwater monitoring wells and are installed using the same techniques. Extraction wells are usually constructed of polyvinyl chloride (PVC) casing and screening. Extraction well diameters typically range from 2 to 12 inches, depending on flow rates and depth; a 4-inch diameter is most common. In general, 4-inch-diameter wells are favored over 2-inch-diameter wells because 4-inch-diameter wells are capable of higher extraction flow rates and generate less frictional loss of vacuum pressure.

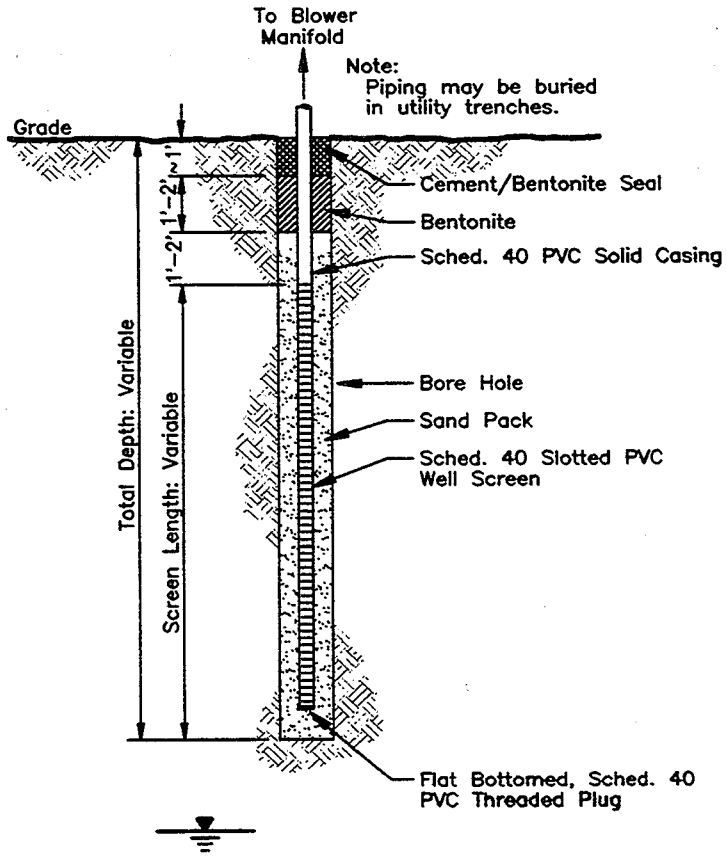
Exhibit II-13 depicts a typical vertical extraction well. Vertical extraction wells are constructed by placing the casing and screen in the center of a borehole. Filter pack material is placed in the annular space between the casing/screen and the walls of the borehole. The filter pack material extends 1 to 2 feet above the top of the well screen and is followed by a 1- to 2-foot-thick bentonite seal. Cement-bentonite grout seals the remaining space up to the surface. Filter pack material and screen slot size must be consistent with the grain size of the surrounding soils.

The location and length of the well screen in vertical extraction wells can vary and should be based on the depth to groundwater, the stratification of the soil, and the location and distribution of contaminants. In general, the length of the screen has little effect on the ROI of an extraction well. However, because the ROI is affected by the intrinsic permeability of the soils in the screened interval (lower intrinsic permeability will result in a smaller ROI, other parameters being equal), the placement of the screen can affect the ROI.

- At a site with homogeneous soil conditions, ensure that the well is screened throughout the contaminated zone. The well screen may be placed as deep as the seasonal low water table. A deeper well helps to ensure remediation of the greatest amount of soil during seasonal low groundwater conditions.

- At a site with stratified soils or lithology, check to see that the screened interval is within the zone of lower permeability because preferred flow will occur in the zones of higher permeability.

Exhibit II-13
Typical Vertical Soil Vapor Extraction Well Construction

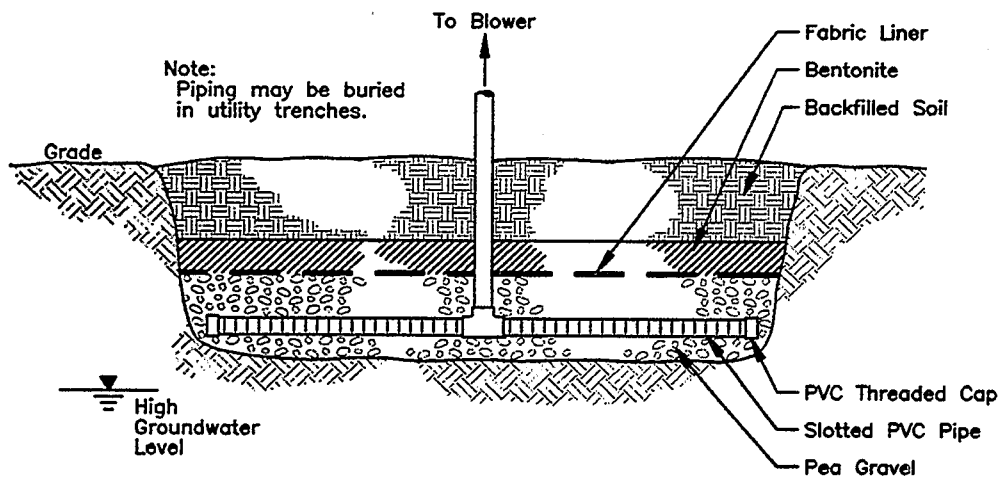


Horizontal Well Construction. Look for horizontal extraction wells or trench systems in shallow groundwater conditions. Exhibit II-14 shows a typical shallow horizontal well construction detail. Horizontal extraction wells are constructed by placing slotted (PVC) piping near the bottom of an excavated trench. Gravel backfill surrounds the piping. A bentonite seal or impermeable liner is added to prevent air leakage from the surface. When horizontal wells are used, the screen must be high enough above the groundwater table that normal groundwater table fluctuations do not submerge the screen. Additionally, vacuum pressures should be monitored such that they do not cause upwelling of the groundwater table that could occlude the well screen(s).

Manifold Piping

Manifold piping connects the extraction wells to the extraction blower. Piping can either be placed above or below grade depending on site operations, ambient temperature, and local building codes. Below-grade piping is most common and is installed in shallow utility trenches that lead from the extraction wellhead vault(s) to a central equipment location. The piping can either be manifolded in the equipment area or connected to a common vacuum main that supplies the wells in series, in which case flow control valves are sited at the wellhead. Piping to the well locations should be sloped toward the well so that condensate or entrained groundwater will flow back toward the well.

Exhibit II-14
Typical Horizontal Soil Vapor Extraction Well Construction



Vapor Pretreatment

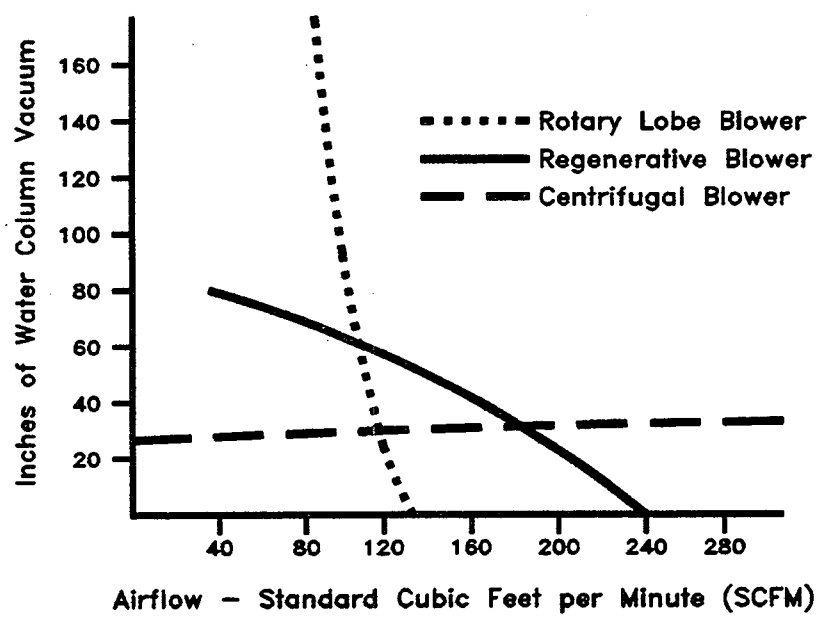
Extracted vapor can contain condensate, entrained groundwater, and particulates that can damage blower parts and inhibit the effectiveness of downstream treatment systems. In order to minimize the potential for damage to blowers, vapors are usually passed through a moisture separator and a particulate filter prior to entering the blower. Check the CAP to verify that both a moisture separator and a particulate filter have been included in the design.

Blower Selection

The type and size of blower selected should be based on both the vacuum required to achieve design vacuum pressure at the extraction wellheads (including upstream and downstream piping losses) and the total flow rate. The flow rate requirement should be based on the sum of the flow rates from the contributing vapor extraction wells. In applications where explosions might occur, blowers must have explosion-proof motors, starters, and electrical systems. Exhibit II-15 depicts the performance curves for the three basic types of blowers that can be used in an SVE system.

- *Centrifugal* blowers (such as squirrel-cage fans) should be used for high-flow (up to 280 standard cubic feet per minute), low-vacuum (less than 30 inches of water) applications.

Exhibit II-15
Performance Curves For Three Types Of Blowers



Notes:

Centrifugal blower type shown is a New York model 2004A at 3500 rpm. Regenerative blower type shown is a Rotron model DR707. Rotary lobe blower type shown is a M-D Pneumatics model 3204 at 3000 rpm.

From "Guidance for Design, Installation and Operation of Soil Venting Systems." Wisconsin Department of Natural Resources, Emergency and Remedial Response Section, PUBL-SW185-93, July 1993.

- *Regenerative and turbine* blowers should be used when a higher (up to 80 inches of water) vacuum is needed.

- *Rotary lobe* and other positive displacement blowers should be used when a very high (greater than 80 inches of water) vacuum and moderate air flow are needed.

Monitoring And Controls

The parameters typically monitored in an SVE system include:

- Pressure (or vacuum)
- Air/vapor flow rate
- Contaminant mass removal rates
- Temperature of blower exhaust vapors

The equipment in an SVE system used to monitor these parameters provides the information necessary to make appropriate system adjustments and track remedial progress. The control equipment in an SVE system allow the flow and vacuum pressure to be adjusted at each extraction well of the system, as necessary. Control equipment typically includes flow control valves. Exhibit II-16 lists typical monitoring and control equipment for an SVE system, where each of these pieces of monitoring equipment should be placed, and the types of equipment that are available.

Optional SVE Components

Additional SVE system components might also be used when certain site conditions exist or pilot studies dictate they are necessary. These components include:

- Injection and passive inlet wells
- Surface seals
- Groundwater depression pumps
- Vapor treatment systems

Injection and Passive Inlet Wells. Air injection and inlet wells are designed to help tune air flow distribution and may enhance air flow rates from the extraction wells by providing an active or passive air source to the subsurface. These wells are often used at sites where a deeper zone (i.e., > 25 feet) is targeted for SVE or where the targeted zone for remediation is isolated from the atmosphere by low permeability materials. They are used also to help prevent short-circuiting of air flow from the atmosphere at sites with shallower target zones. Passive wells have little effect unless they are placed close to the extraction well. In addition, air injection is used to eliminate potential stagnation zones (areas of no flow) that sometimes exist between extraction wells.

Exhibit II-16
Monitoring And Control Equipment

Monitoring Equipment	Location In System	Example Of Equipment
Flow meter	○ At each wellhead ○ Manifold to blower ○ Blower discharge	○ Pitot tube ○ In-line rotameter ○ Orifice plate ○ Venturi or flow tube
Vacuum gauge	○ At each well head or manifold branch ○ Before and after filters upstream of blower ○ Before and after vapor treatment	○ Manometer ○ Magnehelic gauge ○ Vacuum gauge
Vapor temperature sensor	○ Manifold to blower ○ Blower discharge (prior to vapor treatment)	○ Bi-metal dial-type thermometer
Sampling port	○ At each well head or manifold branch ○ Manifold to blower ○ Blower discharge	○ Hose barb ○ Septa fitting
Vapor sample collection equipment (used through a sampling port)	○ At each well head or manifold branch ○ Manifold to blower ○ Blower discharge	○ Tedlar bags ○ Sorbent tubes ○ Sorbent canisters ○ Polypropylene tubing for direct GC injection
Control Equipment		
Flow control valves	○ At each well head or manifold branch ○ Dilution or bleed valve at manifold to blower	○ Ball valve ○ Gate/globe valve ○ Butterfly valve

Air injection wells are similar in construction to extraction wells but can be designed with a longer screened interval in order to ensure uniform air flow. Active injection wells force compressed air into soils. Passive air inlet wells, or inlets, simply provide a pathway that helps extraction wells draw ambient air to the subsurface. Air injection wells should be placed to eliminate stagnation zones, if present, but should not be placed such that the injected air will force contaminants to an area where they will not be recovered (i.e., off-site).

Surface Seals. Surface seals might be included in an SVE system design to prevent surface water infiltration that can reduce air flow rates, reduce emissions of fugitive vapors, prevent vertical short-circuiting of air flow, or increase the design ROI. These results are accomplished because surface seals force fresh air to be drawn from a greater distance from the extraction well. If a surface seal is used, the lower pressure gradients result in decreased flow velocities. This condition may require a higher vacuum to be applied to the extraction well.

Surface seals or caps should be selected to match the site conditions and regular business activities at the site. Options include high density polyethylene (HDPE) liners (similar to landfill liners), clay or bentonite seals (with cover vegetation or other protection), or concrete or asphalt paving. Existing covers (e.g., pavement or concrete slab) might not provide sufficient air confinement if they are constructed with a porous subgrade material.

Groundwater Depression Pumps. Groundwater depression pumping might be necessary at a site with a shallow groundwater table. Groundwater pumps can reduce the upwelling of water into the extraction wells and lower the water table and allow a greater volume of soil to be remediated. Because groundwater depression is affected by pumping wells, these wells must be placed so that the surface of the groundwater is depressed in all areas where SVE is occurring. Groundwater pumping, however, can create two additional waste streams requiring appropriate disposal:

- Groundwater contaminated with dissolved hydrocarbons; and
- Liquid hydrocarbons (i.e., free product, if present).

Vapor Treatment Systems. Look for vapor treatment systems in the SVE design if pilot study data indicate that extracted vapors will contain VOC concentrations in excess of state or local air emission limits. Available vapor treatment options include granular activated carbon (GAC), catalytic oxidation, and thermal oxidation.

GAC is a popular choice for vapor treatment because it is readily available, simple to operate, and can be cost competitive. Catalytic oxidation, however, is generally more economical than GAC when the contaminant mass loading is high. However, catalytic oxidation is not recommended when concentrations of chemical constituents are expected to be sustained at levels greater than 20 percent of their lower explosive limit (LEL). In these cases, a thermal oxidizer is typically employed because the vapor concentration is high enough for the

constituents to burn. Biofilters, an emerging vapor-phase biological treatment technique, can be used for vapors with less than 10 percent LEL, appear to be cost effective, and may also be considered.

Evaluation Of Operation And Monitoring Plans

Make sure that a system operation and monitoring plan has been developed for both the system start-up phase and for long-term operations. Operations and monitoring are necessary to ensure that system performance is optimized and contaminant mass removal is tracked.

Start-Up Operations

The start-up phase should include 7 to 10 days of manifold valving adjustments. These adjustments should optimize contaminant mass removal by concentrating vacuum pressure on the extraction wells that are producing vapors with higher contaminant concentrations, thereby balancing flow and optimizing contaminant mass removal. Flow measurements, vacuum readings, and vapor concentrations should be recorded daily from each extraction vent, from the manifold, and from the effluent stack.

Long-Term Operations

Long-term monitoring should consist of flow-balancing, flow and pressure measurements, and vapor concentration readings. Measurements should take place at biweekly to monthly intervals for the duration of the system operational period.

Exhibit II-17 provides a brief synopsis of system monitoring recommendations.

Exhibit II-17
System Monitoring Recommendations

Phase	Monitoring Frequency	What To Monitor	Where To Monitor
Start-up (7-10 days)	Daily	o Flow o Vacuum o Vapor concentrations	o Extraction vents o Manifold o Effluent stack
Remedial (ongoing)	Biweekly to monthly	o Flow o Vacuum o Vapor concentrations	o Extraction vents o Manifold o Effluent stack

Remedial Progress Monitoring

Monitoring the performance of the SVE system in reducing contaminant concentrations in soils is necessary to determine if remedial progress is proceeding at a reasonable pace.

The mass removed during long-term monitoring intervals can be calculated using vapor concentration and flow rate measurements taken at the manifold. The instantaneous and cumulative mass removal is then plotted versus time. The contaminant mass removed during an operating period can be calculated using the equation provided below. This relationship can be used for each extraction well (and then totalled) or for the system as a whole, depending on the monitoring data that is available.

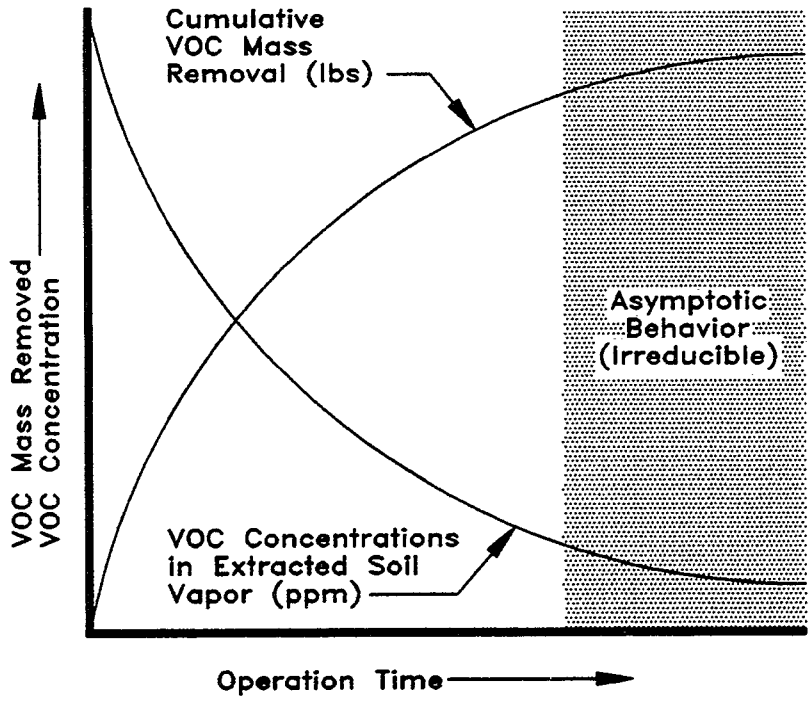
$$M = C \cdot Q \cdot t$$

where: M = cumulative mass removed (kg)
C = vapor concentration (kg/m^3)
Q = extraction flow rate (m^3/hr)
t = operational period (hr)

$$\text{mass removed (kg)} = \frac{kg}{m^3} \cdot \frac{m^3}{hr} \cdot hr$$

Remedial progress of SVE systems typically exhibits asymptotic behavior with respect to both vapor concentration reduction and cumulative mass removal. (See Exhibit II-18.) At this point, the composition of the vapor should be determined and compared with soil vapor samples. This comparison will enable confirmation that there has been a shift in composition toward less volatile components. Soil vapor samples may indicate the composition and extent of the residual contamination. When asymptotic behavior begins to occur, the operator should closely evaluate alternatives that increase mass removal rate such as increasing flow to extraction wells with higher vapor concentrations by terminating vapor extraction from extraction wells with low vapor concentrations or pulsing. Pulsing involves the periodic shutdown and startup operation of extraction wells to allow the subsurface environment to come to equilibrium (shutdown) and then begin extracting vapors again (startup). Other more aggressive steps to curb asymptotic behavior can include installation of additional injection wells or extraction wells.

Exhibit II-18
Relationship Between Concentration Reduction And Mass Removal



If asymptotic behavior is persistent for periods greater than about six months and the concentration rebound is sufficiently small following periods of temporary system shutdown, termination of operations may be appropriate if residual levels are at or below regulatory limits. If not, operation of the system as a bioventing system with reduced vacuum and air flow may be an effective remedial alternative.

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Checklist: Can SVE Be Used At This Site?

This checklist can help you to evaluate the completeness of the CAP and to identify areas that require closer scrutiny. As you go through the CAP, answer the following questions. If the answer to several questions is no, you will want to request additional information to determine if SVE will accomplish the cleanup goals at the site.

1. Factors That Contribute To Permeability Of Soil

Yes	No	
❑	❑	Is the intrinsic permeability greater than 10^{-9} cm^2?
❑	❑	Is the depth to groundwater greater than 3 feet?[1]
❑	❑	Are site soils generally dry?

2. Factors That Contribute To Constituent Volatility

Yes	No	
❑	❑	Is the contaminant vapor pressure greater than 0.5 mm Hg?
❑	❑	If the contaminant vapor pressure is not greater than 0.5 mm Hg, is some type of enhancement (e.g., heated air injection) proposed to increase volatility?
❑	❑	Are the boiling points of the contaminant constituents less than 300°C?
❑	❑	Is the Henry's law constant for the contaminant greater than 100 atm?

[1] If no, this parameter alone may not negate the use of SVE. However, provisions for use of a surface seal, construction of horizontal wells, or for lowering the water table should be incorporated into the CAP.

3. Evaluation Of The SVE System Design

Yes	No	
❑	❑	Does the radius of influence (ROI) for the proposed extraction wells fall in the range 5 to 100 feet?
❑	❑	Has the ROI been calculated for each soil type at the site?
❑	❑	Examine the extraction flow rate. Will these flow rates achieve cleanup in the time allotted for remediation in the CAP?
❑	❑	Is the type of well proposed (horizontal or vertical) appropriate for the site conditions present?
❑	❑	Is the proposed well density appropriate, given the total area to be cleaned up and the radius of influence of each well?
❑	❑	Do the proposed well screen intervals match soil conditions at the site?
❑	❑	Is the blower selected appropriate for the desired vacuum conditions?

4. Optional SVE Components

Yes	No	
❑	❑	Are air injection or passive inlet wells proposed?
❑	❑	Is the proposed air injection/inlet well design appropriate for this site?
❑	❑	Are surface seals proposed?
❑	❑	Are the sealing materials proposed appropriate for this site?
❑	❑	Will groundwater depression be necessary?
❑	❑	If groundwater depression is necessary, are the pumping wells correctly spaced?
❑	❑	Is a vapor treatment system required?
❑	❑	If a vapor treatment system is required, is the proposed system appropriate for the contaminant concentration at the site?

4. Operation And Monitoring Plans

Yes	No	
❑	❑	Does the CAP propose daily monitoring for the first 7 to 10 days of flow measurements, vacuum readings, and vapor concentrations from each extraction vent, the manifold, and the effluent stack?
❑	❑	Does the CAP propose biweekly to monthly monitoring of flow measurements, vacuum readings, and vapor concentrations from each extraction vent, the manifold, and the effluent stack?

Chapter III

Bioventing

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Chapter III
Bioventing

Overview

Bioventing is an in-situ remediation technology that uses indigenous microorganisms to biodegrade organic constituents adsorbed to soils in the unsaturated zone. Soils in the capillary fringe and the saturated zone are not affected. In bioventing, the activity of the indigenous bacteria is enhanced by inducing air (or oxygen) flow into the unsaturated zone (using extraction or injection wells) and, if necessary, by adding nutrients. A bioventing layout using extraction wells is shown in Exhibit III-1; air flow would be reversed if injection wells were used.

When extraction wells are used for bioventing, the process is similar to soil vapor extraction (SVE). However, while SVE removes constituents primarily through volatilization, bioventing systems promote biodegradation of constituents and minimize volatilization (generally by using lower air flow rates than for SVE). In practice, some degree of volatilization and biodegradation occurs when either SVE or bioventing is used. (See Chapter II for a discussion of SVE.)

All aerobically biodegradable constituents can be treated by bioventing. In particular, bioventing has proven to be very effective in remediating releases of petroleum products including gasoline, jet fuels, kerosene, and diesel fuel. Bioventing is most often used at sites with mid-weight petroleum products (i.e., diesel fuel and jet fuel), because lighter products (i.e., gasoline) tend to volatilize readily and can be removed more rapidly using SVE. Heavier products (e.g., lubricating oils) generally take longer to biodegrade than the lighter products. A summary of the advantages and disadvantages of bioventing is shown in Exhibit III-2.

This chapter will assist you in evaluating a corrective action plan (CAP) which proposes bioventing as a remedy for petroleum-contaminated soil. The evaluation process is summarized in a flow diagram shown on Exhibit III-3; this flow diagram serves as a roadmap for the decisions you will make during your evaluation. A checklist has also been provided at the end of this chapter for you to use as a tool to both evaluate the completeness of the CAP and focus attention on areas where additional information may be needed. The evaluation process can be divided into the four steps described below.

Exhibit III-1
Typical Bioventing System Using Vapor Extraction

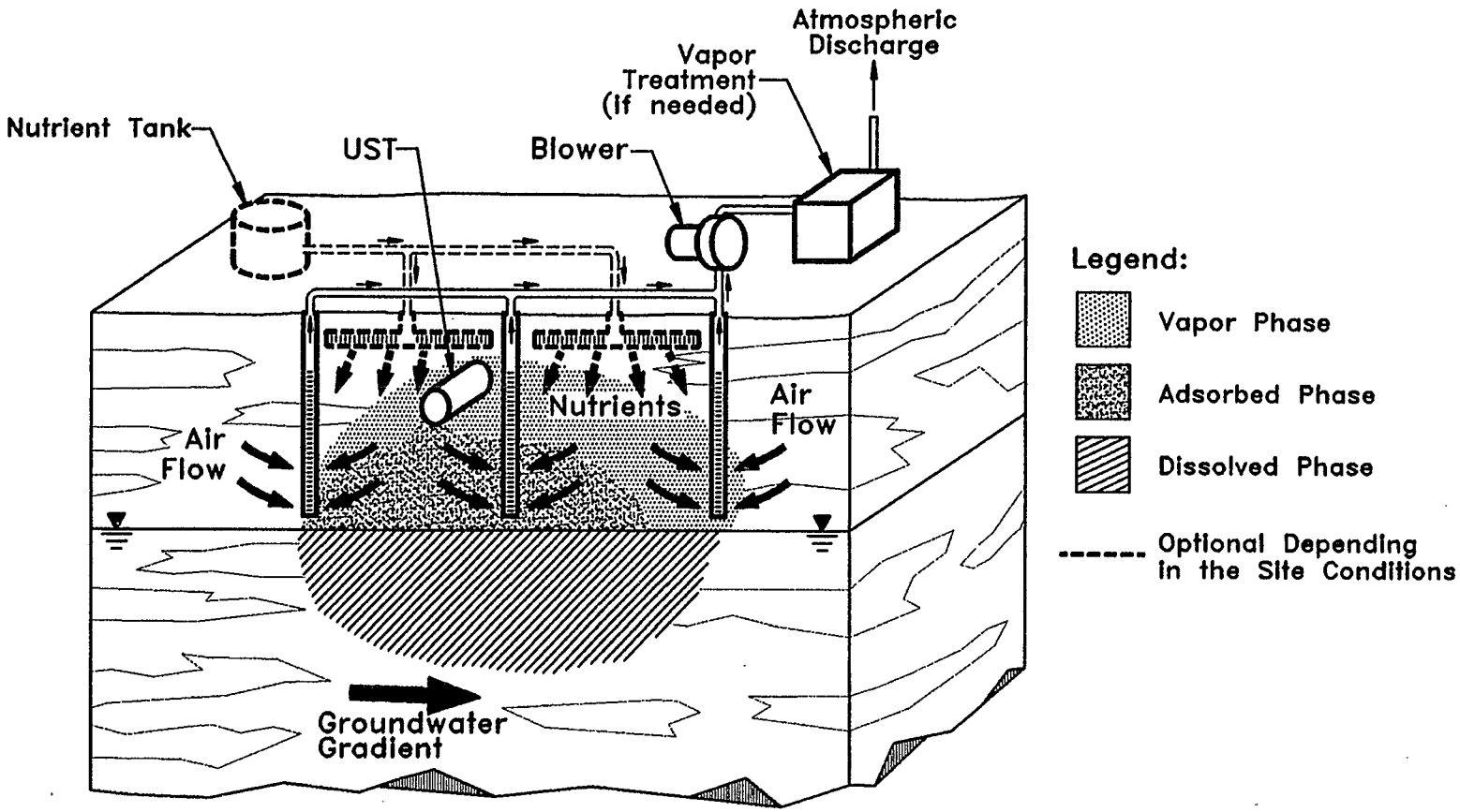


Exhibit III-2
Bioventing Summary

Advantages	Disadvantages
○ Uses readily available equipment; easy to install.	○ High constituent concentrations may initially be toxic to microorganisms.
○ Creates minimal disturbance to site operations. Can be used to address inaccessible areas (e.g., under buildings).	○ Not applicable for certain site conditions (e.g., low soil permeabilities, high clay content, insufficient delineation of subsurface conditions).
○ Requires short treatment times: usually 6 months to 2 years under optimal conditions.	○ Cannot always achieve very low cleanup standards.
○ Is cost competitive: $45-140/ton of contaminated soil.	○ Permits generally required for nutrient injection wells (if used). (A few states also require permits for air injection.)
○ Easily combinable with other technologies (e.g., air sparging, groundwater extraction).	
○ May not require costly offgas treatment.	

- Step 1: ***An initial screening of bioventing effectiveness***, which will allow you to quickly gauge whether bioventing is likely to be effective, moderately effective, or ineffective.

- **Step 2: *A detailed evaluation of bioventing effectiveness***, which provides further screening criteria to confirm whether bioventing is likely to be effective. To complete the detailed evaluation, you will need to identify specific soil properties and product constituent characteristics in the CAP, compare them to ranges where bioventing is effective, evaluate the results of pilot studies reported in the CAP, and conclude whether bioventing is likely to be effective.

- **Step 3: *An evaluation of the bioventing system design***, which will allow you to determine if the rationale for the design has been appropriately defined based on pilot study data or other studies, whether the necessary design components have been specified, and whether the construction process flow designs are consistent with standard practice.

Exhibit III-3
Bioventing Evaluation Process Flow Chart

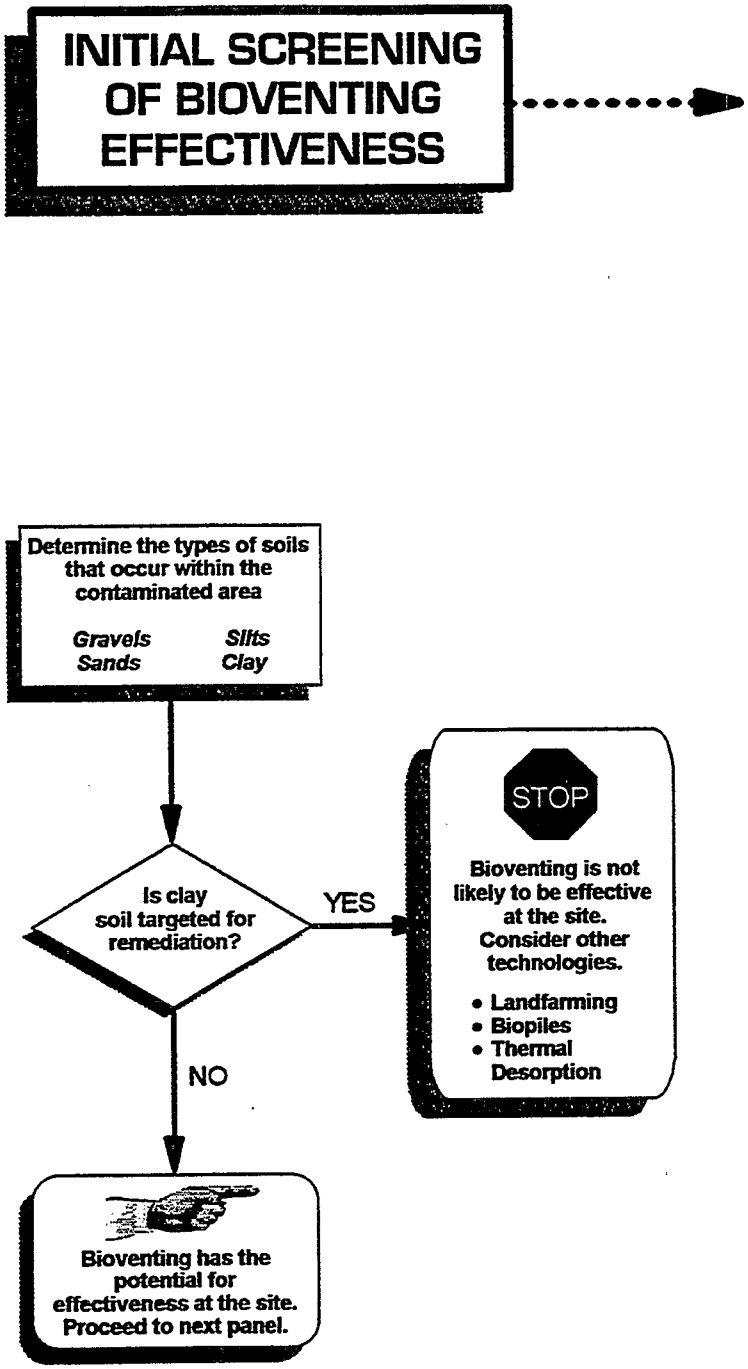


Exhibit III-3
Bioventing Evaluation Process Flow Chart

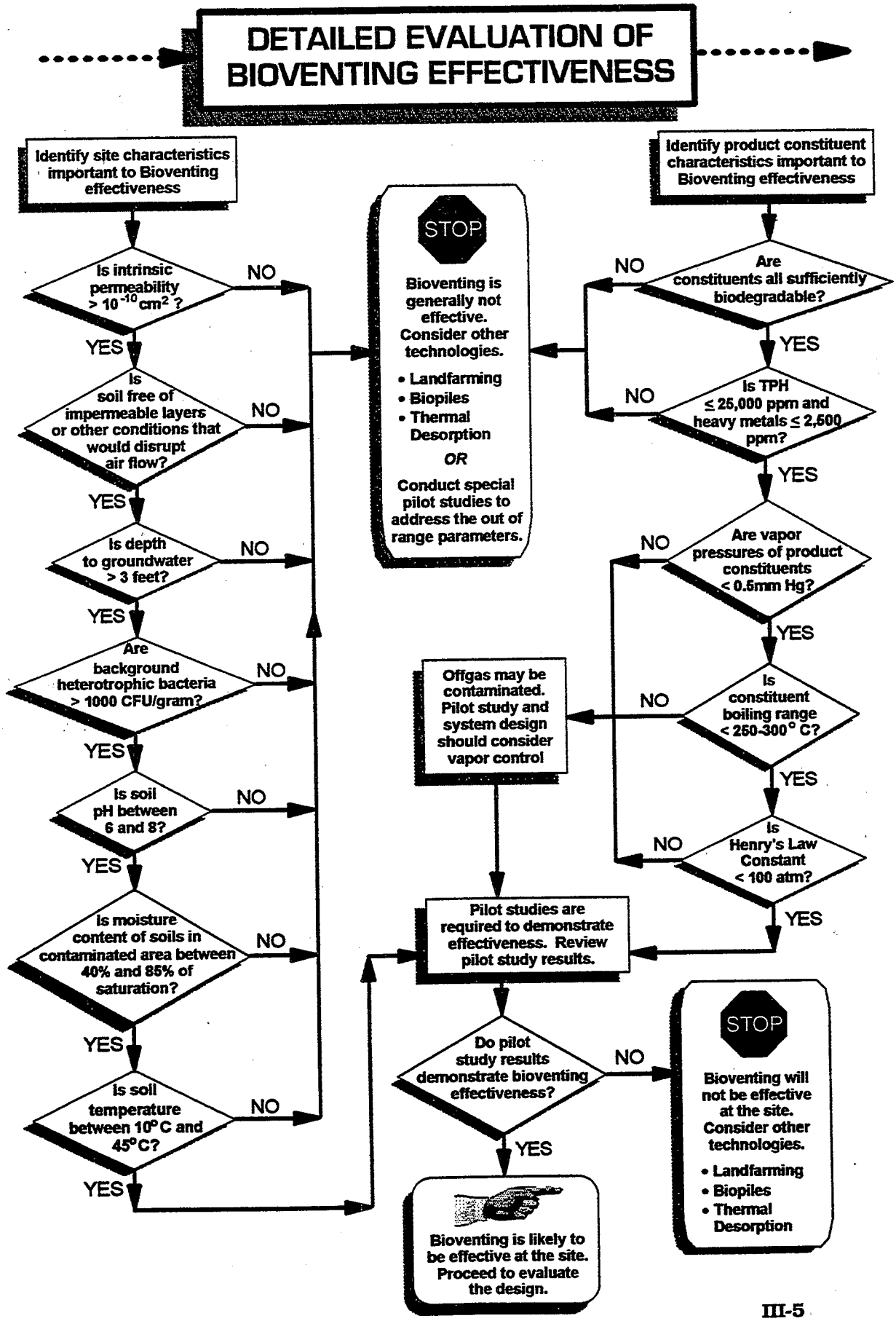
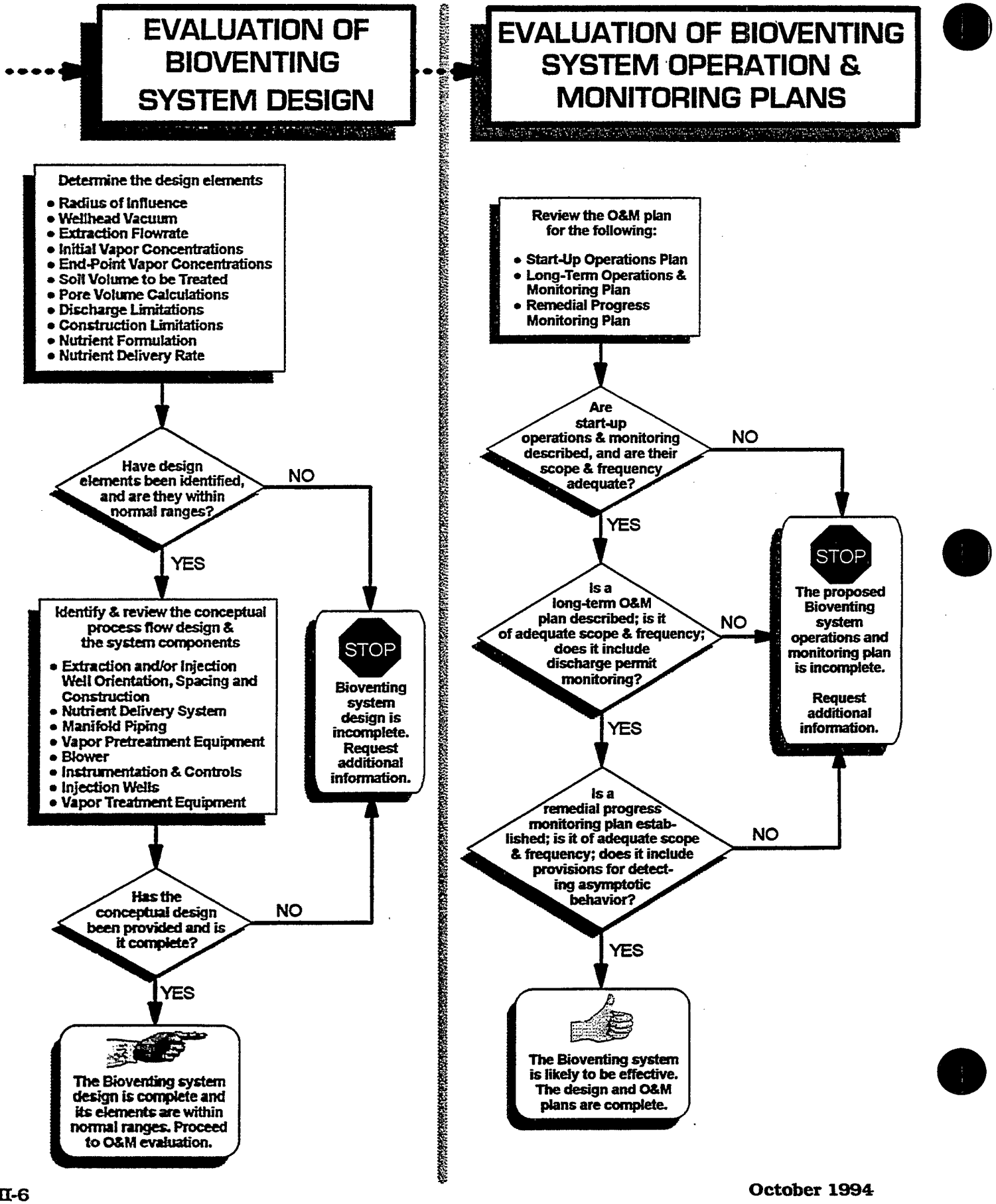


Exhibit III-3
Bioventing Evaluation Process Flow Chart



- **Step 4:** ***An evaluation of the operation and monitoring plans,*** which will allow you to determine whether start-up and long-term system operation monitoring is of sufficient scope and frequency and whether remedial progress monitoring plans are appropriate.

Initial Screening Of Bioventing Effectiveness

This section defines the key factors that should be used to decide whether bioventing has the potential to be effective at a particular site. These factors are:

- The *permeability* of the petroleum-contaminated soils. This will determine the rate at which oxygen can be supplied to the hydrocarbon-degrading microorganisms found in the subsurface.

- The *biodegradability* of the petroleum constituents. This will determine both the rate at which and the degree to which the constituents will be metabolized by microorganisms.

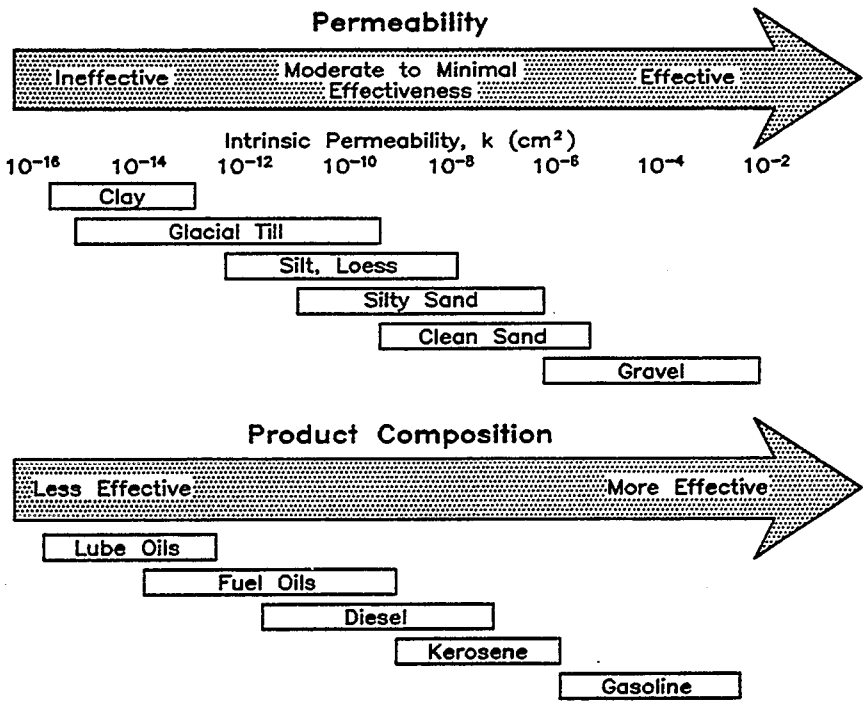
In general, the type of soil will determine its *permeability*. Fine-grained soils (e.g., clays and silts) have lower permeabilities than coarse-grained soils (e.g., sands and gravels). The *biodegradability* of a petroleum product constituent is a measure of its ability to be metabolized by hydrocarbon-degrading bacteria that produce carbon dioxide and water as byproducts of microbial respiration. Petroleum products are generally biodegradable regardless of their molecular weight, as long as indigenous microorganisms have an adequate supply of oxygen and nutrients. For heavier constituents (which are less volatile and less soluble than many lighter components), biodegradation will exceed volatilization as the primary removal mechanism, even though biodegradation is generally slower for heavier constituents than for lighter constituents.

Exhibit III-4 provides a screening tool you can use to make an initial assessment of the potential effectiveness of bioventing. To use this tool, first determine the type of soil present and the type of petroleum product released at the site. Information provided in the following section will allow a more thorough evaluation of effectiveness and will identify areas that could require special design considerations.

Detailed Evaluation Of Bioventing Effectiveness

Once you have completed the initial screening and determined that bioventing may be effective for the soil and petroleum product present, review the CAP further to reconfirm effectiveness.

Exhibit III-4
Initial Screening For Bioventing Effectiveness



Note:
All petroleum products listed are amenable for the bioventing remediation alternative.

While the initial screen focused on soil permeability and constituent biodegradability, the detailed evaluation should consider a broader range of site and constituent characteristics, which are listed in Exhibit III-5.

The remainder of this section describes each of these parameters, why each is important to bioventing, how they can be determined, and the range of each parameter considered appropriate for bioventing.

Exhibit III-5
Key Parameters Used To Evaluate Site Characteristics And Constituent Characteristics

Site Characteristics	Constituent Characteristics
Intrinsic permeability	Chemical structure
Soil structure and stratification	Concentration and toxicity
Microbial presence	Vapor pressure
Soil pH	Product composition and boiling point
Moisture content	Henry's law constant
Soil temperature	
Nutrient concentrations	
Depth to groundwater	

Site Characteristics

Intrinsic Permeability

Intrinsic permeability is a measure of the ability of soils to transmit air and is the *single most important factor* in determining the effectiveness of bioventing because it determines how much oxygen can be delivered (via extraction or injection) to the subsurface bacteria. Hydrocarbon-degrading bacteria use oxygen to metabolize organic material to yield carbon dioxide and water, a process commonly referred to as aerobic respiration. To degrade large amounts of petroleum hydrocarbons, a substantial bacterial population is required which, in turn, requires oxygen for both the metabolic process and the growth of the bacterial mass itself. Approximately 3 to 3½ pounds of oxygen are needed to degrade one pound of petroleum product. Exhibit III-6 shows the relationship of oxygen provided per day from a single vent well for different induced flow rates.

Intrinsic permeability, which will determine the rate at which oxygen can be supplied to the subsurface, varies over 13 orders of magnitude (from 10^{-16} to 10^{-3} cm^2) for the wide range of earth materials, although a more limited range applies for most soil types (10^{-13} to 10^{-5} cm^2). Intrinsic permeability is best determined from field or laboratory tests, but can be estimated within one or two orders of magnitude from soil boring log data and laboratory tests. Procedures for these tests are described in EPA (1991a). Coarse-grained soils (e.g., sands) have higher intrinsic permeability than fine-grained soils (e.g., clays, silts). Note that the ability of a soil to transmit air, which is of prime importance to bioventing, is reduced by the presence of soil water, which can block the

Exhibit III-6
Oxygen Provided Per Day From A Single Well By A Vent System

Air Flow Rate		Oxygen Provided	
SCFM	m^3/min	lb/day	kg/day
1	$2.83 \cdot 10^{-2}$	23	10
5	$1.42 \cdot 10^{-1}$	117	52
10	$2.83 \cdot 10^{-1}$	233	106
20	$5.66 \cdot 10^{-1}$	467	212
50	$1.42 \cdot 10^{0}$	1,170	529
100	$2.83 \cdot 10^{0}$	2,330	1,060

soil pores and reduce air flow. This is especially important in fine-grained soils, which tend to retain water. Use the values presented in Exhibit III-7 to determine if intrinsic permeability is within the effectiveness range for bioventing.

Exhibit III-7
Intrinsic Permeability And Bioventing Effectiveness

Intrinsic Permeability (cm^2)	Bioventing Effectiveness
$k \geq 10^{-8}$	Effective.
$10^{-8} \geq k \geq 10^{-10}$	May be effective; needs further evaluation.
$k < 10^{-10}$	Not effective.

At sites where the soils in the saturated zone are similar to those within the unsaturated zone, hydraulic conductivity of the soils may be used to estimate the permeability of the soils. Hydraulic conductivity is a measure of the ability of soils to transmit water. Hydraulic conductivity can be determined from aquifer tests, including slug tests and pumping tests. You can convert hydraulic conductivity to intrinsic permeability using the following equation:

$$k = K (\mu / \rho g)$$

where:
k = intrinsic permeability (cm^2)
K = hydraulic conductivity (cm/sec)
μ = water viscosity (g/cm · sec)
ρ = water density (g/cm^3)
g = acceleration due to gravity (cm/sec^2)

At 20°C: $\mu/\rho g = 1.02 \cdot 10^{-5}$ cm/sec

To convert k from cm^2 to darcy, multiply by 10^8

Soil Structure And Stratification

Soil structure and stratification are important to bioventing because they affect how and where soil vapors will flow within the soil matrix when extracted or injected. Structural characteristics such as microfracturing can result in higher permeabilities than expected for certain soils (e.g., clays). Increased flow will occur in the fractured but not in the unfractured media. Stratification of soils with different permeabilities can dramatically increase the lateral flow of soil vapors in more permeable strata while reducing the soil vapor flow through less permeable strata. This preferential flow behavior can lead to ineffective or extended remedial times for less-permeable strata or to the possible spreading of contamination if injection wells are used.

You can determine soil intergranular structure and stratification by reviewing soil boring logs for wells or borings and by examining geologic cross-sections. Verify that soil types have been identified, that visual observations of soil structure have been documented, and that boring logs are of sufficient detail to define any soil stratification.

The types of soils and their structures will determine their permeabilities. In general, fine-grained soils composed of clays or silts offer resistance to air flow. However, if the soils are highly fractured, they may have sufficient permeability to use bioventing. Stratified soils may require special consideration in design to ensure that less-permeable strata are adequately vented.

Fluctuations in the groundwater table should also be considered when reviewing the CAP. Significant seasonal or daily (e.g., tidal or precipitation-related) fluctuations may, at times, submerge some of the contaminated soil or a portion of the well screen, making it unavailable for air flow. These fluctuations are most important for horizontal wells, in which screens are placed parallel with the water table surface and a water table rise could occlude the entire length of screen.

Microbial Presence

Soil normally contains large numbers of diverse microorganisms including bacteria, algae, fungi, protozoa, and actinomycetes. In well-aerated soils, which are most appropriate for bioventing, these organisms are generally aerobic. Of these organisms, the bacteria are the most numerous and biochemically active group, particularly at low oxygen levels. Bacteria require a carbon source for cell growth and an energy source to sustain metabolic functions required for growth. Nutrients, including nitrogen and phosphorus, are also required for cell growth.

The metabolic process used by bacteria to produce energy requires a terminal electron acceptor (TEA) to enzymatically oxidize the carbon source to carbon dioxide.

Microbes are classified by the carbon and TEA sources they use to carry out metabolic processes. Bacteria that use organic compounds (such as petroleum constituents and other naturally occurring organics) as their source of carbon are called *heterotrophic*; those that use inorganic carbon compounds such as carbon dioxide are called *autotrophic*. Bacteria that use oxygen as their TEA are called *aerobic*; those that use a compound other than oxygen (e.g., nitrate or sulfate) are called *anaerobic*; and those that can utilize both oxygen and other compounds as TEAs are called *facultative*. For bioventing applications directed at petroleum products, bacteria that are both *aerobic* (or *facultative*) and *heterotrophic* are most important in the degradation process.

To evaluate the presence and population of naturally occurring bacteria that will contribute to degradation of petroleum constituents, laboratory analysis of soil samples from the site should be completed. These analyses, at a minimum, should include plate counts for total heterotrophic bacteria. Although heterotrophic bacteria are normally present in all soil environments, plate counts of less than 1000 colony-forming units (CFU)/gram of soil could indicate the presence of toxic concentrations of inorganic or organic compounds or depletion of oxygen or other essential nutrients. However, concentrations as low as 100 CFU per gram of soil can be increased by bioventing to acceptable levels. The total population of heterotrophic bacterial species that are capable of degrading the specific petroleum constituents present should also be measured. These conditions are summarized in Exhibit III-8.

Exhibit III-8
Heterotrophic Bacteria And Bioventing Effectiveness

Total Heterotrophic Bacteria (prior to bioventing)	Bioventing Effectiveness
> 1000 CFU/gram dry soil	Generally effective.
< 1000 CFU/gram dry soil	May be effective; needs further evaluation to determine if toxic conditions are present.

Soil pH

The optimum pH for bacterial growth is approximately 7; the acceptable range for soil pH in bioventing is between 6 and 8. Soils with pH values outside this range prior to bioventing will require pH adjustments prior to and during bioventing operations. Exhibit III-9 summarizes the effect of soil pH on bioventing effectiveness. Review the CAP to verify that soil pH measurements have been made. If the soil pH is less than 6 or greater than 8, make sure that pH adjustments are included in the bioventing design and operational plans.

Exhibit III-9
Soil pH And Bioventing Effectiveness

Soil pH (prior to bioventing)	Bioventing Effectiveness
$6 \leq pH \leq 8$	Generally effective.
$6 \geq pH \geq 8$	Soils will require amendments to correct pH to effective range.

Moisture Content

Bacteria require moist soil conditions for proper growth. Excessive soil moisture, however, reduces the availability of oxygen, which is also necessary for bacterial metabolic processes, by restricting the flow of air through soil pores. The ideal range for soil moisture is between 40 and 85 percent of the water-holding capacity of the soil. Generally, soils saturated with water prohibit air flow and oxygen delivery to bacteria, while dry soils lack the moisture necessary for bacterial growth.

Airflow is particularly important for soils within the capillary fringe, where a significant portion of the constituents often reside. Fine-grained soils create a thicker capillary fringe than coarse-grained soils. The thickness of the capillary fringe can usually be determined from soil boring logs (i.e., in the capillary fringe, soils are usually described as moist or wet). The capillary fringe usually extends from one to several feet above the elevation of the groundwater table. Moisture content of soils within the capillary fringe may be too high for effective bioventing. Depression of the water table by groundwater pumping may be necessary to biovent soils within the capillary fringe.

Stormwater infiltration can create excessively moist soils in areas that do not have surface covers, such as asphalt or concrete. This may be a persistent problem with fine-grained soils that have slow infiltration rates. Bioventing promotes dehydration of moist soils through increased air flow through the soil, but excessive dehydration hinders bioventing performance and extends operation time.

Soil Temperature

Bacterial growth rate is a function of temperature. Soil microbial activity has been shown to decrease significantly at temperatures below 10°C and essentially to cease at 5°C. Microbial activity of most bacteria important to petroleum hydrocarbon biodegradation also diminishes at temperatures greater than 45°C. Within the range of 10°C to 45°C, the rate of microbial activity typically doubles for every 10°C rise in temperature. In most areas of the U.S., subsurface soils have a fairly constant temperature of about 13°C throughout the year. However, subsurface soil temperatures in the extreme northern states may be lower, reducing the rate of biodegradation.

Nutrient Concentrations

Bacteria require inorganic nutrients such as ammonium and phosphate to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in the site soils but, more frequently, nutrients need to be added to soils to maintain bacterial populations. However, excessive amounts of certain nutrients (i.e., phosphate and sulfate) can repress metabolism.

A rough approximation of minimum nutrient requirements can be based on the stoichiometry of the overall biodegradation process:

$$\text{C-source} + \text{N-source} + O_2 + \text{Minerals} + \text{Nutrients} \longrightarrow \text{Cell mass} + CO_2 + H_2O + \text{products}$$

Different empirical formulas of bacterial cell mass have been proposed; the most widely accepted are $C_5H_7O_2N$ and $C_{60}H_{87}O_{32}N_{12}P$. Using the empirical formulas for cell biomass and other assumptions, the carbon:nitrogen:phosphorus ratios necessary to enhance biodegradation fall in the range of 100:10:1 to 100:1:0.5, depending on the constituents and bacteria involved in the biodegradation process.

Chemical analysis of soil samples from the site should be completed to determine the concentrations of nitrogen (expressed as ammonia) and phosphate that occur naturally in the soil. Using the stoichiometric ratios, the need for nutrient addition can be determined by using an

average concentration of the constituents (carbon source) in the soils to be treated.

Depth To Groundwater

Bioventing is not appropriate for sites with groundwater tables located less than 3 feet below the land surface. Special considerations must be taken for sites with a groundwater table located less than 10 feet below the land surface because groundwater upwelling can occur within bioventing wells under vacuum pressures, potentially occluding screens and reducing or eliminating vacuum-induced soil vapor flow. This potential problem is not encountered if injection wells are used instead of extraction wells to induce air flow. Use Exhibit III-10 to determine whether the water-table depth is of potential concern for use of bioventing.

Exhibit III-10
Depth To Groundwater And Bioventing Effectiveness

Depth To Groundwater	Bioventing Effectiveness
> 10 feet	Effective.
3 feet < depth < 10 feet	Need special controls (i.e., horizontal wells or groundwater pumping).
< 3 feet	Not effective.

Constituent Characteristics

Chemical Structure

The chemical structures of the constituents present in the soils proposed for treatment by bioventing are important for determining the rate at which biodegradation will occur. Although nearly all constituents in petroleum products typically found at UST sites are biodegradable, the more complex the molecular structure of the constituent, the more difficult and less rapid is biological treatment. Most low-molecular-weight (nine carbon atoms or less) aliphatic and monoaromatic constituents are more easily biodegraded than higher-molecular-weight aliphatic or polyaromatic organic constituents. Exhibit III-11 lists, in order of decreasing rate of potential biodegradability, some common constituents found at petroleum UST sites.

Exhibit III-11
Chemical Structure And Biodegradability

Biodegradability	Example Constituents	Products In Which Constituent Is Typically Found
More degradable	n-butane, l-pentane, n-octane	○ Gasoline
	Nonane	○ Diesel fuel
	Methyl butane, dimethylpentenes, methyloctanes	○ Gasoline
	Benzene, toluene, ethylbenzene, xylenes	○ Gasoline
	Propylbenzenes	○ Diesel, kerosene
	Decanes Dodecanes Tridecanes Tetradecanes	○ Diesel ○ Kerosene ○ Heating fuels ○ Lubricating oils
Less degradable	Naphthalenes Fluoranthenes Pyrenes Acenaphthenes	○ Diesel ○ Kerosene ○ Heating oil ○ Lubricating oils

Evaluation of the chemical structure of the constituents proposed for reduction by bioventing at the site will allow you to determine which constituents will be the most difficult to degrade. You should verify that remedial time estimates, biotreatability studies, field-pilot studies (if applicable), and bioventing operation and monitoring plans are based on the constituents that are the most difficult to degrade (or "rate limiting") in the biodegradation process.

Concentration And Toxicity

The presence of very high concentrations of petroleum organics or heavy metals in site soils can be toxic or inhibit the growth and reproduction of bacteria responsible for biodegradation. In addition, very low concentrations of organic material will also result in diminished levels of bacterial activity.

In general, concentrations of petroleum hydrocarbons in excess of 25,000 ppm, or heavy metals in excess of 2,500 ppm, in soils are considered inhibitory and/or toxic to aerobic bacteria. Review the CAP to verify that the average concentrations of petroleum hydrocarbons and heavy metals in the soils to be treated are below these levels. Exhibit III-12 provides the general criteria for constituent concentration and bioventing effectiveness.

Exhibit III-12
Constituent Concentration And Bioventing Effectiveness

Constituent Concentration	Bioventing Effectiveness
Petroleum constituents $\leq$ 25,000 ppm and Heavy metals $\leq$ 2,500 ppm	Effective.
Petroleum constituents > 25,000 ppm or Heavy metals > 2,500 ppm	Ineffective; toxic or inhibitory conditions to bacterial growth exist. Long remediation times likely.

In addition to maximum concentrations, you should consider the cleanup concentrations proposed for the treated soils. Below a certain "threshold" constituent concentration, the bacteria cannot obtain sufficient carbon (from degradation of the constituents) to maintain adequate biological activity. The threshold level can be determined from laboratory studies and should be below the level required for cleanup. Although the threshold limit varies greatly depending on bacteria-specific and constituent-specific features, constituent concentrations below 0.1 ppm are generally not achievable by biological treatment alone. In addition, experience has shown that reductions in total petroleum hydrocarbon concentrations (TPH) greater than 95 percent can be very difficult to achieve because of the presence of "recalcitrant" or nondegradable petroleum species that are included in the TPH analysis. Identify the average starting concentrations and the cleanup concentrations in the CAP for individual constituents and TPH. If a cleanup level lower than 0.1 ppm is required for any individual constituent or a reduction in TPH greater than 95 percent is required to reach the cleanup level for TPH, either a pilot study should be required to demonstrate the ability of bioventing to achieve these reductions at the site or another technology should be considered. These conditions are summarized in Exhibit III-13.

Exhibit III-13
Cleanup Concentrations And Bioventing Effectiveness

Cleanup Requirement	Bioventing Effectiveness
Constituent concentration > 0.1 ppm and TPH reduction < 95%	Effective.
Constituent concentration ≤ 0.1 ppm or TPH reduction ≥ 95%	Potentially ineffective; pilot studies are required to demonstrate reductions.

Vapor Pressure

Vapor pressure is important in evaluating the extent to which constituents will be volatilized rather than biodegraded. The vapor pressure of a constituent is a measure of its tendency to evaporate. More precisely, it is the pressure that a vapor exerts when in equilibrium with its pure liquid or solid form. Constituents with higher vapor pressures are generally volatilized rather than undergoing biodegradation. Constituents with vapor pressures higher than 0.5 mm Hg will likely be volatilized by the induced air stream before they biodegrade. Constituents with vapor pressures lower than 0.5 mm Hg will not volatilize to a significant degree and can instead undergo *in situ* biodegradation by bacteria.

As previously discussed, petroleum products contain many different chemical constituents. Each constituent will be volatilized (rather than biodegraded) to different degrees by a bioventing system, depending on its vapor pressure. If concentrations of volatile constituents are significant, treatment of extracted vapors may be needed. Exhibit III-14 lists vapor pressures of select petroleum constituents.

Product Composition And Boiling Point

Boiling point is another measure of constituent volatility. Because of their complex constituent compositions, petroleum products are often classified by their boiling point ranges (rather than vapor pressures). In general, nearly all petroleum-derived organic compounds are capable of biological degradation, although constituents of higher molecular weights and higher boiling points require longer periods of time to be

Exhibit III-14
Vapor Pressures Of Common Petroleum Constituents

Constituent	Vapor Pressure (mm Hg at 20°C)
Methyl t-butyl ether	245
Benzene	76
Toluene	22
Ethylene dibromide	11
Ethylbenzene	7
Xylenes	6
Naphthalene	0.5
Tetraethyl lead	0.2

degraded. Products with boiling points of less than about 250°C to 300°C will volatilize to some extent and can be removed by a combination of volatilization and biodegradation in a bioventing system. The boiling point ranges for common petroleum products are shown in Exhibit III-15.

Exhibit III-15
Petroleum Product Boiling Ranges

Product	Boiling Range (°C)
Gasoline	40 to 205
Kerosene	175 to 325
Diesel fuel	200 to 338
Heating oil	> 275
Lubricating oils	Nonvolatile

Henry's Law Constant

Another method of gauging the volatility of a constituent is by noting its Henry's law constant. Henry's law constant is the partition coefficient that relates the concentration of a constituent dissolved in water to its partial pressure in the vapor under equilibrium conditions.

In other words, it describes the relative tendency for a dissolved constituent to exist in the vapor phase. Henry's law constants for several common constituents found in petroleum products are shown in Exhibit III-16. Constituents with Henry's law constants of greater than 100 atmospheres are generally considered volatile and are more likely to be volatilized rather than biodegraded.

Exhibit III-16
Henry's Law Constant Of Common Petroleum Constituents

Constituent	Henry's Law Constant (atm)
Tetraethyl lead	4,700
Ethylbenzene	359
Xylenes	266
Benzene	230
Toluene	217
Naphthalene	72
Ethylene dibromide	34
Methy t-butyl ether	27

Pilot Scale Studies

After you have examined the data in the CAP to gauge the potential effectiveness of bioventing, you will be in a position to decide if bioventing is likely to be highly effective, somewhat effective, or ineffective for site conditions. In general, remedial approaches that rely on biological processes should be subject to field pilot studies to verify and quantify the potential effectiveness of the approach and provide data necessary to design the system. For bioventing, these studies may range in scope and complexity from a simple soil column test or microbial count to field respirometry tests and soil vapor extraction (or injection) pilot studies. The scope of pilot testing or laboratory studies should be commensurate with the size of the area to be remediated, the reduction in constituent concentration required, and the results of the initial effectiveness screening.

A list and description of commonly used laboratory and pilot-scale studies is provided below.

- *Soil Vapor Extraction and Injection Treatability Tests* are generally used to determine the radius of influence that an extraction well or injection well can exert in the surrounding soils, the optimum vapor

flow rate and pressure (or vacuum) that should be applied to the wells, and the concentration of petroleum constituents in the induced air stream. The test most often includes short-term vapor extraction or air injection from a single well while measuring the pressure effect in monitoring wells or probes spaced at increasing distances from the extraction well or the injection well. The test can assist in determining the spacing, number, and type of wells needed for the full-scale system. It is usually not economically attractive to perform this test for sites with areas smaller than 5,000 cubic yards of *in situ* contaminated soil or for sites with soil permeabilities greater than 10^{-8} cm^2.

- *Respirometry Studies* are generally used to determine the oxygen transport capacity of the site soils and to estimate the biodegradation rates under field conditions. The test includes short-term injection of an oxygen/inert gas mixture into a well that has been screened in the contaminated soil horizon. Carbon dioxide, inert gas (typically helium), and oxygen concentrations are measured in the injection well and surrounding wells periodically for about 1 to 5 days. The measurements are then compared to baseline concentrations of the gases prior to injection. Increases in carbon dioxide and decreases in oxygen concentrations are indications of biological metabolism of constituents; the inert gas concentration provides the baseline for these calculations. Temperature of the extracted vapor may also be monitored to serve as an additional indicator of biological activities. Field respirometry studies are usually only needed for sites with large areas of contamination, perhaps greater than 100,000 cubic yards of *in situ* soils requiring remediation; at sites where soil permeability is less than 10^{-8} cm^2; or when reductions of more than 80 percent of the constituents that have vapor pressures less than 0.5 mm Hg are required.

- *Laboratory Microbial Screening* tests are used to determine the presence of a population of naturally-occurring bacteria that may be capable of degrading petroleum product constituents. Samples of soils from the site are analyzed in an offsite laboratory. Microbial plate counts determine the number of colony forming units (CFU) of heterotrophic bacteria and petroleum-degrading bacteria are present per unit mass of dry soil. These tests are relatively inexpensive.

- *Laboratory Biodegradation Studies* can be used to estimate the rate of oxygen delivery and to determine if the addition of inorganic nutrients is necessary. However, laboratory studies cannot duplicate field conditions, and field tests are more reliable. There are two kinds of laboratory studies: *slurry studies* and *column studies*. *Slurry studies*, which are more common and less costly, involve the preparation of

numerous "soil microcosms" consisting of small samples of site soils mixed into a slurry with site groundwater. The microcosms are divided into several groups which may include control groups that are "poisoned" to destroy any bacteria, non-nutrified test groups that have been provided oxygen but not nutrients, and nutrified test groups which are supplied both oxygen and nutrients. Microcosms from each group are analyzed periodically (usually weekly) for the test period duration (usually 4 to 12 weeks) for bacterial population counts and constituent concentrations. Results of slurry studies should be considered as representing optimal conditions because slurry microcosms do not consider the effects of limited oxygen delivery or soil heterogeneity. *Column studies* are set up in a similar way using columns of site soils and may provide more realistic expectations of bioventing performance.

Evaluation Of The Bioventing System Design

Once you have completed the detailed evaluation of bioventing effectiveness, you can evaluate the design of the system. The CAP should include a discussion of the design basis for the system and the conceptual design. Detailed engineering design documents might also be included, depending on state requirements. Further detail about information to look for in the discussion of the design is provided below.

Rationale For The Design

The rationale for the design includes the fundamental design decisions and requirements that form the foundation for the system design. For bioventing systems, the design should include the following information:

- *Design Radius of Influence* (ROI) is an estimate of the maximum distance from a vapor extraction well (or injection well) at which sufficient air flow can be induced to sustain acceptable degradation rates. Establishing the design ROI is not a trivial task because it depends on many factors including intrinsic permeability of the soil, soil chemistry, moisture content, and desired remediation time. The ROI should usually be determined through field pilot studies but can be estimated from air flow modeling or other empirical methods. Generally, the design ROI can range from 5 feet (for fine-grained soils) to 100 feet (for coarse-grained soils). For sites with stratified geology, radii of influence should be defined for each soil type. The ROI is important in determining the appropriate number and spacing of extraction or injection wells.

- *Wellhead Pressure* is the pressure (or vacuum) that is required at the top of the vent well to produce the desired induced air stream flow rate from the well. Although wellhead pressure (or vacuum) is usually determined through field pilot studies, it can be estimated and typically ranges from 3 to 100 inches of water vacuum for extraction and 10 to 50 psi for injection. Less permeable soils generally require higher vacuum or pressure to produce a reasonable radius of influence. It should be noted, however, that high vacuum pressures can cause upwelling of the water table and occlusion of the extraction well screens. For air injection, high pressure may push the contaminated vapor to previously uncontaminated soil and ground water.

- *Induced Vapor Flow Rate* is the volumetric flow rate of soil vapor that will be induced by each extraction or injection well and establishes the oxygen delivery rate to the *in situ* treatment area. The induced vapor flow rate, radius of influence, and wellhead pressure are all interdependent (i.e., a certain vapor flow rate requires a certain wellhead pressure and radius of influence). The induced vapor flow rate should be determined from pilot studies, but it may be calculated using mathematical or physical models (EPA, 1993). The flow rate will contribute to the operational time requirements of the bioventing system. Typical induced flow rates can range from 5 to 100 CFM per well.

- *Initial Constituent Vapor Concentrations* can be measured during pilot studies or estimated from soil gas samples or soil samples. They are used to estimate constituent mass extraction rate to determine whether treatment of extracted vapors will be required prior to atmospheric discharge or reinjection. Be advised that state regulations may not allow reinjection.

- *Required Final Constituent Concentrations* in soils or vapors are either defined by state regulations as "remedial action levels" or determined on a site-specific basis using transport modeling and risk assessment. They will determine what areas of the site require treatment and when bioventing operations can be terminated.

- *Required Remedial Cleanup Time* may also influence the design of the system. The designer may vary the well spacing to speed remediation to meet cleanup deadlines, if required.

- *Soil Volume To Be Treated* is determined by state action levels or a site-specific risk assessment using site characterization data for the soils.

- *Pore Volume Calculations* are used along with extraction flow rate to determine the pore volume exchange rate and, therefore, oxygen delivery rate. The exchange rate is calculated by dividing the soil pore space within the treatment zone by the design vapor extraction rate. The pore space within the treatment zone is calculated by multiplying the soil porosity by the volume of soil to be treated. Some literature suggests that one pore volume of soil vapor should be extracted at least weekly for effective remedial progress.

  You can calculate the time required to exchange one pore volume of soil vapor using the following equation:

$$E = \frac{\varepsilon V}{Q}$$

where:
E = pore volume exchange time (hr)
ε = soil porosity (m^3 vapor/m^3 soil)
V = volume of soil to be treated (m^3 soil)
Q = total vapor extraction flowrate (m^3 vapor/hr)

$$E = \frac{(m^3 \text{ vapor} / m^3 \text{ soil}) \cdot (m^3 \text{ soil})}{(m^3 \text{ vapor} / \text{hr})} = \text{hr}$$

- *Discharge Limitations And Monitoring Requirements* are usually established by state air quality regulations. Such requirements must be considered by designers of a bioventing system to ensure that monitoring ports are included in the system for sites where volatile constituents will be extracted. Discharge limitations imposed by state air quality regulations will determine whether offgas treatment is required.

- *Site Construction Limitations*, such as buildings, utilities, buried objects, and residences, must be identified and considered in the design process.

- *Nutrient Formulation and Delivery Rate*, which can be established through either field or laboratory pilot studies, determines if nutrients are required.

Components Of A Bioventing System

Once the design basis is defined, the design of the bioventing system can be developed. A typical bioventing system design will include the following components and information:

- Extraction well (or injection well) orientation, placement, and construction details
- Piping design
- Vapor pretreatment design (if necessary)
- Vapor treatment system selection (if necessary)
- Blower specification
- Instrumentation and control design
- Monitoring locations

Nutrient additions are sometimes included in bioventing designs. If nutrients are added, the design should specify the nutrient addition well orientation, placement, and construction details. Note that state regulations may either require permits for nutrient injection wells or prohibit them entirely. Exhibit III-17 is a conceptual schematic diagram for a bioventing system using vapor extraction.

The following subsections provide guidance for selecting the appropriate system configuration, standard system components, and additional system components to adequately address petroleum contaminated soils at a particular UST site.

Extraction Wells

Well Orientation. A bioventing system can use either vertical or horizontal extraction wells. Orientation of the wells should be based on site-specific needs and conditions. Exhibit III-18 lists site conditions and the corresponding appropriate well orientation.

Exhibit III-17
Schematic Of Bioventing System Using Vapor Extraction

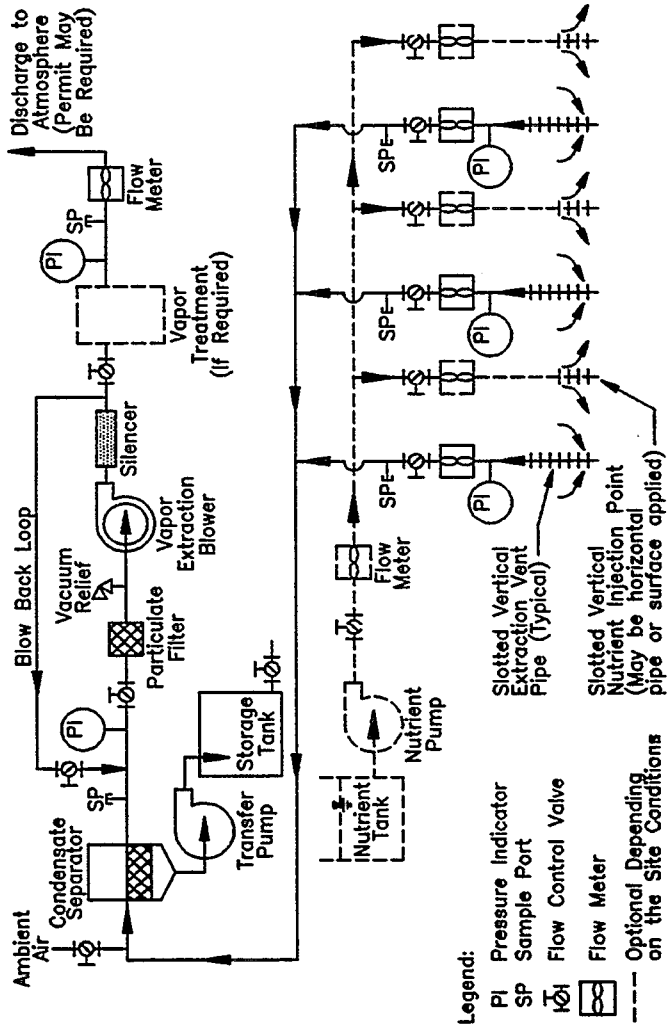


Exhibit III-18
Well Orientation And Site Conditions

Well Orientation	Site Conditions
Vertical extraction well	○ Shallow to deep contamination (5 to 100+ feet). ○ Depth to groundwater > 10 feet.
Horizontal extraction well	○ Shallow contamination (< 25 feet). More effective than vertical wells at depths < 10 feet. Construction difficult at depths > 25 feet. ○ Zone of contamination confined to a specific stratigraphic unit.

Well Placement and Number of Wells. You can determine the number and location of extraction wells by using several methods. In the first method, divide the area of the site requiring treatment by the area corresponding to the design ROI of a single well to obtain the total number of wells needed. Then space the wells evenly within the treatment area to provide areal coverage so that the areas of influence cover the entire area of contamination.

$$\text{Number of wells needed} = \frac{\text{Treatment area } (m^2)}{\text{Area for single extraction well } (m^2 \text{ / well})}$$

In the second method, determine the total extraction flow rate needed to exchange the soil pore volume within the treatment area in a reasonable amount of time (3 to 7 days). Determine the number of wells required by dividing the total extraction flow rate needed by the flow rate achievable with a single well.

$$\text{Number of wells needed} = \frac{\varepsilon V / t_e}{q}$$

where: ε = soil porosity (m^3 vapor / m^3 soil)
V = volume of soil in treatment area (m^3 soil)
q = vapor extraction rate from single extraction well (m^3 vapor/hr).
t_e= time for exchange of pore volume(s), (hrs)

In the example below, a 7-day exchange time is used.

$$\text{Number of wells needed} = \frac{\left(\frac{m^3 \text{ vapor}}{m^3 \text{ soil}}\right) \cdot \left(\frac{(m^3 \text{ soil})}{168 \text{ hrs}}\right)}{\frac{m^3 \text{ vapor}}{hr}}$$

Consider the following additional factors in evaluating proposed well spacing.

- In areas of high contaminant concentrations, closer well spacing is desired to increase oxygen flow and accelerate contaminant degradation rates.

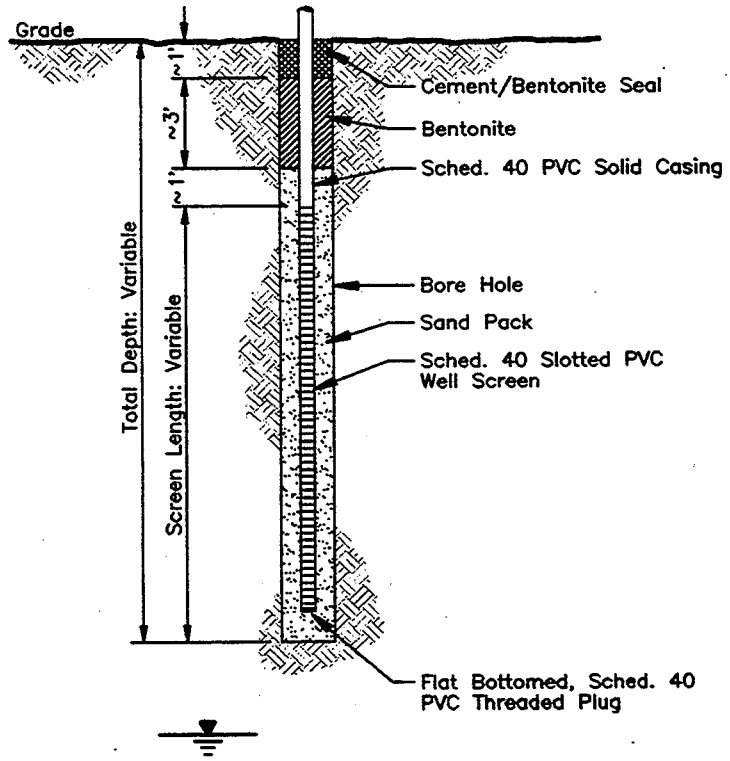
- Wells may be spaced slightly farther apart if a surface seal is planned for installation or if one already exists. A surface seal increases the radius of influence by forcing air to be drawn from a greater distance by preventing short-circuiting from land surface. However, passive vent wells or air injection wells may be required to supplement the flow of air in the subsurface.

- In stratified or structured soils, well spacings may be irregular. Wells screened in zones of lower intrinsic permeability must be spaced closer together than wells screened in zones of higher intrinsic permeability.

Well Construction. *Vertical Well Construction.* Vertical extraction wells are similar in construction to monitoring wells and are installed using the same techniques. Extraction wells are usually constructed of polyvinyl chloride (PVC) casing and screen. Extraction well diameters typically range from 2 to 12 inches, depending on flow rates and depth; a 4-inch diameter is most common.

Exhibit III-19 depicts a typical vertical extraction well. Vertical extraction wells are constructed by placing the casing and screen in the center of a borehole. Filter pack material is placed in the annular space between the casing/screen and the walls of the borehole. The filter pack material extends 1-2 feet above the top of the well screen and is

Exhibit III-19
Typical Bioventing Vertical Well Construction



followed by a 1-2 foot thick bentonite seal. Cement-bentonite grout seals the remaining space up to the surface. Filter pack material and screen slot size must be consistent with the grain size of the surrounding soils.

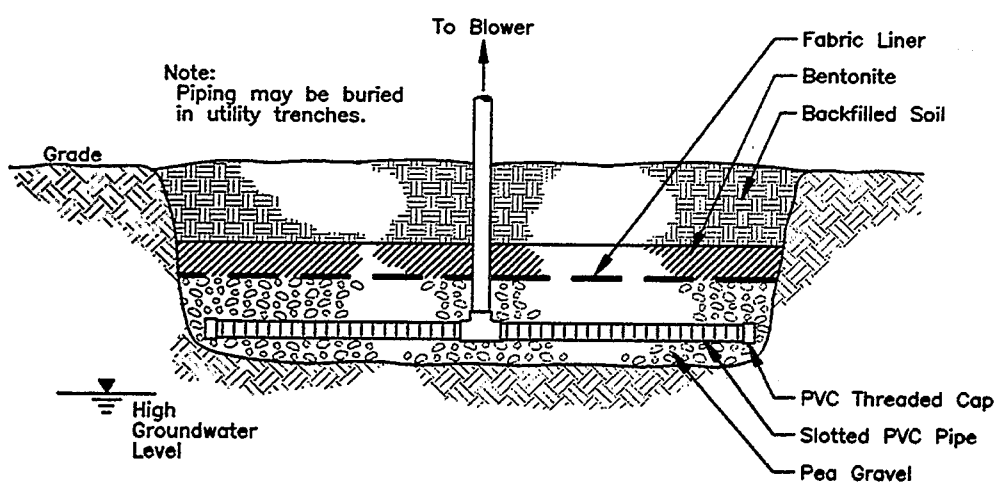
The location and length of the well screen in vertical extraction or injection wells can vary and should be based on the depth to groundwater, the stratification of the soil, and the location and distribution of contaminants. In general, the length of the screen has little effect on the ROI of an extraction or injection well. However, because the ROI is affected by the intrinsic permeability of the soils in the screened interval (lower intrinsic permeability will result in a smaller ROI, other parameters being equal), the placement of the screen can affect the ROI.

- At a site with homogeneous soil conditions, ensure that the well is screened throughout the contaminated zone. The well screen may be placed as deep as the seasonal low water table. A deep well helps to ensure remediation of the greatest amount of soil during seasonal low groundwater conditions.

- At a site with stratified soils or lithology, the screened interval can be placed at a depth corresponding to a zone of lower permeability. This placement will help ensure that air passes through this zone rather than merely flow through adjacent zones of higher permeability.

Horizontal Well Construction. Horizontal extraction wells or trench systems are generally used in shallow groundwater conditions. Exhibit III-20 shows a typical shallow horizontal well construction detail. Horizontal extraction wells are constructed by placing slotted PVC piping near the bottom of an excavated trench. Gravel bedding surrounds the piping. A bentonite seal or impermeable liner prevents air leakage from the surface. When horizontal wells are used, the screen must be high enough above the groundwater table so that normal groundwater table fluctuations do not submerge the screen. Additionally, if vacuum extraction is used, pressures should be monitored to ensure that induced groundwater upwelling does not occlude the screen(s).

Exhibit III-20
Typical Horizontal Well



Air Injection Wells

Air injection wells are similar in construction to extraction wells, but air injection wells can be designed with a longer screened interval in order to ensure uniform air flow. Other design criteria for injection wells' orientation, well placement, and well construction are the same as that of extraction wells described above. Horizontal wells are also applicable for air injection. Active injection wells force compressed air into soils. Passive injection wells, or inlets, simply provide a pathway that helps extraction wells draw air from the atmosphere into the subsurface. Air injection wells should be placed to eliminate stagnation zones, but should not force contaminants to an area where they will not be recovered (i.e., off-site) or could cause adverse health or safety effects.

Air injection wells can be used alone or, more commonly, in conjunction with extraction wells. The injection well/extraction well combination is often used at sites that are covered with an impermeable cap (e.g., pavement or buildings) because the cap restricts direct air flow to the subsurface. They are used also to help prevent short-circuiting the air flow which may be restricted by preferential pathways in the subsurface. In addition, air injection can be used to eliminate potential stagnation zones (areas of no flow), which sometimes exist between extraction wells.

Air injection wells are seldom used by themselves primarily because the contaminated offgas can not be collected. Without the ability to collect the offgas, contaminated vapor may spread to previously uncontaminated areas. Also the offgas can not be used to evaluate the extent of subsurface biological activities. In most cases, air injections are limited to removing low or non-volatile petroleum products.

Manifold Piping

Manifold piping connects to the extraction or injection blower. Piping can either be placed above or below grade depending on site operations, ambient temperature, and local building codes. Below-grade piping is the more common and is installed in shallow utility trenches that lead from the wellhead vault to a central equipment location. The piping can either be manifolded in the equipment area or connected to a common pressure (or vacuum) main that supplies the wells in series, in which case flow control valves are sited at the wellhead. Piping to extraction well locations should be sloped toward the well so that condensate or entrained groundwater will flow back toward the well.

Vapor Pretreatment

Extracted vapor can contain condensate, entrained groundwater, and particulates that can damage blower parts and inhibit the effectiveness of downstream treatment systems. In order to minimize the potential for damage, vapors are usually passed through a moisture separator and a particulate filter prior to entering the blower. Check the CAP to verify that both a moisture separator and a particulate filter have been included in the design.

Blower Selection

The type and size of blower selected should be based on (1) the vacuum or pressure required to achieve design pressure at the wellheads (including upstream and downstream piping losses) and (2) the total flow rate. The flow rate requirement should be based on the sum of the flow rates from the contributing extraction or injection wells. In applications where explosions may occur, be sure the CAP specifies blowers with explosion-proof motors, starters, and electrical systems. Exhibit III-21 depicts the performance curves for the three basic types of blowers that can be used in a bioventing system.

- *Centrifugal* blowers (such as squirrel-cage fans) should be used for high-flow, low-pressure, or low-vacuum applications (less than 20 inches of water).

- *Regenerative and turbine* blowers should be used when a higher pressure or vacuum (up to 80 inches of water) is needed.

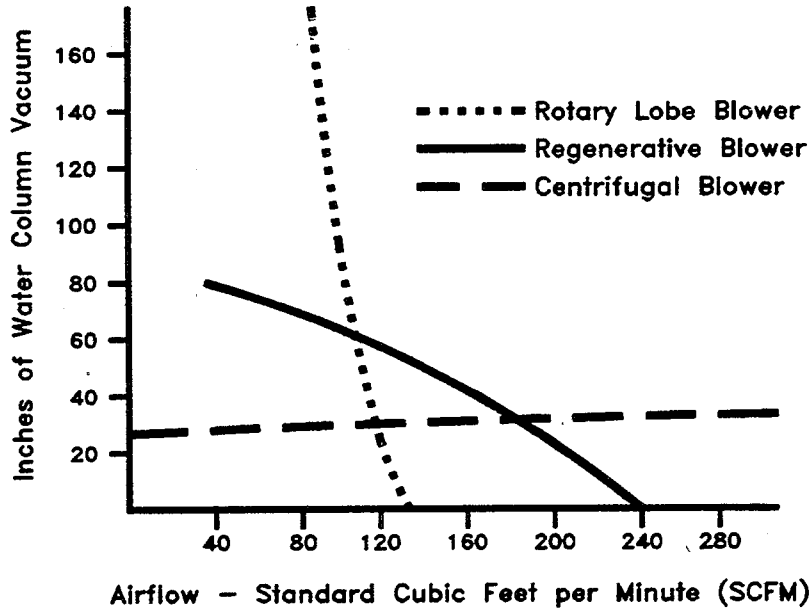
- *Rotary lobe* and other positive displacement blowers should be used when a very high pressure or vacuum (greater than 80 inches of water) is needed. Rotary lobe blowers are not generally applicable to bioventing systems.

Instrumentation and Controls

The parameters typically monitored in a bioventing system include:

- Pressure (or vacuum)
- Air/vapor flow rate
- Carbon dioxide and/or oxygen concentration in extracted vapor
- Contaminant mass extraction rates
- Temperature
- Nutrient delivery rate (if nutrients are added)

Exhibit III-21
Performance Curves For Three Types Of Blowers



Notes:

Centrifugal blower type shown is a New York model 2004A at 3500 rpm. Regenerative blower type shown is a Rotron model DR707. Rotary lobe blower type shown is a M-D Pneumatics model 3204 at 3000 rpm.

From "Guidance for Design, Installation and Operation of Soil Venting Systems." Wisconsin Department of Natural Resources, Emergency and Remedial Response Section, PUBL-SW185-93, July 1993.

The monitoring equipment in a bioventing system enables you to observe the progress of remediation and to control each component of the system. Exhibit III-22 describes where each of these pieces of monitoring equipment is typically placed and the types of equipment that are available.

Optional Bioventing Components

Additional bioventing system components might be used when certain site conditions exist or when pilot studies dictate they are necessary. These components include:

- Nutrient delivery systems (if needed)
- Surface seals
- Groundwater depression pumps
- Vapor treatment systems.

Exhibit III-22
Monitoring Equipment

Instrument	Location In System	Example Of Equipment
Flow meter	○ At each well head ○ Manifold to blower ○ Blower discharge ○ Nutrient manifold	○ Pitot tube ○ In-line rotameter ○ Orifice plate ○ Turbine wheel ○ Venturi or flow tube
Vacuum/Pressure gauge	○ At each well head or manifold branch ○ Before and after filters before blower ○ Before and after vapor treatment	○ Manometer ○ Magnehelic gauge ○ Vacuum gauge
Sampling port	○ At each well head or manifold branch ○ Manifold to blower ○ Blower discharge	○ Hose barb ○ Septa fitting
Flow control valves	○ At each well head or manifold branch ○ Dilution or bleed valve at manifold to blower	○ Ball valve ○ Gate valve ○ Dilution/ambient air bleed valve
Vapor temperature sensor	○ Manifold to blower ○ Blower discharge (prior to vapor treatment)	○ Bi-metal dial-type thermometer
Vapor sample collection equipment (used through a sampling port)	○ At each well head or manifold branch ○ Manifold to blower ○ Blower discharge	○ Tedlar bags ○ Sorbent tubes ○ Sorbent canisters ○ Polypropylene tubing for direct GC injection
Control Equipment		
Flow control valves	○ At each well head or manifold branch ○ Dilution or bleed valve at manifold to blower	○ Ball valve ○ Gate/globe valve ○ Butterfly valve

Each of these system components is discussed below.

Nutrient Delivery Systems. If the addition of nutrients is required to support biological growth, a nutrient delivery system will be needed. Nutrients are usually supplied to the subsurface through topical application or by injection through horizontal trenches or wells. Topical application is either by hand-spraying or through conventional irrigation systems (e.g., sprinklers). Horizontal wells are similar in design to those used for extraction, and typically consist of slotted or perforated PVC pipe installed in shallow (< 2 feet) trenches laid in a gravel bed. Nutrient solutions can be prepared from solid formulations used in agricultural applications of sodium tripolyphosphate and ammonium salts, and should be added monthly to quarterly. Nutrient delivery systems may also be used to add solutions to adjust pH as required.

Surface Seals. Surface seals might be included in a bioventing system design in order to prevent surface water infiltration that can reduce air flow rates, to reduce fugitive emissions, to prevent short-circuiting of air flow, or to increase the design ROI. These results are accomplished because surface seals force fresh air to travel a greater distance from the extraction or injection well. If a surface seal is used, the lower pressure gradients result in decreased flow velocities. This condition may require a higher vacuum or pressure to be applied to the extraction or injection well.

Surface seals or caps should be selected to match the site conditions and regular business activities at the site. Options include high density polyethylene (HDPE) liners (similar to landfill liners), clay or bentonite seals, or concrete or asphalt paving. Existing covers (e.g., pavement or concrete slabs) might not be applicable if they are constructed with a porous subgrade material.

Groundwater Pumps. Groundwater depression pumping might be necessary at a site with a shallow groundwater table or to expose contaminated soils in the capillary or saturated zone. Groundwater pumps reduce the upwelling of water into the extraction wells or lower the water table and allow a greater volume of soil to be remediated. Because groundwater depression is affected by pumping wells, these wells must be placed so that the surface of the groundwater is depressed in all areas where bioventing is to occur. Groundwater pumping, however, can create two additional waste streams requiring appropriate disposal:

- Groundwater contaminated with dissolved hydrocarbons; and
- Liquid hydrocarbons (i.e., free product), if present.

Vapor Treatment. Look for vapor treatment systems in the bioventing design if pilot study data indicate that extracted vapors will contain VOC concentrations in excess of established air quality limits. Commonly available treatment options are granular activated carbon (GAC), catalytic oxidation, or thermal oxidation for vapor treatment.

GAC is a popular choice for vapor treatment because it is readily available, simple to operate, and can be cost effective. Catalytic oxidation, however, is generally more economical than GAC when the contaminant mass loading is high. However, catalytic oxidation is not recommended when concentrations of chemical constituents are expected to be sustained at levels greater than 20 percent of their lower explosive limit (LEL). In these cases, a thermal oxidizer is typically employed because the vapor concentration is high enough for the constituents to burn. Biofilters, an emerging vapor-phase biological treatment technique, can be used for vapors with less than 10 percent LEL, appear to be cost effective, and may also be considered.

Evaluation Of Operation And Monitoring Plans

It is important to make sure that a system operation and monitoring plan has been developed for both the system start-up phase and for long-term operations. Operations and monitoring are necessary to ensure that system performance is optimized and contaminant mass extraction and degradation are tracked. Monitoring of remedial progress for bioventing systems is more difficult than for SVE systems in that mass removal cannot be directly measured in extracted vapors. Typically, both VOC concentrations (extracted mass) and carbon dioxide concentrations (a product of microbial respiration) must both be monitored.

Systems involving only injection wells will have an especially limited capability for performance monitoring because it is not possible to collect the offgas. The monitoring plan should include subsurface soil sampling to track constituent reduction and biodegradation conditions. Also, to ensure the injected air is not causing contamination of the atmosphere or previously uncontaminated soil or ground water, samples from each medium should be analyzed for potential constituents.

Start-Up Operations

The start-up phase should include 7 to 10 days of manifold valving adjustments. These adjustments should balance flow to optimize carbon dioxide production and oxygen uptake rate while, to the extent possible, minimizing volatilization by concentrating pressure (or vacuum) on the

wells that are in areas of higher contaminant concentrations. To accomplish this, flow measurements, pressure or vacuum readings, carbon dioxide concentrations, oxygen concentrations, and VOC concentrations should be recorded daily from each extraction well, from the manifold, and from the effluent stack. Nutrient delivery (if needed) should not be performed until after start-up operations are complete.

Long-Term Operations

Long-term monitoring should consist of flow-balancing, flow and pressure measurements, carbon dioxide measurements, oxygen measurements, and VOC concentration readings. Measurements should take place at weekly or biweekly intervals for the duration of the system operational period. Nutrient addition, if necessary, should occur on a periodic basis rather than continuously. Some literature suggests that nutrient solutions be injected in wells or trenches or applied to the surface at monthly or quarterly intervals. Exhibit III-23 provides a brief synopsis of system monitoring recommendations.

Exhibit III-23
System Monitoring Recommendations

Phase	Frequency	What To Monitor	Where To Monitor
Start-up	At least daily	o Flow o Vacuum readings o VOCs o Carbon dioxide o Oxygen	o Extraction vents o Manifold o Effluent stack
Remedial	Weekly to bi-weekly	o Flow o Vacuum o VOCs o Carbon dioxide o Oxygen	o Extraction vents o Manifold o Effluent stack

Remedial Progress Monitoring

Monitoring the performance of the bioventing system in reducing contaminant concentrations in soils is necessary to determine if remedial progress is proceeding at a reasonable pace. A variety of methods can be used.

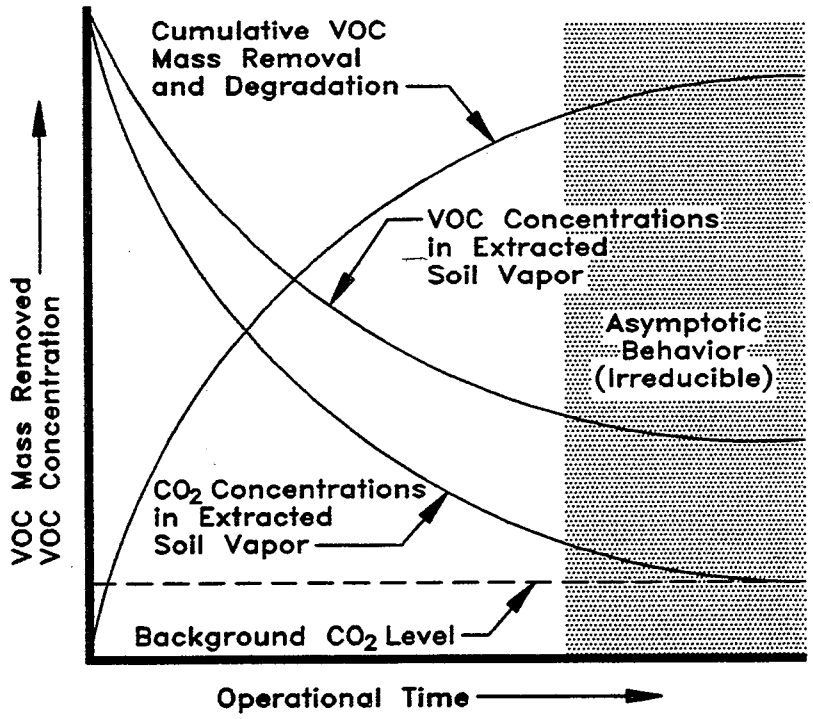
Since concentrations of petroleum constituents may be reduced due to both volatilization and biodegradation, both processes should be monitored in order to track the cumulative effect. The constituent mass

extraction component can be tracked and calculated using the VOC concentrations measured in the extraction manifold multiplied by the extraction flow rate. The constituent mass that is degraded is more difficult to quantify but can be monitored qualitatively by observing trends in carbon dioxide and oxygen concentrations in the extracted soil vapors.

Remedial progress of bioventing systems typically exhibits asymptotic behavior with respect to VOC, oxygen, and carbon dioxide concentrations in extracted vapors as shown in Exhibit III-24. When asymptotic behavior begins to occur, the operator should closely evaluate alternatives that may increase bioventing effectiveness (e.g., increasing extraction flow rate or nutrient addition frequency). Other, more aggressive steps to curb asymptotic behavior can include adding injection wells, additional extraction wells, or injecting concentrated solutions of bacteria.

If asymptotic behavior is persistent for periods greater than about 6 months, modification of the system design and operations (e.g., pulsing of injection or extraction air flow) may be appropriate. If asymptotic behavior continues, termination of operations may be appropriate.

Exhibit III-24
VOC/CO_2 Concentration Reduction And Constituent Mass Removal And Degradation Behavior For Bioventing Systems



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Checklist: Can Bioventing Be Used At This Site?

This checklist can help you evaluate the completeness of the CAP and to identify areas that require closer scrutiny. As you go through the CAP, answer the following questions. If the answer to several questions is no, you should request additional information to determine if bioventing will accomplish cleanup goals at the site.

1. Site Characteristics

Yes	No	
❑	❑	Is the soil intrinsic permeability greater than 10^{-10} cm^2?
❑	❑	Is the soil free of impermeable layers or other conditions that would disrupt air flow?
❑	❑	Is the total heterotrophic bacteria count > 1,000 CFU/gram dry soil?
❑	❑	Is soil pH between 6 and 8?
❑	❑	Is the moisture content of soil in contaminated area between 40% to 85% of saturation?
❑	❑	Is soil temperature between 10°C and 45°C during the proposed treatment season?
❑	❑	Is the carbon:nitrogen:phosphorus ratio between 100:10:5 and 100:1:0.5?
❑	❑	Is the depth to groundwater > 3 feet?[1]

2. Constituent Characteristics

Yes	No	
❑	❑	Are constituents all sufficiently biodegradable?
❑	❑	Is the concentration of Total Petroleum Hydrocarbon ≤ 25,000 ppm and heavy metals ≤ 2,500 ppm?
❑	❑	If there are constituents with vapor pressures greater than 0.5 mm Hg, boiling ranges above 300°C, or Henry's law constants greater than 100 atm/mole fraction, has the CAP addressed the potential environmental impact of the volatilized constituents?

[1] This parameter alone may not negate the use of bioventing. However, provisions for the construction of horizontal wells or trenches or for lowering the water table should be incorporated into the CAP.

3. Evaluation Of The Bioventing System Design

Yes	No	
❑	❑	Will the induced air flow rates achieve cleanup in the time allotted for remediation in the CAP?
❑	❑	Does the radius of influence (ROI) for the proposed extraction or injection wells fall in the range of 5 to 100 feet?
❑	❑	Has the ROI been calculated for each soil type at the site?
❑	❑	Is the type of well proposed (horizontal or vertical) appropriate for the site conditions present?
❑	❑	Is the proposed well density appropriate, given the total area to be cleaned up and the radius of influence of each well?
❑	❑	Do the proposed well screen intervals match soil conditions at the site?
❑	❑	Are air injection wells proposed?
❑	❑	Is the proposed air injection well design appropriate for this site?
❑	❑	Is the selected blower appropriate for the desired vacuum conditions?

4. Optional Bioventing Components

Yes	No	
❑	❑	If nutrient delivery systems will be needed, are designs for those systems provided?
❑	❑	Are surface seals proposed?
❑	❑	Are the proposed sealing materials appropriate for this site?
❑	❑	Will groundwater depression be necessary?
❑	❑	If groundwater depression is necessary, are the pumping wells correctly spaced?
❑	❑	Is a vapor treatment system required?
❑	❑	If a vapor treatment system is required, is the proposed system appropriate for the contaminant concentration at the site?

5. Operation And Monitoring Plans

Yes	No	
❑	❑	Is monitoring of offgas vapors for VOC and carbon dioxide concentration proposed?
❑	❑	Is subsurface soil sampling proposed for tracking constituent reduction and biodegradation conditions?
❑	❑	Are manifold valving adjustments proposed for the start-up phase?
❑	❑	Is nutrient addition (if necessary) proposed to be controlled on a periodic rather than continuous basis?

Chapter IV

Biopiles

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Chapter IV
Biopiles

Overview

Biopiles, also known as biocells, bioheaps, biomounds, and compost piles, are used to reduce concentrations of petroleum constituents in excavated soils through the use of biodegradation. This technology involves heaping contaminated soils into piles (or "cells") and stimulating aerobic microbial activity within the soils through the aeration and/or addition of minerals, nutrients, and moisture. The enhanced microbial activity results in degradation of adsorbed petroleum-product constituents through microbial respiration. Biopiles are similar to landfarms in that they are both above-ground, engineered systems that use oxygen, generally from air, to stimulate the growth and reproduction of aerobic bacteria which, in turn, degrade the petroleum constituents adsorbed to soil. While landfarms are aerated by tilling or plowing, biopiles are aerated most often by forcing air to move by injection or extraction through slotted or perforated piping placed throughout the pile. (Chapter V provides a detailed description of landfarming.) A typical biopile cell is shown in Exhibit IV-1.

Biopiles, like landfarms, have been proven effective in reducing concentrations of nearly all the constituents of petroleum products typically found at underground storage tank (UST) sites. Lighter (more volatile) petroleum products (e.g., gasoline) tend to be removed by evaporation during aeration processes (i.e., air injection, air extraction, or pile turning) and, to a lesser extent, degraded by microbial respiration. Depending upon your state's regulations for air emissions of volatile organic compounds (VOCs), you may need to control the VOC emissions. Control involves capturing the vapors before they are emitted to the atmosphere, passing them through an appropriate treatment process, and then venting them to the atmosphere. The mid-range hydrocarbon products (e.g., diesel fuel, kerosene) contain lower percentages of lighter (more volatile) constituents than does gasoline. Biodegradation of these petroleum products is more significant than evaporation. Heavier (non-volatile) petroleum products (e.g., heating oil, lubricating oils) do not evaporate during biopile aeration; the dominant mechanism that breaks down these petroleum products is biodegradation. However, higher molecular weight petroleum constituents such as those found in heating and lubricating oils, and, to a lesser extent, in diesel fuel and kerosene, require a longer period of time to degrade than do the constituents in gasoline. A summary of the advantages and disadvantages of biopiles is shown in Exhibit IV-2.

Exhibit IV-1
Typical Biopile System

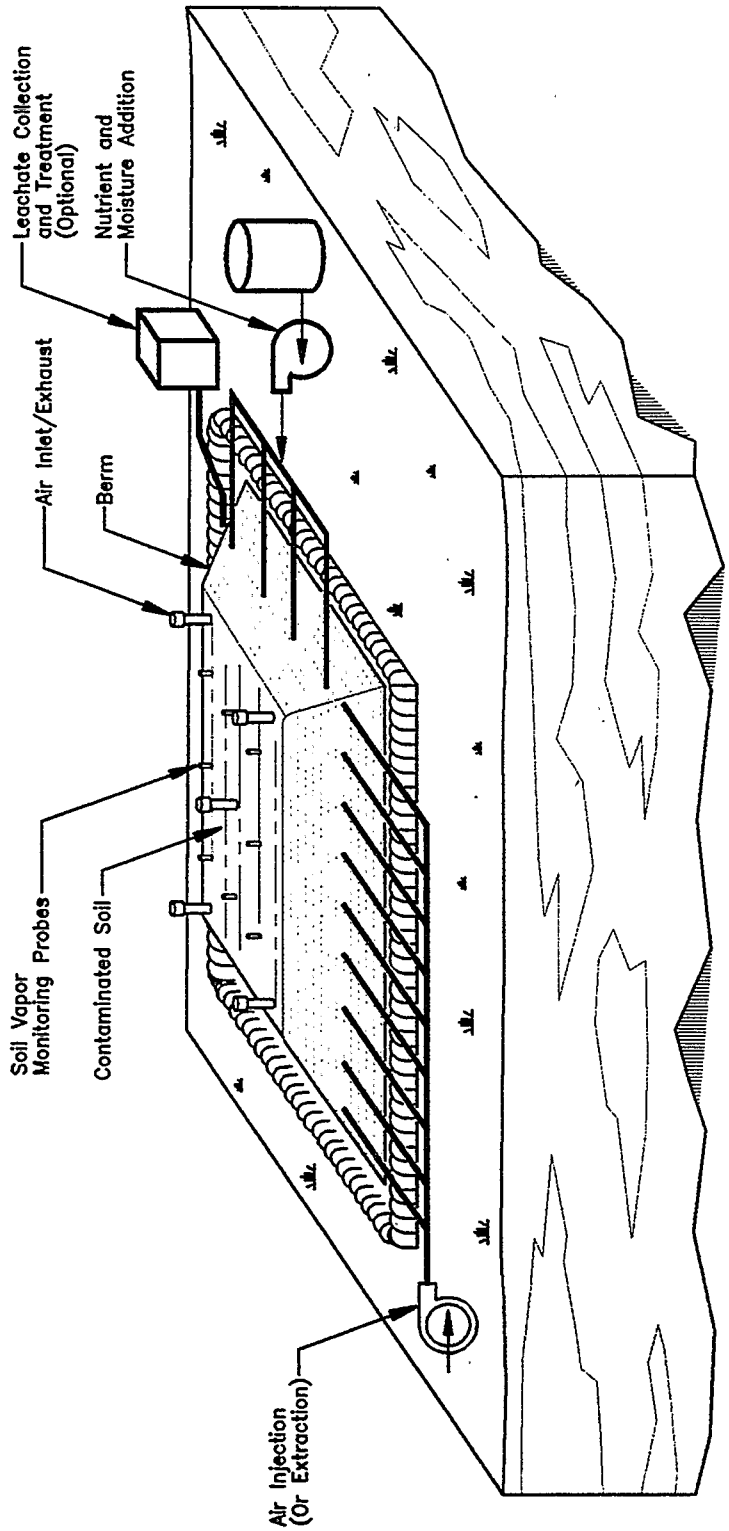


Exhibit IV-2
Advantages And Disadvantages Of Biopiles

Advantages	Disadvantages
○ Relatively simple to design and implement.	○ Concentration reductions > 95% and constituent concentrations < 0.1 ppm are very difficult to achieve.
○ Short treatment times: usually 6 months to 2 years under optimal conditions.	○ May not be effective for high constituent concentrations (> 50,000 ppm total petroleum hydrocarbons).
○ Cost competitive: $30-90/ton of contaminated soil.	○ Presence of significant heavy metal concentrations (> 2,500 ppm) may inhibit microbial growth.
○ Effective on organic constituents with slow biodegradation rates.	○ Volatile constituents tend to evaporate rather than biodegrade during treatment.
○ Requires less land area than landfarms.	○ Requires a large land area for treatment, although less than landfarming.
○ Can be designed to be a closed system; vapor emissions can be controlled.	○ Vapor generation during aeration may require treatment prior to discharge.
○ Can be engineered to be potentially effective for any combination of site conditions and petroleum products.	○ May require bottom liner if leaching from the biopile is a concern.

This chapter will assist you in evaluating a corrective action plan (CAP) that proposes biopiles as a remedy for petroleum-contaminated soil. The evaluation guidance is presented in the three steps described below. The evaluation process, summarized in a flow diagram shown in Exhibit IV-3, will serve as a roadmap for the decisions you will make during your evaluation. A checklist has been provided at the end of this chapter for you to use as a tool for evaluating the completeness of the CAP and for focusing on areas where additional information may be needed. Because a biopile system can be engineered to be potentially effective for any combination of site conditions and petroleum products, the evaluation process for this technology does not include initial screening. The evaluation process can be divided into the following steps.

○ **Step 1:** ***An evaluation of biopile effectiveness***, in which you can identify the soil, constituent, and climatic factors that contribute to the effectiveness of biopiles and compare them to acceptable operating ranges. To complete the evaluation, you will need to compare these properties to ranges in which biopiles are effective.

Exhibit IV-3
Biopile Evaluation Process Flow Chart

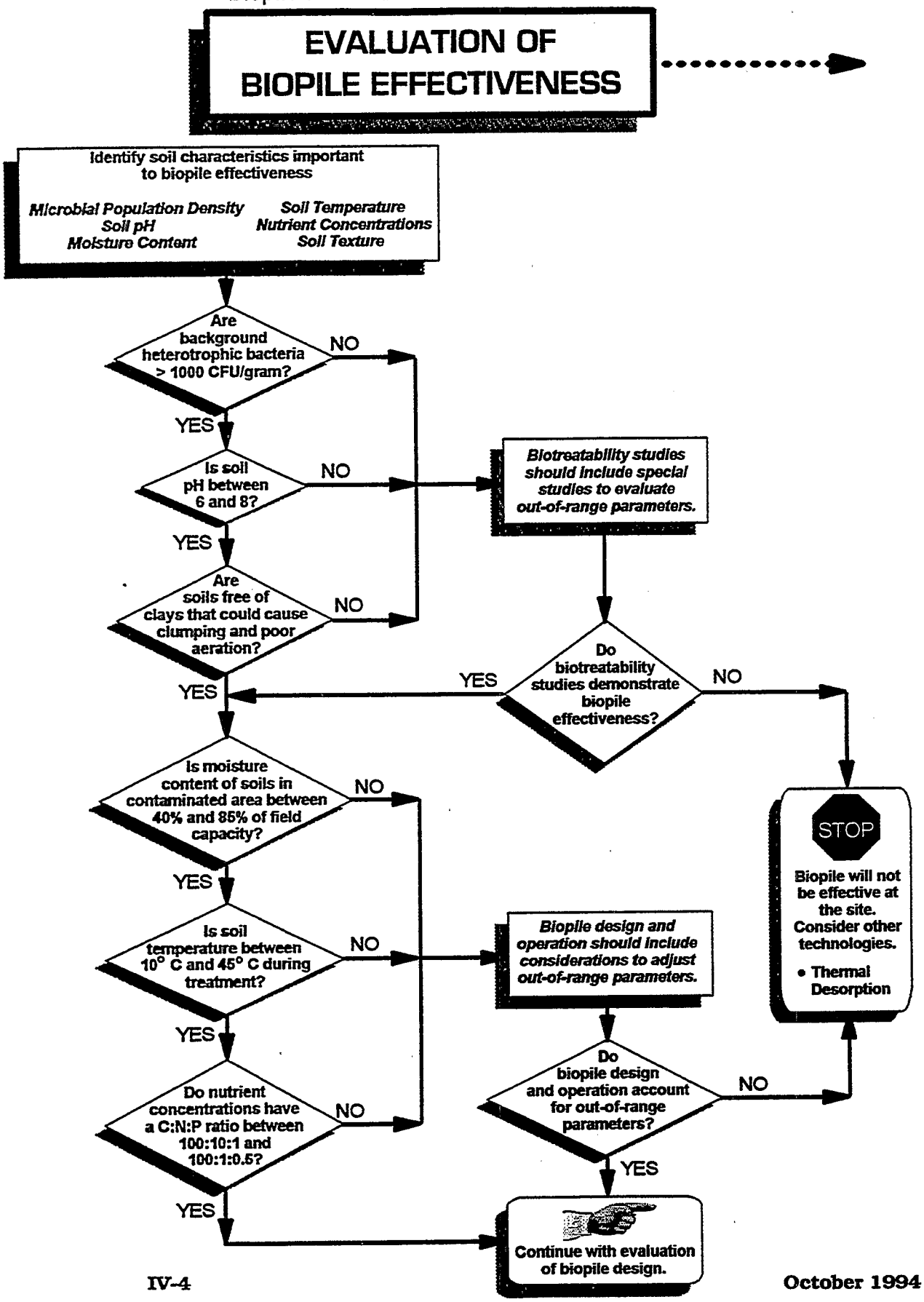


Exhibit IV-3
Biopile Evaluation Process Flow Chart

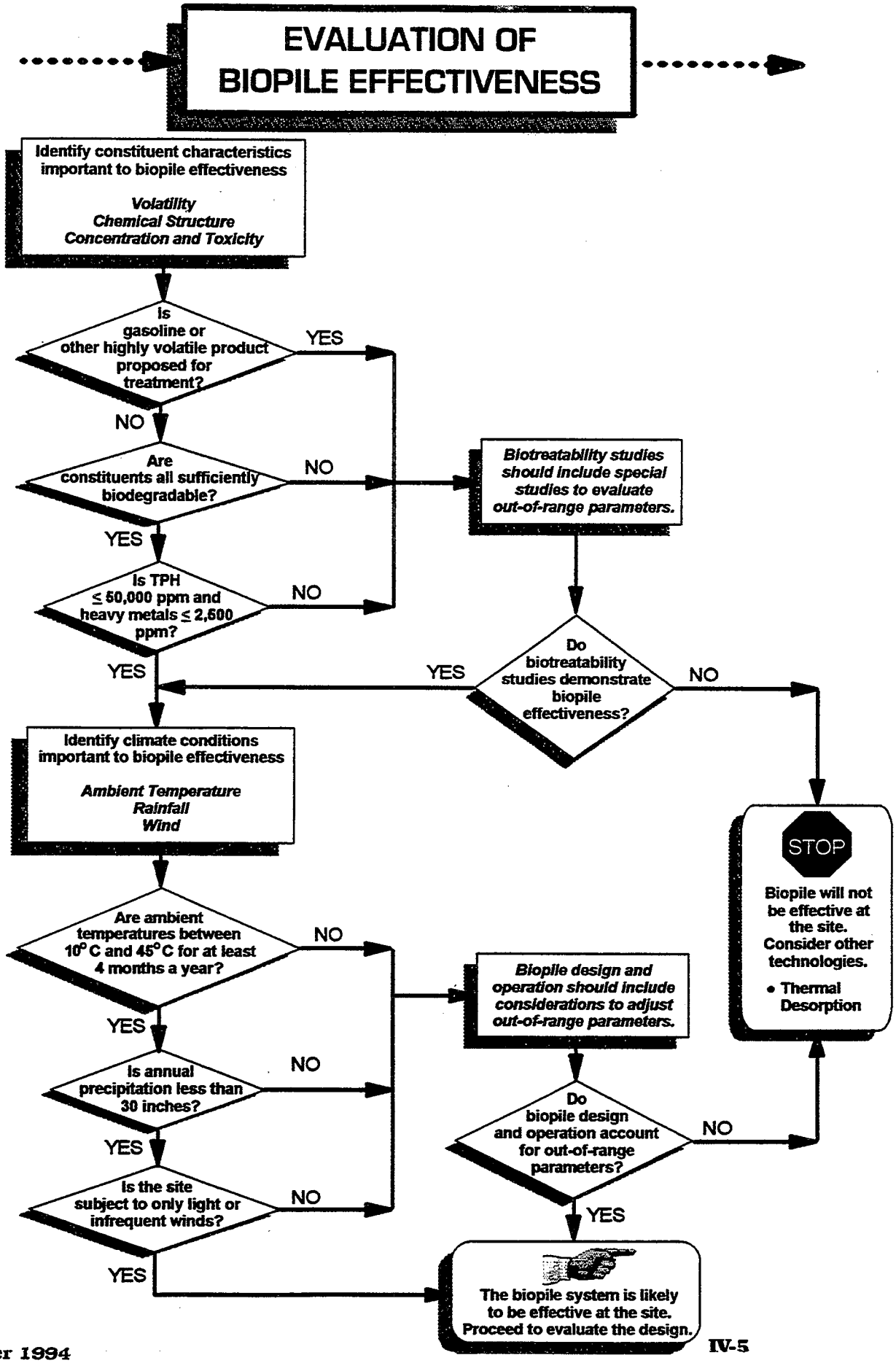
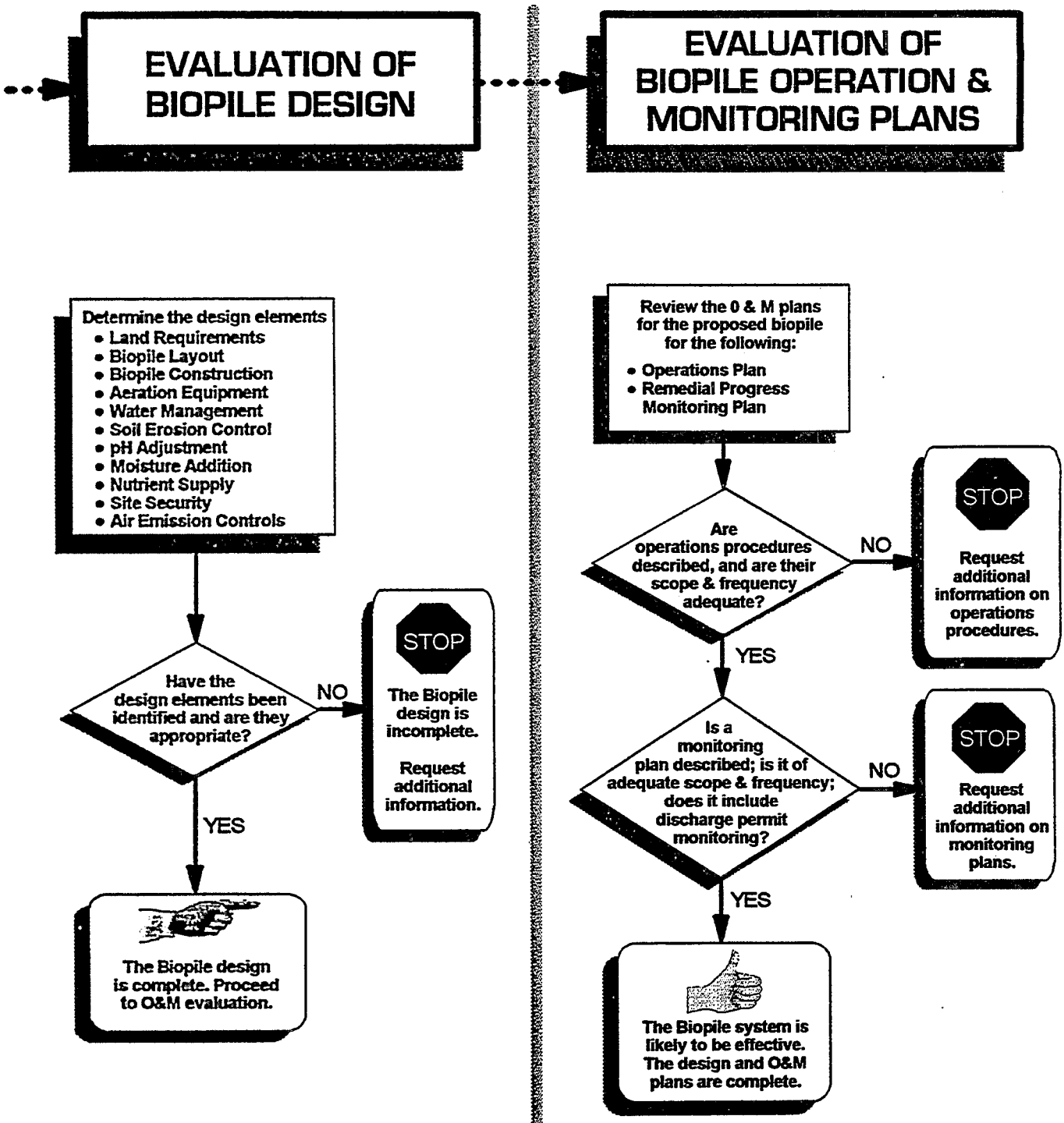


Exhibit IV-3
Biopile Evaluation Process Flow Chart



- **Step 2: An *evaluation of the biopile system design*** will allow you to determine if the rationale for the design has been appropriately defined, whether the necessary design components have been specified, and whether the construction designs are consistent with standard practice.

- **Step 3: An *evaluation of the operation and monitoring plans,*** which are critical to the effectiveness of biopiles, will allow you to determine whether start-up and long-term system operation and monitoring plans are of sufficient scope.

Evaluation Of Biopile Effectiveness

The effectiveness of a biopile system depends on many parameters which are listed in Exhibit IV-4. The parameters are grouped into three categories: soil characteristics, constituent characteristics, and climatic conditions.

Exhibit IV-4
Parameters Used To Evaluate The Effectiveness Of Biopile Systems

Soil Characteristics	Constituent Characteristics	Climatic Conditions
Microbial population density	Volatility	Ambient temperature
Soil pH	Chemical structure	Rainfall
Moisture content	Concentration and toxicity	Wind
Soil temperature		
Nutrient concentrations		
Soil texture		

The following paragraphs contain descriptions of each parameter that include: why it is important; how it can be determined; and what its appropriate range is. During your evaluation, remember that because a biopile is an above-ground treatment technique, most parameters (except climatic conditions) can be controlled during the design and operation of the biopile. Therefore, during your evaluation, identify those parameters that fall outside the effective ranges provided and verify that the system design and proposed operating specifications compensate for any site conditions that are less than optimal.

Soil Characteristics

Microbial Population Density

Soil normally contains large numbers of diverse microorganisms including bacteria, algae, fungi, protozoa, and actinomycetes. In well-drained soils, which are most appropriate for biopiles, these organisms are generally aerobic. Of these organisms, bacteria are the most numerous and biochemically active group, particularly at low oxygen levels. Bacteria require a carbon source for cell growth and an energy source to sustain metabolic functions required for growth. Bacteria also require nitrogen and phosphorus for cell growth. Although sufficient types and quantities of microorganisms are usually present in the soil for landfarming, recent applications of ex-situ soil treatment include blending the soil with cultured microorganisms or animal manure (typically from chickens or cows). Incorporating manure serves to both augment the microbial population and provide additional nutrients. Recently, the use of a certain fungi for biodegradation of organic contaminants has been proposed based on promising laboratory tests.

The metabolic process used by bacteria to produce energy requires a terminal electron acceptor (TEA) to enzymatically oxidize the carbon source to carbon dioxide. Microbes are classified by the carbon and TEA sources they use to carry out metabolic processes. Bacteria that use organic compounds (e.g., petroleum constituents and other naturally occurring organics) as their source of carbon are *heterotrophic*; those that use inorganic carbon compounds (e.g., carbon dioxide) are *autotrophic*. Bacteria that use oxygen as their TEA are *aerobic*; those that use a compound other than oxygen, (e.g., nitrate, sulfate), are *anaerobic*; and those that can utilize both oxygen and other compounds as TEAs are *facultative*. For applications directed at cleaning up petroleum products, only bacteria that are both *aerobic* (or *facultative*) and *heterotrophic* are important in the degradation process.

In order to evaluate the presence and population of naturally occurring bacteria that will contribute to degradation of petroleum constituents, conduct laboratory analyses of soil samples from the site. These analyses, at a minimum, should include plate counts for total heterotrophic bacteria. Plate count results are normally reported in terms of colony-forming units (CFUs) per gram of soil. Microbial population densities in typical soils range from 10^4 to 10^7 CFU/gram of soil. For biopiles to be effective the minimum heterotrophic plate count should be 10^3 CFU/gram or greater. Plate counts lower than 10^3 could indicate the presence of toxic concentrations of organic or inorganic (e.g., metals) compounds. In this situation, biopiles may still be effective if the soil is conditioned or amended to reduce the toxic concentrations and increase the microbial population density. More elaborate laboratory tests are sometimes conducted to identify the bacterial species present. This may be desirable if there is uncertainty about whether

microbes capable of degrading specific petroleum hydrocarbons occur naturally in the soil. If insufficient numbers or types of microorganisms are present, the population density may be increased by introducing cultured microbes that are available from numerous different vendors. See Exhibit IV-5 for the relationship between counts of total heterotrophic bacteria and the effectiveness of biopiles.

Exhibit IV-5
Heterotrophic Bacteria And Biopile Effectiveness

Total Heterotrophic Bacteria (prior to biopile operation)	Biopile Effectiveness
> 1,000 CFU/gram dry soil	Generally effective.
< 1,000 CFU/gram dry soil	May be effective; needs further evaluation to determine if toxic conditions are present.

The use of fungi (specifically the white rot fungus) is emerging as a remedial technology that may be effective on many types of organic contaminants. These fungi do not metabolize contaminants; degradation occurs outside their cells. The fungi degrade lignin, which must be supplied to them, usually in the form of sawdust or woodchips blended with the soil. In the process of degrading lignin, the fungi excrete other chemicals that degrade the organic contaminants. This process is called co-metabolism. Although the technology has not as yet been subject to extensive field testing, laboratory tests show it can degrade organic chemicals to non-detectable levels.

Soil pH

To support bacterial growth, the soil pH should be within the 6 to 8 range, with a value of about 7 (neutral) being optimal. Soils with pH values outside this range prior to biopile operation will require pH adjustment during construction of the biopile and during operation of the biopile. Soil pH within the biopile soils can be raised through the addition of lime and lowered by adding elemental sulfur during construction. Liquid solutions may also be injected into the biopile during operations to adjust pH. However, mixing with soils during construction results in more uniform distribution. Exhibit IV-6 summarizes the effect of soil pH on biopile effectiveness. Review the CAP to verify that soil pH measurements have been made. If the soil pH is less than 6 or greater than 8, make sure that pH adjustments, in the form of soil amendments, are included in the construction plans for the biopile and that the operations plan includes monitoring of pH.

Exhibit IV-6
Soil pH And Biopile Effectiveness

Soil pH (prior to biopile construction)	Biopile Effectiveness
$6 \leq pH \leq 8$	Generally effective.
$6 > pH > 8$	Biopile soils will require amendments to correct pH to effective range.

Moisture Content

Soil microorganisms require moist soil conditions for proper growth. Excessive soil moisture, however, restricts the movement of air through the subsurface thereby reducing the availability of oxygen which is essential for aerobic bacterial metabolic processes. In general, soils should be moist but not wet or dripping wet. The ideal range for soil moisture is between 40 and 85 percent of the water-holding capacity (field capacity) of the soil or about 12 percent to 30 percent by weight. Periodically, moisture must be added to the biopile because soils become dry as a result of evaporation, which is increased during aeration operations. Excessive accumulation of moisture can occur within biopiles in areas with high precipitation or poor drainage. These conditions should be considered in the biopile design. For example, an impermeable cover can mitigate excess infiltration and potential erosion of the biopile. Exhibit IV-7 shows the optimal range for soil moisture content.

Exhibit IV-7
Soil Moisture And Biopile Effectiveness

Soil Moisture	Biopile Effectiveness
40% $\leq$ field capacity $\leq$ 85%	Effective.
Field capacity < 40%	Periodic moisture addition is needed to maintain proper bacterial growth.
Field capacity > 85%	Biopile design should include special water drainage considerations or impervious cover.

Soil Temperature

Bacterial growth rate is a function of temperature. Soil microbial activity has been shown to significantly decrease at temperatures below 10°C and to essentially cease below 5°C. The microbial activity of most bacteria important to petroleum hydrocarbon biodegradation also diminishes at temperatures greater than 45°C. Within the range of 10°C

to 45°C, the rate of microbial activity typically doubles for every 10°C rise in temperature. Because soil temperature varies with ambient temperature, there will be certain periods during the year when bacterial growth and, therefore, constituent degradation will diminish. When ambient temperatures return to the growth range, bacterial activity will be gradually restored.

In colder parts of the United States, such as the Northeastern states, optimum operating temperatures typically exist for periods of 7 to 9 months. In very cold climates, special precautions can be taken, including enclosing the biopile within a greenhouse-type structure, injecting heated air into the biopile, or introducing special bacteria capable of activity at lower temperatures. In warm regions, optimum temperatures for biopile effectiveness can last all year. Exhibit IV-8 shows how soil temperature affects biopile operation.

Exhibit IV-8
Soil Temperature And Biopile Effectiveness

Soil Temperature	Biopile Effectiveness
10°C ≤ soil temperature ≤ 45°C	Effective.
10°C > soil temperature > 45°C	Not generally effective; microbial activity diminished during seasonal temperature extremes but restored during periods within the effective temperature range. Temperature-controlled enclosures, heated (or cooled) air injection, or special bacteria required for areas with extreme temperatures.

Nutrient Concentrations

Microorganisms require inorganic nutrients such as nitrogen and phosphorus to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in the site soils but, more frequently, nutrients need to be added to the biopile soils to maintain bacterial populations. However, excessive amounts of certain nutrients (i.e., phosphate and sulfate) can repress microbial metabolism. The typical carbon:nitrogen:phosphorus ratio necessary for biodegradation falls in the range of 100:10:1 to 100:1:0.5, depending on the specific constituents and microorganisms involved in the biodegradation process.

The naturally occurring available nitrogen and phosphorus content of the soil should be determined by chemical analyses of samples collected from the site. These types of analyses are routinely conducted in agronomic laboratories that test soil fertility for farmers. These concentrations can be compared to the nitrogen and phosphorus requirements calculated from the stoichiometric ratios of the biodegradation process. A conservative approximation of the amount of nitrogen and phosphorus required for optimum degradation of petroleum products can be calculated by assuming that the total mass of hydrocarbon in the soil represents the mass of carbon available for biodegradation. This simplifying assumption is valid because the carbon content of the petroleum hydrocarbons commonly encountered at UST sites is approximately 90 percent carbon by weight.

As an example, assume that at a LUST site the volume of contaminated soil is 90,000 ft^3, the average TPH concentration in the contaminated soil is 1,000 mg/kg, and the soil bulk density is 50 kg/ft^3 (1.75 g/cm^3).

The mass of contaminated soil is equal to the product of volume and bulk density:

$$\text{soil mass} = 90{,}000\ ft^3 \times \frac{50\ kg}{ft^3} = 4.5 \times 10^6\ kg$$

The mass of the contaminant (and carbon) is equal to the product of the mass of contaminated soil and the average TPH concentration in the contaminated soil:

$$\text{contaminant mass} =$$
$$4.5 \times 10^6\ kg \times 1{,}000\ \frac{mg}{kg} = 4.5 \times 10^3\ kg \approx 10{,}000\ lbs$$

Using the C:N:P ratio of 100:10:1, the required mass of nitrogen would be 1,000 lbs, and the required mass of phosphorus would be 100 lbs. After converting these masses into concentration units (56 mg/kg for nitrogen and 5.6 mg/kg for phosphorus), they can be compared with the results of the soil analyses to determine if nutrient addition is necessary. If nitrogen addition is necessary, slow release sources should be used. Nitrogen additions can lower soil pH, depending on the amount and type of nitrogen added.

Soil Texture

Texture affects the permeability, moisture content, and bulk density of the soil. To ensure that oxygen addition (by air extraction or injection), nutrient distribution, and moisture content of the soils can be maintained within effective ranges, you must consider the texture of the soils. For example, soils that tend to clump together (such as clays) are difficult to aerate and result in low oxygen concentrations. It is also difficult to uniformly distribute nutrients throughout these soils. They also retain water for extended periods following a precipitation event.

You should identify whether clayey soils are proposed for the biopile at the site. Soil amendments (e.g., gypsum) and bulking materials (e.g., sawdust, or straw) should be blended into the soil as the biopile is being constructed to ensure that the biopile medium has a loose or divided texture. Clumpy soil may require shredding or other means of pretreatment during biopile construction to incorporate these amendments.

Constituent Characteristics

Volatility

The volatility of contaminants proposed for treatment in biopiles is important because volatile constituents tend to evaporate from the biopile into the air during extraction or injection, rather than being biodegraded by bacteria. Constituent vapors in air that is injected into the biopile will dissipate into the atmosphere unless the biopile is covered and collection piping is installed beneath the cover. If air is added to the pile by applying a vacuum to the aeration piping, volatile constituent vapors will pass into the extracted air stream which can be treated, if necessary. In some cases (where allowed), it may be acceptable to reinject the extracted vapors back into the soil pile for additional degradation. It is important to optimize the aeration rate to the biopile. Evaporation of volatile constituents can be reduced by minimizing the air extraction or injection rate, which also reduces degradation rates by reducing oxygen supply to bacteria.

Petroleum products generally encountered at UST sites range from those with a significant volatile fraction, such as gasoline, to those that are primarily nonvolatile, such as heating and lubricating oils. Petroleum products generally contain more than one hundred different constituents that possess a wide range of volatility. In general, gasoline, kerosene, and diesel fuels contain constituents with sufficient volatility to evaporate from a biopile. Depending upon state-specific regulations for air emissions of volatile organic compounds (VOCs), control of VOC emissions may be required. Control involves capturing vapors before they are emitted to the atmosphere and then passing them through an appropriate treatment process before being vented to the atmosphere.

Chemical Structure

The chemical structures of the contaminants present in the soils proposed for treatment by biopiles are important in determining the rate at which biodegradation will occur. Although nearly all constituents in petroleum products typically found at UST sites are biodegradable, the more complex the molecular structure of the constituent, the more difficult and less rapid is biological treatment. Most low molecular-weight (nine carbon atoms or less) aliphatic and monoaromatic constituents are more easily biodegraded than higher molecular weight aliphatic or

polyaromatic organic constituents. Exhibit IV-9 lists, in order of decreasing rate of potential biodegradability, some common constituents found at petroleum UST sites.

Exhibit IV-9
Chemical Structure And Biodegradability

Biodegradability	Example Constituents	Products In Which Constituent Is Typically Found
More degradable	n-butane, l-pentane, n-octane	○ Gasoline
	Nonane	○ Diesel fuel
	Methyl butane, dimethylpentenes, methyloctanes	○ Gasoline
	Benzene, toluene, ethylbenzene, xylenes	○ Gasoline
	Propylbenzenes	○ Diesel, kerosene
	Decanes	○ Diesel
	Dodecanes	○ Kerosene
	Tridecanes	○ Heating fuels
	Tetradecanes	○ Lubricating oils
Less degradable	Naphthalenes	○ Diesel
	Fluoranthenes	○ Kerosene
	Pyrenes	○ Heating oil
	Acenaphthenes	○ Lubricating oils

Evaluation of the chemical structure of the constituents proposed for reduction by biopiles at the site will allow you to determine which constituents will be the most difficult to degrade. You should verify that remedial time estimates, biotreatability studies, field-pilot studies (if applicable), and biopile operation and monitoring plans are based on the constituents that are most difficult to degrade (or "rate limiting") in the biodegradation process.

Concentration And Toxicity

The presence of very high concentrations of petroleum organics or heavy metals in site soils can be toxic or inhibit the growth and reproduction of bacteria responsible for biodegradation in biopiles. Conversely, very low concentrations of organic material will result in diminished levels of microbial activity.

In general, soil concentrations of total petroleum hydrocarbons (TPH) in the range of 10,000 to 50,000 ppm, or heavy metals exceeding 2,500 ppm, are considered inhibitory and/or toxic to most microorganisms. If TPH concentrations are greater than 10,000 ppm, or the concentration of heavy metals is greater than 2,500 ppm, then the contaminated soil should be thoroughly mixed with clean soil to dilute the contaminants so that the average concentrations are below toxic levels. Exhibit IV-10 provides the general criteria for constituent concentration and biopile effectiveness.

Exhibit IV-10
Constituent Concentration And Biopile Effectiveness

Constituent Concentration	Biopile Effectiveness
Petroleum constituents $\leq$ 50,000 ppm and Heavy metals $\leq$ 2,500 ppm	Effective, however, if contaminant concentration is > 10,000 ppm, then soil should be blended with clean soil to reduce the concentration of the contaminants.
Petroleum constituents > 50,000 ppm or Heavy metals > 2,500 ppm	Ineffective; toxic or inhibitory conditions to bacterial growth exist. Dilution by blending necessary.

In addition to maximum concentrations, you should consider the cleanup goals proposed for the biopile soils. Below a certain "threshold" constituent concentration, the bacteria cannot obtain sufficient carbon (from degradation of the constituents) to maintain adequate biological activity. The threshold level can be determined from laboratory studies and should be below the level required for cleanup. Although the threshold limit varies greatly depending on bacteria-specific and constituent-specific features, generally constituent concentrations below 0.1 ppm are not achievable by biological treatment alone. In addition, experience has shown that reductions in TPH concentrations greater than 95 percent can be very difficult to achieve because of the presence of "recalcitrant" or nondegradable hydrocarbon species that are included in the TPH analysis. If a cleanup level lower than 0.1 ppm is required for any individual constituent or a reduction in TPH greater than 95 percent is required to reach the cleanup level for TPH, either a pilot study is required to demonstrate the ability of a biopile system to achieve these reductions at the site or another technology should be considered. Exhibit IV-11 shows the relationship between cleanup requirements and biopile effectiveness.

Exhibit IV-11
Cleanup Requirements And Biopile Effectiveness

Cleanup Requirement	Biopile Effectiveness
Constituent concentration > 0.1 ppm and TPH reduction < 95%	Effective.
Constituent concentration ≤ 0.1 ppm or TPH reduction ≥ 95%	Potentially ineffective; pilot studies are required to demonstrate contaminant reductions.

Climatic Conditions

Ambient Temperature

The ambient temperature is important because it influences soil temperature. As described previously, the temperature of the soils in the biopile impacts bacterial activity and, consequently, biodegradation. The optimal temperature range for biopiles is 10°C to 45°C. Special considerations (e.g., heating, covering, or enclosing) in biopile design can overcome the effects of colder climates and extend the length of the bioremediation season.

Rainfall

Some biopile designs do not include covers, leaving the biopile exposed to climatic factors including rainfall, snow, and wind, as well as ambient temperatures. Rainwater that falls on the biopile area will increase the moisture content of the soil and cause erosion. As previously described, effective biopile operation requires a proper range of moisture content. During and following a significant precipitation event, the moisture content of the soils may be temporarily in excess of that required for effective bacterial activity. On the other hand, during periods of drought, moisture content may be below the effective range and additional moisture may need to be added.

If the site is located in an area subject to annual rainfall of greater than 30 inches during the biopile season, a rain shield (such as a cover, tarp, plastic tunnel, or greenhouse structure) should be considered in the design of the biopile. In addition, rainfall runon and runoff from the biopile area should be controlled using berms at the perimeter of the biopile. A leachate collection system at the bottom of the biopile and a leachate treatment system may also be necessary to prevent groundwater contamination from the biopile.

Wind

Erosion of the biopile soils can occur during windy periods. Wind erosion can be limited by applying moisture periodically to the surface of the biopile or by enclosing or covering the biopile.

Biotreatability Evaluation

Biotreatability studies are especially desirable if toxicity is a concern or natural soil conditions are not conducive to biological activity. Biotreatability studies are usually performed in the laboratory and should be planned so that, if successful, the proper parameters are developed to design and implement the biopile system. If biotreatability studies do not demonstrate effectiveness, field trials or pilot studies will be needed prior to implementation, or another remedial approach should be evaluated. If the soil, constituents, and climatic characteristics are within the range of effectiveness for biopiles, review biotreatability studies to confirm that biopiles have the potential for effectiveness and to verify that the parameters needed to design the full-scale biopile system have been obtained. Biotreatability studies should provide data on contaminant biodegradability, ability of indigenous microorganisms to degrade contaminants, optimal microbial growth conditions and biodegradation rates, and sufficiency of natural nutrients and minerals.

There are two types of biotreatability studies generally used to demonstrate biopile effectiveness: (1) Flask Studies and (2) Pan Studies. Both types of studies begin with the characterization of the baseline physical and chemical properties of the soils to be treated in the biopile. Typical physical and chemical analyses performed on site soil samples for biotreatability studies are listed on Exhibit IV-12. The specific objectives of these analyses are to:

- Determine the types and concentrations of contaminants in the soils that will be used in the biotreatability studies.

- Assess the initial concentrations of constituents present in the study samples so that reductions in concentration can be evaluated.

- Determine if nutrients (nitrogen and phosphorus) are present in sufficient concentrations to support enhanced levels of bacterial activity.

- Evaluate parameters that may inhibit bacterial growth (e.g., toxic concentrations of metals, pH values lower than 6 or higher than 8).

Exhibit IV-12
Physical And Chemical Parameters For Biotreatability Studies

Parameter	Measured Properties
Soil toxicity	Type and concentration of contaminant and/or metals present, pH.
Soil texture	Grain size, clay content, moisture content, porosity, permeability, bulk density.
Nutrients	Nitrate, phosphate, other anions and cations.
Contaminant biodegradability	Total organic carbon concentration, volatility, chemical structure.

After you have characterized the soil samples, perform bench studies to evaluate biodegradation effectiveness. Flask (or bottle) studies which are simple and inexpensive, are used to test for biodegradation in water or soils using soil/water slurry microcosms. Flask studies may use a single slurry microcosm that is sampled numerous times or may have a series of slurry microcosms, each sampled once. Flask studies are less desirable than pan studies for evaluation of biopile effectiveness and are primarily used for evaluation of water-phase bioremedial technologies. Pan studies use soils, without dilution in an aqueous slurry, placed in steel or glass pans as microcosms that more closely resemble biopiles.

In either pan or flask studies, degradation is measured by tracking constituent concentration reduction and changes in bacterial population and other parameters over time. A typical treatment evaluation using pan or flask studies may include the following types of studies.

- *No Treatment Control Studies* measure the rate at which the existing bacteria can degrade constituents under oxygenated conditions without the addition of supplemental nutrients.

- *Nutrient Adjusted Studies* determine the optimum adjusted C:N:P ratio to achieve maximum degradation rates using microcosms prepared with different concentrations of nutrients.

- *Inoculated Studies* are performed if bacterial plate counts indicate that natural microbial activity is insufficient to promote sufficient degradation. Microcosms are inoculated with bacteria known to degrade the constituents at the site and are analyzed to determine if degradation can be increased by inoculation.

- *Sterile Control Studies* measure the degradation rate due to abiotic processes (including volatilization) as a baseline comparison with the other studies that examine biological processes. Microcosm soils are sterilized to eliminate bacterial activity. Abiotic degradation rates are then measured over time.

Review the CAP to determine that biotreatability studies have been completed, biodegradation is demonstrated, nutrient application and formulation have been evaluated and defined, and potential inhibitors or toxic conditions have been identified.

Evaluation Of The Biopile Design

Once you have verified that biopiles have the potential to be effective, you can evaluate the design of the biopile system. The CAP should include a discussion of the rationale for the design and present the conceptual engineering design. Detailed engineering design documents might also be included, depending on state requirements. Further detail about information to look for in the discussion of the design is provided below.

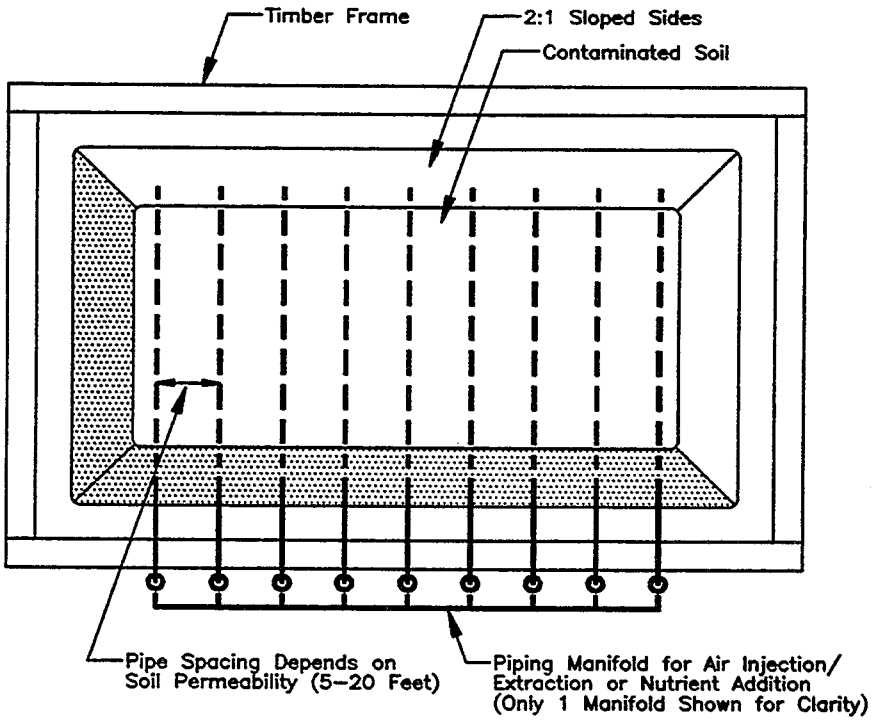
- *Land Requirements* can be determined by dividing the amount of soil to be treated by the height of the proposed biopile(s). The typical height of biopiles varies between 3 and 10 feet. Additional land area around the biopile(s) will be required for sloping the sides of the pile, for containment berms, and for access. The length and width of biopiles is generally not restricted unless aeration is to occur by manually turning the soils. In general, biopiles which will be turned should not exceed 6 to 8 feet in width.

- *Biopile Layout* is usually determined by the configuration of and access to the land available for the biopile(s). The biopile system can include single or multiple piles.

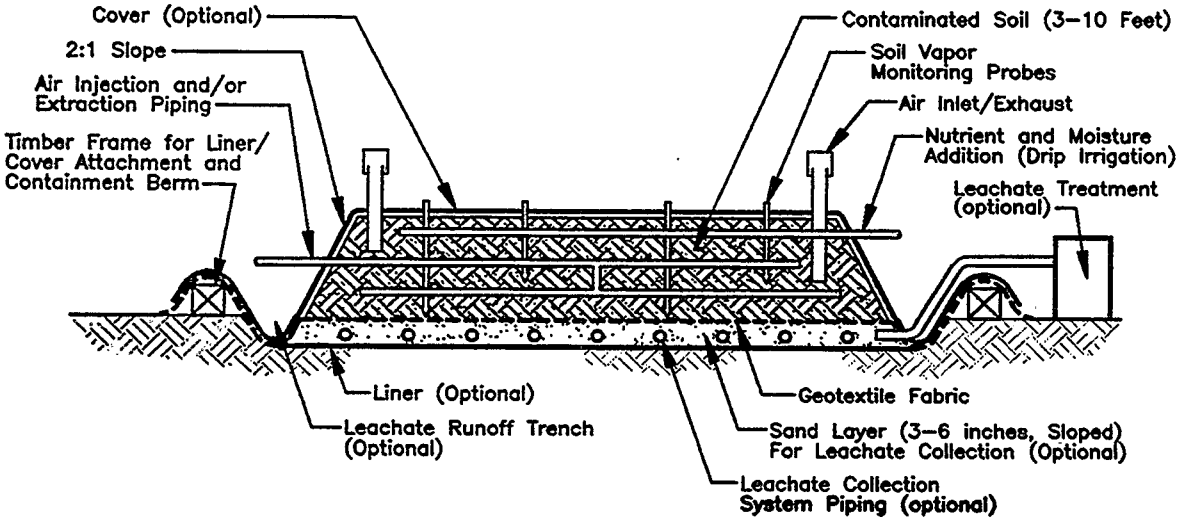
- *Biopile Construction* includes: site preparation (grubbing, clearing, and grading); berms; liners and covers(if necessary); air injection, extraction and/or collection piping arrangement; nutrient and moisture injection piping arrangement; leachate collection and treatment systems; soil pretreatment methods (e.g., shredding, blending, amendments for fluffing, pH control); and enclosures and appropriate vapor treatment facilities (where needed). The construction design of a typical biopile is shown as Exhibit IV-13.

- *Aeration Equipment* usually includes blowers or fans which will be attached to the aeration piping manifold unless aeration is to be accomplished by manually turning the soil.

Exhibit IV-13
Construction Design Of A Typical Biopile



PLAN VIEW
NOT TO SCALE



CROSS SECTION
NOT TO SCALE

- *Water Management* systems for control of runon and runoff are necessary to avoid saturation of the treatment area or washout of the soils in the biopile area. Runon is usually controlled by earthen berms or ditches that intercept and divert the flow of stormwater. Runoff can be controlled by diversion within the bermed treatment area to a retention pond where the runoff can be stored, treated, or released under a National Pollution Discharge Elimination System (NPDES) permit.

- *Soil Erosion Control* from wind or water generally includes sloping the sides of the pile, covering the pile, constructing water management systems, and spraying to minimize dust.

- *pH Adjustment, Moisture Addition, and Nutrient Supply* methods usually include incorporation of solid fertilizers, lime and/or sulfur into the soils while constructing the biopile, or injection of liquid nutrients, water and acid/alkaline solutions preferably through a dedicated piping system during operation of the biopile. The composition of nutrients and acid or alkaline solutions/solids for pH control is developed in biotreatability studies, and the frequency of their application is modified during biopile operation as needed.

- *Site Security* may be necessary to keep trespassers out of the treatment area. If the biopile is accessible to the public, a fence or other means of security is recommended to deter public contact with the contaminated material within the biopile area.

- *Air Emission Controls* (e.g., covers or structural enclosures) may be required if volatile constituents are present in the biopile soils. For compliance with air quality regulations, the volatile organic emissions should be estimated based on initial concentrations of the petroleum constituents present. Vapors in extracted or injected air should be monitored during the initial phases of biopile operation for compliance with appropriate permits or regulatory limits on atmospheric discharges. If required, appropriate vapor treatment technology should be specified, including operation and monitoring parameters.

Evaluation Of Operation And Remedial Progress Monitoring Plans

It is important to make sure that system operation and monitoring plans have been developed for the biopile operation. Regular monitoring is necessary to ensure optimization of biodegradation rates, to track constituent concentration reductions, and to monitor vapor emissions, migration of constituents into soils beneath the biopile (if unlined), and groundwater quality. If appropriate, ensure that monitoring to determine compliance with stormwater discharge or air quality permits is also proposed.

Operations Plan

Make certain that the plan for operating the biopile system described in the CAP includes the anticipated frequency of aeration, nutrient addition, and moisture addition. The plan should be flexible and modified based on the results of regular monitoring of the biopile soils. The plan should also account for seasonal variations in ambient temperature and rainfall. In general, aeration and moisture and nutrient applications should be more frequent in the warmer, drier months. If the biopile is covered with impervious sheeting (e.g., plastic or geofabric/ geotextile), the condition of the cover must be checked periodically to ensure that it remains in place and that it is free of rips, tears, or other holes. Provision should be made for replacement of the cover in the event that its condition deteriorates to the point where it is no longer effective.

Remedial Progress Monitoring Plan

Make certain that the monitoring plan for the biopile system is described in detail and include monitoring of biopile soils for constituent reduction and biodegradation conditions (e.g., CO_2, O_2, CH_4, H_2S), air monitoring for vapor emissions if volatile constituents are present, soil and groundwater monitoring to detect potential migration of constituents beyond the biopile area, and runoff water sampling (if applicable) for discharge permits. Make sure that the number of samples collected, sampling locations, and collection methods are in accordance with state regulations. A monitoring plan for a typical biopile operation is shown in Exhibit IV-14.

Soils within the biopile should be monitored at least quarterly during treatment to determine pH, moisture content, bacterial population, nutrient content, and constituent concentrations. For biopiles using air extraction or for those using air injection and off-gas collection, biodegradation conditions can be tracked by measuring oxygen and carbon dioxide concentrations in the vapor extracted from the biopile. These measurements should be taken weekly during the first 3 months of operation. The results of these analyses, which may be done using electronic instruments, field test kits, or in a field laboratory are critical to the optimal operation of the biopile. The results should be used to adjust air injection or extraction flow rates, nutrient application rates, moisture addition frequency and quantity, and pH. Optimal ranges for these parameters should be maintained to achieve maximum degradation rates.

Exhibit IV-14
Typical Remedial Progress Monitoring Plan For Biopiles

Medium To Be Monitored	Purpose	Sampling Frequency	Parameters To Be Analyzed
Soil in the biopile	Determine constituent degradation and biodegradation conditions.	Monthly to quarterly during the operation.	Bacterial population, constituent concentrations, pH, ammonia, phosphorus, moisture content, other rate limiting conditions.
Air extracted or collected from the biopile	Determine constituent degradation and biodegradation conditions.	Weekly during the first 3 months then monthly or quarterly.	CO_2, O_2, CH_4, H_2S, VOCs.
Air	Site personnel and population health hazards.	Twice during the first two weeks of operation, quarterly thereafter or to meet air quality requirements.	Volatile constituents, particulates.
Runoff water	Soluble or suspended constituents.	As required for NPDES permit.	As specified for NPDES permit; also hazardous organics.
Soil beneath the biopile	Migration of constituents.	Quarterly or twice per biopile season.	Hazardous constituents.
Groundwater downgradient of biopile	Migration of soluble constituents.	Once per biopile season (annually).	Hazardous, soluble constituents.

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Checklist: Can Biopiles Be Used At This Site?

This checklist can help you to evaluate to completeness of the CAP and to identify areas that require closer scrutiny. As you go through the CAP, answer the following questions. If the answer to several questions is no and biotreatability studies demonstrate marginal to ineffective results, request additional information to determine if biopiles will accomplish cleanup goals at the site.

1. Soil Characteristics That Contribute To Biopile Effectiveness

Yes	No	
❑	❑	Is the total heterotrophic bacteria count > 1,000 CFU/gram dry soil?
❑	❑	Is the soil pH between 6 and 8?
❑	❑	Is the soil moisture between 40% and 85%?
❑	❑	Is the soil temperature between 10°C and 45°C?
❑	❑	Is the carbon:nitrogen:phosphorous ratio between 100:10:1 and 100:1:0.5?
❑	❑	Does the soil divide easily and tend not to clump together?

2. Constituent Characteristics That Contribute To Biopile Effectiveness

Yes	No	
❑	❑	Are products to be treated primarily kerosene or heavier (i.e., not gasoline), or will air emissions be monitored and, if necessary, controlled?
❑	❑	Are most of the constituents readily degradable?
❑	❑	Are total petroleum constituents $\leq$ 50,000 ppm and total heavy metals $\leq$ 2,500 ppm?

3. Climatic Conditions That Contribute To Biopile Effectiveness

Yes	No	
❑	❑	Is the rainfall less than 30 inches during the biopile season?
❑	❑	Are high winds unlikely?

4. Biotreatability Evaluation

Yes	No	
❑	❑	Has a biotreatability study been conducted?
❑	❑	Was biodegradation demonstrated, nutrient application and formulation defined, and potential inhibitors or toxic conditions checked?

5. Evaluation Of Biopile Design

Yes	No	
❑	❑	Is sufficient land available considering the biopile depth and additional space for berms and access?
❑	❑	Is runon and runoff controlled?
❑	❑	Are erosion control measures specified?
❑	❑	Are the frequency of application and composition of nutrients and pH adjustment materials specified?
❑	❑	Is moisture addition needed?
❑	❑	Are other sub-optimal natural site conditions addressed in the biopile design (e.g., low temperatures, poor soil texture, and excessive rainfall)?
❑	❑	Is the site secured?
❑	❑	Are air emissions estimated and will air emissions monitoring be conducted?
❑	❑	Are provisions included for air emissions controls, if needed?

6. Operation And Monitoring Plans

Yes	No	
❑	❑	Are frequencies of aeration, nutrient addition, and moisture addition provided in the operation plan?
❑	❑	Is monitoring for constituent reduction and biodegradation conditions proposed?

6. Operation And Monitoring Plans (continued)

Yes	No	
❑	❑	Are air, soil, and surface runoff water sampling (if applicable) proposed to ensure compliance with appropriate permits?
❑	❑	Are the proposed number of samples to be collected, sampling locations, and collection methods in accordance with state regulations?
❑	❑	Is quarterly (or more frequent) monitoring for soil pH, moisture content, bacterial population, nutrient content, and constituent concentrations proposed?

Chapter V

Landfarming

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Chapter V
Landfarming

Overview

Landfarming, also known as land treatment or land application, is an above-ground remediation technology for soils that reduces concentrations of petroleum constituents through biodegradation. This technology usually involves spreading excavated contaminated soils in a thin layer on the ground surface and stimulating aerobic microbial activity within the soils through aeration and/or the addition of minerals, nutrients, and moisture. The enhanced microbial activity results in degradation of adsorbed petroleum product constituents through microbial respiration. If contaminated soils are shallow (i.e., ≤ 3 feet below ground surface), it may be possible to effectively stimulate microbial activity without excavating the soils. If petroleum-contaminated soil is deeper than 5 feet, the soils should be excavated and reapplied on the ground surface. A typical landfarming operation is shown in Exhibit V-1.

Landfarming has been proven effective in reducing concentrations of nearly all the constituents of petroleum products typically found at underground storage tank (UST) sites. Lighter (more volatile) petroleum products (e.g., gasoline) tend to be removed by evaporation during landfarm aeration processes (i.e., tilling or plowing) and, to a lesser extent, degraded by microbial respiration. Depending upon your state's regulations for air emissions of volatile organic compounds (VOCs), you may need to control the VOC emissions. Control involves capturing the vapors before they are emitted to the atmosphere, passing them through an appropriate treatment process, and then venting them to the atmosphere. The mid-range hydrocarbon products (e.g., diesel fuel, kerosene) contain lower percentages of lighter (more volatile) constituents than does gasoline. Biodegradation of these petroleum products is more significant than evaporation. Heavier (non-volatile) petroleum products (e.g., heating oil, lubricating oils) do not evaporate during landfarm aeration; the dominant mechanism that breaks down these petroleum products is biodegradation. However, higher molecular weight petroleum constituents such as those found in heating and lubricating oils, and, to a lesser extent, in diesel fuel and kerosene, require a longer period of time to degrade than do the constituents in gasoline. A summary of the advantages and disadvantages of landfarming is shown in Exhibit V-2.

The policies and regulations of your state determine whether landfarming is allowed as a treatment option. Before reading this chapter, consider whether your state allows the use of this remedial option.

Exhibit V-1
Typical Landfarming Operation

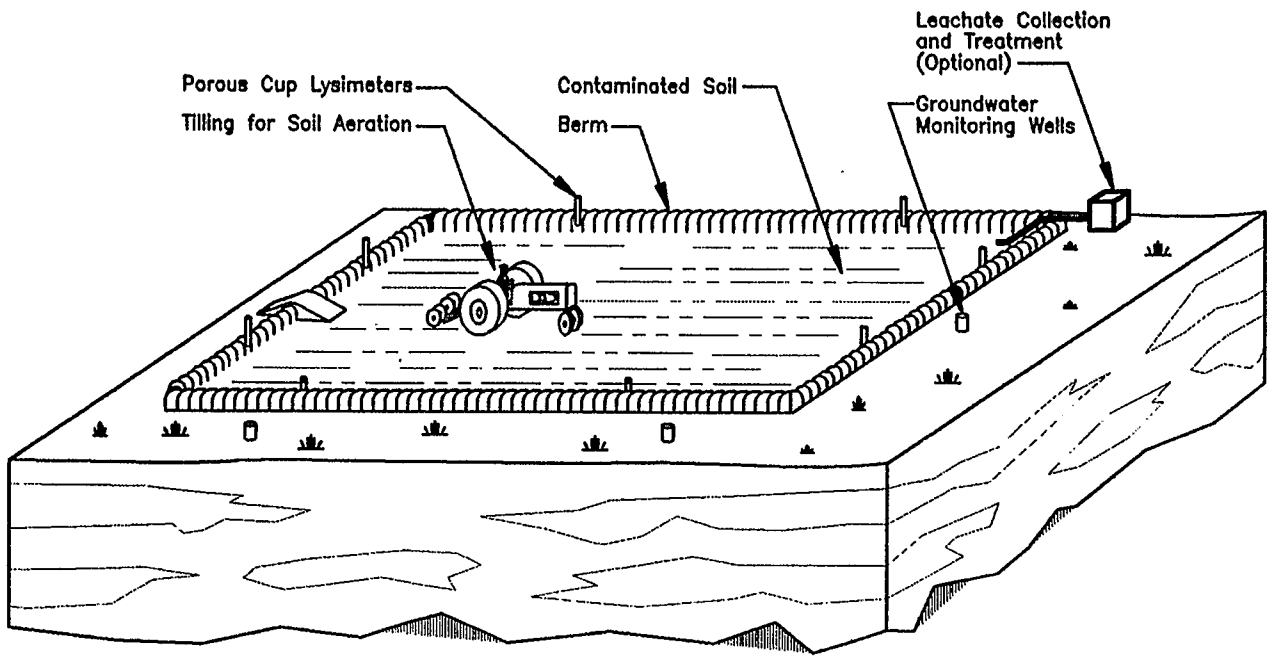


Exhibit V-2
Advantages And Disadvantages Of Landfarming

Advantages	Disadvantages
○ Relatively simple to design and implement.	○ Concentration reductions > 95% and constituent concentrations < 0.1 ppm are very difficult to achieve.
○ Short treatment times: usually 6 months to 2 years under optimal conditions.	○ May not be effective for high constituent concentrations (> 50,000 ppm total petroleum hydrocarbons).
○ Cost competitive: $30-60/ton of contaminated soil.	○ Presence of significant heavy metal concentrations (> 2,500 ppm) may inhibit microbial growth.
○ Effective on organic constituents with slow biodegradation rates.	○ Volatile constituents tend to evaporate rather than biodegrade during treatment.
	○ Requires a large land area for treatment.
	○ Dust and vapor generation during landfarm aeration may pose air quality concerns.
	○ May require bottom liner if leaching from the landfarm is a concern.

This chapter will assist you in evaluating a corrective action plan (CAP) that proposes landfarming as a remedy for petroleum contaminated soil. The evaluation guidance is presented in the three steps described below. The evaluation process, which is summarized in a flow diagram shown in Exhibit V-3, will serve as a roadmap for the decisions you will make during your evaluation. A checklist has also been provided at the end of this chapter to be used as a tool to evaluate the completeness of the CAP and to help you focus on areas where additional information may be needed. The evaluation process can be divided into the following steps.

○ **Step 1:** ***An evaluation of landfarming effectiveness***, in which you can identify the soil, constituent, and climatic factors that contribute to the effectiveness of landfarming and compare them to acceptable operating ranges. To complete the evaluation, you will need to compare these properties to ranges where landfarming is effective.

Exhibit V-3
Landfarming Evaluation Process Flow Chart

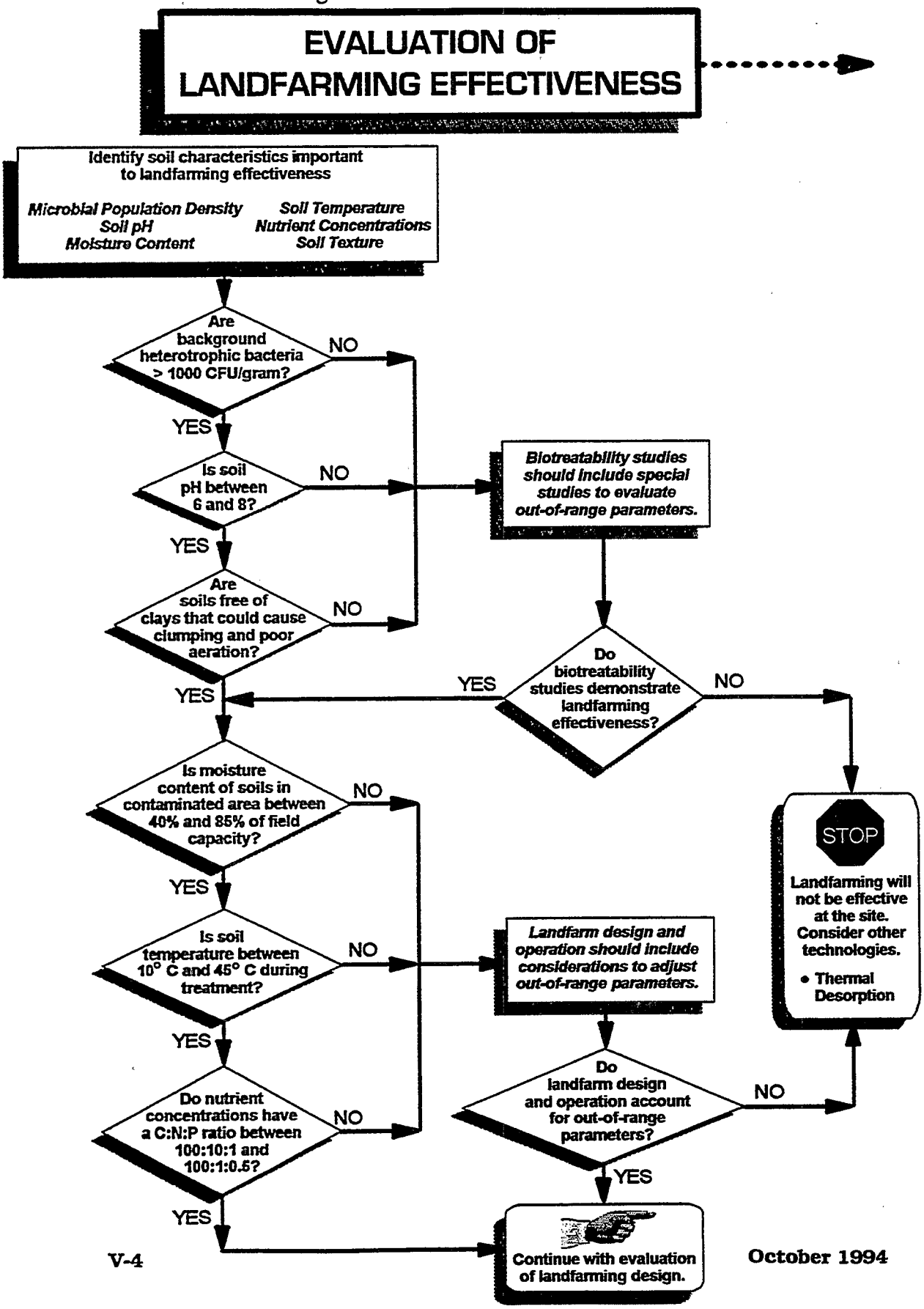


Exhibit V-3
Landfarming Evaluation Process Flow Chart

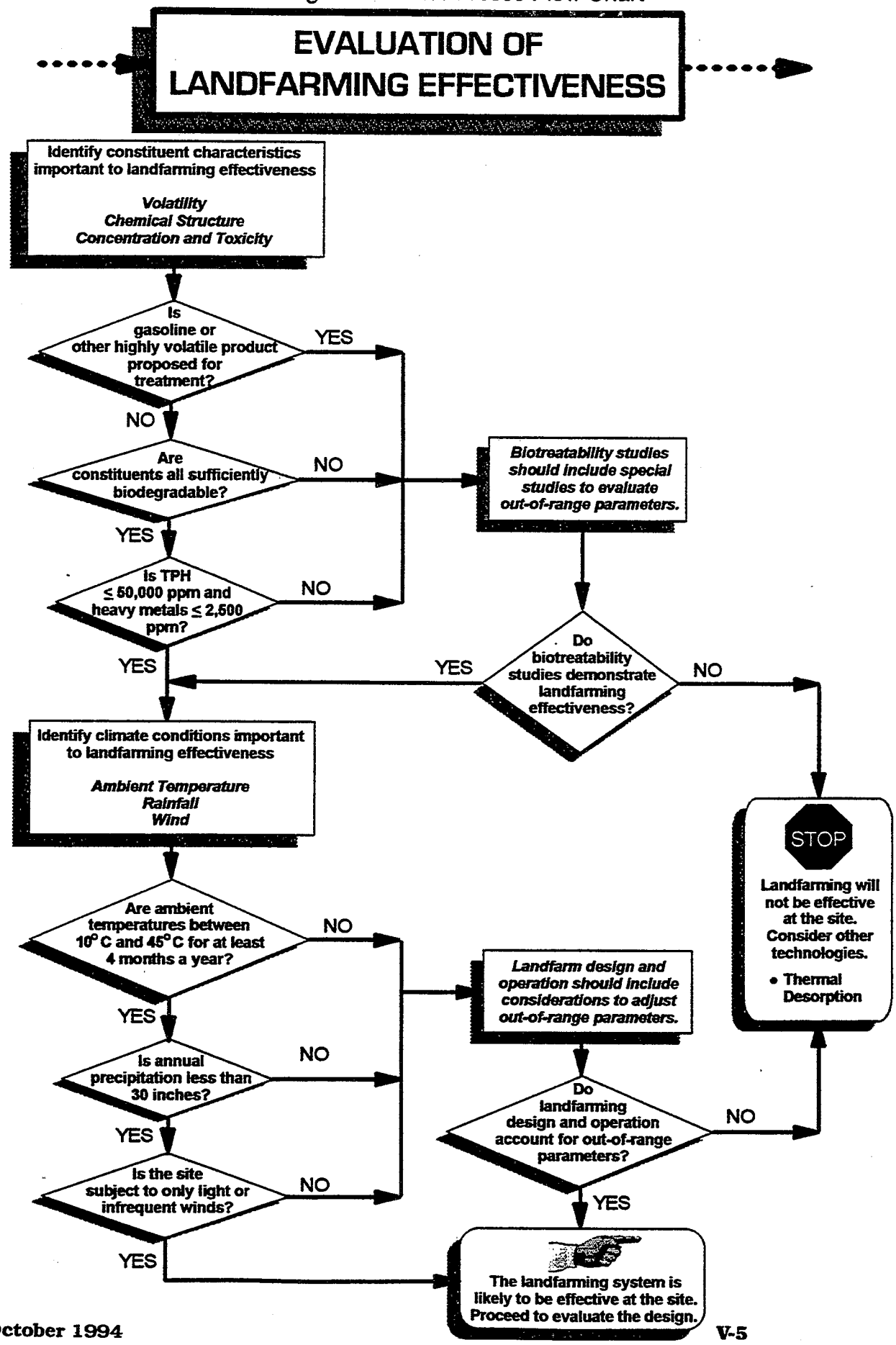
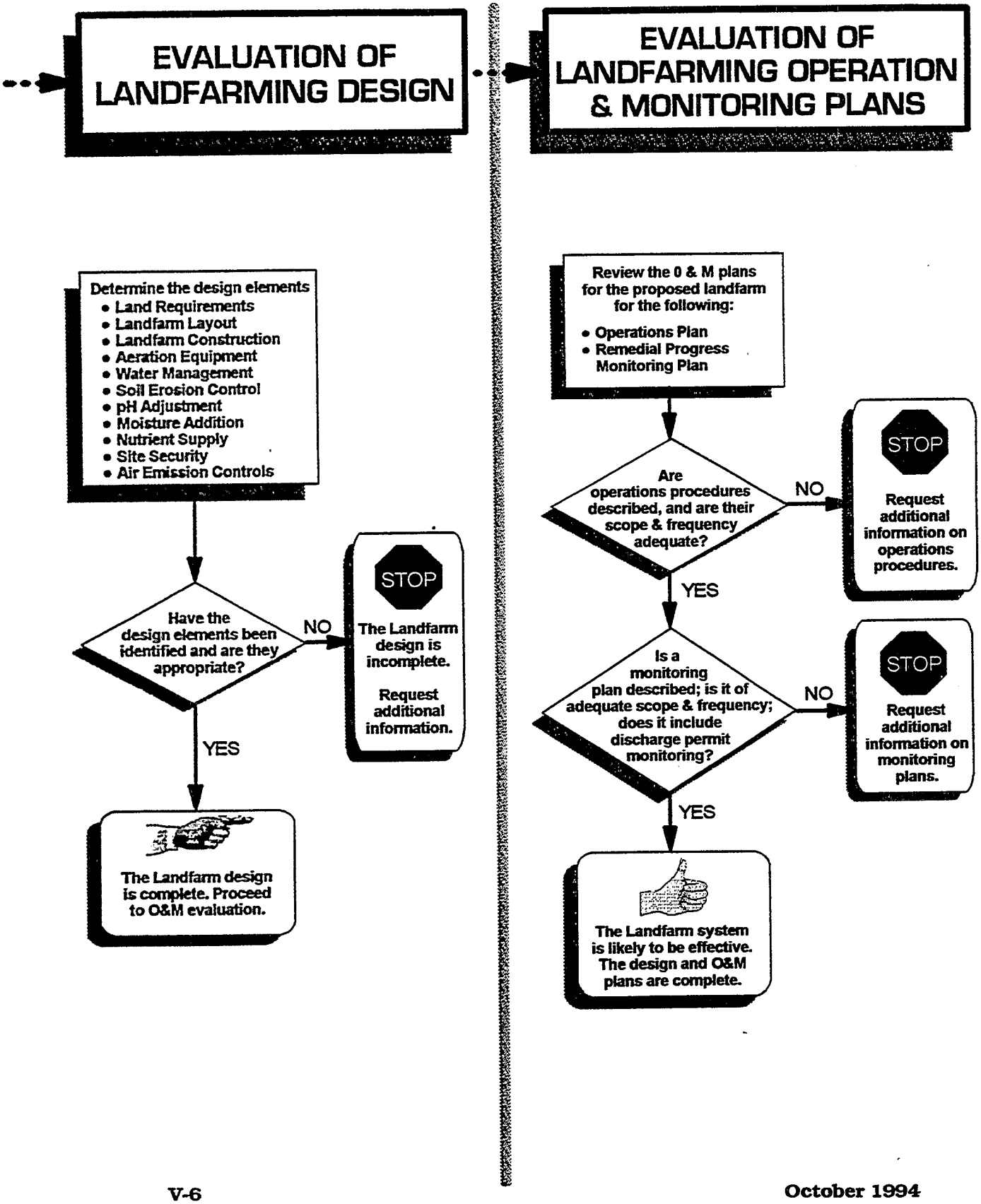


Exhibit V-3
Landfarming Evaluation Process Flow Chart



- **Step 2:** ***An evaluation of the landfarming system design*** will allow you to determine if the rationale for the design has been appropriately defined, whether the necessary design components have been specified, and whether the construction designs are consistent with standard practice.

- **Step 3:** ***An evaluation of the operation and monitoring plans,*** which are critical to the effectiveness of landfarming, will allow you to determine whether start-up and long-term system operation and monitoring plans are of sufficient scope and frequency.

Evaluation Of Landfarming Effectiveness

The effectiveness of landfarming depends on many parameters which are listed in Exhibit V-4. The parameters are grouped into three categories: soil characteristics, constituent characteristics, and climatic conditions.

Exhibit V-4
Parameters Used To Evaluate The Effectiveness Of Landfarming

Soil Characteristics	Constituent Characteristics	Climatic Conditions
Microbial population density	Volatility	Ambient temperature
Soil pH	Chemical structure	Rainfall
Moisture content	Concentration and toxicity	Wind
Soil temperature		
Nutrient concentrations		
Texture		

The following paragraphs contain descriptions of each parameter that include: why it is important; how it can be determined; and what its appropriate range is. During your evaluation, remember that because landfarming is an above-ground treatment technique, most parameters (except climatic conditions) can be controlled during the design and operation of the landfarm. Therefore, during your evaluation, identify those parameters that fall outside the effectiveness ranges provided and verify that the system design and proposed operating specifications compensate for any site conditions that are less than optimal.

Soil Characteristics

Microbial Population Density

Soil normally contains large numbers of diverse microorganisms including bacteria, algae, fungi, protozoa, and actinomycetes. In well-drained soils, which are most appropriate for landfarming, these organisms are generally aerobic. Of these organisms, bacteria are the most numerous and biochemically active group, particularly at low oxygen levels. Bacteria require a carbon source for cell growth and an energy source to sustain metabolic functions required for growth. Bacteria also require nitrogen and phosphorus for cell growth. Although sufficient types and quantities of microorganisms are usually present in the soil, recent applications of ex-situ soil treatment include blending the soil with cultured microorganisms or animal manure (typically from chickens or cows). Incorporating manure serves to both augment the microbial population and provide additional nutrients.

The metabolic process used by bacteria to produce energy requires a terminal electron acceptor (TEA) to enzymatically oxidize the carbon source to carbon dioxide. Microbes are classified by the carbon and TEA sources they use to carry out metabolic processes. Bacteria that use organic compounds (e.g., petroleum constituents and other naturally occurring organics) as their source of carbon are *heterotrophic*; those that use inorganic carbon compounds (e.g., carbon dioxide) are *autotrophic*. Bacteria that use oxygen as their TEA are *aerobic*; those that use a compound other than oxygen, (e.g., nitrate, sulfate), are *anaerobic*; and those that can utilize both oxygen and other compounds as TEAs are *facultative*. For landfarming applications directed at petroleum products, only bacteria that are both *aerobic* (or *facultative*) and *heterotrophic* are important in the degradation process.

In order to evaluate the presence and population of naturally occurring bacteria that will contribute to degradation of petroleum constituents, conduct laboratory analyses of soil samples from the site. These analyses, at a minimum, should include plate counts for total heterotrophic bacteria. Plate count results are normally reported in terms of colony-forming units (CFUs) per gram of soil. Microbial population densities in typical soils range from 10^4 to 10^7 CFU/gram of soil. For landfarming to be effective, the minimum heterotrophic plate count should be 10^3 CFU/gram or greater. Plate counts lower than 10^3 could indicate the presence of toxic concentrations of organic or inorganic (e.g., metals) compounds. In this situation, landfarming may still be effective if the soil is conditioned or amended to reduce the toxic concentrations and increase the microbial population density. More elaborate laboratory tests are sometimes conducted to identify the bacterial species present. This may be desirable if there is uncertainty about whether or not microbes capable of degrading specific petroleum

hydrocarbons occur naturally in the soil. If insufficient numbers or types of microorganisms are present, the population density may be increased by introducing cultured microbes that are available from vendors. Exhibit V-5 shows the relationship between plate counts of total heterotrophic bacteria and the effectiveness of landfarming.

Exhibit V-5
Heterotrophic Bacteria And Landfarming Effectiveness

Total Heterotrophic Bacteria (prior to landfarming)	Landfarming Effectiveness
> 1000 CFU/gram dry soil	Generally effective.
< 1000 CFU/gram dry soil	May be effective; needs further evaluation to determine if toxic conditions are present.

Soil pH

To support bacterial growth, the soil pH should be within the 6 to 8 range, with a value of about 7 (neutral) being optimal. Soils with pH values outside this range prior to landfarming will require pH adjustment prior to and during landfarming operations. Soil pH within the landfarm can be raised through the addition of lime and lowered by adding elemental sulfur. Exhibit V-6 summarizes the effect of soil pH on landfarming effectiveness. Review the CAP to verify that soil pH measurements have been made. If the soil pH is less than 6 or greater than 8, make sure that pH adjustments, in the form of soil amendments, are included in the design and operational plans for the landfarm.

Exhibit V-6
Soil pH And Landfarming Effectiveness

Soil pH (prior to landfarming)	Landfarming Effectiveness
$6 \leq pH \leq 8$	Generally effective.
$6 > pH > 8$	Landfarm soils will require amendments to correct pH to effective range.

Moisture Content

Soil microorganisms require moisture for proper growth. Excessive soil moisture, however, restricts the movement of air through the subsurface thereby reducing the availability of oxygen which is also necessary for aerobic bacterial metabolic processes. In general, the soil should be moist but not wet or dripping wet. The ideal range for soil moisture is between 40 and 85 percent of the water-holding capacity (field capacity) of the soil or about 12 percent to 30 percent by weight. Periodically, moisture must be added in landfarming operations because soils become dry as a result of evaporation, which is increased during aeration operations (i.e., tilling and/or plowing). Excessive accumulation of moisture can occur at landfarms in areas with high precipitation or poor drainage. These conditions should be considered in the landfarm design. For example, an impervious cover can mitigate excessive infiltration and potential erosion of the landfarm. Exhibit V-7 shows the optimal range for soil moisture content.

Exhibit V-7
Soil Moisture And Landfarming Effectiveness

Soil Moisture	Landfarming Effectiveness
40% $\leq$ field capacity $\leq$ 85%	Effective.
Field capacity < 40%	Periodic moisture addition is needed to maintain proper bacterial growth.
Field capacity > 85%	Landfarm design should include special water drainage considerations.

Soil Temperature

Bacterial growth rate is a function of temperature. Soil microbial activity has been shown to decrease significantly at temperatures below 10°C and to essentially cease below 5°C. The microbial activity of most bacteria important to petroleum hydrocarbon biodegradation also diminishes at temperatures greater than 45°C. Within the range of 10°C to 45°C, the rate of microbial activity typically doubles for every 10°C rise in temperature. Because soil temperature varies with ambient temperatures, there will be certain periods during the year when bacterial growth and, therefore, constituent degradation, will diminish. When ambient temperatures return to the growth range, bacterial activity will be gradually restored. The period of the year when the ambient temperature is within the range for microbial activity is commonly called the "landfarming season."

In colder parts of the United States, such as the Northeastern states, the length of the landfarming season is shorter, typically ranging from only 7 to 9 months. In very cold climates, special precautions can be taken, including enclosing the landfarm within a greenhouse-type structure or introducing special bacteria (psychrophiles), which are capable of activity at lower temperatures. In warm regions, the landfarming season can last all year. Exhibit V-8 shows how soil temperature affects landfarming operation.

Exhibit V-8
Soil Temperature And Landfarming Effectiveness

Soil Temperature	Landfarming Effectiveness
10°C ≤ soil temperature ≤ 45°C	Effective.
10°C > soil temperature > 45°C	Not generally effective; microbial activity diminished during seasonal temperature extremes but restored during periods within the effective temperature range. Temperature-controlled enclosures or special bacteria required for areas with extreme temperatures.

Nutrient Concentrations

Microorganisms require inorganic nutrients such as nitrogen and phosphorus to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in the site soils but, more frequently, nutrients need to be added to landfarm soils to maintain bacterial populations. However, excessive amounts of certain nutrients (i.e., phosphate and sulfate) can repress microbial metabolism. The typical carbon:nitrogen:phosphorus ratio necessary for biodegradation falls in the range of 100:10:1 to 100:1:0.5, depending upon the specific constituents and microorganisms involved in the biodegradation process.

The naturally occurring available nitrogen and phosphorus content of the soil should be determined by chemical analyses of samples collected from the site. These types of analyses are routinely conducted in agronomic laboratories that test soil fertility for farmers. These concentrations can be compared to the nitrogen and phosphorus requirements calculated from the stoichiometric ratios of the biodegradation process. A conservative approximation of the amount of nitrogen and phosphorus required for optimum degradation of petroleum products can be calculated by assuming that the total mass of hydrocarbon in the soil represents the mass of carbon available for biodegradation. This simplifying assumption is valid because the carbon

content of the petroleum hydrocarbons commonly encountered at UST sites is approximately 90 percent carbon by weight.

As an example, assume that at a LUST site the volume of contaminated soil is 90,000 ft^3, the average TPH concentration in the contaminated soil is 1,000 mg/kg, and the soil bulk density is 50 kg/ft^3 (1.75 g/cm^3).

The mass of contaminated soil is equal to the product of volume and bulk density:

$$\text{soil mass} = 90{,}000\ ft^3 \times \frac{50\ kg}{ft^3} = 4.5 \times 10^6\ kg$$

The mass of the contaminant (and carbon) is equal to the product of the mass of contaminated soil and the average TPH concentration in the contaminated soil:

$$\text{contaminant mass} =$$
$$4.5 \times 10^6\ kg \times 1{,}000\ \frac{mg}{kg} = 4.5 \times 10^3\ kg \approx 10{,}000\ lbs$$

Using the C:N:P ratio of 100:10:1, the required mass of nitrogen would be 1,000 lbs, and the required mass of phosphorus would be 100 lbs. After converting these masses into concentration units (56 mg/kg for nitrogen and 5.6 mg/kg for phosphorus), they can be compared with the results of the soil analyses to determine if nutrient addition is necessary. If nitrogen addition is necessary, slow release sources should be used. Nitrogen addition can lower pH, depending on the amount and type of nitrogen added.

Soil Texture

Texture affects the permeability, moisture content, and bulk density of the soil. To ensure that oxygen addition (by tilling or plowing), nutrient distribution, and moisture content of the soils can be maintained within effective ranges, you must consider the texture of the soils. For example, soils which tend to clump together (such as clays) are difficult to aerate and result in low oxygen concentrations. It is also difficult to uniformly distribute nutrients throughout these soils. They also retain water for extended periods following a precipitation event.

You should identify whether clayey soils are proposed for landfarming at the site. Soil amendments (e.g., gypsum) and bulking materials (e.g., sawdust, or straw) should be blended into the soil as the landfarm is being constructed to ensure that the landfarming medium has a loose or divided texture. Clumpy soil may require shredding or other means of pretreatment during landfarm construction to incorporate these amendments.

Constituent Characteristics

Volatility

The volatility of contaminants proposed for treatment by landfarming is important because volatile constituents tend to evaporate from the landfarm, particularly during tilling or plowing operations, rather than being biodegraded by bacteria. Constituent vapors emitted from a landfarm will dissipate into the atmosphere unless the landfarm is enclosed within a surface structure such as a greenhouse or plastic tunnel or covered with a plastic sheet.

Petroleum products generally encountered at UST sites range from those with a significant volatile fraction, such as gasoline, to those that are primarily nonvolatile, such as heating and lubricating oils. Petroleum products generally contain more than one hundred different constituents that possess a wide range of volatility. In general, gasoline, kerosene, and diesel fuels contain constituents with sufficient volatility to evaporate from a landfarm. Depending upon state-specific regulations for air emissions of volatile organic compounds (VOCs), control of VOC emissions may be required. Control involves capturing vapors before they are emitted to the atmosphere and then passing them through an appropriate treatment process before being vented to the atmosphere.

Chemical Structure

The chemical structures of the contaminants present in the soils proposed for treatment by landfarming are important in determining the rate at which biodegradation will occur. Although nearly all constituents in petroleum products typically found at UST sites are biodegradable, the more complex the molecular structure of the constituent, the more difficult, and less rapid, is biological treatment. Most low molecular-weight (nine carbon atoms or less) aliphatic and monoaromatic constituents are more easily biodegraded than higher molecular weight aliphatic or polyaromatic organic constituents. Exhibit V-9 lists, in order of decreasing rate of potential biodegradability, some common constituents found at petroleum UST sites.

Evaluation of the chemical structure of the constituents proposed for reduction by landfarming at the site will allow you to determine which constituents will be the most difficult to degrade. You should verify that remedial time estimates, biotreatability studies, field-pilot studies (if applicable), and landfarm operation and monitoring plans are based on the constituents that are most difficult to degrade (or "rate limiting") in the biodegradation process.

Exhibit V-9
Chemical Structure And Biodegradability

Biodegradability	Example Constituents	Products In Which Constituent Is Typically Found
More degradable	n-butane, n-pentane, n-octane	○ Gasoline
	Nonane	○ Diesel fuel
	Methyl butane, dimethylpentenes, methyloctanes	○ Gasoline
	Benzene, toluene, ethylbenzene, xylenes	○ Gasoline
	Propylbenzenes	○ Diesel, kerosene
	Decanes	○ Diesel
	Dodecanes	○ Kerosene
	Tridecanes	○ Heating fuels
	Tetradecanes	○ Lubricating oils
Less degradable	Naphthalenes	○ Diesel
	Fluoranthenes	○ Kerosene
	Pyrenes	○ Heating oil
	Acenaphthenes	○ Lubricating oils

Concentration And Toxicity

The presence of very high concentrations of petroleum organics or heavy metals in site soils can be toxic or inhibit the growth and reproduction of bacteria responsible for biodegradation in landfarms. In addition, very low concentrations of organic material will also result in diminished levels of bacteria activity.

In general, soil concentrations of total petroleum hydrocarbons (TPH) in the range of 10,000 to 50,000 ppm, or heavy metals exceeding 2,500 ppm, are considered inhibitory and/or toxic to most microorganisms. If TPH concentrations are greater than 10,000 ppm, or the concentration of heavy metals is greater than 2,500 ppm, then the contaminated soil should be thoroughly mixed with clean soil to dilute the contaminants so that the average concentrations are below toxic levels. Exhibit V-10 provides the general criteria for constituent concentration and landfarming effectiveness.

Exhibit V-10
Constituent Concentration And Landfarming Effectiveness

Constituent Concentration	Landfarming Effectiveness
Petroleum constituents ≤ 50,000 ppm and Heavy metals ≤ 2,500 ppm	Effective; however, if contaminant concentration is > 10,000 ppm, the soil may need to be blended with clean soil to reduce the concentration of the contaminants.
Petroleum constituents > 50,000 ppm or Heavy metals > 2,500 ppm	Ineffective; toxic or inhibitory conditions to bacterial growth exist. Dilution by blending necessary.

In addition to maximum concentrations, you should consider the cleanup goals proposed for the landfarm soils. Below a certain "threshold" constituent concentration, the bacteria cannot obtain sufficient carbon (from degradation of the constituents) to maintain adequate biological activity. The threshold level can be determined from laboratory studies and should be below the level required for cleanup. Although the threshold limit varies greatly depending on bacteria-specific and constituent-specific features, generally constituent concentrations below 0.1 ppm are not achievable by biological treatment alone. In addition, experience has shown that reductions in TPH concentrations greater than 95 percent can be very difficult to achieve because of the presence of "recalcitrant" or nondegradable species that are included in the TPH analysis. If a cleanup level lower than 0.1 ppm is required for any individual constituent or a reduction in TPH greater than 95 percent is required to reach the cleanup level for TPH, either a pilot study is required to demonstrate the ability of landfarming to achieve these reductions at the site or another technology should be considered. Exhibit V-11 shows the relationship between cleanup requirements and landfarming effectiveness.

Climatic Conditions

Typical landfarms are uncovered and, therefore, exposed to climatic factors including rainfall, snow, and wind, as well as ambient temperatures.

Ambient Temperature

The ambient temperature is important because it influences soil temperature. As described previously, the temperature of the soils in the landfarm impacts bacterial activity and, consequently, biodegradation. The optimal temperature range for landfarming is 10°C to 45°C. Special considerations (e.g., heating, covering, or enclosing) can overcome the effects of colder climates and extend the length of the landfarming season.

Exhibit V-11
Cleanup Requirements And Landfarming Effectiveness

Cleanup Requirement	Landfarming Effectiveness
Constituent concentration > 0.1 ppm and TPH reduction < 95%	Effective.
Constituent concentration ≤ 0.1 ppm or TPH reduction ≥ 95%	Potentially ineffective; pilot studies are required to demonstrate contaminant reduction.

Rainfall

Rainwater that falls directly onto, or runs onto, the landfarm area will increase the moisture content of the soil and cause erosion. As previously described, effective landfarming requires a proper range of moisture content. During and following a significant precipitation event, the moisture content of the soils may be temporarily in excess of that required for effective bacterial activity. On the other hand, during periods of drought, moisture content may be below the effective range and additional moisture may need to be added.

If the site is located in an area subject to annual rainfall of greater than 30 inches during the landfarming season, a rain shield (such as a tarp, plastic tunnel, or greenhouse structure) should be considered in the design of the landfarm. In addition, rainfall runon and runoff from the landfarm should be controlled using berms at the perimeter of the landfarm. A leachate collection system at the bottom of the landfarm and a leachate treatment system may also be necessary to prevent groundwater contamination from the landfarm.

Wind

Erosion of landfarm soils can occur during windy periods and particularly during tilling or plowing operations. Wind erosion can be limited by plowing soils into windrows and applying moisture periodically.

Biotreatability Evaluation

Biotreatability studies are especially desirable if toxicity is a concern or natural soil conditions are not conducive to biological activity. Biotreatability studies are usually performed in the laboratory and should be planned so that, if successful, the proper parameters are developed to design and implement the landfarming approach. If biotreatability studies do not demonstrate effectiveness, field trials or pilot studies will be needed prior to implementation, or another remedial approach should be evaluated. If the soil, constituents, and climatic characteristics are within the range of effectiveness for landfarming, review biotreatability studies to confirm that landfarming has the potential for effectiveness and to verify that the parameters needed to design the full-scale landfarm have been obtained. Biotreatability studies should provide data on contaminant biodegradability, ability of indigenous microorganisms to degrade contaminants, optimal microbial growth conditions and biodegradation rates, and sufficiency of natural nutrients and minerals.

There are two types of biotreatability studies generally used to demonstrate landfarming effectiveness: (1) Flask Studies and (2) Pan Studies. Both types of studies begin with the characterization of the baseline physical and chemical properties of the soils to be treated in the landfarm. Typical physical and chemical analyses performed on site soil samples for biotreatability studies are listed on Exhibit V-12. The specific objectives of these analyses are to:

- Determine the types and concentrations of contaminants in the soils that will be used in the biotreatability studies.
- Assess the initial concentrations of constituents present in the study samples so that reductions in concentration can be evaluated.
- Determine if nutrients (nitrogen and phosphorus) are present in sufficient concentrations to support enhanced levels of bacterial activity.
- Evaluate parameters that may inhibit bacterial growth (e.g., toxic concentrations of metals, pH values lower than 6 or higher than 8).

After the characterization of the soil samples is complete, perform bench studies to evaluate biodegradation effectiveness. Flask (or bottle) studies, which are simple and inexpensive, are used to test for biodegradation in water or soils using soil/water slurry microcosms. Flask studies may use a single slurry microcosm that is sampled numerous times or may have a series of slurry microcosms, each sampled once. Flask studies are less desirable than pan studies for evaluation of landfarming effectiveness and are primarily used for evaluation of water-phase bioremedial technologies. Pan studies use soils, without dilution in an aqueous slurry, placed in steel or glass pans as microcosms that more closely resemble landfarming.

Exhibit V-12
Physical And Chemical Parameters For Biotreatability Studies

Parameter	Measured Properties
Soil toxicity	Type and concentration of contaminant and/or metals present, pH.
Soil texture	Grain size, clay content, moisture content, porosity, permeability, bulk density.
Nutrients	Nitrate, phosphate, other anions and cations.
Contaminant biodegradability	Total organic carbon concentration, volatility, chemical structure.

In either pan or flask studies, degradation is measured by tracking constituent concentration reduction and changes in bacterial population and other parameters over time. A typical treatment evaluation using pan or flask studies may include the following types of studies.

- *No Treatment Control Studies* measure the rate at which the existing bacteria can degrade constituents under oxygenated conditions without the addition of supplemental nutrients.

- *Nutrient Adjusted Studies* determine the optimum adjusted C:N:P ratio to achieve maximum degradation rates using microcosms prepared with different concentrations of nutrients.

- *Inoculated Studies* are performed if bacterial plate counts indicate that natural microbial activity is insufficient to promote sufficient degradation. Microcosms are inoculated with bacteria known to degrade the constituents at the site and are analyzed to determine if degradation can be increased by inoculation.

- *Sterile Control Studies* measure the degradation rate due to abiotic processes (including volatilization) as a baseline comparison with the other studies that examine biological processes. Microcosm soils are sterilized to eliminate bacterial activity. Abiotic degradation rates are then measured over time.

Review the CAP to determine that biotreatability studies have been completed, biodegradation is demonstrated, nutrient application and formulation have been evaluated and defined, and no potential inhibitors or toxic conditions have been identified.

Evaluation Of The Landfarm Design

Once you have verified that landfarming has the potential for effectiveness, you can evaluate the design of the landfarm. The CAP should include a discussion of the rationale for the design and present the conceptual engineering design. Detailed engineering design documents might also be included, depending on state requirements. Further detail about information to look for in the discussion of the design is provided below.

- *Land Requirements* can be determined by dividing the amount of soil to be treated by the depth of the landfarm soils. The depth of landfarms can vary between 12 inches and 18 inches depending on the capabilities of the tilling equipment to be used. Very powerful tillers can reach as much as 24 inches deep to aerate landfarm soils. Additional land area around the landfarm will be required for containment berms and for access.

- *Landfarm Layout* is usually determined by the configuration of and access to the land available for the landfarm. The landfarm can include single or multiple plots.

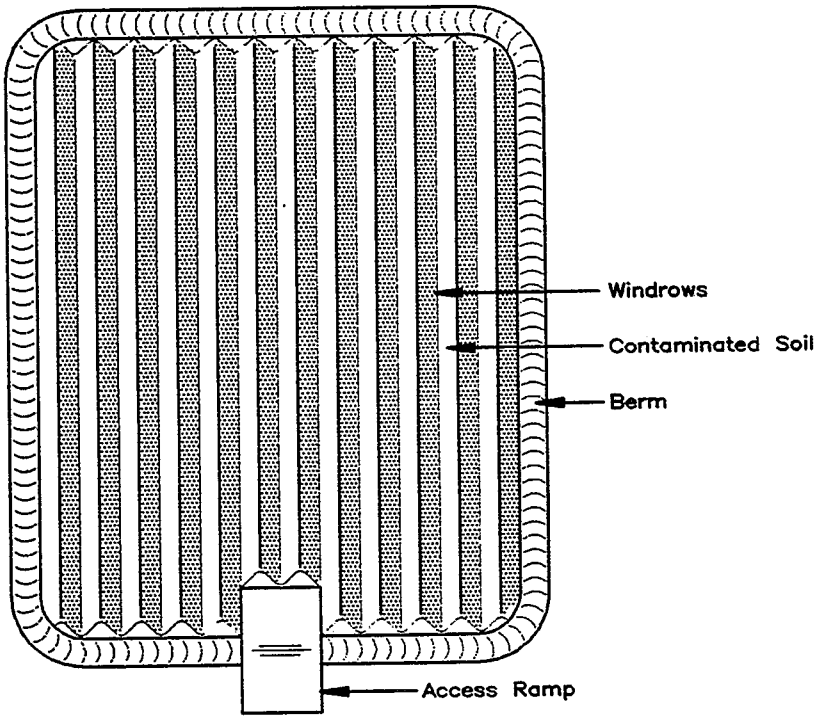
- *Landfarm Construction* includes: site preparation (grubbing, clearing and grading); berms; liners (if necessary); leachate collection and treatment systems; soil pretreatment methods (e.g., shredding, blending and amendments for fluffing, pH control); and enclosures and appropriate vapor treatment facilities (where needed). The construction design of a typical landfarm is shown as Exhibit V-13.

- *Aeration Equipment* usually includes typical agricultural equipment such as roto-tillers. The most favorable method is to use a disking device towed behind a tractor so that aerated soils are not tamped by the tractor tires.

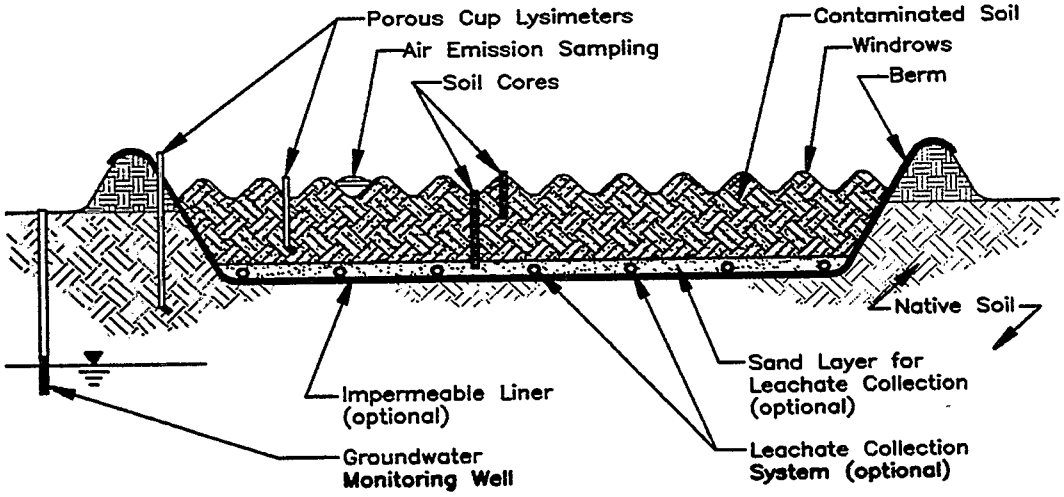
- *Water Management* systems for control of runon and runoff are necessary to avoid saturation of the treatment area or washout of the soils in the landfarm. Runon is usually controlled by earthen berms or ditches that intercept and divert the flow of stormwater. Runoff can be controlled by diversion within the bermed treatment area to a retention pond where the runoff can be stored, treated, or released under a National Pollution Discharge Elimination System (NPDES) permit.

- *Soil Erosion Control* from wind or water generally includes terracing the soils into windrows, constructing water management systems, and spraying to minimize dust.

Exhibit V-13
Construction Design Of A Typical Landfarm



PLAN VIEW
NOT TO SCALE



CROSS SECTION
NOT TO SCALE

- *pH Adjustment and Nutrient Supply* methods usually include periodic application of solid fertilizers, lime and/or sulfur while disking to blend soils with the solid amendments, or applying liquid nutrients using a sprayer. The composition of nutrients and acid or alkaline solutions/solids for pH control is developed in biotreatability studies and the frequency of their application is modified during landfarm operation as needed.

- *Site Security* may be necessary to keep trespassers out of the treatment area. If the landfarm is accessible to the public, a fence or other means of security is recommended to deter public contact with the contaminated material within the landfarm.

- *Air Emission Controls* (e.g., covers or structural enclosures) may be required if volatile constituents are present in the landfarm soils. For compliance with air quality regulations, the volatile organic emissions should be estimated based on initial concentrations of the petroleum constituents present. Vapors above the landfarm should be monitored during the initial phases of landfarm operation for compliance with appropriate permits or regulatory limits on atmospheric discharges. If required, appropriate vapor treatment technology should be specified, including operation and monitoring parameters.

Evaluation Of Operation And Remedial Progress Monitoring Plans

It is important to make sure that system operation and monitoring plans have been developed for the landfarming operation. Regular monitoring is necessary to ensure optimization of biodegradation rates, to track constituent concentration reductions, and to monitor vapor emissions, migration of constituents into soils beneath the landfarm (if unlined), and groundwater quality. If appropriate, ensure that monitoring to determine compliance with stormwater discharge or air quality permits is also proposed.

Operations Plan

Make certain that the plan for operating the landfarm described in the CAP includes the anticipated frequency of aeration, nutrient addition, and moisture addition. The plan should be flexible and modified based on the results of regular monitoring of the landfarm soils. The plan should also account for seasonal variations in ambient temperature and rainfall. In general, aeration and moisture and nutrient applications should be more frequent in the warmer, drier months. If the landfarm is covered with impervious sheeting (e.g., plastic or geofabric/textile), the condition of the cover must be checked periodically to ensure that it remains in place and that it is free of rips, tears, or other holes.

Provision should be made for replacement of the cover in the event that its condition deteriorates to the point where it is no longer effective. Particularly in the more northern states, operations may be suspended altogether during the winter months.

Remedial Progress Monitoring Plan

Make certain that the monitoring plan for the landfarm is described in detail and includes monitoring of landfarm soils for constituent reduction and biodegradation conditions (e.g., CO_2, O_2, CH_4, H_2S), air monitoring for vapor emissions if volatile constituents are present, soil and groundwater monitoring to detect potential migration of constituents beyond the landfarm, and runoff water sampling (if applicable) for discharge permits. Make sure that the number of samples collected, sampling locations, and collection methods are in accordance with state regulations. A monitoring plan for a typical landfarm operation is shown in Exhibit V-14.

Soils within the landfarm should be monitored at least quarterly during the landfarming season to determine pH, moisture content, bacterial population, nutrient content, and constituent concentrations. The results of these analyses, which may be done using electronic instruments, field test kits, or in a field laboratory are critical to the optimal operation of the landfarm. The results should be used to adjust aeration frequency, nutrient application rates, moisture addition frequency and quantity, and pH. Optimal ranges for these parameters should be maintained to achieve maximum degradation rates.

Exhibit V-14
Typical Remedial Progress Monitoring Plan For Landfarming

Medium To Be Monitored	Purpose	Sampling Frequency	Parameters To Be Analyzed
Soil in the landfarm	Determine constituent degradation and biodegradation conditions.	Monthly to quarterly during the landfarming season.	Bacterial population, constituent concentrations, pH, ammonia, phosphorus, moisture content, other rate limiting conditions.
Air	Site personnel and population health hazards.	During first two aerations, quarterly thereafter or to meet air quality requirements.	Volatile constituents, particulates.
Runoff water	Soluble or suspended constituents.	As required for NPDES permit.	As specified for NPDES permit; also hazardous organics.
Soil beneath the landfarm	Migration of constituents.	Quarterly or twice per landfarming season.	Hazardous constituents.
Groundwater downgradient of landfarm	Migration of soluble constituents.	Once per landfarming season (annually).	Hazardous, soluble constituents.

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Checklist: Can Landfarming Be Used At This Site?

This checklist can help you to evaluate the completeness of the CAP and to identify areas that require closer scrutiny. As you go through the CAP, answer the following questions. If the answer to several questions is no and biotreatability studies demonstrate marginal to ineffective results, request additional information to determine if landfarming will accomplish cleanup goals at the site.

1. Soil Characteristics That Contribute To Landfarming Effectiveness

Yes	No	
❑	❑	Is the total heterotrophic bacteria count > 1,000 CFU/gram dry soil?
❑	❑	Is the soil pH between 6 and 8?
❑	❑	Is the soil moisture between 40% and 85%?
❑	❑	Is the soil temperature between 10°C and 45°C?
❑	❑	Is the carbon:nitrogen:phosphorous ratio between 100:10:1 and 100:1:0.5?
❑	❑	Does the soil divide easily and tend not to clump together?

2. Constituent Characteristics That Contribute To Landfarming Effectiveness

Yes	No	
❑	❑	Are products to be treated primarily kerosene or heavier (i.e., not gasoline), or will air emissions be monitored and, if necessary, controlled?
❑	❑	Are most of the constituents readily degradable?
❑	❑	Are total petroleum constituents $\leq$ 50,000 ppm and total heavy metals $\leq$ 2,500 ppm?

3. Climatic Conditions That Contribute To Landfarming Effectiveness

Yes	No	
❑	❑	Is the rainfall less than 30 inches during the landfarming season?
❑	❑	Are high winds unlikely?

4. Biotreatability Evaluation

Yes	No	
❑	❑	Has a biotreatability study been conducted?
❑	❑	Were biodegradation demonstrated, nutrient application and formulation defined, and potential inhibitors or toxic conditions checked?

5. Evaluation Of Landfarm Design

Yes	No	
❑	❑	Is sufficient land available considering the landfarm depth and additional space for berms and access?
❑	❑	Are runon and runoff controlled?
❑	❑	Are erosion control measures specified?
❑	❑	Are the frequency of application and composition of nutrients and pH adjustment materials specified?
❑	❑	Is moisture addition needed?
❑	❑	Are other sub-optimal natural site conditions addressed in the landfarm design?
❑	❑	Is the site secured?
❑	❑	Are air emissions estimated and will air emissions monitoring be conducted?
❑	❑	Are provisions included for air emissions controls, if needed?

6. Operation And Monitoring Plans

Yes	No	
❑	❑	Is monitoring for stormwater discharge or air quality permits (if applicable) proposed?
❑	❑	Does the operation plan include the anticipated frequency of aeration, nutrient addition, and moisture addition?
❑	❑	Does the monitoring plan propose measuring constituent reduction and biodegradation conditions in the landfarm soils?

6. Operation And Monitoring Plans (continued)

Yes	No	
❑	❑	Are air, soil, and surface runoff water sampling (if applicable) proposed to ensure compliance with appropriate permits?
❑	❑	Are the proposed numbers of samples to be collected, sampling locations, and collected methods in accordance with state regulations?
❑	❑	Is quarterly (or more frequent) monitoring for soil pH, moisture content, bacterial population, nutrient content, and constituent concentrations proposed?

Chapter VI

Low-Temperature Thermal Desorption

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Chapter VI
Low-Temperature Thermal Desorption

Low-Temperature Thermal Desorption (LTTD), also known as low-temperature thermal volatilization, thermal stripping, and soil roasting, is an *ex-situ* remedial technology that uses heat to physically separate petroleum hydrocarbons from excavated soils. Thermal desorbers are designed to heat soils to temperatures sufficient to cause constituents to volatilize and desorb (physically separate) from the soil. Although they are not designed to decompose organic constituents, thermal desorbers can, depending upon the specific organics present and the temperature of the desorber system, cause some of the constituents to completely or partially decompose. The vaporized hydrocarbons are generally treated in a secondary treatment unit (e.g., an afterburner, catalytic oxidation chamber, condenser, or carbon adsorption unit) prior to discharge to the atmosphere. Afterburners and oxidizers destroy the organic constituents. Condensers and carbon adsorption units trap organic compounds for subsequent treatment or disposal.

Some pre- and postprocessing of soil is necessary when using LTTD. Excavated soils are first screened to remove large (> 2 inches in diameter) objects. These may be sized (e.g., crushed or shredded) and then introduced back into the feed material. After leaving the desorber, soils are cooled, re-moistened to control dust, and stabilized (if necessary) to prepare them for disposal/reuse. Treated soil may be redeposited onsite, used as cover in landfills, or incorporated into asphalt.

Thermal desorption systems fall into two general classes -- stationary facilities and mobile units. Contaminated soils are excavated and transported to stationary facilities; mobile units can be operated directly onsite. Desorption units are available in a variety of process configurations including rotary desorbers, asphalt plant aggregate dryers, thermal screws, and conveyor furnaces.

LTTD has proven very effective in reducing concentrations of petroleum products including gasoline, jet fuels, kerosene, diesel fuel, heating oils, and lubricating oils. LTTD is applicable to constituents that are volatile at temperatures as great as 1,200°F. Exhibit VI-1 provides an illustration of a typical LTTD operation. The advantages and disadvantages of LTTD are listed in Exhibit VI-2.

Exhibit VI-1
Parallel Flow (Co-Current) Rotary Low-Temperature Thermal Desorption System

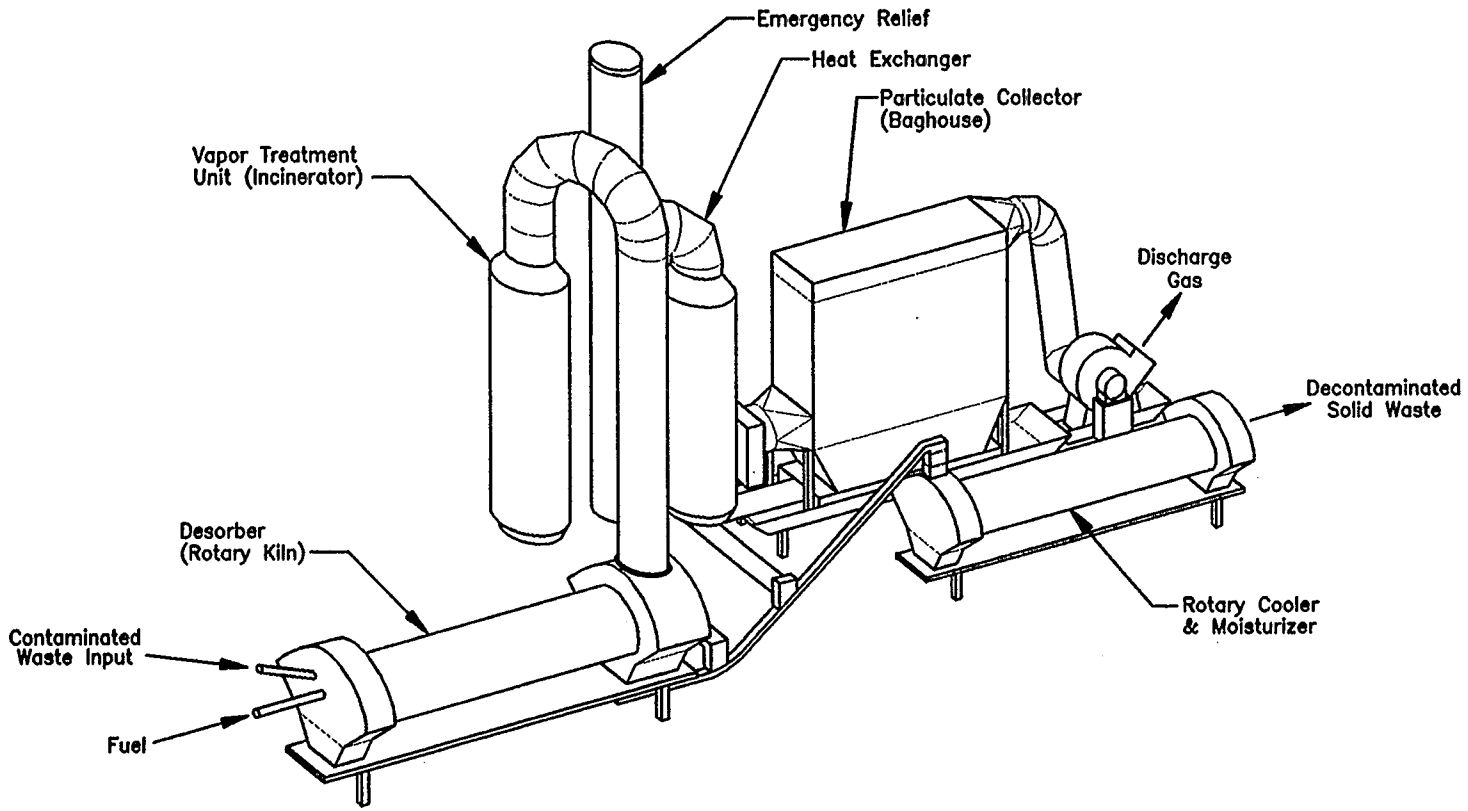


Exhibit VI-2
Advantages And Disadvantages Of LTTD

Advantages	Disadvantages
○ Readily available equipment for onsite or offsite treatment.	○ Requires excavation of soils; generally limited to 25 feet below land surface.
○ Very rapid treatment time; most commercial systems capable of over 25 tons per hour throughput.	○ Onsite treatment will require significant area (> ½ acre) to locate LTTD unit and store process soils.
○ Cost competitive for large volumes (> 1,000 yd^3) of soils: $30-70/ton of contaminated soil, exclusive of excavation and transportation costs.	○ Offsite treatment will require costly transportation of soils and possibly manifesting.
○ Can be used to mitigate "hot spot" source areas with very high concentrations of petroleum hydrocarbons.	○ Soils excavated from below the groundwater table require dewatering prior to treatment because of high moisture content.
○ Easily combinable with other technologies, such as air sparging or groundwater extraction.	
○ Treated soil can be redeposited onsite or used for landfill cover (if permitted by a regulatory agency).	
○ Can consistently reduce TPH to below 10 ppm and BTEX below 100 ppb (and sometimes lower).	

This chapter will assist you in evaluating a corrective action plan (CAP) which proposes LTTD as a remedy for petroleum-contaminated soil. It is not intended to serve as a guide for designing, operating, monitoring, or permitting thermal desorption systems. Further, LTTD processes generate additional waste streams (e.g., gaseous and/or liquid) that require treatment and typically come under the authority of different regulatory agencies. Desorption units are permitted by these other agencies and must comply with monitoring and treatment requirements that are beyond the purview of most UST programs. The evaluation process is summarized in a flow diagram shown on Exhibit VI-3 and will serve as a roadmap for the decisions you will make during your evaluation. A checklist has also been provided at the end of this chapter to be used as a tool to evaluate the completeness of the CAP

Exhibit VI-3
Low-Temperature Thermal Desorption Process Flow Chart

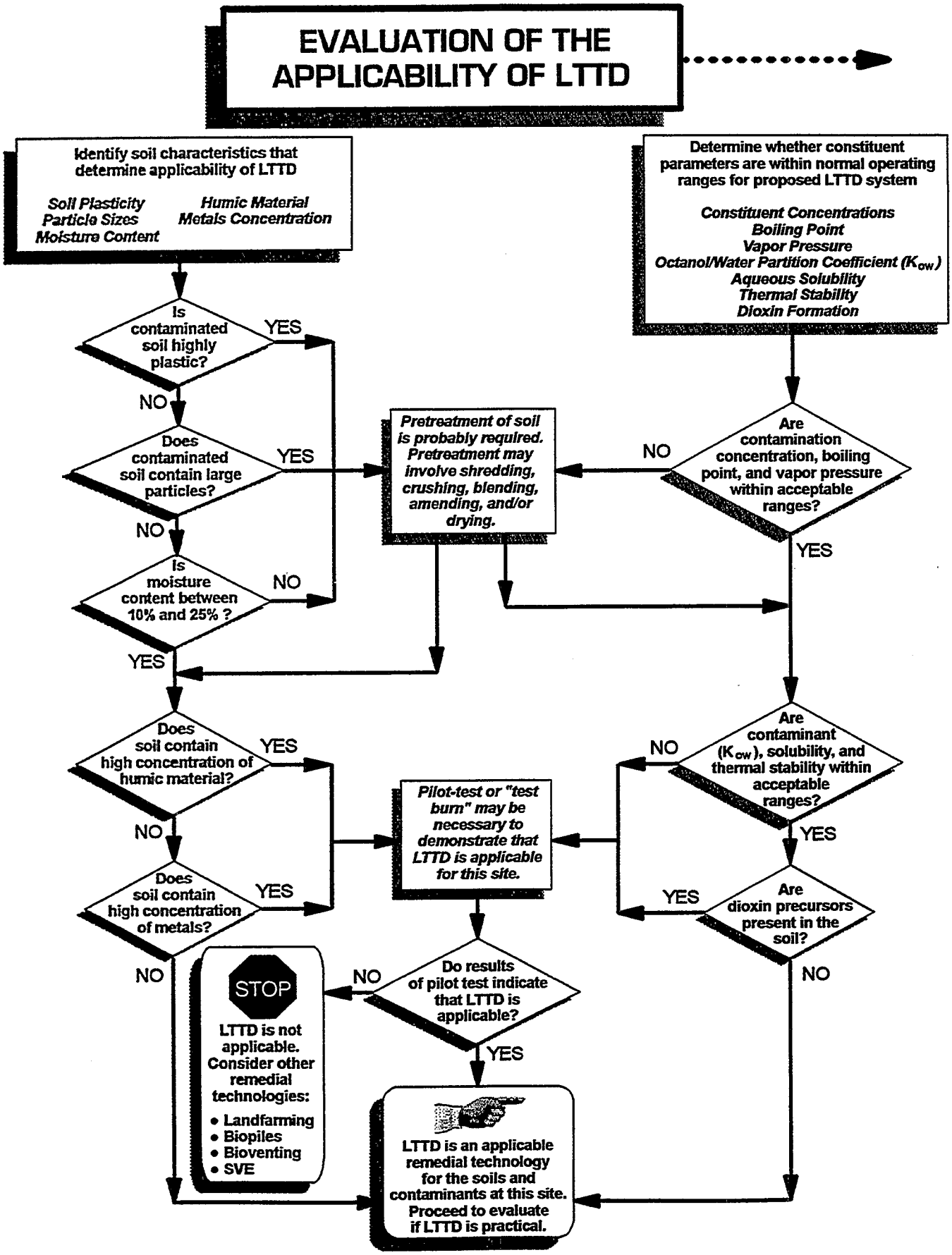


Exhibit VI-3
Low-Temperature Thermal Desorption Process Flow Chart

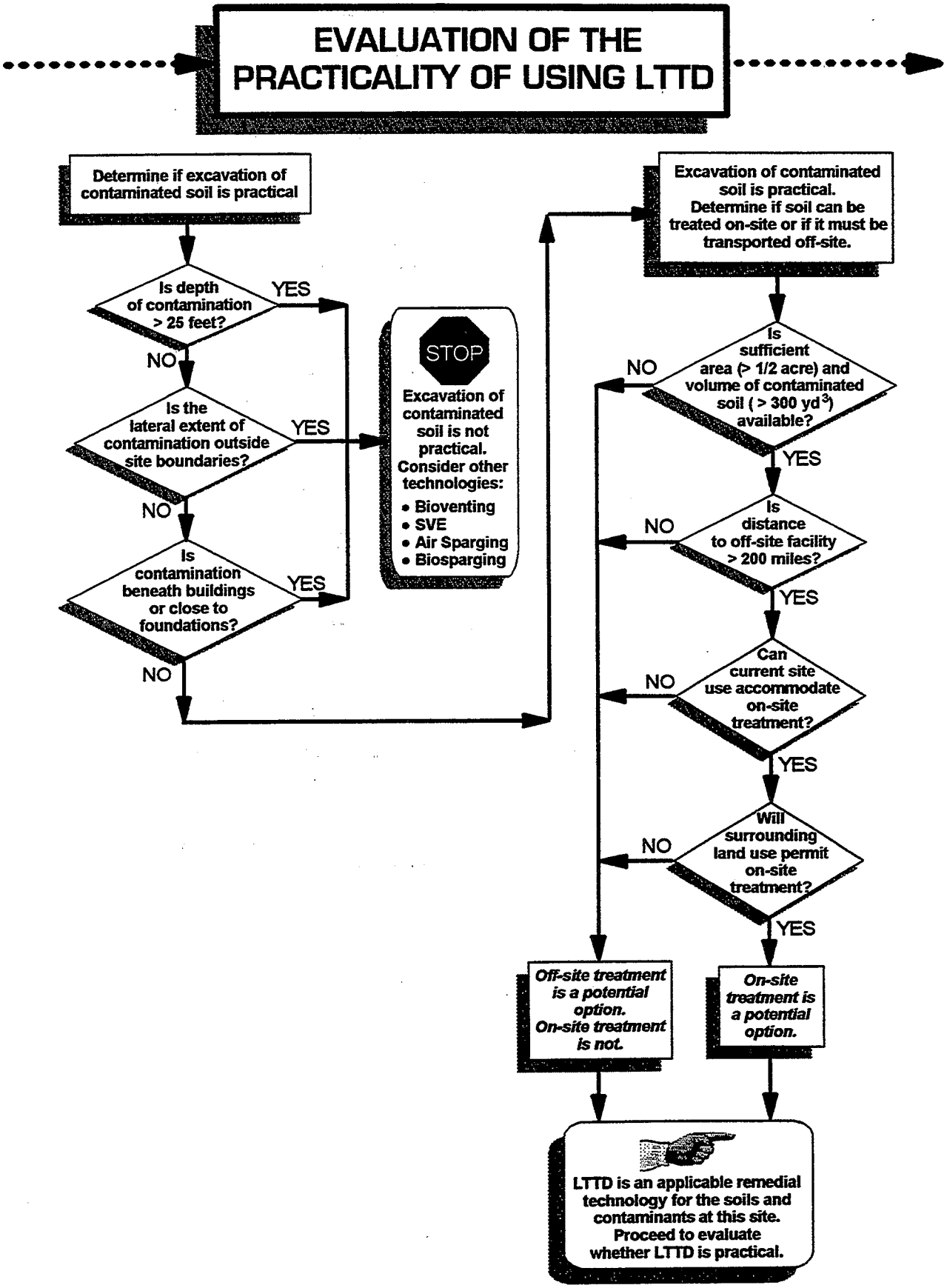
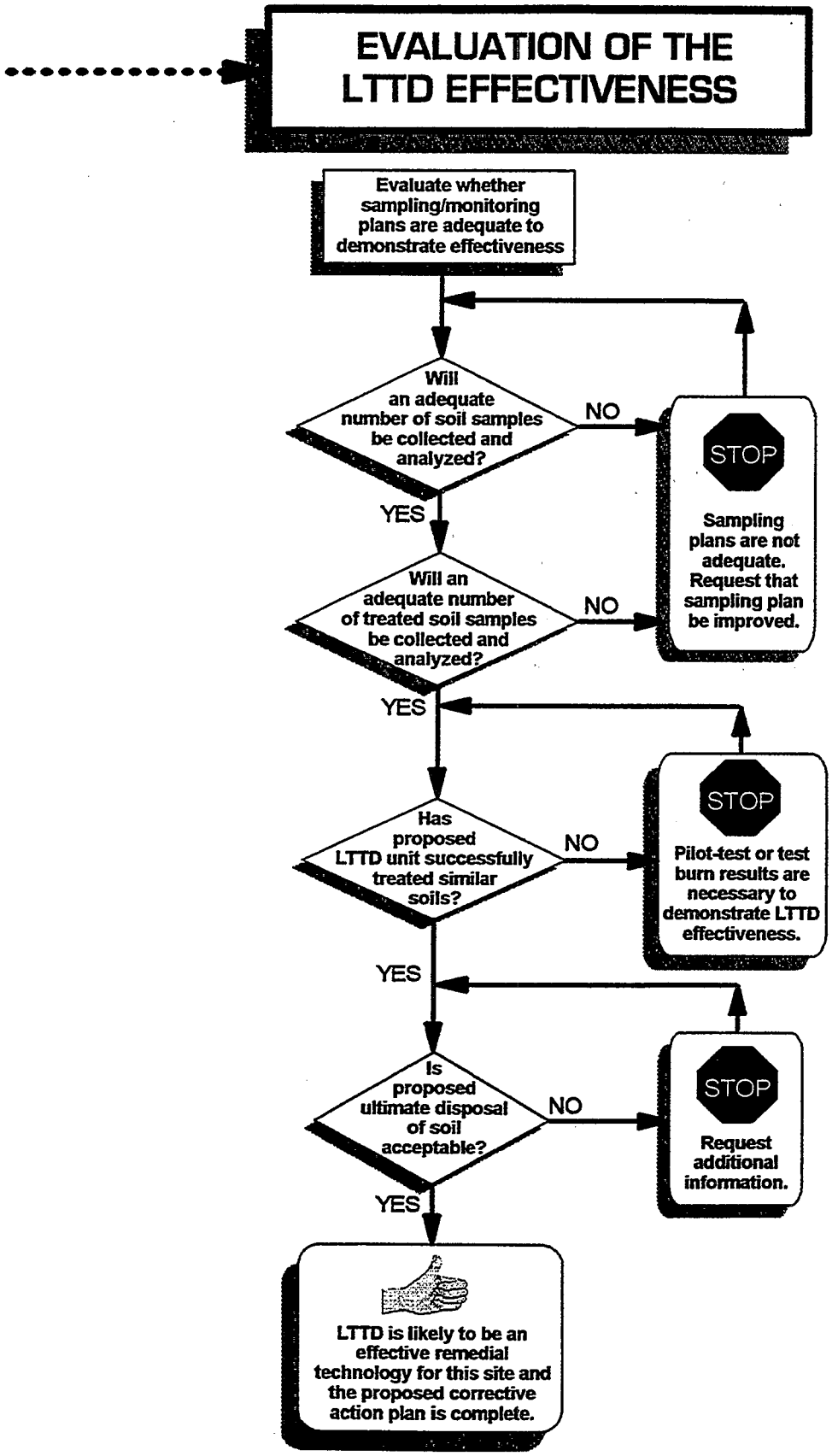


Exhibit VI-3
Low-Temperature Thermal Desorption Process Flow Chart



and to help focus attention on areas where additional information may be needed. The evaluation process is divided into the following three steps:

- **Step 1:** ***An evaluation of the applicability of LTTD.*** Factors that influence the applicability of thermal desorption include physical and chemical properties of the soil and constituents present at the site, and the process operating conditions of the desorption system. To complete the evaluation, you will need to verify that these properties are within the range of LTTD effectiveness. Pre- and post-treatment of the soil should be also be considered. If factors are outside the demonstrated range of LTTD effectiveness, then pilot studies (e.g. test burns) may be appropriate to verify that LTTD will be effective.

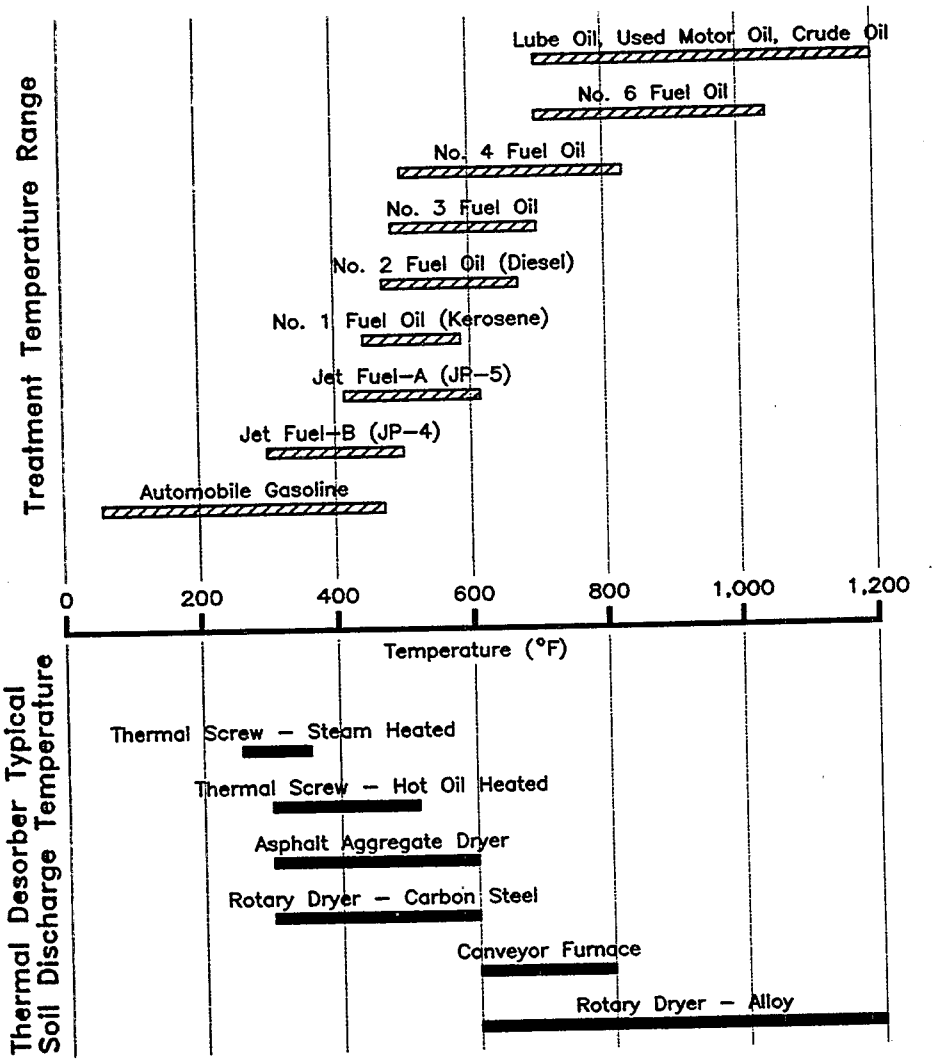
- **Step 2:** ***An evaluation of the practicality of using LTTD.*** Determination of the practicality of using thermal desorption depends upon site-specific factors such as volume of contaminated soil, horizontal and vertical extent of contamination, site area, site usage and surrounding land use. In addition, desorption process parameters (e.g., soil processing rate, mobile vs stationary unit) and target residual levels should also be considered. Other considerations include economic factors and disposition of treated soils.

- **Step 3:** ***An evaluation of LTTD effectiveness.*** The effectiveness of LTTD treatment systems may be evaluated by either (1) calculating the percent reduction in constituent concentrations by comparing the pre- and post-treatment levels in the soil or, (2) determining if residual contaminant levels are at or below regulatory limits. Monitoring plans should specify an adequate number of samples of treated soil to be analyzed.

Evaluation Of The Applicability Of LTTD

This section defines the key parameters that should be used to decide whether LTTD will be a viable remedy for a particular site. In order to determine if LTTD is an applicable remedial alternative, factors to be considered include the characteristics of the soil and constituents present at the site, as well as the LTTD process operating conditions. Thermal desorption is applicable to a wide range of organic constituents, including most petroleum hydrocarbon fuels (Exhibit VI-4). Specific soil and constituent characteristics that influence the applicability of LTTD are summarized in Exhibit VI-5.

Exhibit VI-4
Recommended Treatment Temperatures For Selected Petroleum Products



Legend:

Recommended Product Treatment Temperature Range

Typical Thermal Desorber Soil Discharge Temperature

Exhibit VI-5
Key Soil And Constituent Characteristics That Influence Applicability Of LTTD

Soil Characteristics	Constituent Characteristics
Soil plasticity	Contaminant concentrations
Particle size distribution	Boiling point range
Moisture content	Vapor pressure
Heat capacity	Octanol/water partition coefficient
Concentration of humic material	Aqueous solubility
Metals concentration	Thermal stability
Bulk density	Dioxin formation

The remainder of this section describes each of these parameters, why each is important to LTTD, how each can be determined, and the range of each parameter considered appropriate for LTTD.

Soil Characteristics

Essentially all soil types are amenable for treatment by LTTD systems. However, different soils may require varying degrees and types of pretreatment. For example, coarse-grained soils (e.g., gravel and cobbles) may require crushing; fine-grained soils that are excessively cohesive (e.g., clay) may require shredding.

Soil Plasticity

The plasticity of the soil is a measure of its ability to deform without shearing and is to some extent a function of water content. Plastic soils tend to stick to screens and other equipment, and agglomerate into large clumps. In addition to slowing down the feed rate, plastic soils are difficult to treat. Heating plastic soils requires higher temperatures because of the low surface area to volume ratio and increased moisture content. Also, because plastic soils tend to be very fine-grained, organic compounds tend to be tightly sorbed. Thermal treatment of highly plastic soils requires pretreatment, such as shredding or blending with more friable soils or other amendments (e.g., gypsum).

Plasticity characteristics are formally measured using a set of parameters known as Atterberg Limits. Atterberg Limits are defined as the moisture contents which define a soil's liquid limit, plastic limit, and sticky limit. The range of water content where the soil is in a plastic state is defined as the plasticity index.

The plasticity index is the difference between the soil's liquid and plastic limits, and indicates the range of water content through which the soil remains plastic. Thus, the greater the plastic index, the more likely the soil will clump. In general, clumping is most likely for silt and clay soils.

From a practical standpoint, formal determination of a soil's plasticity index is unnecessary. One of the first stages in the LTTD treatment train is screening to remove material larger than about 2 inches in diameter. Desorption unit operators will take the steps necessary to ensure that the soils will move freely through the treatment process, whether this requires shredding, blending, or amending. If the soils are to be blended, the characteristics of the blending stock should be determined to ensure that no contaminants are present that could adversely affect treatment of the soils excavated from the UST site.

Particle Size Distribution

Particle size distribution is important for proper selection of the type of thermal desorber and pretreatment process to be used. Material larger than 2 inches in diameter will need to be crushed or removed. Crushed material is recycled back into the feed to be processed. Coarser-grained soils tend to be free-flowing and do not agglomerate into clumps. They typically do not retain excessive moisture, therefore, contaminants are easily desorbed. Finer-grained soils tend to retain soil moisture and agglomerate into clumps. When dry, they may yield large amounts of particulates that may require recycling after being intercepted in the baghouse. Other consequences of fine-grained soils are discussed under Soil Plasticity and Moisture Content.

Moisture Content

The solids processing capacity of a thermal desorption system is inversely proportional to the moisture content of the feed material. The presence of moisture in the excavated soils to be treated in the LTTD unit will determine the residence time required and heating requirements for effective removal of contaminants. In order for desorption of petroleum constituents to occur, most of the soil moisture must be evaporated in the desorber. This process can require significant additional thermal input to the desorber and excessive residence time for the soil in the desorber (Exhibit VI-6). In general, soil moisture content ranges from 5 to 35 percent. Exhibit VI-7 shows the applicability of various LTTD system configurations for various soil moisture ranges. For LTTD treatment, the optimal soil moisture range is from 10 to 25 percent. For moisture content above 10 percent by weight,

Exhibit VI-6
Energy Demand Versus Soil Moisture Content

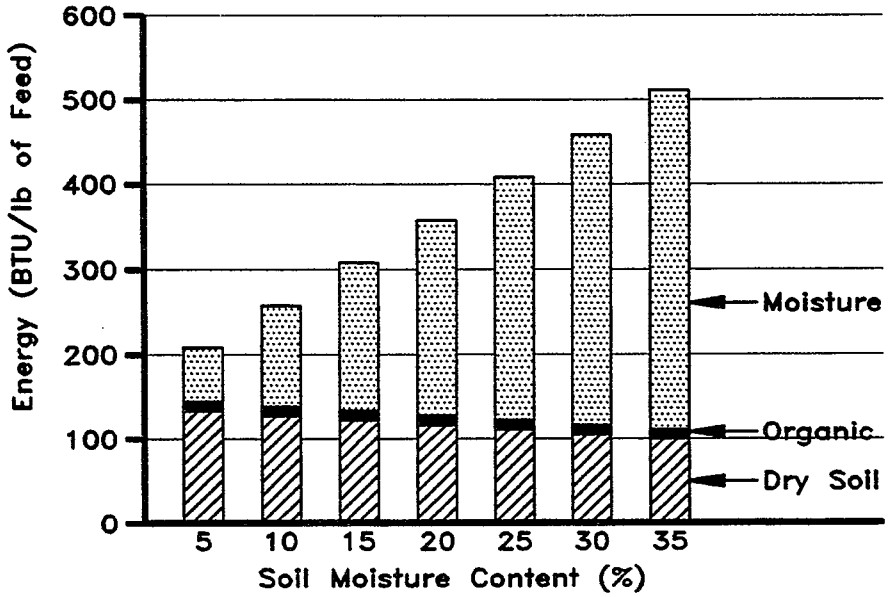
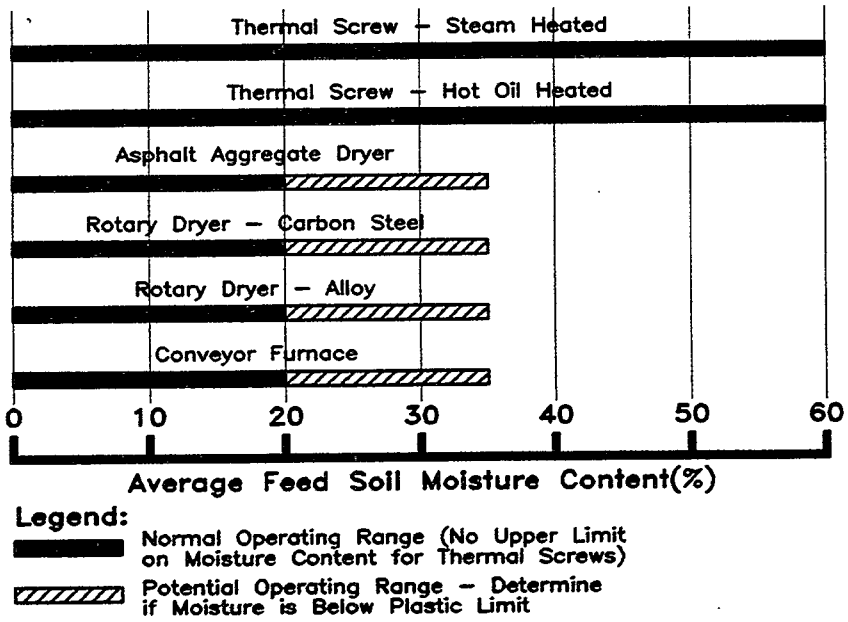


Exhibit VI-7
Feed Soil Moisture Content Limits



moisture is the major heat sink in the system. Moisture content also influences plasticity which affects handling of the soil. Soils with excessive moisture content (> 20 percent) must be dewatered. Typical dewatering methods include air drying (if storage space is available to spread the soils), mixing with drier soils, or mechanical dewatering. For example, if 10 feet of soil will be excavated, including 1 foot in the capillary fringe, and 9 feet of drier soil, the excavated soils when mixed would likely be suitable for LTTD.

If soils located beneath the water table or those with moisture contents greater than 20 to 35 percent are proposed for treatment by LTTD, you should verify that dewatering is planned. If the soil is to be mixed with drier soils there needs to be a sufficient volume of this material available to produce a mixture with an acceptable moisture level.

Heat Capacity

Heat capacity of soil partially determines the amount of heat that must be transferred to raise the temperature of the soil sufficiently to volatilize the organic contaminants. However, since the typical range in heat capacity values of various soils is relatively small, variations are not likely to have a major impact on application of thermal desorption processes.

Concentration Of Humic Material

Humic material is composed of organic material formed by the decay of vegetation. Humic material is found in high concentrations in peat and other highly organic soils. The presence of humic material can cause analytical interferences, yielding a false positive indication of the presence of TPH or BTEX. Organic material in soil also enhances the adsorption of certain organic compounds, making desorption more difficult.

Metals Concentration

In the past, various lead compounds (e.g., tetraethyl lead) were commonly used as fuel additives to boost the octane rating in gasoline. Although the use of lead has been discontinued, sites of older spills may have relatively high lead concentrations in the soil. The presence of metals in soil can have two implications: (1) limitations on disposal of the solid wastes generated by desorption, and (2) attention to air pollution control regulations that limit the amount of metals that may be released in stack emissions. At normal LTTD operating temperatures, heavy metals are not likely to be significantly separated from soils.

Bulk Density

Bulk density is required to estimate the mass of contaminated soil from the volume of soil excavated. The typical *in situ* (bank) bulk density range is 80-120 lb/ft^3. *Ex situ* (excavated) soil bulk density ranges from 75 to 90 percent of the *in situ* bulk density.

Constituent Characteristics

The concentrations and characteristics of constituents are the key parameters to be evaluated during screening studies to evaluate the potential use of thermal desorption processes. The thermal treatment contractor will want to know the concentration of total petroleum hydrocarbons (TPH) in the soil. A number of state and local regulatory agencies require testing of the soils for other specific hazardous characteristics. The following analyses may be required to be conducted during screening studies:

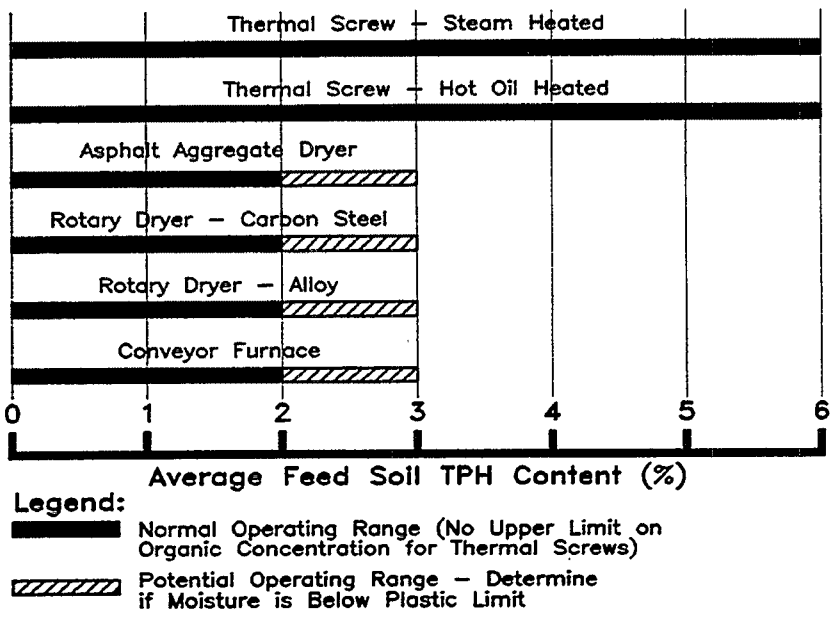
- Benzene, toluene, ethylbenzene, xylenes (BTEX)
- Total organic halides (TOX)
- Toxicity Characteristic Leaching Procedure (TCLP) for volatiles, semivolatiles, and metals
- Total metals
- Polychlorinated biphenyls (PCBs)
- Ignitability
- Corrosivity
- Reactivity

Constituent Concentrations

Constituent concentrations have several impacts on the thermal desorption process. The selection of the appropriate LTTD process configuration is dependent to some extent on constituent concentrations because they influence the soil treatment temperature and residence time required to meet soil cleanup criteria. Each petroleum product possesses a heating value that is a measure of the amount of thermal energy that will be released when the product is burned. High concentrations of petroleum products in soil can result in high soil heating values. Heat released from soils can result in overheating and damage to the desorber. Soils with heating values > 2,000 Btu/lb require blending with cleaner soils to dilute the high concentration of hydrocarbons. High hydrocarbon concentrations in the offgas may exceed the thermal capacity of the afterburner and potentially result in the release of untreated vapors into the atmosphere.

Excessive constituent levels in soil could also potentially result in the generation of vapors in the desorber at concentrations exceeding the lower explosive limit (LEL). The LEL for most organics is generally 1-5 percent by volume. For safety reasons, the concentration of organic compounds in the exhaust gas of a thermal desorption device operating in an oxygen-rich environment should be limited to < 25 percent of the lower explosive limit. For directly heated rotary dryers, the maximum concentration of TPH in feed material that can be treated without exceeding the lower explosive limits is generally in the range of 1-3 percent. If the organic content exceeds 3 percent, the soil must be blended with soil that has a lower organics content to avoid exceeding the LEL. Systems that operate in an inert atmosphere (e.g., thermal screws) do not have limitations on the concentration of organics that can be processed. In an inert atmosphere, the concentration of oxygen is too low (< 2 percent by volume) to support combustion. Exhibit VI-8 shows feed soil TPH concentration limits for various LTTD system configurations.

Exhibit VI-8
Feed Soil TPH Concentration Limits



Boiling Point Range

Petroleum products are often classified by their boiling point ranges. Because the boiling point of a compound is a measure of its volatility, the applicability of LTTD at a site can be estimated from the boiling point range of the petroleum product present. In general, most petroleum-related organics are capable of removal by LTTD, but higher molecular weight (and higher boiling point) constituents require longer residence time in the desorber and higher desorber operating temperatures. Heavier products tend to break down before volatilizing, or they may form non-toxic wax-like compounds that do not volatilize. The boiling point ranges for common petroleum products are shown in Exhibit VI-9.

Exhibit VI-9
Petroleum Product Boiling Ranges

Product	Boiling Range (°C)	Boiling Range (°F)
Gasoline	40 to 225	104 to 437
Kerosene	180 to 300	356 to 572
Diesel fuel	200 to 338	392 to 640
Heating oil	> 275	> 527
Lubricating oils	Nonvolatile	Nonvolatile

Most desorbers operate at temperatures between 300°F-1,000°F. Desorbers constructed of special alloys can operate at temperatures up to 1,200°F. More volatile products (e.g., gasoline) can be desorbed at the lower operating range, while semivolatile products (e.g., kerosene, diesel fuel) generally require temperatures in excess of 700°F, and relatively nonvolatile products (e.g., heating oil, lubricating oils) require even higher temperatures.

Vapor Pressure

Vapor pressure is the force per unit area exerted by a vapor in an equilibrium state with its pure solid, liquid, or solution at a given temperature. Along with boiling point, vapor pressure is used to measure a compound's volatility. Vapor pressure influences the rate of thermal desorption and increases exponentially with an increase in temperature. Therefore, modest increases in desorption temperature result in large increases in the rate of desorption.

Octanol/Water Partition Coefficient (K_{ow})

The octanol/water partition coefficient (K_{ow}) represents the ratio of the solubility of a compound in octanol (a non-polar solvent) to its solubility in water (a polar solvent). The higher the K_{ow}, the more non-polar the compound. Log K_{ow} is generally used as a relative indicator of the tendency of an organic compound to absorb to soil. Log K_{ow} values are generally inversely related to aqueous solubility and directly proportional to molecular weight. Compounds with high Log K_{ow} values tend to remain sorbed to soil for a long period of time and are more difficult to desorb than compounds with low values.

Aqueous Solubility

Aqueous solubility is a measure of the extent to which a compound will dissolve in water. Solubility is generally inversely related to molecular weight: the higher the molecular weight, the lower the solubility. Compounds with higher molecular weight are also generally more difficult to desorb from soil than are compounds with lower molecular weight.

Thermal Stability

Petroleum hydrocarbons are not expected to significantly decompose/combust in LTTD units, provided that the offgas temperature is below the temperature at which a compound will spontaneously combust (the autoignition temperature). Autoignition temperature is, therefore, an indicator of the thermal stability of petroleum hydrocarbons, and the degree of thermal decomposition is related to the maximum temperature exposure.

Dioxin Formation

Dioxins can be formed from the thermal destruction of PCBs and other chlorinated compounds. The petroleum hydrocarbons typically present at UST sites do not contain PCBs; therefore, formation of dioxins is usually not of concern. Waste oils that contain chlorinated hydrocarbons may, however, be potential precursors of dioxins. Soils from waste oil spills should be analyzed for PCBs and other chlorinated hydrocarbons.

Process Operating Conditions

Process operating conditions are dependent upon the type of thermal desorption system and vary over a wide range. Each system configuration has its own advantages and disadvantages, and each is

applicable for treatment of specific ranges of constituents (Exhibit VI-10). LTTD systems vary in the manner in which the soils are transported through the desorber, the method used to heat the soils; the temperature at which the desorber operates; the time required to treat the soils; and the offgas treatment method used to control emissions.

Types Of Low-Temperature Thermal Desorption Systems

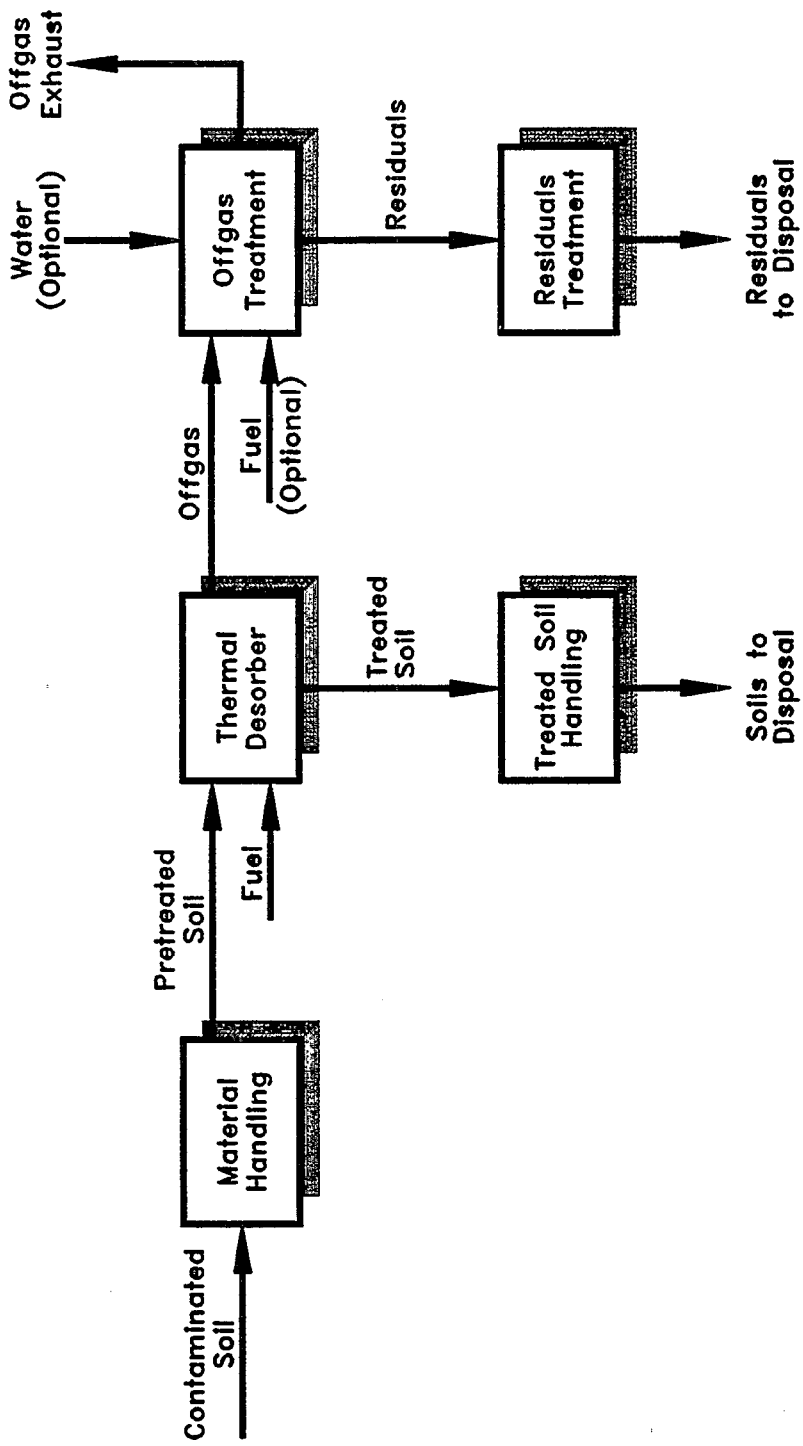
The term thermal desorber describes the primary treatment operation that heats petroleum-contaminated materials and desorbs organic materials into a purge gas. Mechanical design features and process operating conditions vary considerably among the various types of LTTD systems. Desorption units are available in the following configurations: rotary dryer, asphalt plant aggregate dryer, thermal screw, and conveyor furnace. Systems may either be stationary facilities or mobile units. Contaminated soils are excavated and transported to stationary facilities, while mobile units can be operated directly on the site of the contaminated soil.

Although all LTTD systems use heat to separate (desorb) organic contaminants from the soil matrix, each system has a different configuration with its own set of advantages and disadvantages. The decision to use one system over another depends on the nature of the contaminants as well as machine availability, system performance, and economic considerations. System performance may be evaluated on the basis of pilot tests (e.g., test burns) or examination of historical machine performance records. Pilot tests to develop treatment conditions are generally not necessary for petroleum-contaminated soils.

Mechanical design features and process operating conditions vary among the different types of LTTD systems. The four systems mentioned above are briefly described below, and the advantages and disadvantages of each are listed.

Rotary Dryers. Rotary dryer systems use a cylindrical metal reactor (drum) that is inclined slightly from the horizontal. A burner located at one end provides heat to raise the temperature of the soil sufficiently to desorb organic contaminants. The flow of soil may be either cocurrent with or countercurrent to the direction of the purge gas flow. As the drum rotates, soil is conveyed through the drum. Lifters raise the soil, carrying it to near the top of the drum before allowing it to fall through the heated purge gas. Mixing in a rotary dryer enhances heat transfer by convection and allow soils to be rapidly heated. Rotary desorber units are manufactured for a wide range of treatment capacities; these units may be either stationary or mobile.

Exhibit VI-10
Thermal Desorption System Schematic Design



The maximum soil temperature that can be obtained in a rotary dryer depends on the composition of the dryer shell. The soil discharge temperature of carbon steel drums is typically 300°-600° F. Alloy drums are available that can increase the soil discharge temperature to 1,200° F. Most rotary dryers that are used to treat petroleum contaminated soil are made of carbon steel. After the treated soil exits the rotary dryer, it enters a cooling conveyor where water is sprayed on the soil for cooling and dust control. Water addition may be conducted in either a screw conveyor or a pugmill.

Besides the direction of purge gas flow relative to soil feed direction, there is one major difference in configuration between countercurrent and cocurrent rotary dryers. The purge gas from a countercurrent rotary dryer is typically only 350°F-500°F and does not require cooling before entering the baghouse where fine particles are trapped. A disadvantage is that these particles may not have been decontaminated and are typically recycled to the dryer. Countercurrent dryers have several advantages over cocurrent systems. They are more efficient in transferring heat from purge gas to contaminated soil, and the volume and temperature of exit gas are lower, allowing the gas to go directly to a baghouse without needing to be cooled. The cooler exit gas temperature and smaller volume eliminates the need for a cooling unit, which allows downstream processing equipment to be smaller. Countercurrent systems are effective on petroleum products with molecular weights lower than No.2 fuel oil.

In cocurrent systems, the purge gas is 50°-100°F hotter than the soil discharge temperature. The result is that the purge gas exit temperature may range from 400°-1,000°F and cannot go directly to the baghouse. Purge gas first enters an afterburner to decontaminate the fine particles, then goes into a cooling unit prior to introduction into the baghouse. Because of the higher temperature and volume of the purge gas, the baghouse and all other downstream processing equipment must be larger than in a countercurrent system. Cocurrent systems do have several advantages over countercurrent systems. The afterburner is located upstream of the baghouse ensuring that fine particles are decontaminated. In addition, because the heated purge gas is introduced at the same end of the drum as the feed soil, the soil is heated faster, resulting in a longer residence time. Higher temperatures and longer residence time mean that cocurrent systems can be used to treat soils contaminated with heavier petroleum products. Cocurrent systems are effective for light and heavy petroleum products including No. 6 fuel oil, crude oil, motor oil, and lubricating oil.

Asphalt Plant Aggregate Dryers. Hot-mix asphalt plants use aggregate that has been processed in a dryer before it is mixed with liquid asphalt. The use of petroleum contaminated soils for aggregate material is widespread. Aggregate dryers may either be stationary or mobile. Soil treatment capacities range from 25-150 tons per hour. The soil may be incorporated into the asphalt as a recycling process or the treated soil may be used for other purposes.

Asphalt rotary dryers are normally constructed of carbon steel and have a soil discharge temperature of 300°-600°F. Typically, asphalt plant aggregate dryers are identical to countercurrent rotary desorbers described above and are effective on the same types of contaminants. The primary difference is that an afterburner is not required for incorporation of clean aggregate into the asphalt mix. In some areas, asphalt plants that use petroleum contaminated soil for aggregate may be required to be equipped with an afterburner.

Thermal Screws. A thermal screw desorber typically consists of a series of 1-4 augers. The auger system conveys, mixes, and heats contaminated soils to volatilize moisture and organic contaminants into a purge gas stream. Augers can be arranged in series to increase the soil residence time, or they can be configured in parallel to increase throughput capacity. Most thermal screw systems circulate a hot heat-transfer oil through the hollow flights of the auger and return the hot oil through the shaft to the heat transfer fluid heating system. The heated oil is also circulated through the jacketed trough in which each auger rotates. Thermal screws can also be steam-heated. Systems heated with oil can achieve soil temperatures of up to 500°F, and steam-heated systems can heat soil to approximately 350°F.

Most of the gas generated during heating of the heat-transfer oil does not come into contact the waste material and can be discharged directly to the atmosphere without emission controls. The remainder of the flue gas maintains the thermal screw purge gas exit temperature above 300°F. This ensures that volatilized organics and moisture do not condense. In addition, the recycled flue gas has a low oxygen content (< 2 percent by volume) which minimizes oxidation of the organics and reduces the explosion hazard. If pretreatment analytical data indicates a high organic content (> 4 percent), use of a thermal screw is recommended. After the treated soil exits the thermal screw, water is sprayed on the soil for cooling and dust control. Thermal screws are available with soil treatment capacities ranging from 3-15 tons per hour.

Since thermal screws are indirectly heated, the volume of purge gas from the primary thermal treatment unit is less than one half of the volume from a directly-heated system with an equivalent soil processing capacity. Therefore, offgas treatment systems consist of relatively small unit operations that are well suited to mobile applications. Indirect heating also allows thermal screws to process materials with high organic contents since the recycled flue gas is inert, thereby reducing the explosion hazard.

Conveyor Furnace. A conveyor furnace uses a flexible metal belt to convey soil through the primary heating chamber. A one-inch-deep layer of soil is spread evenly over the belt. As the belt moves through the system, soil agitators lift the belt and turn the soil to enhance heat transfer and volatilization of organics. The conveyor furnace can heat soils to temperatures from 300°-800°F. At the higher temperature range, the conveyor furnace is more effective in treating some heavier petroleum hydrocarbons than are oil or steam-heated thermal screws, asphalt plant aggregate dryers, and carbon steel rotary dryers. After the treated soil exits the conveyor furnace, it is sprayed with water for cooling and dust control. As of February, 1993, only one conveyor furnace system was currently in use for the remediation of petroleum contaminated soil. This system is mobile and can treat 5-10 tons of soil per hour.

OffGas Treatment

Treatment systems for LTTD system offgas are designed to address three types of air pollutants: particulates, organic vapors, and carbon monoxide. Particulates are controlled with both wet (e.g., venturi scrubbers) and dry (e.g., cyclones, baghouses) unit operations. Rotary dryers and asphalt aggregate dryers most commonly use dry gas cleaning unit operations. Cyclones are used to capture large particulates and reduce the particulate load to the baghouse. Baghouses are used as the final particulate control device. Thermal screw systems typically use a venturi scrubber as the primary particulate control.

The control of organic vapors is achieved by either destruction or collection. Afterburners are used downstream of rotary dryers and conveyor furnaces to destroy organic contaminants and oxidize carbon monoxide. Conventional afterburners are designed so that exit gas temperatures reach 1,400°-1,600°F. Organic destruction efficiency typically ranges from 95 to > 99 percent.

Condensers and activated carbon may also be used to treat the offgas from thermal screw systems. Condensers may be either water-cooled or electrically-cooled systems to decrease offgas temperatures to 100°-140°F. The efficiency of condensers for removing organic compounds ranges from 50 to > 95 percent. Noncondensible gases exiting the condenser are normally treated by a vapor-phase activated carbon treatment system. The efficiency of activated carbon adsorption systems for removing organic contaminants ranges from 50-99 percent. Condensate from the condenser is processed through a phase separator where the non-aqueous phase organic component is separated and disposed of or recycled. The remaining water is then processed through activated carbon and used to rehumidify treated soil.

Treatment Temperature

Treatment temperature is a key parameter affecting the degree of treatment of organic components. The required treatment temperature depends upon the specific types of petroleum contamination in the soil. Exhibit VI-4 illustrates the recommended treatment temperatures for various petroleum products and the operating temperature ranges for various LTTD systems. The actual temperature achieved by an LTTD system is a function of the moisture content and heat capacity of the soil, soil particle size, and the heat transfer and mixing characteristics of the thermal desorber.

Residence Time

Residence time is a key parameter affecting the degree to which decontamination is achievable. Residence time depends upon the design and operation of the system, characteristics of the contaminants and the soil, and the degree of treatment required.

Pilot Testing

The requirement for pilot testing of petroleum-contaminated soils, in which a quantity of soil from the site is processed through the LTTD system (a "test burn"), is specified by state and local regulations. The results of preliminary testing of soil samples should identify the relevant constituent properties, and examination of the machine's performance records should indicate how effective the system will be in treating the soil. However, it should be noted that the proven effectiveness of a particular system for a specific site or waste does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at other sites. If a test burn is conducted, it is important to

ensure that the soil tested is representative of average conditions and that enough samples are analyzed before and after treatment to confidently determine whether LTTD will be effective.

Determination Of The Practicality Of Using LTTD

This section identifies the factors that determine whether LTTD is a practical remedial alternative. While many of these factors are dependent upon site-specific characteristics (e.g., the location and volume of contaminated soils, site layout), practicality is also determined by regulatory, logistical, and economic considerations. The economics of LTTD as a remedial option are highly site-specific. Economic factors include site usage (because excavation and onsite soil treatment at a retail site (e.g., gasoline station, convenience store) will most likely prevent the business from operating for an extended period of time), the cost of LTTD per unit volume of soil relative to other remedial options, and the location of the nearest applicable LTTD system (because transportation costs are a function of distance). Further discussion of the economics of LTTD use is beyond the scope of this manual.

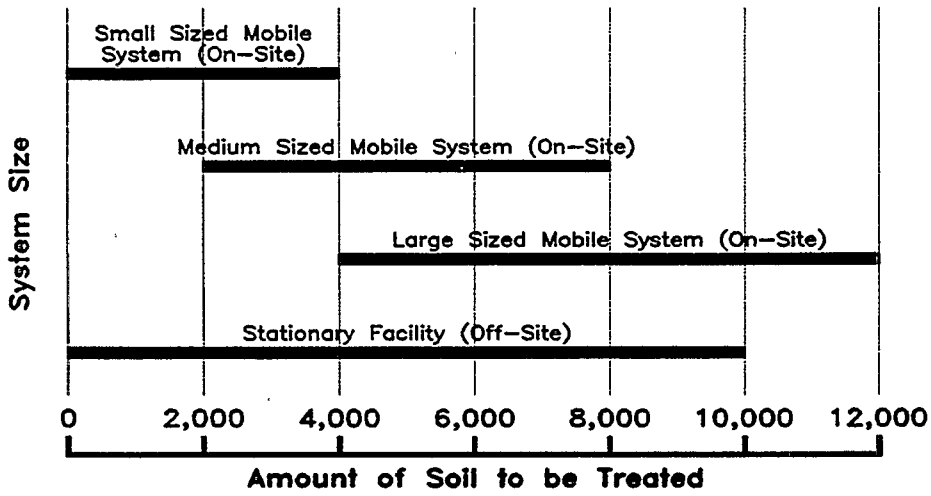
Vertical And Horizontal Extent Of Contamination

Because soils to be treated in an LTTD unit must be excavated, their location must be suitable for removal by excavation techniques. Soils that are located more than 25 feet below the land surface cannot be removed by conventional equipment. In addition, soils that are located beneath a building or near building foundations cannot be excavated without removal of the building itself. In addition, as mentioned previously, soils located beneath the groundwater table can be excavated but generally cannot be treated in the LTTD unit unless dried, dewatered, or blended with other soils to reduce moisture content.

You should identify the location of the proposed excavation and verify that soils to be excavated are less than 25 feet below land surface, above the water table, and not beneath or near buildings or other structures.

The vertical and horizontal extent of contamination determines the volume of soil that must be treated. The cost of remediation and time required for processing is directly proportional to the volume of contaminated soil to be treated. Volume also determines whether onsite treatment is viable. A small mobile LTTD system with a throughput capacity of 5 to 15 tons per hour may be able to stockpile materials and operate in an area as small as ¼ acre. Exhibit VI-11 shows the relationship between thermal desorber size and the amount of soil to be treated.

Exhibit VI-11
Thermal Desorption Size Versus Amount Of Soil To Be Treated



System Characteristics	System Type: Small Mobile (On–Site)	Medium Mobile (On–Site)	Large Mobile (On–Site)	Stationary Facility (Off–Site)
No. of Trailers	1–2	3–6	7–10	NA
Primary Burner Capacity (MM Btu/Hr)	5–15	15–30	30–50	30–120
Secondary Burner Capacity (MM Btu/Hr)	5–15[a]	15–30[a]	30–50	30–100[b]
Soil Processing Capacity (Tons/Hour)	5–15	15–30	25–100	30–300

[a] Systems with Condensers do not include Afterburners.

[b] Some Fixed Base Asphalt Aggregate Dryers do not include Afterburners.

Site Layout

Site layout factors influence whether excavation of soils is possible at all. If excavation is possible, consideration can be given to whether onsite thermal treatment is a viable option. Site layout factors that must be considered in evaluating onsite thermal desorption treatment include:

- Amount of space available for stockpiling treated and untreated materials and operating process equipment,
- Space required for continuation of daily business, and
- Minimum distances required by fire and safety codes for operating thermal desorption equipment in the vicinity of petroleum storage facilities.

The amount of area available to stockpile soils and operate processing equipment may dictate the maximum size of the treatment system that can be operated at the site. In general, onsite treatment operations will require a minimum of ½ acre. This has further economic implications because the costs associated with LTTD are strongly affected by the physical size and soil processing capacity of the thermal treatment system.

Adjacent Land Use

When land adjacent to an UST site is being used for schools, parks, health care facilities, high-value commercial development, or dense residential development, problems may develop in obtaining permits for the use of onsite thermal desorption. Air discharge restrictions may require the use of expensive control measures that could make onsite treatment economically infeasible. Thermal desorption units are most economical when they are operated on a 24-hour-per-day schedule. However, noise considerations may limit hours of operation in some locations.

Other Considerations

Treatment goals are also important when considering the use of LTTD. For soils contaminated with lighter petroleum hydrocarbons, residual TPH levels can be reduced to 10 ppm or less. Some newer rotary units can consistently achieve TPH levels of < 1 ppm and BTEX levels < 100 ppb. System effectiveness can be evaluated based on the treatment records for a specific machine.

Treated soils are typically disposed of in a landfill, used as cover in landfills, incorporated into asphalt, or returned to the site to backfill the excavation. Final disposition of the soil depends upon the residual levels of contaminants in the treated soil and economic factors such as transportation and disposal costs, as well as costs for clean material to backfill the excavation. It should be noted that treatment processes may alter the physical properties of the material. A thorough geotechnical evaluation of the treated material may be necessary to determine its suitability for use in an engineering application (e.g., road bed, building foundation support, grading and filling).

Evaluation Of The Effectiveness Of LTTD

For sites with petroleum contaminated soils, the primary concern is to reduce the residual concentration of the organic constituents to or below regulatory levels. This criterion applies to both the soil surrounding the excavation and the soil that was excavated and thermally treated. An appropriate number of soil samples should be collected from around the walls and bottom of the excavation. These samples should then be analyzed for the requisite parameters to ensure that all of the soil that must be thermally treated has been excavated.

The effectiveness of an LTTD treatment system may be evaluated by either (1) determining whether residual contaminant levels are at or below regulatory limits or (2) calculating the percent reduction in soil constituent concentrations by comparing pre- and post-treatment levels. Monitoring plans should specify an adequate number of samples of treated soil to be analyzed. A typical sample density is one sample per 100 cubic yards of treated soil. Exhibit VI-12 lists typical monitoring locations and frequency for petroleum contaminated soils treated by LTTD.

Exhibit VI-12
Monitoring Recommendations

Phase	Frequency	Where To Monitor	What To Monitor
Excavation	At proposed limit of excavation	o Excavation walls o Excavation floor	o TPH, constituents of concern
LTTD treatment	Every 100 cu.yd. of feed soil and treated soil	o Feed soil o Treated soil	o TPH, constituents of concern

Operation of LTTD units requires various permits and demonstration of compliance with permit requirements. Monitoring requirements for LTTD systems are by their nature different from monitoring required at an UST site. Monitoring of LTTD system waste streams (e.g., concentrations of particulates, volatiles, and carbon monoxide in stack gas) are required by the agency(ies) issuing the permits for operation of the facility. Compliance with limits specified by the permits is the responsibility of the LTTD facility owner/operator. Other LTTD system operating parameters (e.g., desorber temperature, soil feed rate, afterburner temperature) are also the responsibility of the LTTD facility owner/operator.

References

U.S. Environmental Protection Agency (EPA). *Low-temperature Thermal Treatment Technology: Applications Analysis Report.* Cincinnati, OH: U.S. EPA, Office of Research and Development. EPA/540/AR-92/019, 1992.

Troxler, W.L., J.J. Cudahy, R.P. Zink, and S.I. Rosenthal. *Thermal Desorption Applications Manual for Treating Nonhazardous Petroleum Contaminated Soils.* Cincinnati, OH: U.S. EPA, Office of Research and Development, 1994.

Anderson, W.C., ed. *Innovative Site Remediation Technology: Thermal Desorption, Volume 6.* Washington, D.C.: U.S. EPA, Office of Solid Waste and Emergency Response. EPA 542-B-93-011, 1993.

Checklist: Can LTTD Be Used At This Site?

This checklist can help you to evaluate the completeness of the CAP and to identify areas that require closer evaluation. As you go through the CAP, answer the following questions.

1. Evaluation Of LTTD Effectiveness

Yes	No	
❑	❑	Do soils have high plasticity?
❑	❑	Do soils contain large rocks or debris?
❑	❑	Is moisture content > 35%?
❑	❑	Is the TPH concentration > 2% by weight?
❑	❑	Are hydrocarbons highly volatile?

If the answer to any of the above questions is yes, then the soils require pretreatment.

❑	❑	Do the soils have a high concentration of humic material?
❑	❑	Do the soils have a high concentration of heavy metals?
❑	❑	Are contaminant K_{ow}s relatively high?
❑	❑	Are dioxin precursors present in the soils?

If the answer to any of the above questions is yes, then a pilot test or "test burn" should be conducted to demonstrate that LTTD is an applicable remedial technology.

❑	❑	Do the results of the pilot test indicate that LTTD is applicable?

2. Evaluation Of The Practicality Of Using LTTD

Yes	No	
❑	❑	Is the depth of contaminated soil 25 feet or less below land surface?
❑	❑	Is contaminated soil contained within site boundaries?
❑	❑	Is there no contamination beneath buildings or near building foundations?

If the answer to any of the above questions is no, then excavation of the soil is not practical; therefore, LTTD is not practical. Consider an *in situ* remedial technology instead.

❑	❑	Is sufficient land area available for operation of equipment and temporary storage (staging) of contaminated soil and treated soil?
❑	❑	Is the distance to an off-site facility prohibitively far?
❑	❑	Will surrounding land use permit operation of an onsite system in the neighborhood?

If the answer to any of the above questions is no, then excavated soils must be transported to an off-site facility for treatment.

3. Evaluation Of The Effectiveness Of Using LTTD

Yes	No	
❑	❑	Will an adequate number of *in situ* soil samples be collected and analyzed?
❑	❑	Will an adequate number of treated soil samples be collected and analyzed?

3. Evaluation Of The Effectiveness Of Using LTTD (continued)

Yes	No	
❑	❑	Has the proposed desorption unit successfully treated similar soils with similar contaminant concentration levels?
❑	❑	Is the proposed ultimate disposal of the soil (e.g., return to excavation, transport to landfill for cover) acceptable?

If the answer to any of the above questions is no, then additional information is necessary to evaluate whether LTTD is likely to be an effective remedial technology.

Chapter VII

Air Sparging

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Chapter VII
Air Sparging

Overview

Air sparging (AS) is an *in situ* remedial technology that reduces concentrations of volatile constituents in petroleum products that are adsorbed to soils and dissolved in groundwater. This technology, which is also known as "in situ air stripping" and "in situ volatilization," involves the injection of contaminant-free air into the subsurface saturated zone, enabling a phase transfer of hydrocarbons from a dissolved state to a vapor phase. The air is then vented through the unsaturated zone. Air sparging is most often used together with soil vapor extraction (SVE), but it can also be used with other remedial technologies. When air sparging is combined with SVE, the SVE system creates a negative pressure in the unsaturated zone through a series of extraction wells to control the vapor plume migration. This combined system is called AS/SVE. Chapter II provides a detailed discussion of SVE.

The existing literature contains case histories describing both the success and failure of air sparging; however, since the technology is relatively new, there are few cases with substantial documentation of performance. When used appropriately, air sparging has been found to be effective in reducing concentrations of volatile organic compounds (VOCs) found in petroleum products at underground storage tank (UST) sites. Air sparging is generally more applicable to the lighter gasoline constituents (i.e., benzene, ethylbenzene, toluene, and xylene [BTEX]), because they readily transfer from the dissolved to the gaseous phase. Air sparging is less applicable to diesel fuel and kerosene. Appropriate use of air sparging may require that it be combined with other remedial methods (e.g., SVE or pump-and-treat). Exhibit VII-1 provides an illustration of an air sparging system with SVE. Exhibit VII-2 provides a summary of the advantages and disadvantages of air sparging.

This chapter will assist you in evaluating a corrective action plan (CAP) that proposes air sparging as a remedy for petroleum-contaminated soil. The evaluation guidance is presented in the four steps described below. The evaluation process, which is summarized in a flow diagram shown in Exhibit VII-3, serves as a roadmap for the decisions you will make during your evaluation. A checklist has also been provided at the end of the chapter for you to use as a tool both to evaluate the completeness of the CAP and to focus on areas where additional information may be needed.

Exhibit VII-1
Air Sparging System With SVE

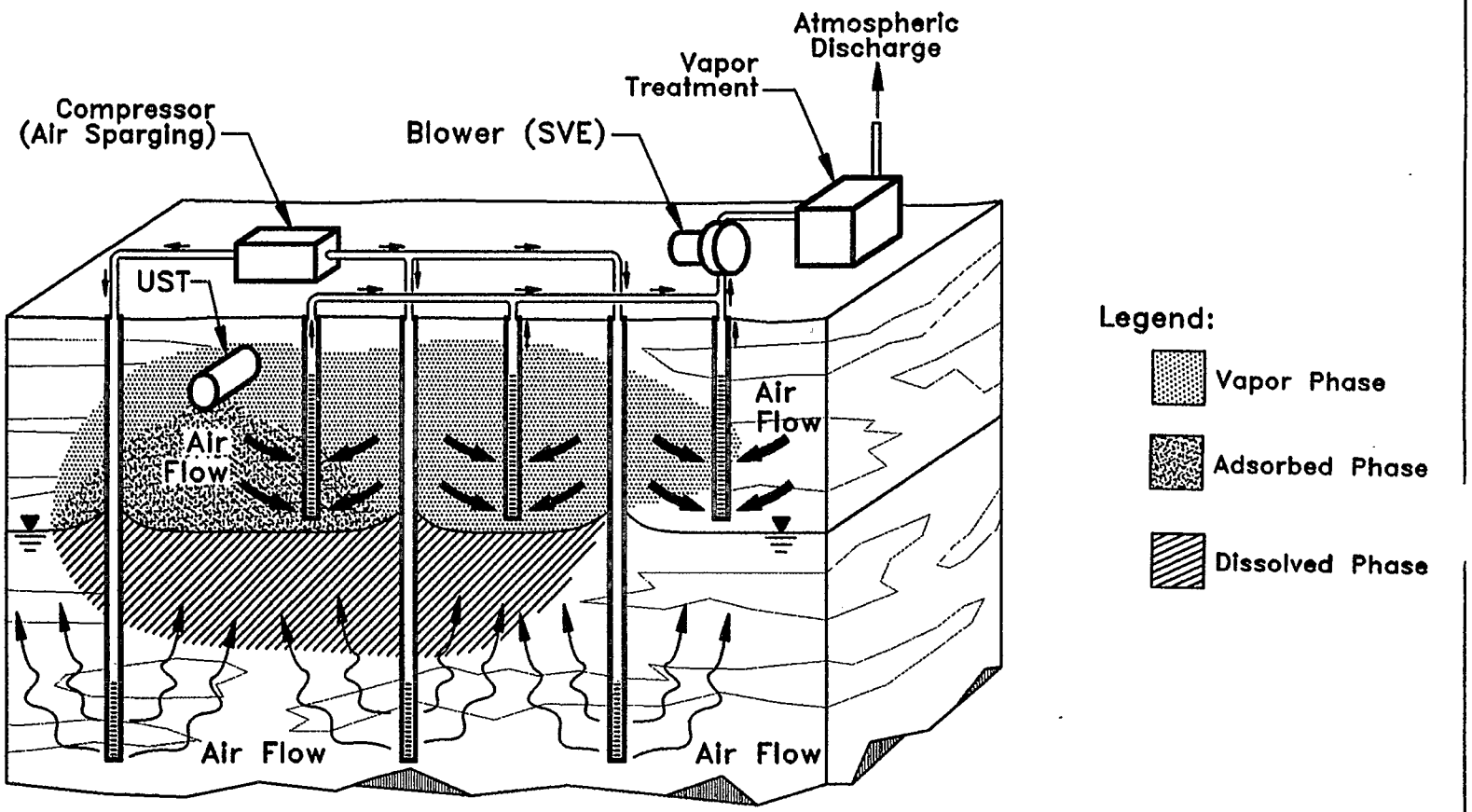


Exhibit VII-2
Advantages And Disadvantages Of Air Sparging

Advantages	Disadvantages
○ Readily available equipment; easy installation.	○ Cannot be used if free product exists (i.e., any free product must be removed prior to air sparging).
○ Implemented with minimal disturbance to site operations.	○ Cannot be used for treatment of confined aquifers.
○ Short treatment times: usually less than 1 to 3 years under optimal conditions.	○ Stratified soils may cause air sparging to be ineffective.
○ At about $20-50/ton of saturated soil, air sparging is less costly than aboveground treatment systems.	○ Some interactions among complex chemical, physical, and biological processes are not well understood.
○ Requires no removal, treatment, storage, or discharge considerations for groundwater.	○ Lack of field and laboratory data to support design considerations.
○ Can enhance removal by SVE.	○ Potential for inducing migration of constituents.
	○ Requires detailed pilot testing and monitoring to ensure vapor control and limit migration.

- **Step 1:** ***An initial screening of air sparging effectiveness*** allows you to quickly gauge whether air sparging is likely to be effective, moderately effective, or ineffective. You can use the initial screening process as a yardstick to determine whether the technology has the potential to be effective.

- **Step 2:** ***A detailed evaluation of air sparging effectiveness*** provides further screening criteria to confirm whether air sparging is likely to be effective. You will need to find specific soil and product constituent characteristics and properties, compare them to ranges where air sparging is effective, and evaluate pilot study plans.

- **Step 3:** ***An evaluation of the air sparging system design*** allows you to determine if basic design information has been defined, if necessary design components have been specified, if construction process flow designs are consistent with standard practice, and if a detailed field pilot scale test has been properly performed.

Exhibit VII-3
Air Sparging Evaluation Process Flow Chart

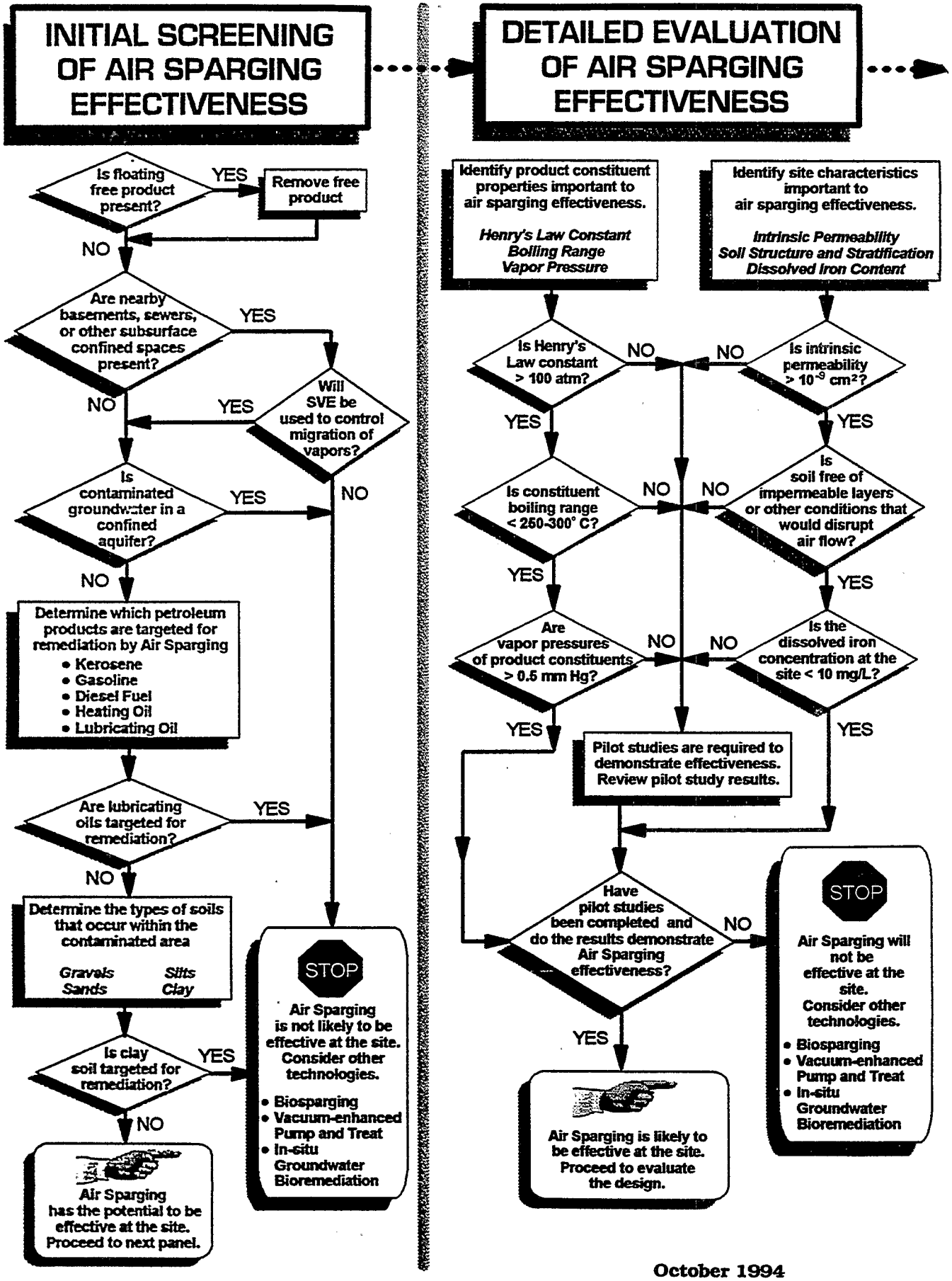
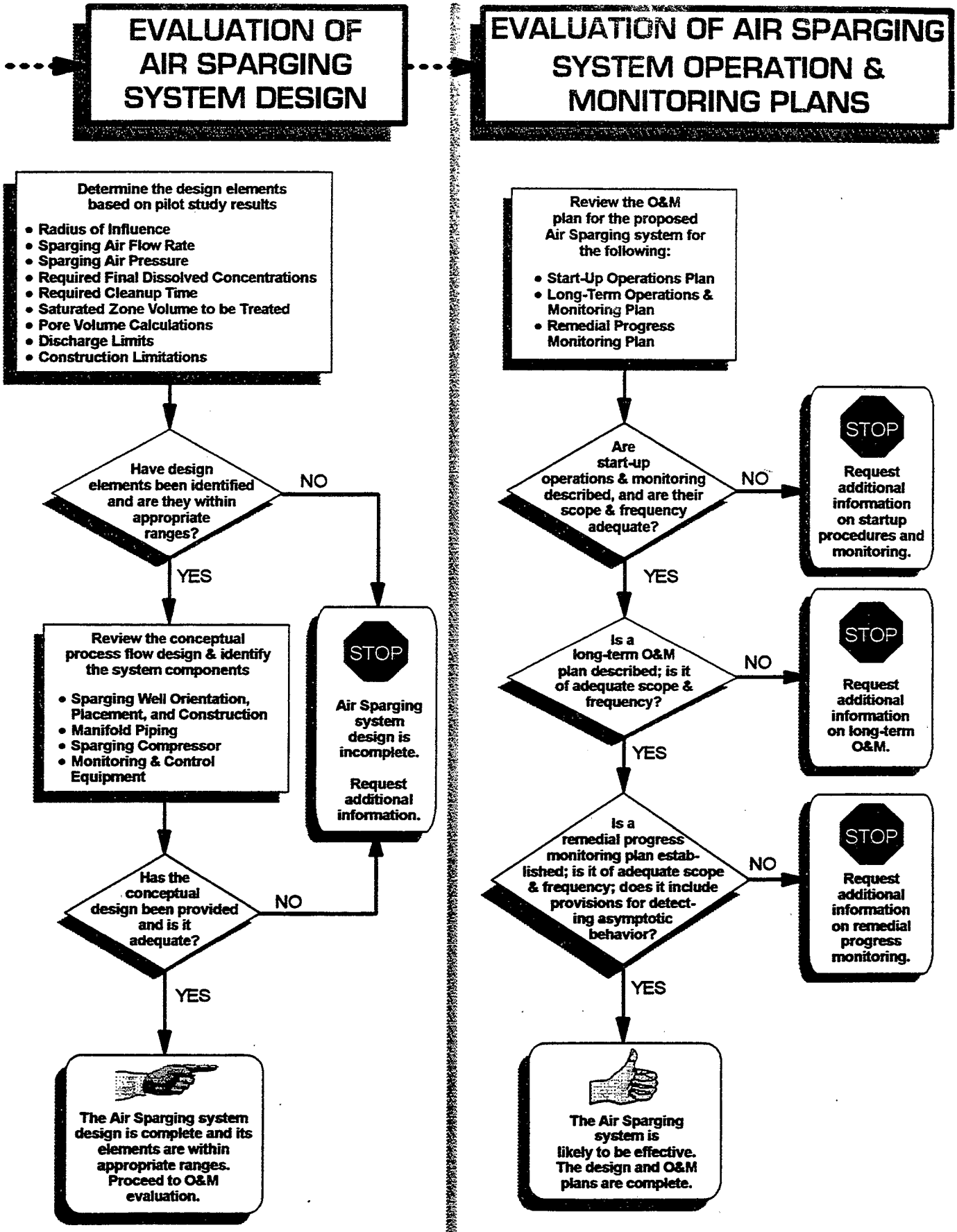


Exhibit VII-3
Air Sparging Evaluation Process Flow Chart



- **Step 4:** ***An evaluation of the operation and monitoring plans*** allows you to determine whether start-up and long-term system operation and monitoring is of sufficient scope and frequency and whether remedial progress monitoring plans are appropriate.

Initial Screening Of Air Sparging Effectiveness

This section allows you to perform an initial screening of whether air sparging will be effective at a site. First, you need to determine if site-specific factors which prohibit the use of air sparging are present. Second, you need to determine if the key parameters which contribute to the effectiveness and design are within appropriate ranges for air sparging.

Air sparging should not be used if the following site conditions exist:

- *Free product is present.* Air sparging can create groundwater mounding which could potentially cause free product to migrate and contamination to spread.

- *Nearby basements, sewers, or other subsurface confined spaces are present at the site.* Potentially dangerous constituent concentrations could accumulate in basements unless a vapor extraction system is used to control vapor migration.

- *Contaminated groundwater is located in a confined aquifer system.* Air sparging cannot be used to treat groundwater in a confined aquifer because the injected air would be trapped by the saturated confining layer and could not escape to the unsaturated zone.

The effectiveness of air sparging depends primarily on two factors:

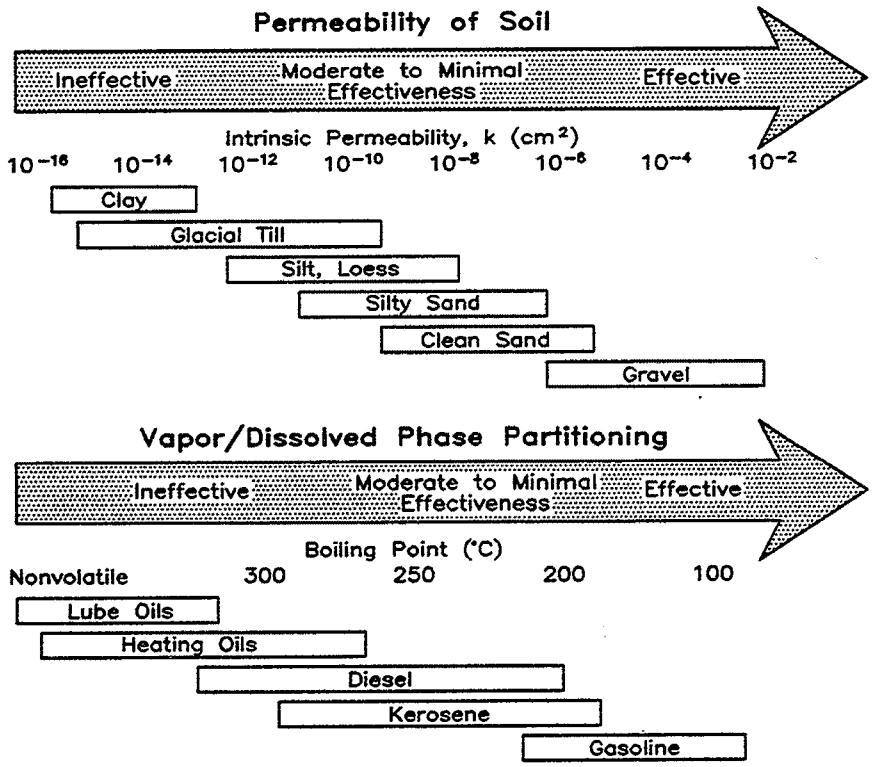
- *Vapor/dissolved phase partitioning* of the constituents determines the equilibrium distribution of a constituent between the dissolved phase and the vapor phase. Vapor/dissolved phase partitioning is, therefore, a significant factor in determining the rate at which dissolved constituents can be transferred to the vapor phase.

- *Permeability* of the soil determines the rate at which air can be injected into the saturated zone. It is the other significant factor in determining the mass transfer rate of the constituents from the dissolved phase to the vapor phase.

Effectiveness of air sparging can be gauged by determining these two factors. In general, air sparging is more effective for constituents with greater volatility and lower solubility and for soils with higher permeability.

Exhibit VII-4 can be used as a screening tool to help you assess the general effectiveness of air sparging for a given site. It provides boiling point ranges for the petroleum products typically encountered at UST sites as a rough gauge for vapor/dissolved phase partitioning. The higher boiling point products contain more constituents of higher volatility (but not necessarily lower solubility) which generally results in greater partitioning to the vapor phase from the dissolved phase. Exhibit VII-4 also provides the range of intrinsic permeabilities for soil types typically encountered at UST sites.

Exhibit VII-4
Initial Screening For Air Sparging Effectiveness



Detailed Evaluation Of Air Sparging Effectiveness

Once you have completed the initial screening and determined that air sparging may have the potential to be effective for the soils and petroleum product present, evaluate the CAP further to confirm that air sparging will be effective.

Begin by reviewing the two major components that determine the effectiveness of air sparging: (1) the vapor/dissolved phase partitioning of the constituents and (2) the permeability of the soils. The combined effect of these two components determines the rate at which the constituent mass will be removed (i.e., the constituent mass removal rate). This rate will decrease as air sparging operations proceed and concentrations of dissolved constituents are reduced. They also determine the placement and number of air sparge points required to address the dissolved phase plume.

Many site-specific and constituent-specific parameters can be used to determine vapor/dissolved partitioning and permeability. These parameters are summarized in Exhibit VII-5. The remainder of this section describes each parameter, why it is important to air sparging, how it can be determined, and its range for effective air sparging.

Exhibit VII-5
Key Parameters Used To Evaluate Vapor/Dissolved Phase Partitioning And Permeability Of Soil

Constituent Vapor/Dissolved Phase Partitioning	Permeability Of Soil
Henry's law constant	Intrinsic permeability
Product composition and boiling point	Soil structure and stratification
Vapor pressure	Iron concentration dissolved in groundwater
Constituent concentration	
Solubility	

Factors That Contribute To Constituent Vapor/Dissolved Phase Partitioning

Henry's Law Constant

The most important characteristic to evaluate vapor/dissolved phase partitioning is the Henry's law constant, which quantifies the relative tendency of a dissolved constituent to transfer to the vapor phase. Henry's law states that, for ideal gases and solutions under equilibrium conditions, the ratio of the partial pressure of a constituent in the vapor

phase to the concentration of the constituent in the dissolved phase is constant. That is:

$$P_a = H_a X_a$$

where:

P_a = partial pressure of constituent a in air (atm)
H_a = Henry's law constant (atm)
X_a = Solution concentration of constituent (mole fraction)

Henry's law constants for several constituents commonly found in petroleum products are shown in Exhibit VII-6. Constituents with Henry's law constants greater than 100 atmospheres are generally considered amenable to removal by air sparging.

Exhibit VII-6
Henry's Law Constant Of Common Petroleum Constituents

Constituent	Henry's Law Constant At 20°C (atm)
Tetraethyl lead	4700
Ethylbenzene	359
Xylenes	266
Benzene	230
Toluene	217
Naphthalene	72
Ethylene dibromide	34
Methyl t-butyl ether	27

Product Composition And Boiling Point

Because petroleum products are often classified by their boiling point range and because the boiling point of a compound is a measure of its volatility, vapor/dissolved phase partitioning of the dissolved petroleum product can be estimated from its boiling point range. However, because vapor/dissolved phase partitioning is a function of both volatility and solubility, boiling point range should be used only as a gauge to consider effectiveness for the product in general.

The most commonly encountered petroleum products from UST releases are gasoline, kerosene, diesel fuel, heating oils, and lubricating oils. Petroleum products are a complex mixture often containing more than 100 separate compounds. Each compound responds to air sparging with differing levels of success based on its individual volatility. Shown in Exhibit VII-7 are the boiling point ranges for common petroleum products.

Exhibit VII-7
Petroleum Product Boiling Point Ranges

Product	Boiling Point Range (°C)
Gasoline	40 to 225
Kerosene	180 to 300
Diesel fuel	200 to 338
Heating oil	> 275
Lubricating oils	Nonvolatile

In general, constituents in petroleum products with boiling points less than 250°C to 300°C are sufficiently volatile for removal from the saturated zone by air sparging. Nearly all gasoline constituents and a portion of kerosene and diesel fuel constituents can be removed from the saturated zone by air sparging. Heating and lubricating oils cannot be removed by air sparging. However, air sparging can promote biodegradation of semivolatile and nonvolatile constituents (see Chapter VIII: Biosparging).

Vapor Pressure

Vapor pressure is another means by which the volatility of a constituent can be determined and used as a gauge for vapor/dissolved phase partitioning. The vapor pressure of a chemical is a measure of its tendency to evaporate. More precisely, it is the pressure that a vapor exerts when in equilibrium with its pure liquid or solid form. Constituents with higher vapor pressures are generally transferred from the dissolved phase to the vapor phase more easily. Those constituents with vapor pressures higher than 0.5 mm Hg are considered to be amenable to air sparging. Exhibit VII-8 presents vapor pressures of some common petroleum constituents.

Exhibit VII-8
Vapor Pressures Of Common Petroleum Constituents

Constituent	Vapor Pressure (mm Hg at 20°C)
Methyl t-butyl ether	245
Benzene	76
Toluene	22
Ethylene dibromide	11
Ethylbenzene	7
Xylenes	6
Naphthalene	0.5
Tetraethyl lead	0.2

Constituent Concentrations

If it is determined that air sparging is a potentially viable technology for the site, the initial and the target cleanup levels for the contaminants in the groundwater must be evaluated. No apparent upper level of contaminant concentration exists for air sparging to be effective; however, if floating free product is present, air sparging is not suitable because induced groundwater mounding can spread the contamination. Thus, any free product must be removed prior to initiating air sparging.

The achievable cleanup level may vary greatly depending on the contaminant type and soil concentrations. Exhibit VII-9 presents examples of the effectiveness of air sparging (used with SVE). After varying operational durations, each system reached a residual contaminant level that could not be lowered (listed as the final concentration).

Solubility

The aqueous solubility of a constituent is a measure of the maximum weight of the constituent that can be dissolved in water. Solubility, like volatility, is a component of the vapor/dissolved phase partitioning behavior for a constituent. However, solubility is less important than vapor pressure and Henry's law constant and should not be used as the sole gauge for air sparging effectiveness. Thus, no threshold value can be provided. Constituents with relatively high solubility, such as benzene, can still exhibit sufficiently high vapor/dissolved phase partitioning for air sparging when they possess high volatility (vapor pressure). When considering a constituent for removal by air sparging, however, it is important to consider that sparging creates turbulence in the subsurface which will enhance dissolution of constituents adsorbed to saturated zone soils. Constituents with relatively high solubilities and low Henry's law constants, such as MTBE and ethylene dibromide, could be mobilized through dissolution but not removed effectively by air sparging. Exhibit VII-10 lists the solubilities of several constituents typically found in petroleum products at UST sites.

Factors That Contribute To Permeability Of Soil

Intrinsic Permeability

Intrinsic permeability is a measure of the ability of soils to transmit fluids and is the *single most important characteristic of the soil* in determining the effectiveness of air sparging. Intrinsic permeability varies over 13 orders of magnitude (from 10^{-16} to 10^{-3} cm^2) for the wide range of earth materials, although a more limited range applies to most soil types (10^{-13} to 10^{-5} cm^2). Although the intrinsic permeability of the

Exhibit VII-9
Summary Of Air Sparging Applications (Used With SVE)

Site	Soil Type	Depth to Groundwater (feet)	Product	Cleanup Time (months)	Initial Groundwater Concentrations (mg/L)	Final Groundwater Concentrations (mg/L)
A	Alluvial sands, silts, and clay	6.5-16	gasoline	2	BTEX: 4-25	BTEX: 0.25-8
B	Silty sand, interfering clay layer	6.5	gasoline	5	Benzene: 3-6	59% average reduction
E	NR	NR	gasoline	10	Benzene: > 30	Benzene: < 5
F	Sand, silt	8-13	gasoline	24	BTEX: 6-24	BTEX: 0.38-7.6
G	Fine-coarse sand, gravel	15.5-16	gasoline	2	BTEX: 21	BTEX: < 1

BTEX = Benzene, Toluene, Ethylbenzene, and Xylene
NR = Not Reported

Source: Adapted from R.A. Brown et al., *Treatment of a Solvent Contaminated Site with Air Sparging/Soil Vapor Extraction.*

Exhibit VII-10
Solubility Of Common Petroleum Constituents

Constituent	Solubility (mg/L at 20°C)
Methyl t-butyl ether	48,000
Ethylene dibromide	4,310
Benzene	1,780
Toluene	515
Xylene	185
Ethylbenzene	152
Naphthalene	30
Tetraethyl lead	0.0025

saturated zone (for air sparging) and unsaturated zone (when SVE is used) is best determined from field tests, it can be estimated from soil boring logs and laboratory tests. Coarse-grained soils (e.g., sands) have greater intrinsic permeability than fine-grained soils (e.g., clays and silts). Use the values shown in Exhibit VII-11 to determine if intrinsic permeability is within the range of effectiveness for air sparging.

Exhibit VII-11
Intrinsic Permeability And Air Sparging Effectiveness

Intrinsic Permeability (k)(cm^2)	Air Sparging Effectiveness
$k \geq 10^{-9}$	Generally effective
$10^{-9} \geq k \geq 10^{-10}$	May be effective; needs further evaluation
$k < 10^{-10}$	Marginal effectiveness to ineffective

Intrinsic permeability of saturated-zone soils is usually determined in the field by aquifer pump tests that measure hydraulic conductivity. You can convert hydraulic conductivity to intrinsic permeability using the following equation:

$$k = K\ (\mu/\rho g)$$

where:
- k = intrinsic permeability (cm^2)
- K = hydraulic conductivity (cm/sec)
- μ = water viscosity (g/cm · sec)
- ρ = water density (g/cm^3)
- g = acceleration due to gravity (cm/sec^2)

At 20°C: $\mu/\rho g = 1.02 \cdot 10^{-5}$ cm/sec

To convert k from cm^2 to darcy, multiply by 10^8

Intrinsic permeability of the unsaturated zone can be estimated from the intrinsic permeability of the saturated zone if similar soil types are present or can be determined in the field by conducting permeability tests or SVE pilot studies. (See Chapter II: Soil Vapor Extraction.)

Soil Structure And Stratification

The types of soil present and their micro- and macro-structures control the air sparging pressure and the distribution of air in the saturated zone. For example, fine-grained soils require higher sparging air pressures because gas pockets have a tendency to form in these types of soils, thereby further reducing the minimal effectiveness of sparging for treating them. Greater lateral dispersion of the air is likely in fine-grained soils and can result in lateral displacement of the groundwater and contaminants if groundwater control is not maintained.

Soil characteristics will also determine the preferred zones of vapor flow in the vadose zone, thereby indicating the ease with which vapors can be controlled and extracted using SVE (if used).

Stratified or highly variable heterogeneous soils typically create the greatest barriers to air sparging. Both the injected air and the stripped vapors will travel along the paths of least resistance (coarse-grained zones) and could travel a great lateral distance from the injection point. This phenomenon could result in the contaminant-laden sparge vapors migrating outside the vapor extraction control area.

Information about soil type, structure, and stratification can be determined from boring logs or geologic cross-section maps. You should verify that soil types have been identified and visual observations of soil structure have been documented.

Iron Concentration Dissolved In Groundwater

The presence of dissolved iron (Fe^{+2}) in groundwater can reduce the permeability of the saturated zone soils during air sparging operations. When dissolved iron is exposed to oxygen, it is oxidized to insoluble iron (Fe^{+3}) oxide which can precipitate within the saturated zone and occlude soil pore space, thereby reducing the region available for air (and groundwater) flow, and reducing permeability. Precipitation of iron oxide occurs predominantly in the saturated zone near air sparging well screens where oxygen content (from injected air) is the highest. This oxidation can render air sparging wells useless after even short periods of operation and necessitate the installation of new wells in different locations.

You should verify that laboratory measurements of total dissolved iron have been completed for groundwater samples from the site. Use Exhibit VII-12 to determine the range where dissolved iron is a concern for air sparging effectiveness.

Exhibit VII-12
Dissolved Iron And Air Sparging Effectiveness

Dissolved Iron Concentration (mg/L)	Air Sparging Effectiveness
$Fe^{+2} < 10$	Air sparging effective
$10 \leq Fe^{+2} \leq 20$	Air sparging wells require periodic testing and may need periodic replacement
$Fe^{+2} > 20$	Air sparging not recommended

Field Pilot-Scale Studies

Field pilot studies are necessary to adequately design and evaluate any air sparging system. However, pilot tests should not be conducted if free product is known to exist at the groundwater table, if uncontrolled vapors could migrate into confined spaces, sewers, or buildings, or if the contaminated groundwater is in an unconfined aquifer. The air sparge well used for pilot testing is generally located in an area of moderate constituent concentrations. Testing the system in areas of extremely low constituent concentrations may not provide sufficient data. In addition, because sparging can induce migration of constituents, pilot tests are generally not conducted in areas of extremely high constituent concentrations. The air sparging pilot study should include an SVE pilot study if SVE is to be included in the design of the air sparging system.

Pilot studies for air sparging often include SVE pilot testing to determine if SVE can be used to effectively control the vapor plume. Pilot studies, therefore, should include the installation of a single sparge point, several vapor extraction points (if SVE is to be included in the design), and soil gas monitoring points to evaluate vapor generation rates and to define the vapor plume. Existing groundwater monitoring wells (normally not fewer than three to five wells around the plume) that have been screened above the saturated zone and through the dissolved phase plume can be used to monitor both dissolved and vapor phase migration, to monitor for changes in dissolved oxygen, and to measure changes in the depth to the groundwater table surface. Additional vapor probes should be used to further define the vapor plume and identify any preferential migration pathways. These probes should be designed and installed as discussed in Chapter II: Soil Vapor Extraction.

If SVE is to be used in the air sparging system, the first portion of the test should be conducted using vapor extraction only and evaluated as described in Chapter II: Soil Vapor Extraction without the air sparging system being operated. This portion of the pilot test will establish the baseline vapor extraction levels, the extent of the non-sparged vapor plume, the SVE well radius of influence, and the intrinsic permeability of the unsaturated zone (discussed in Chapter II). The air sparging portion of the test should be conducted with the sparging point operating at variable sparge pressures (e.g., 5 pounds per square inch-gauge [psig], 10 psig) and different depths (e.g., 5 feet, 10 feet below the dissolved phase plume). It is essential that vapor equilibrium be obtained prior to changing the sparge rate or depth. When no change in vapor emission rates from baseline occurs, the air sparging system may not be controlling the sparge vapor plume, possibly due to soil heterogeneity. Assess the potential for this problem by reviewing the site's soil lithology, typically documented on soil boring logs. During this test, the hydraulic gradient and VOC concentrations in soil vapors extracted from monitoring wells must be monitored until equilibrium is reached.

The final portion of the pilot test is the concurrent operation of the SVE pilot system and the air sparging system. This portion of the test will determine the optimum SVE system (i.e., the number and orientation of wells) that will capture the sparged VOCs for various sparging rates. In addition, this portion of the test requires monitoring of VOC emissions, sparging pressure and flow rates, SVE vacuum and flow rates, monitoring well vapor concentrations, and dissolved constituent concentrations. Exhibit VII-13 presents a summary of the Pilot Test Data Objectives.

Evaluation Of The Air Sparging System Design

Once you have verified that air sparging is applicable to your site, you can evaluate the design of the system. The CAP should include a discussion of the rationale for the system design and the results of the pilot tests. Detailed engineering design documents might also be included, depending on individual state requirements. Discussion of the SVE portion of the design is included in Chapter II: Soil Vapor Extraction.

Rationale For The Design

The following factors should be considered as you evaluate the design of the air sparging system in the CAP.

- *Design ROI* for air sparging wells. The ROI is the most important parameter to be considered in the design of the air sparging system. The ROI is defined as the greatest distance from a sparging well at which sufficient sparge pressure and airflow can be induced to enhance the mass transfer of contaminants from the dissolved phase to the vapor phase. The ROI will help determine the number and spacing of the sparging wells.

Exhibit VII-13
Pilot Test Data Objectives

Data Requirement	Source
SVE Test Portion (if necessary)	
SVE radius of influence (ROI)	Monitoring point pressure gauges
Wellhead and monitoring point vacuum	Well head pressure gauge
Initial contaminant vapor concentrations	SVE exhaust flame ionization detector (FID) readings (or other suitable detection device)
Initial hydraulic gradient	Water level tape at monitoring wells or pressure transducers and data logger
Air Sparging Test Portion	
Air sparging ROI	Monitoring point pressure gauge
Sparging rate	Compressor discharge flow gauge
Sparging vapor concentrations	Monitoring well and vapor point FID readings (or other suitable detection device)
Hydraulic gradient influence	Water level tape at monitoring wells or pressure transducers and data logger
Dissolved oxygen and carbon dioxide	Dissolved oxygen and carbon dioxide probes at monitoring wells
Combined Test (if necessary)	
Sparging/SVE capture rates	Pressure/flow gauges
Constituent vapor concentrations	Blower discharge and monitoring points

The ROI should be determined based on the results of pilot tests. One should be careful, however, when evaluating pilot test results because the measurement of air flow, increased dissolved oxygen, or the presence of air bubbles in a monitoring point can be falsely interpreted as an air flow zone that is thoroughly permeated with injected air. However, these observations may only represent localized sparging around sparsely distributed air flow channels. The ROI depends primarily on the hydraulic conductivity of the aquifer material in which sparging takes place. Other factors that affect the ROI include soil heterogeneities, and differences between lateral and vertical permeability of the soils. Generally, the design ROI can range from 5 feet for fine-grained soils to 100 feet for coarse-grained soils.

- *Sparging Air Flow Rate.* The sparging air flow rate required to provide sufficient air flow to enhance mass transfer is site-specific and will be determined via the pilot test. Typical air flow rates range from 3 to 25 standard cubic feet per minute (scfm) per injection well. Pulsing of the air flow (i.e., turning the system on and off at specified intervals) may provide better distribution and mixing of the air in the contaminated saturated zone, thereby allowing for greater contact with the dissolved phase contaminants. The vapor extraction system should have a

greater flow capacity and greater area of influence than the air sparging system. The air sparging rate should vary between 20 percent and 80 percent of the soil vapor extraction flow rate.

- *Sparging Air Pressure* is the pressure at which air is injected into the saturated zone. The saturated zone requires pressures greater than the static water pressure (1 psi for every 2.3 ft of hydraulic head) and the head necessary to overcome capillary forces of the water in the soil pores near the injection point. A typical system will be operated at approximately 10 to 15 psig. Excessive pressure may cause fracturing of the soils and create permanent air channels that can significantly reduce air sparging effectiveness.

- *Initial Constituent Vapor Concentrations* are measured during pilot studies. They are used to estimate constituent mass removal rates and system operational time requirements and to determine whether treatment of extracted vapors will be required prior to atmospheric discharge or reinjection.

- *Required Final Dissolved Constituent Concentrations* in the saturated zone will determine which areas of the site require treatment and when air sparging system operations can be terminated. These levels are usually defined by state regulations as *remedial action levels.* In some states, these levels are determined on a site-specific basis using transport modeling and risk assessment.

- *Required Remedial Cleanup Time* may influence the design of the system. The designer may vary the spacing of the sparging wells to speed remediation to meet cleanup deadlines, if required.

- *Saturated Zone Volume To Be Treated* is determined by state action levels or a site-specific risk assessment using site characterization data for the groundwater.

- *Pore Volume Calculations* are used along with extraction flow rate to determine the pore volume exchange rate. Some literature suggests that at a minimum one pore volume of soil vapor should be extracted daily for effective remedial progress.

- *Discharge Limitations And Monitoring Requirements* are usually established by state regulations but must be considered by designers of an air sparging system which uses SVE to ensure that monitoring ports are included in the system hardware. Discharge limitations imposed by state air quality regulations will determine whether offgas treatment is required.

- *Site Construction Limitations* (e.g., building locations, utilities, buried objects, residences) must be identified and considered in the design process.

What Are The Typical Components Of An Air Sparging System?

Once the rationale for the design is defined, the design of the air sparging system can be developed. A typical air sparging system design may include the following components and information:

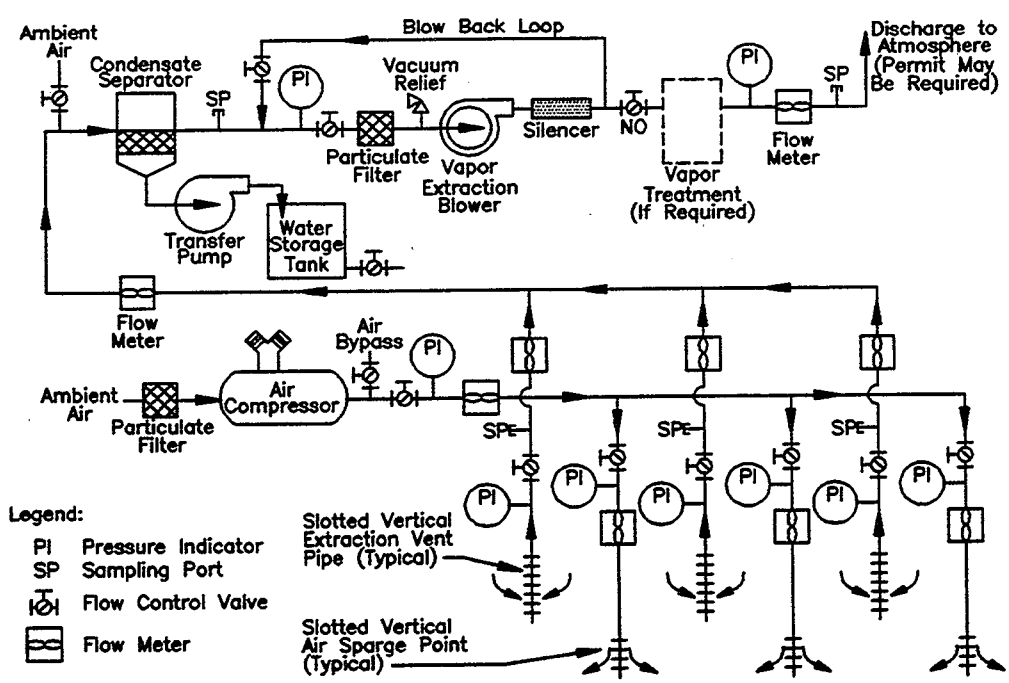
- Well orientation, placement, and construction details.
- Manifold piping.
- Compressed air equipment.
- Monitoring and controls.

If an SVE system is used for vapor control, the following components and information will also be needed:

- Vapor pretreatment design.
- Vapor treatment system selection.
- Blower specification.

Exhibit VII-14 provides a schematic diagram of a typical air sparging system used with SVE. Chapter II: Soil Vapor Extraction should be consulted for information on the design of the SVE portion of the remedial system (if necessary) including vapor pretreatment design, vapor treatment system selection, and blower specification.

Exhibit VII-14
Schematic Of Air Sparging System Used With SVE



Sparge And Extraction Wells

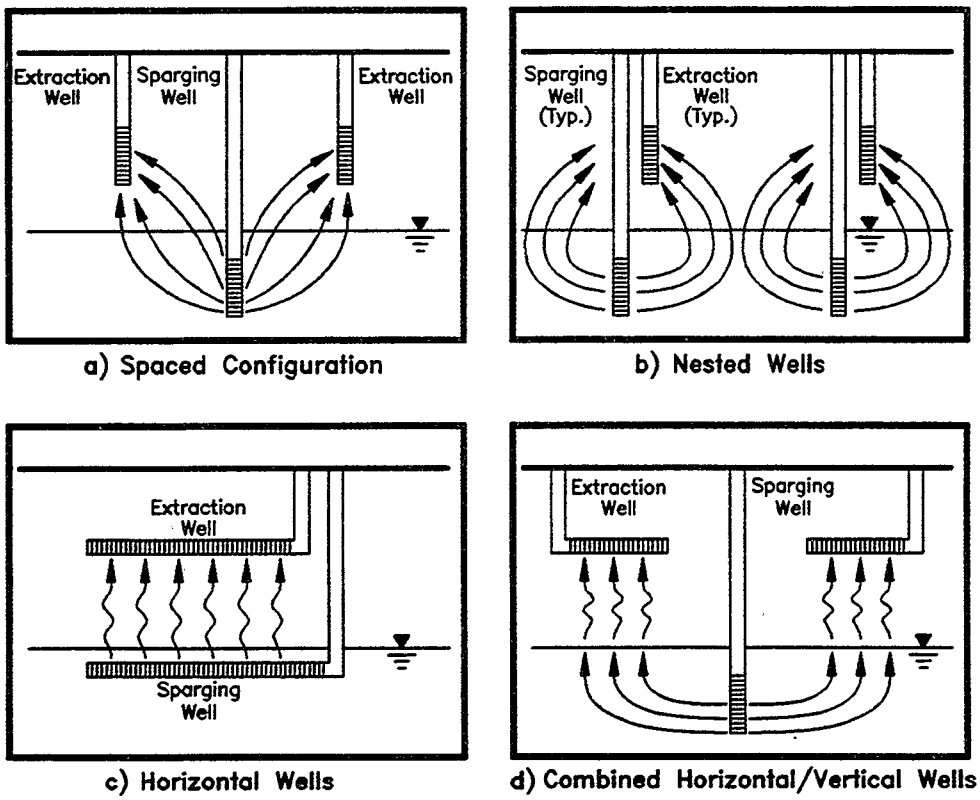
Well Orientation. An air sparging system can use either vertical or horizontal sparge wells. Well orientation should be based on site-specific needs and conditions. For example, horizontal systems should be considered when evaluating sites that will require 10 or more sparge or extraction points or if the affected area is under an operational facility. Exhibit VII-15 lists site conditions and the corresponding appropriate well orientation.

Exhibit VII-15
Well Orientation And Site Conditions

Well Orientation	Site Conditions
Vertical wells	o Deep contamination (> 25 feet) o Depth to groundwater (> 10 feet) o Fewer than 10 wells
Horizontal wells	o Shallow groundwater table (< 25 feet) o Zone of contamination within a specific stratigraphic unit o System under an operational facility

Well Placement And Number of Wells. Exhibit VII-16, Air Sparging/Vapor Extraction Well Configurations, shows various configurations that can be used in laying out air sparging systems used in conjunction with SVE. The essential goals in configuring the wells and monitoring points are (1) to optimize the influence on the plume, thereby maximizing the removal efficiency of the system and (2) to provide optimum monitoring and vapor extraction points to ensure minimal migration of the vapor plume and no undetected migration of either the dissolved phase or vapor phase plumes. In shallow applications, in large plume areas, or in locations under buildings or pavements, horizontal vapor extraction wells are very cost effective and efficient for controlling vapor migration. Exhibit VII-17 is a typical layout of a system that surrounds and contains a plume and includes air sparging and SVE wells.

Exhibit VII-16
Air Sparging/Soil Vapor Extraction Well Configurations



Source: "Advances in Air Sparging Design," The Hazardous Waste Consultant, Vol. 11, Issue 1, January/February 1993, p. 1-4.

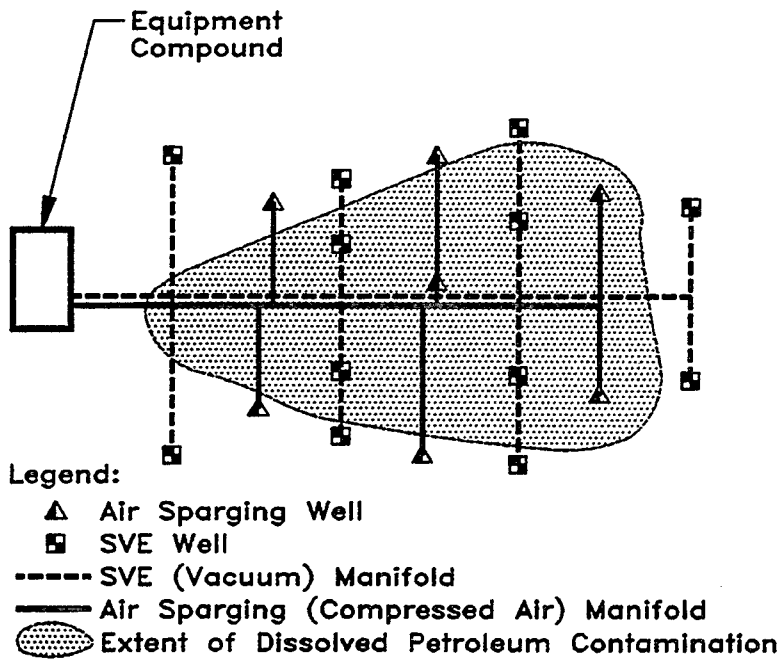
The number and location of extraction wells can be determined by using several methods as discussed in Chapter II: Soil Vapor Extraction. However, the following general points should be considered:

- Closer well spacing is often appropriate in areas of high contaminant concentrations in order to enhance air distribution and removal rates.

- If a surface seal exists or is planned for the design, the extraction wells can be spaced slightly farther apart because air is drawn from a greater distance and not directly from the surface.

- At sites with stratified soils, wells screened in strata with low permeabilities might require closer well spacing than wells screened in strata with higher permeabilities.

Exhibit VII-17
Combined Air Sparging/SVE System Layout



Well Construction. The air sparging (injection) wells are generally constructed of 1 to 5 inch PVC or stainless steel pipe. The screened interval is normally from 1 to 3 feet and is generally set from 5 to 15 feet below the deepest extent of adsorbed contaminants. Setting the screen at a deeper interval requires higher pressures on the system but generally does not achieve higher sparge rates. Increased screened intervals do not improve system efficiency because air tends to exit at the top portion of the screen. Air sparging wells must be properly grouted to prevent short circuiting of the air. Horizontal injection wells should be designed and installed carefully to ensure that air exits from along the entire screen length. Perforated pipe, rather than well screening, is sometimes preferable. Exhibits VII-18 and VII-19 present typical vertical and horizontal air sparging well constructions, respectively.

Injection wells should be fitted with check valves to prevent potential line fouling caused by pressure in the saturated zone forcing water up the point when the system is shut down. Each air sparging well should also be equipped with a pressure gauge and flow regulator to enable adjustments in sparging air distribution. Refer to Chapter II: Soil Vapor Extraction for vapor extraction well details.

Exhibit VII-18
Typical Vertical Air Sparging Well Construction

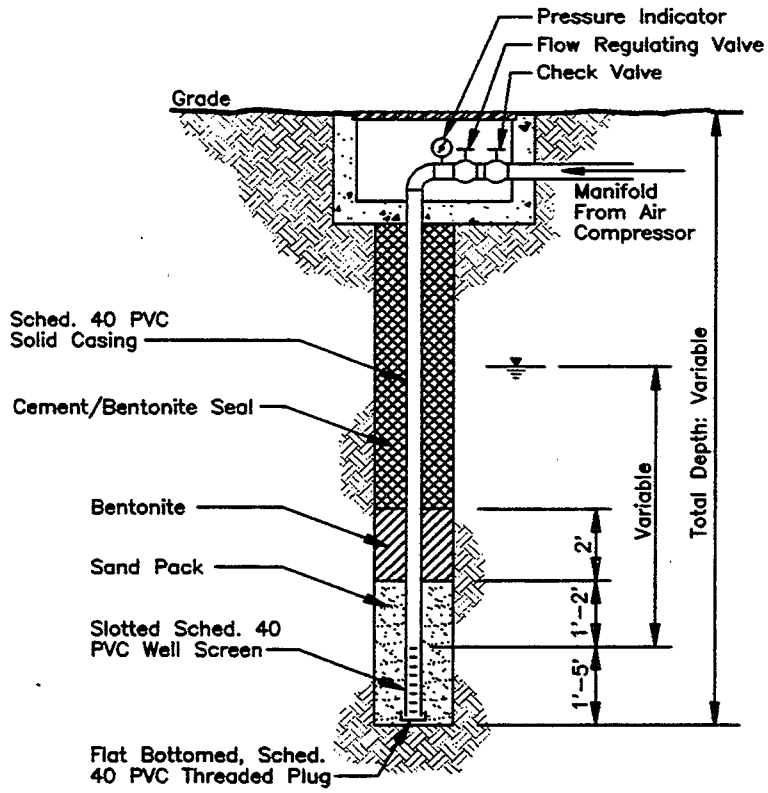
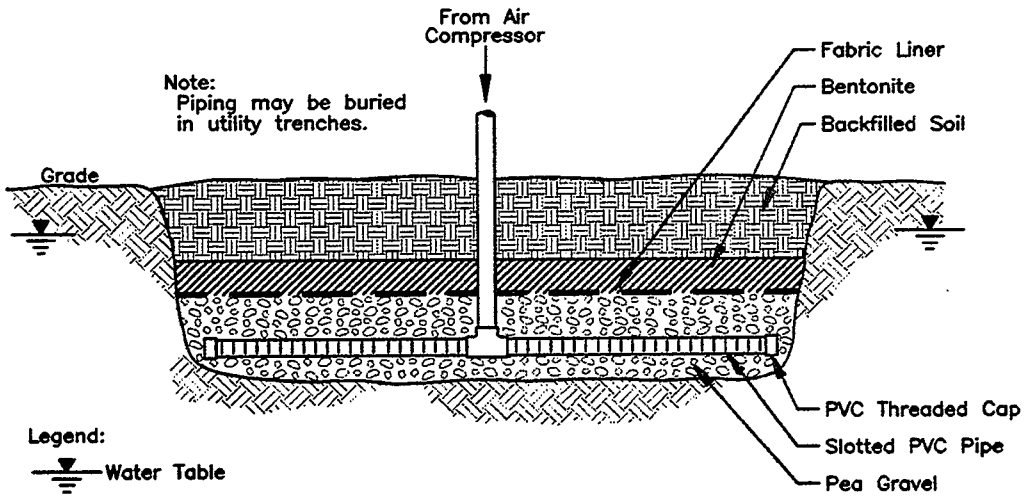


Exhibit VII-19
Typical Horizontal Air Sparging Well Construction



Manifold Piping

Manifold piping connects the sparging wells to the air compressor. Piping can be placed either above or below grade depending on site operations, ambient temperature, and local building codes. Below-grade piping is more common and is installed in shallow utility trenches that lead from the sparging wellhead vault(s) to a central equipment location. The piping can be either manifolded in the equipment area or connected to a common compressor main that supplies the wells in series, in which case flow control valves are located at the wellhead. Piping to the well locations should be sloped toward the well so that condensate or entrained groundwater will flow back toward the well.

The pressurized air distribution system can be made of metal pipe or rubber-reinforced air hose. PVC pipe should not be connected directly to the compressor because of the high temperatures of air leaving the compressor which can diminish the integrity of the PVC. If pipe trenches are used for the distribution system, they must be sealed to prevent short circuiting of air flow.

Compressed Air Equipment

An oil-free compressor or a standard compressor equipped with downstream coalescing and particulate filters should be used to ensure that no contaminants are injected into the saturated zone. The compressor should be rated for continuous duty at the maximum expected flow rate and pressure to provide adequate flexibility during full operations.

Monitoring And Controls

The parameters typically monitored in an air sparging system include:

- Pressure (or vacuum)
- Air/vapor flow rate

The equipment in an air sparging system used to monitor these parameters provides the information necessary to make appropriate system adjustments and track remedial progress. The control equipment in an air sparging system allow the flow and sparge pressure to be adjusted at each sparging well of the system, as necessary. Control equipment typically includes flow control valves/regulators.
Exhibit VII-20 lists typical monitoring and control equipment for an air sparging system, where each of these pieces of equipment should be placed, and the types of equipment that are available.

Exhibit VII-20
Monitoring And Control Equipment

Monitoring Equipment	Location In System	Example Of Equipment
Flow meter	○ At each injection and vapor extraction well head ○ Manifold to blower ○ Stack discharge	○ Pitot tube ○ In-line rotameter ○ Orifice plate ○ Venturi or flow tube
Pressure gauge	○ At each injection and vapor extraction well head or manifold branch ○ Before blower (before and after filters) ○ Before and after vapor treatment	○ Manometer ○ Magnehelic gauge ○ Vacuum gauge
Vapor or air sparge temperature sensor	○ Manifold to blower ○ Blower or compressor discharge (prior to vapor treatment)	○ Bi-metal dial-type thermometer ○ Thermocouple
Sampling port	○ At each vapor extraction well head or manifold branch ○ Manifold to blower ○ Blower discharge	○ Hose barb ○ Septa fitting
Control Equipment		
Flow control valves/ regulators	○ At each vapor extraction well head or manifold branch ○ Dilution or bleed valve at manifold to blower ○ At header to each sparge point	○ Ball valve ○ Gate valve ○ Dilution/ambient air bleed valve ○ Gate valve ○ Dilution/ambient air bleed valve

Evaluation Of Operation And Monitoring Plans

The system operation and monitoring plan should include both system startup and long-term operations. Operations and monitoring are necessary to ensure optimal system performance and to track the rate of contaminant mass removal.

Startup Operations

The startup phase should begin with only the SVE portion of the system (if used) as described in Chapter II. After the SVE system is adjusted, the air sparging system should be started. Startup operations should include 7 to 10 days of manifold valving adjustments to balance injection rates and optimize mass flow rates. Injection and extraction rates, pressures, depth to groundwater, hydraulic gradient, and VOC levels should be recorded hourly during initial startup until the flow is stabilized. Injection rates should then be monitored daily. Vapor concentration should also be monitored in any nearby utility lines, basements, or other subsurface confined spaces. Other monitoring of the system should be done in accordance with the SVE requirements from Chapter II.

Long-Term Operations

Long-term monitoring should consist of contaminant level measurements (in the groundwater, vapor wells, and blower exhaust), flow-balancing (including flow and pressure measurements), and vapor concentration readings. Measurements should take place at biweekly to monthly intervals for the duration of the system operational period.

Samples collected during sparging operations may give readings that show lower concentrations of dissolved contaminants than those found in the surrounding aquifer. These readings could lead to the erroneous conclusion that remediation is occurring throughout the aquifer. Therefore, contaminant concentrations should be determined shortly following system shutdown, when the subsurface environment has reached equilibrium.

Exhibit VII-21 provides a brief synopsis of system monitoring requirements.

Remedial Progress Monitoring

Monitoring the performance of the air sparging system in reducing contaminant concentrations in the saturated zone is necessary to determine if remedial progress is proceeding at a reasonable pace. A variety of methods can be used. One method includes monitoring contaminant levels in the groundwater and vapors in the monitoring wells and blower exhaust, respectively. The vapor and contaminant concentrations are then each plotted against time.

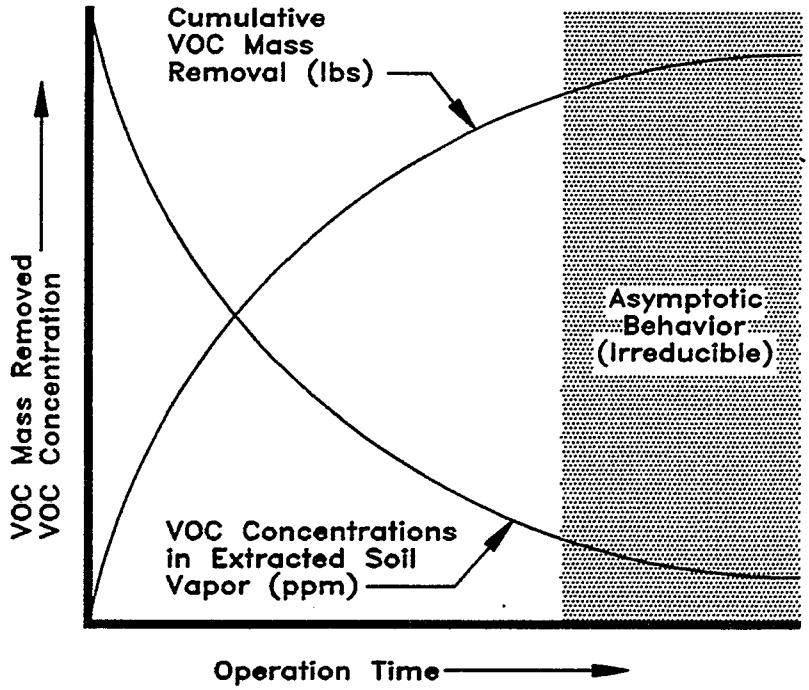
Exhibit VII-21
System Monitoring Recommendations

Phase	Monitoring Frequency	What To Monitor	Where To Monitor
Startup (7-10 days)	At least daily	○ Sparge pressure ○ Flow ○ Vacuum readings (SVE) ○ Vapor concentrations (SVE)	○ Air sparging wellhead ○ Sparge and extraction wells ○ Manifold ○ Effluent stack
Long-term (ongoing)	Biweekly to monthly	○ Flow (SVE) ○ Vacuum readings (SVE) ○ Sparge pressure ○ Vapor concentrations (SVE)	○ Extraction vents ○ Manifold ○ Air sparging wellhead ○ Effluent stack
	Quarterly to annually	○ Dissolved constituent concentrations	○ Groundwater monitoring wells

Remedial progress of air sparging systems typically exhibits asymptotic behavior with respect to both dissolved-phase and vapor-phase concentration reduction (Exhibit VII-22). Systems that use SVE can monitor progress through mass removal calculations. (See Chapter II: Soil Vapor Extraction for calculations.) When asymptotic behavior begins to occur, the operator should evaluate alternatives that increase the mass transfer removal rate (e.g., pulsing, or turning off the system for a period of time and then restarting it). Other more aggressive steps to further reduce constituent concentrations can include installation of additional air sparging or extraction wells.

If asymptotic behavior is persistent for periods greater than about 6 months and the concentration rebound is sufficiently small following periods of temporary system shutdown, the appropriate regulatory officials should be consulted; termination of operations may be appropriate.

Exhibit VII-22
Concentration Reduction And Mass Removal Behavior For Both Air Sparging And SVE Systems



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Checklist: Can Air Sparging Be Used At This Site?

This checklist can help you to evaluate the completeness of the CAP and to identify areas that require closer scrutiny. As you go through the CAP, answer the following questions. If the answer to several questions is no, you will want to request additional information to determine if air sparging will accomplish the cleanup goals at the site.

1. Factors That Contribute To The Vapor/Dissolved Phase Partitioning Of The Constituents

Yes	No	
❑	❑	Is the Henry's law constant for the contaminant greater than 100 atm?
❑	❑	Are the boiling points of the contaminant constituents less than 300°C?
❑	❑	Is the contaminant vapor pressure greater than 0.5 mm Hg?

2. Factors That Contribute To Permeability Of Soil

Yes	No	
❑	❑	Is the intrinsic permeability greater than 10^{-9} cm^2?
❑	❑	Is the soil free of impermeable layers or other conditions that would disrupt air flow?
❑	❑	Is the dissolved iron concentration at the site < 10 mg/L?

3. Evaluation Of The Air Sparging System Design

Yes	No	
❑	❑	Does the radius of influence (ROI) for the proposed air sparging wells fall in the range 5 to 100 feet?
❑	❑	Has the ROI been calculated for each soil type at the site?
❑	❑	Examine the sparging air flow rate. Will these flow rates provide sufficient vapor/dissolved phase partitioning of constituents to achieve cleanup in the time allotted for remediation in the CAP?

3. Evaluation Of The Air Sparging System Design (continued)

Yes	No	
❑	❑	Examine the sparging air pressure. Will the proposed pressure be sufficient to overcome the hydraulic head and capillary forces?
❑	❑	Is the number and placement of wells appropriate, given the total area to be cleaned up and the radius of influence of each well?
❑	❑	Do the proposed well screen intervals account for contaminant plume location at the site?
❑	❑	Is the proposed well configuration appropriate for the site conditions present?
❑	❑	Is the air compressor selected appropriate for the desired sparge pressure?

4. Operation And Monitoring Plans

Yes	No	
❑	❑	Does the CAP propose starting up the SVE system prior to starting the air sparging system?
❑	❑	Are manifold valving adjustments proposed during the first 7 to 10 days of operation?
❑	❑	Is monitoring for sparge pressure and flows, vacuum readings (for SVE), groundwater depth, vapor concentrations, dissolved oxygen levels, carbon dioxide levels, and pH proposed for the first 7 to 10 days of operation?
❑	❑	Is weekly to biweekly monitoring of groundwater pH and levels of contaminants, carbon dioxide, and dissolved oxygen proposed following startup?
❑	❑	Is weekly to biweekly monitoring of the effluent stack for levels of contaminants, oxygen, and carbon dioxide proposed following startup?

Chapter VIII

Biosparging

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Chapter VIII
Biosparging

Overview

Biosparging is an in-situ remediation technology that uses indigenous microorganisms to biodegrade organic constituents in the saturated zone. In biosparging, air (or oxygen) and nutrients (if needed) are injected into the saturated zone to increase the biological activity of the indigenous microorganisms. Biosparging can be used to reduce concentrations of petroleum constituents that are dissolved in groundwater, adsorbed to soil below the water table, and within the capillary fringe. Although constituents adsorbed to soils in the unsaturated zone can also be treated by biosparging, bioventing is typically more effective for this situation. (Chapter III provides a detailed description of bioventing.)

The biosparging process is similar to air sparging. However, while air sparging removes constituents primarily through volatilization, biosparging promotes biodegradation of constituents rather than volatilization (generally by using lower flow rates than are used in air sparging). In practice, some degree of volatilization and biodegradation occurs when either air sparging or biosparging is used. (Air sparging is discussed in Chapter VII.)

When volatile constituents are present, biosparging is often combined with soil vapor extraction or bioventing (collectively referred to as vapor extraction in this chapter), and can also be used with other remedial technologies. When biosparging is combined with vapor extraction, the vapor extraction system creates a negative pressure in the vadose zone through a series of extraction wells that control the vapor plume migration. Chapters II and III provide detailed discussions of soil vapor extraction and bioventing, respectively. Exhibit VIII-1 provides a conceptual drawing of a biosparging system with vapor extraction.

The existing literature contains case histories describing both the successes and failures of biosparging; however, because the technology is relatively new, few cases provide substantial documentation of performance. When used appropriately, biosparging is effective in reducing petroleum products at underground storage tank (UST) sites. Biosparging is most often used at sites with mid-weight petroleum products (e.g., diesel fuel, jet fuel); lighter petroleum products (e.g., gasoline) tend to volatilize readily and to be removed more rapidly using air sparging. Heavier products (e.g., lubricating oils) generally take longer to biodegrade than the lighter products, but biosparging can still be used at these sites. Exhibit VIII-2 provides a summary of the advantages and disadvantages of biosparging.

Exhibit VIII-1
Biosparging System (Used With Soil Vapor Extraction)

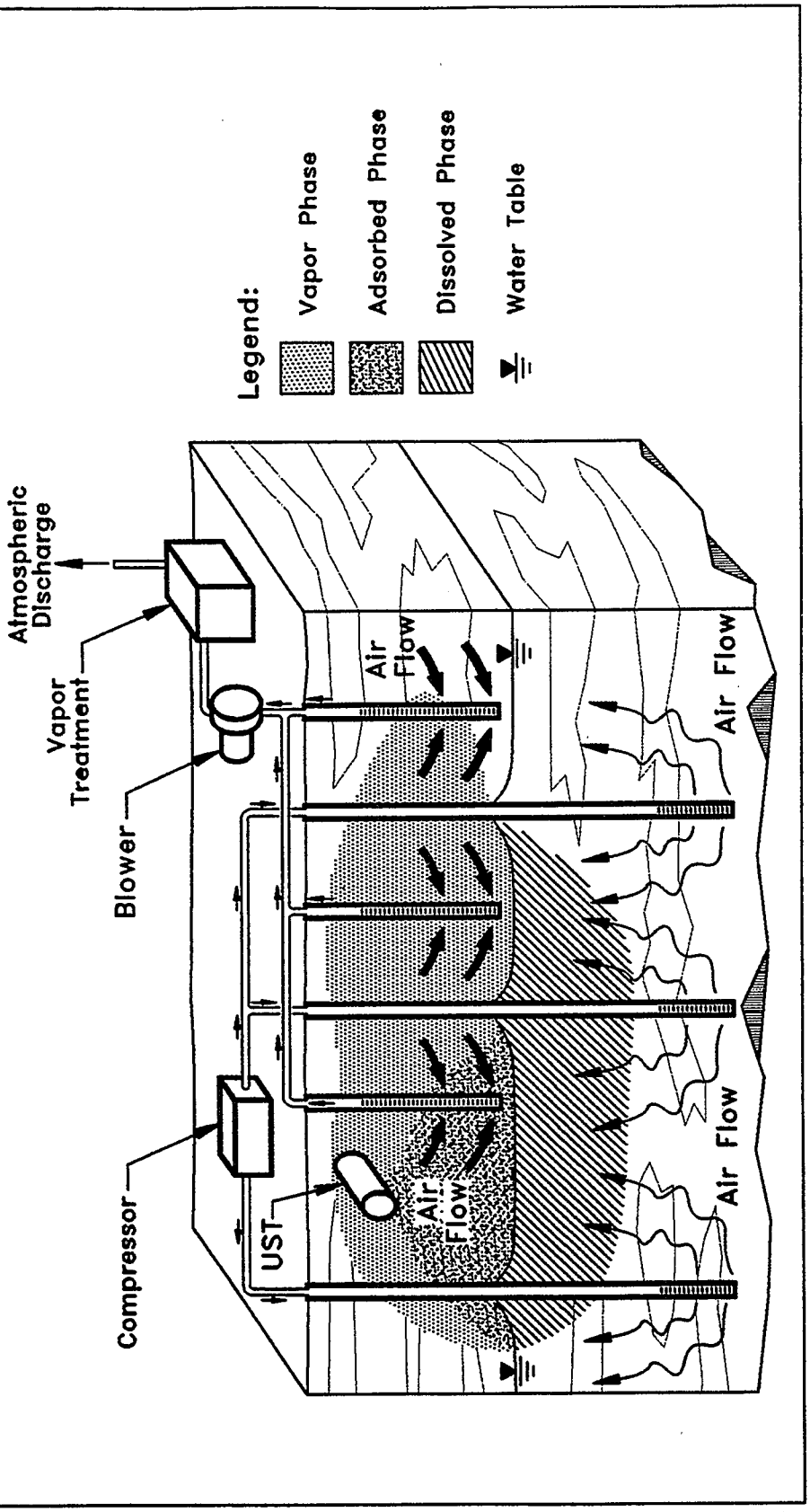


Exhibit VIII-2
Advantages And Disadvantages Of Biosparging

Advantages	Disadvantages
○ Readily available equipment; easy to install.	○ Can only be used in environments where air sparging is suitable (e.g., uniform and permeable soils, unconfined aquifer, no free-phase hydrocarbons, no nearby subsurface confined spaces).
○ Creates minimal disturbance to site operations.	○ Some interactions among complex chemical, physical, and biological processes are not well understood.
○ Short treatment times, 6 months to 2 years under favorable conditions.	○ Lack of field and laboratory data to support design considerations.
○ Is cost competitive.	○ Potential for inducing migration of constituents.
○ Enhances the effectiveness of air sparging for treating a wider range of petroleum hydrocarbons.	
○ Requires no removal, treatment, storage, or discharge of groundwater.	
○ Low air injection rates minimize potential need for vapor capture and treatment.	

This chapter will assist you in evaluating a corrective action plan (CAP) that proposes biosparging as a remedy for petroleum-contaminated groundwater and soil. The evaluation process is summarized in a flow diagram shown in Exhibit VIII-3, which serves as a roadmap for the decisions you will make during your evaluation. A checklist has also been provided at the end of this chapter for you to use as a tool to both evaluate the completeness of the CAP and to focus attention on areas where additional information may be needed. The evaluation process can be divided into the four steps described below.

○ **Step 1:** ***An initial screening of biosparging effectiveness*** allows you to quickly gauge whether biosparging is likely to be effective, moderately effective, or ineffective.

○ **Step 2:** ***A detailed evaluation of biosparging effectiveness*** provides further screening criteria to confirm whether biosparging is likely to be effective. You will need to identify site and constituent characteristics, compare them to ranges where biosparging is effective, and evaluate pilot study plans.

Exhibit VIII-3
Biosparging Evaluation Process Flow Chart

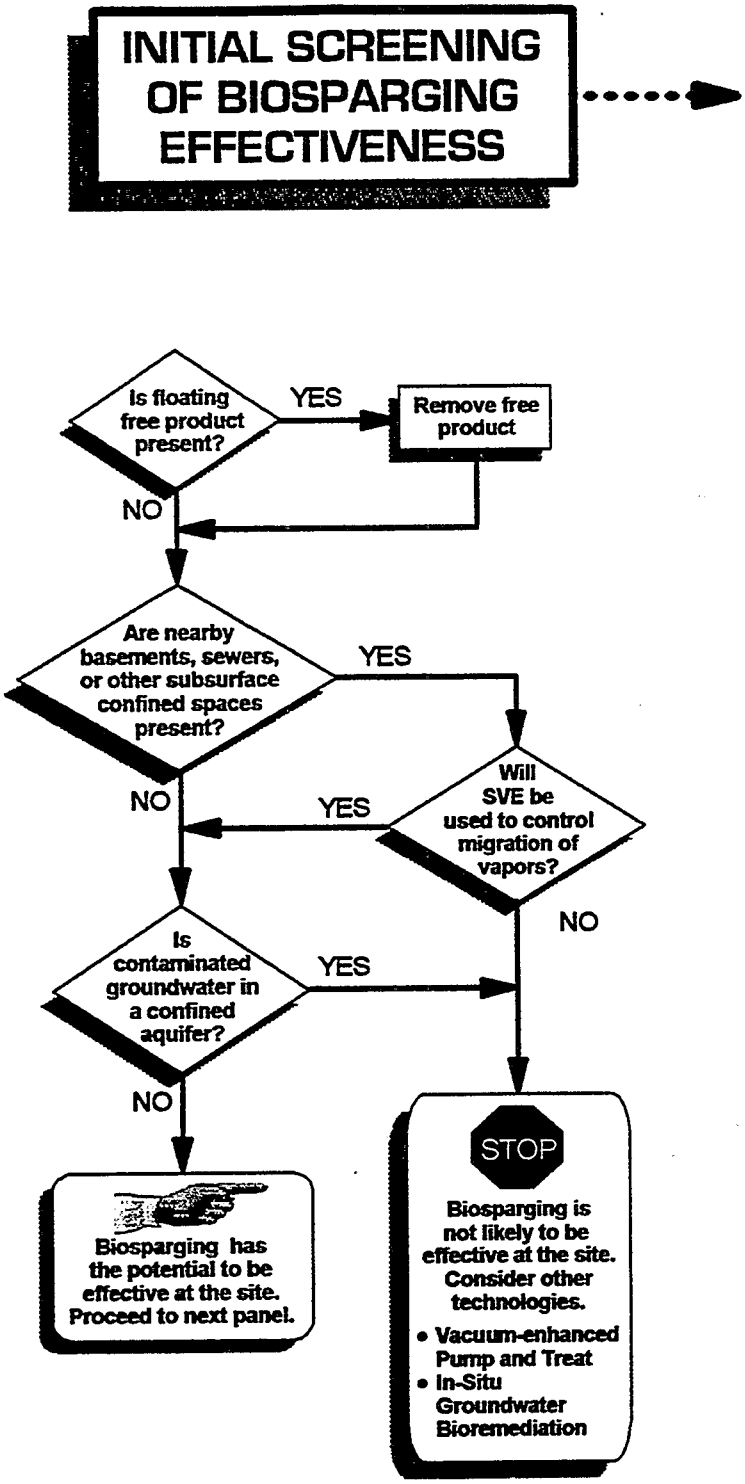


Exhibit VIII-3
Biosparging Evaluation Process Flow Chart

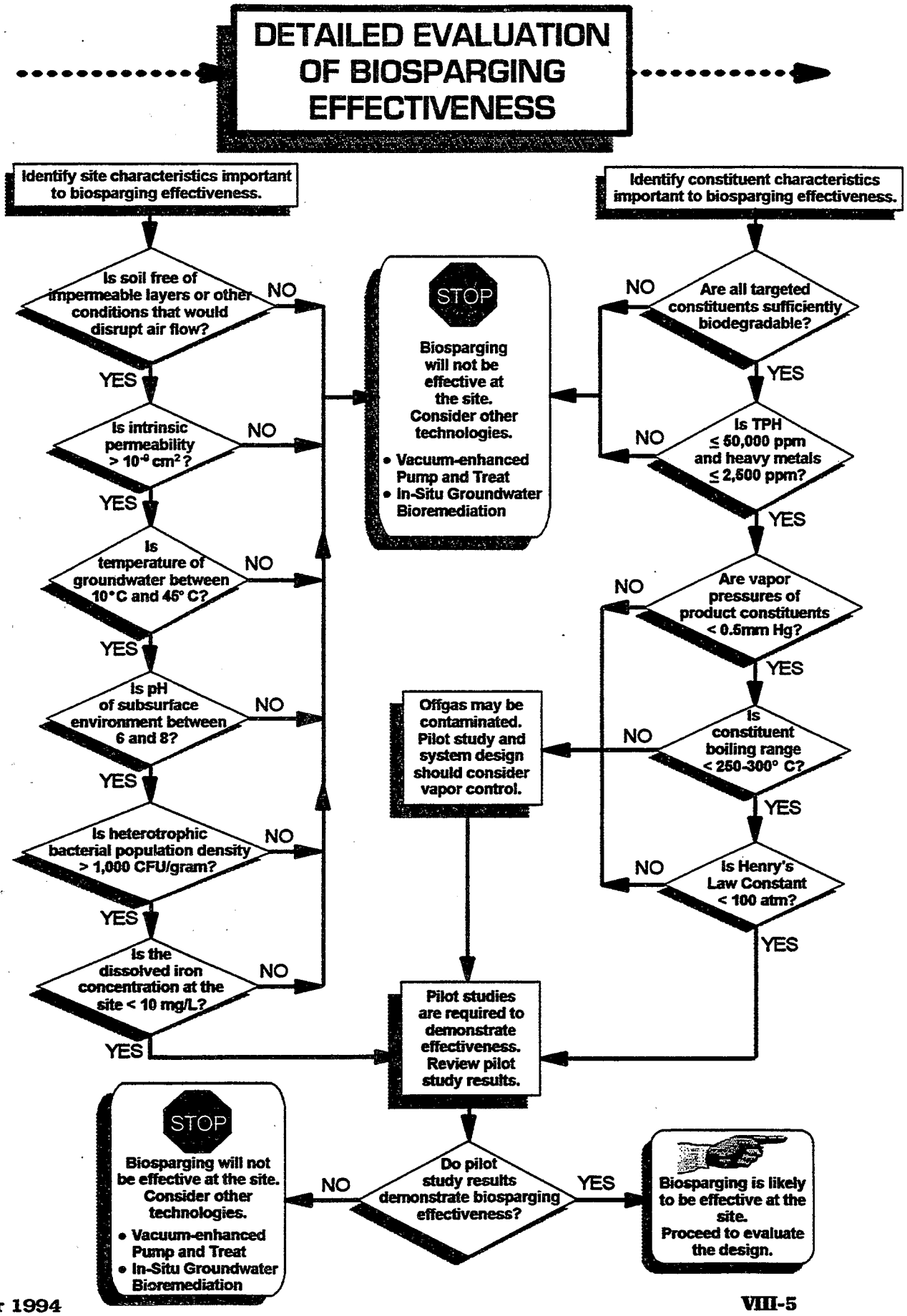
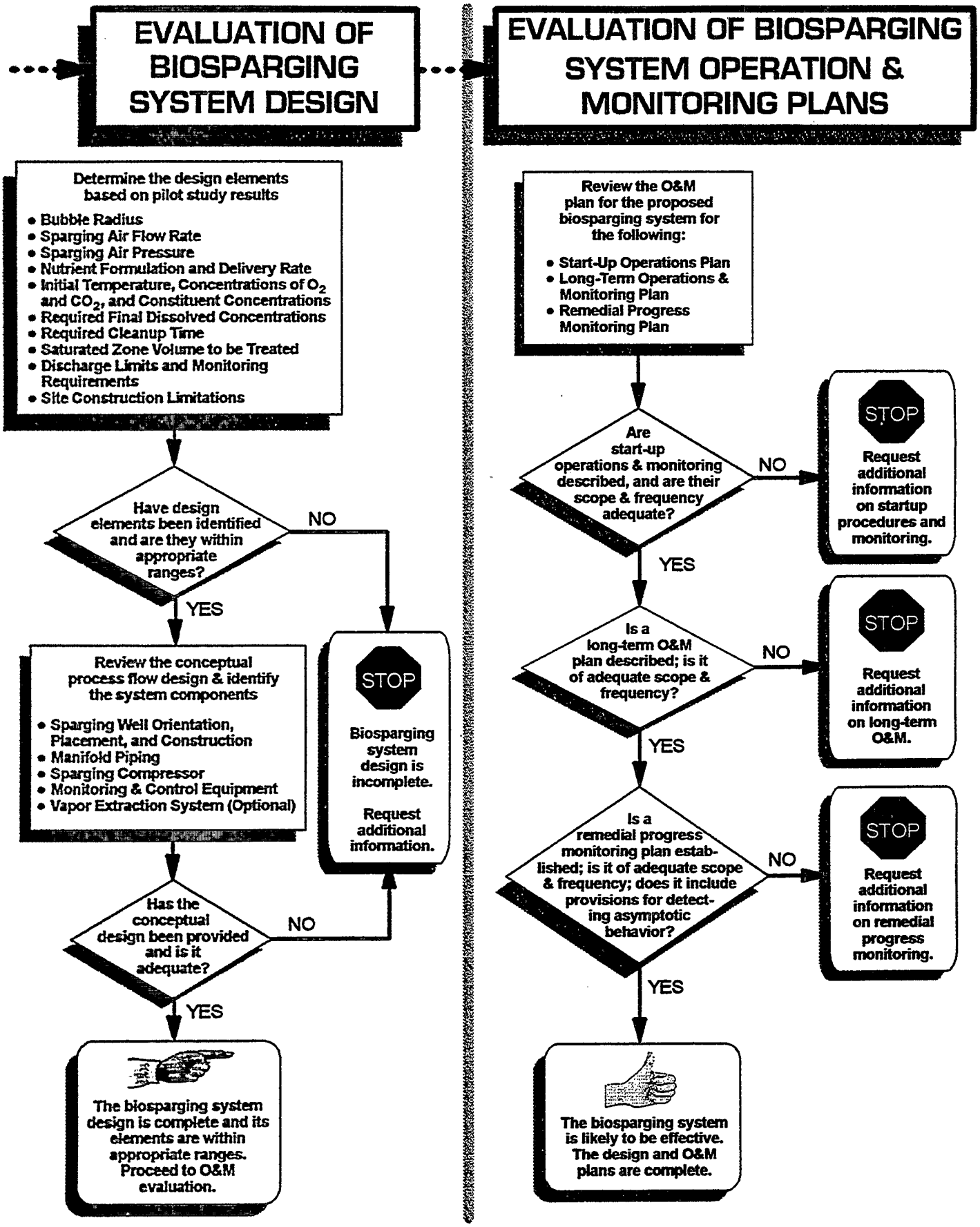


Exhibit VIII-3
Biosparging Evaluation Process Flow Chart



- **Step 3:** ***An evaluation of the biosparging system design*** allows you to determine whether basic design information has been defined, whether necessary design components have been specified, whether construction process flow designs are consistent with standard practice, and if a detailed field pilot scale test has been properly performed.

- **Step 4:** ***An evaluation of the operation and monitoring plans*** allows you to determine whether start-up and long-term system operation and monitoring is of sufficient scope and frequency and whether remedial progress monitoring plans are appropriate.

Initial Screening Of Biosparging Effectiveness

This section allows you to perform an initial screening of whether biosparging will be effective at a site. First, you need to determine whether or not any site-specific factors which could prohibit the use of biosparging are present. Second, you need to determine if the key parameters which contribute to the effectiveness and design are within appropriate ranges for biosparging.

Biosparging should not be used if the following site conditions exist:

- *Free product is present.* Biosparging can create groundwater mounding which could cause free product to migrate and contamination to spread.

- *Basements, sewers, or other subsurface confined spaces are located near the site.* Potentially dangerous constituent concentrations could accumulate in basements and other subsurface confined spaces unless a vapor extraction system is used to control vapor migration.

- *Contaminated groundwater is located in a confined aquifer system.* Biosparging cannot be used to treat groundwater in a confined aquifer because the air sparged into the aquifer would be trapped by the saturated confining layer and could not escape to the unsaturated zone.

The effectiveness of biosparging depends primarily on two factors:

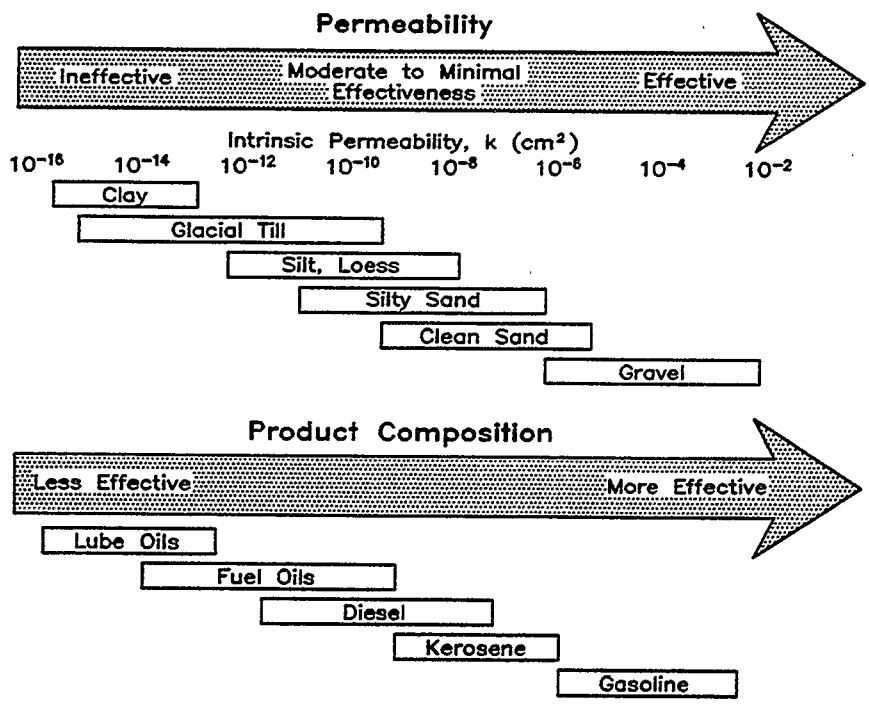
- The *permeability* of the soil which determines the rate at which oxygen can be supplied to the hydrocarbon-degrading microorganisms in the subsurface.

- The *biodegradability* of the petroleum constituents which determines both the rate at which and the degree to which the constituents will be degraded by microorganisms.

In general, the type of soil will determine its *permeability*. Fine-grained soils (e.g., clays and silts) have lower permeabilities than coarse-grained soils (e.g., sands and gravels). The *biodegradability* of a petroleum constituent is a measure of its ability to be metabolized by hydrocarbon-degrading bacteria or other microorganisms. Petroleum constituents are generally biodegradable, regardless of their molecular weight, as long as indigenous microorganisms have an adequate supply of oxygen and nutrients. For heavier constituents (which are generally less volatile and less soluble than lighter constituents), biodegradation will exceed volatilization as the primary removal mechanism, even though biodegradation is generally slower for heavier constituents than for lighter constituents.

Exhibit VIII-4 is an initial screening tool that you can use to help assess the potential effectiveness of biosparging for a given site. To use this tool, first determine the type of soil present and the type of petroleum product released at the site. Information provided in the following section will allow a more thorough evaluation of effectiveness and will identify areas that could require special design considerations.

Exhibit VIII-4
Initial Screening For Biosparging Effectiveness



Note:
All petroleum products listed are amenable for the biosparging remediation alternative.

Detailed Evaluation Of Biosparging Effectiveness

Once you have completed the initial screening and determined that biosparging may be effective for the soils and petroleum product present, evaluate the CAP further to confirm that biosparging will be effective.

While the initial screen focused on soil permeability and constituent biodegradability, the detailed evaluation should consider a broader range of site and constituent characteristics, which are listed in Exhibit VIII-5.

Exhibit VIII-5
Key Parameters Used To Evaluate The Suitability Of Biosparging

Site Characteristics	Constituent Characteristics
Intrinsic permeability	Chemical structure
Soil structure and stratification	Concentration and toxicity
Temperature	Vapor pressure
pH	Product composition and boiling point
Microbial population density	Henry's law constant
Nutrient concentrations	
Dissolved iron concentration	

The remainder of this section describes each parameter, why it is important to biosparging, how it can be determined, and its range for effective biosparging. If a vapor extraction system is considered for vapor control requirements, additional factors such as depth to groundwater and moisture content of the unsaturated zone should be examined to determine if vapor extraction is suitable. See Chapter II: Soil Vapor Extraction for the evaluation of the vapor extraction component, if used.

Site Characteristics That Affect Biosparging

Intrinsic Permeability

Intrinsic permeability is a measure of the ability of soil to transmit fluids and is the *single most important characteristic of the soil* in determining the effectiveness of biosparging because it controls how well oxygen can be delivered to the subsurface microorganisms. Aerobic hydrocarbon-degrading bacteria use oxygen to metabolize organic material to yield carbon dioxide and water. To degrade large amounts of a petroleum product, a substantial bacterial population is required which, in turn, requires oxygen for both metabolic processes and an increase in the overall bacterial population. Approximately 3 to 3½ pounds of oxygen are needed to degrade one pound of petroleum product.

Intrinsic permeability varies over 13 orders of magnitude (from 10^{-16} to 10^{-3} cm^2) for the wide range of earth materials, although a more limited range applies to most soil types (10^{-13} to 10^{-5} cm^2). Intrinsic permeability of the saturated zone for biosparging is best determined from field tests, but it can also be estimated from soil boring logs and laboratory tests. Procedures for these tests are described in EPA (1991a). Coarse-grained soils (e.g., sands) have greater intrinsic permeability than fine-grained soils (e.g., clays and silts). Use the values shown in Exhibit VIII-6 to determine if the intrinsic permeability of the soils at the site are within the range of effectiveness for biosparging.

Exhibit VIII-6
Intrinsic Permeability And Biosparging Effectiveness

Intrinsic Permeability (k)(cm^2)	Biosparging Effectiveness
$k > 10^{-9}$	Generally effective.
$10^{-9} \geq k \geq 10^{-10}$	May be effective; needs further evaluation.
$k < 10^{-10}$	Marginal effectiveness to ineffective.

Intrinsic permeability of saturated-zone soils is usually determined in the field by aquifer pump tests that measure hydraulic conductivity. You can convert hydraulic conductivity to intrinsic permeability using the following equation:

$$k = K\ (\mu/\rho g)$$

where:
- k = intrinsic permeability (cm^2)
- K = hydraulic conductivity (cm/sec)
- μ = water viscosity (g/cm · sec)
- ρ = water density (g/cm^3)
- g = acceleration due to gravity (cm/sec^2)

At 20°C: $\mu/\rho g = 1.02 \cdot 10^{-5}$ cm/sec

Convert k from cm^2 to darcy, multiply by 10^8.

Intrinsic permeability of the unsaturated zone can be estimated from the intrinsic permeability of the saturated zone if similar soil types are present. Alternatively, it can be determined in the field by conducting permeability tests or soil vapor extraction pilot studies. (See Chapter II: Soil Vapor Extraction.)

Soil Structure And Stratification

The types of soil present and their micro- and macro-structures will control the biosparging pressure and distribution of oxygen and nutrients in the saturated zone. For example, fine-grained soils require higher sparging air pressures because air flow is restricted through smaller pores, thereby reducing the efficiency of oxygen distribution. In general, air injection rates used in biosparging are low enough that vapor migration is not a major concern. However, this rate must be assessed on a site-by-site basis.

Soil characteristics also determine the preferred zones of vapor flow in the unsaturated zone, thereby indicating the ease with which vapors can be controlled and extracted (if vapor extraction is used). Stratified or highly variable heterogeneous soils typically create the greatest impediments to biosparging. Both the injected air and the stripped vapors will travel along the paths of least resistance (coarse-grained zones) and could travel a great lateral distance from the injection point. This phenomenon could result in enhanced migration of constituents.

Information about soil type, structure, and stratification can be determined from boring logs or geologic cross-section maps. You should verify that soil types have been identified and that visual observations of soil structure have been documented.

Temperature Of The Groundwater

Bacterial growth rate is a function of temperature. Subsurface microbial activity has been shown to decrease significantly at temperatures below 10°C and essentially to cease below 5°C. Microbial activity of most bacterial species important to petroleum hydrocarbon biodegradation also diminishes at temperatures greater than 45°C. Within the range of 10°C to 45°C, the rate of microbial activity typically doubles for every 10°C rise in temperature. In most cases, because biosparging is an in-situ technology, the bacteria are likely to experience stable groundwater temperatures with only slight seasonal variations. In most areas of the U.S., the average groundwater temperature is about 13°C, but groundwater temperatures may be somewhat lower or higher in the extreme northern and southern states.

pH Levels

The optimum pH for bacterial growth is approximately 7; the acceptable range for biosparging is between 6 and 8. If the groundwater pH is outside of this range, it is possible to adjust the pH prior to and during biosparging operations. However, pH adjustment is often not cost-effective because natural buffering capacity of the groundwater system generally necessitates continuous adjustment and monitoring throughout the biosparging operation. In addition, efforts to adjust pH

may lead to rapid changes in pH, which are also detrimental to bacterial activity.

Microbial Population Density

Soil normally contains large numbers of diverse microorganisms including bacteria, algae, fungi, protozoa, and actinomycetes. Of these organisms, the bacteria are the most numerous and biochemically active group, particularly at low oxygen levels. Bacteria require a carbon source for cell growth and an energy source to sustain metabolic functions required for growth. Nutrients, including nitrogen and phosphorus, are also required for cell growth. The metabolic process used by bacteria to produce energy requires a terminal electron acceptor (TEA) to enzymatically oxidize the carbon source to carbon dioxide.

Microbes are classified by the carbon and TEA sources they use to carry out metabolic processes. Bacteria that use organic compounds (such as petroleum constituents and other naturally occurring organics) as their source of carbon are *heterotrophic*; those that use inorganic carbon compounds such as carbon dioxide are *autotrophic*. Bacteria that use oxygen as their TEA are *aerobic*; those that use a compound other than oxygen (e.g., nitrate or sulfate) are *anaerobic*; and those that can utilize both oxygen and other compounds as TEAs are *facultative*. For biosparging applications directed at petroleum products, bacteria that are both *aerobic* (or *facultative*) and *heterotrophic* are most important in the degradation process.

To evaluate the presence and population density of naturally occurring bacteria that will contribute to degradation of petroleum constituents, laboratory analysis of soil samples from the site (collected from below the water table) should be conducted. These analyses, at a minimum, should include plate counts for total heterotrophic bacteria. Plate count results are normally reported in terms of colony-forming units (CFUs) per gram of soil. Microbial population densities in typical soils range from 10^4 to 10^7 CFU/gram of soil. For biosparging to be effective, the minimum heterotrophic plate count should be 10^3 CFU/gram or greater. Plate counts lower than 10^3 could indicate the presence of toxic concentrations of organic or inorganic (e.g., metals) compounds. These conditions are summarized in Exhibit VIII-7.

Even when plate counts are lower than 10^3, biosparging may still be effective if the soil is conditioned or amended to reduce the toxic concentrations and increase the microbial population density. More elaborate laboratory tests are sometimes conducted to identify the bacterial species present. Such tests may be desirable if you are uncertain whether or not microbes capable of degrading specific petroleum hydrocarbons occur naturally in the soil. If insufficient numbers or types of microorganisms are present, the population density may be increased by introducing cultured microbes that are available from numerous vendors. These conditions are summarized in Exhibit VIII-7.

Exhibit VIII-7
Heterotrophic Bacteria And Biosparging Effectiveness

Total Heterotrophic Bacteria (prior to biosparging)	Biosparging Effectiveness
> 1,000 CFU/gram dry soil	Generally effective.
< 1,000 CFU/gram dry soil	May be effective; needs further evaluation to determine if toxic conditions are present.

Nutrient Concentrations

Bacteria require inorganic nutrients such as nitrogen and phosphate to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in the aquifer but, more frequently, nutrients need to be added to maintain adequate bacterial populations. However, excessive amounts of certain nutrients (i.e., phosphate and sulfate) can repress metabolism.

A rough approximation of minimum nutrient requirements can be based on the stoichiometry of the overall biodegradation process:

$$\text{C-source} + \text{N-source} + O_2 + \text{Minerals} + \text{Nutrients} \longrightarrow$$
$$\text{Cell mass} + CO_2 + H_2O + \text{other metabolic by-products}$$

Different empirical formulas of bacterial cell mass have been proposed; the most widely accepted are $C_5H_7O_2N$ and $C_{60}H_{87}O_{32}N_{12}P$. Using the empirical formulas for cell biomass and other assumptions, the carbon:nitrogen:phosphorus ratios necessary to enhance biodegradation fall in the range of 100:10:1 to 100:1:0.5, depending on the constituents and bacteria involved in the biodegradation process.

Chemical analyses of soil samples from the site (collected from below the water table) should be completed to determine the available concentrations of nitrogen (expressed as ammonia) and phosphate that are naturally in the soil. These types of analyses are routinely conducted in agronomic laboratories that test soil fertility for farmers. Using the stoichiometric ratios, the need for nutrient addition can be determined by using an average concentration of the constituents (carbon source) in the soils to be treated. If nitrogen addition is necessary, slow release sources should be used. Nitrogen addition can lower pH, depending on the amount and type of nitrogen added.

Iron Concentration Dissolved In Groundwater

The presence of dissolved ferrous iron (Fe^{+2}) in groundwater can reduce the permeability of the saturated zone soils during the sparging operations. When dissolved iron is exposed to oxygen, it is oxidized to ferric iron (Fe^{+3}) oxide which, because it is less soluble than ferrous iron,

can precipitate within the saturated zone and occlude soil pore space. On a large scale this could reduce the region available for air (and groundwater) flow, thereby reducing permeability. Precipitation of iron oxide occurs predominantly in the saturated zone near sparging well screens where oxygen content (from injected air) is the highest. This oxidation can render sparging wells useless after even short periods of operation; installation of new wells in different locations would then be required.

Verify that laboratory measurements of total dissolved iron have been completed for groundwater samples from the site. Use Exhibit VIII-8 to determine the range in which dissolved iron is a concern for biosparging effectiveness.

Exhibit VIII-8
Dissolved Iron And Biosparging Effectiveness

Dissolved Iron Concentration (mg/L)	Biosparging Effectiveness
$Fe^{+2} < 10$	Biosparging effective.
$10 \leq Fe^{+2} \leq 20$	Sparging wells require periodic testing and may need periodic replacement.
$Fe^{+2} > 20$	Biosparging not recommended.

Constituent Characteristics That Affect Biosparging

Chemical Structure

The chemical structures of the constituents to be treated by biosparging are important for determining the rate at which biodegradation will occur. Although nearly all constituents in petroleum products typically found at UST sites are biodegradable, the more complex the molecular structure of the constituent, the more difficult and less rapid is biological treatment. Most low-molecular-weight (nine carbon atoms or less) aliphatic and monoaromatic constituents are more easily biodegraded than higher-molecular-weight aliphatic or polyaromatic organic constituents. Exhibit VIII-9 lists, in order of decreasing rate of potential biodegradability, some common constituents found at petroleum UST sites.

Evaluation of the chemical structure of the constituents proposed for reduction by biosparging at the site will allow you to determine which constituents will be the most difficult to degrade. You should verify that remedial time estimates, biotreatability studies, field-pilot studies (if applicable), and biosparging operation and monitoring plans are based on the constituents that are the most difficult to degrade (or "rate limiting") in the biodegradation process.

Exhibit VIII-9
Chemical Structure And Biodegradability

Biodegradability	Example Constituents	Products In Which Constituent Is Typically Found
More degradable	n-butane, l-pentane, n-octane	○ Gasoline
	Nonane	○ Diesel fuel
	Methyl butane, dimethylpentenes, methyloctanes	○ Gasoline
	Benzene, toluene, ethylbenzene, xylenes	○ Gasoline
	Propylbenzenes	○ Diesel, kerosene
	Decanes Dodecanes Tridecanes Tetradecanes	○ Diesel ○ Kerosene ○ Heating fuels ○ Lubricating oils
Less degradable	Naphthalenes Fluoranthenes Pyrenes Acenaphthenes	○ Diesel ○ Kerosene ○ Heating oil ○ Lubricating oils

Concentration And Toxicity

The presence of very high concentrations of petroleum organics or heavy metals in site soils can be toxic or inhibit the growth and reproduction of bacteria responsible for biodegradation. In addition, very low concentrations of organic material will also result in diminished levels of bacterial activity.

In general, concentrations of petroleum hydrocarbons in excess of 50,000 ppm, or heavy metals in excess of 2,500 ppm, in soils are considered inhibitory and/or toxic to aerobic bacteria. Review the CAP to verify that the average concentrations of petroleum hydrocarbons and heavy metals in the soils and groundwater to be treated are below these levels. Exhibit VIII-10 provides the general criteria for constituent concentration and biosparging effectiveness.

In addition to maximum concentrations, you should consider the cleanup concentrations proposed for the treated soils. Below a certain "threshold" constituent concentration, the bacteria cannot obtain sufficient carbon (from degradation of the constituents) to maintain adequate biological activity. The threshold level can be determined from

Exhibit VIII-10
Constituent Concentration And Biosparging Effectiveness

Constituent Concentration	Biosparging Effectiveness
Petroleum constituents ≤ 50,000 ppm and Heavy metals ≤ 2,500 ppm	Effective.
Petroleum constituents > 50,000 ppm or Heavy metals > 2,500 ppm	Ineffective; toxic or inhibitory conditions to bacterial growth exist. Long remediation times likely.

laboratory studies and should be below the level required for cleanup. Although the threshold limit varies greatly depending on bacteria-specific and constituent-specific features, constituent concentrations below 0.1 ppm are generally not achievable by biological treatment alone. In addition, experience has shown that reductions in total petroleum hydrocarbon concentrations (TPH) greater than 95 percent can be very difficult to achieve because of the presence of "recalcitrant" or nondegradable petroleum hydrocarbons that are included in the TPH analysis. Identify the average starting concentrations and the cleanup concentrations in the CAP for individual constituents and TPH. If a cleanup level lower than 0.1 ppm is required for any individual constituent or a reduction in TPH greater than 95 percent is required to reach the cleanup level for TPH, either a pilot study should be required to demonstrate the ability of biosparging to achieve these reductions at the site or another technology should be considered. These conditions are summarized in Exhibit VIII-11.

Exhibit VIII-11
Cleanup Concentrations And Biosparging Effectiveness

Cleanup Requirement	Biosparging Effectiveness
Constituent concentration > 0.1 ppm and TPH reduction < 95%	Effective.
Constituent concentration ≤ 0.1 ppm or TPH reduction ≥ 95%	Potentially ineffective; pilot studies are required to demonstrate reductions.

Vapor Pressure

Vapor pressure is important in evaluating the extent to which constituents will be volatilized rather than biodegraded. The vapor pressure of a constituent is a measure of its tendency to evaporate. More precisely, it is the pressure that a vapor exerts when in equilibrium with its pure liquid or solid form. Constituents with higher vapor pressures are generally volatilized rather than biodegraded. In general, constituents with vapor pressures higher than 0.5 mm Hg will likely be volatilized by the induced air stream before they biodegrade. Constituents with vapor pressures lower than 0.5 mm Hg will not volatilize to a significant degree and can instead undergo *in situ* biodegradation by bacteria.

As previously discussed, petroleum products contain many different chemical constituents. Each constituent will be volatilized (rather than biodegraded) to different degrees by a biosparging system, depending on its vapor pressure. If concentrations of volatile constituents are significant, use of a vapor extraction system and treatment of extracted vapors may be needed. Exhibit VIII-12 lists vapor pressures of select petroleum constituents.

Exhibit VIII-12
Vapor Pressures Of Common Petroleum Constituents

Constituent	Vapor Pressure (mm Hg at 20°C)
Methyl t-butyl ether	245
Benzene	76
Toluene	22
Ethylene dibromide	11
Ethylbenzene	7
Xylenes	6
Naphthalene	0.5
Tetraethyl lead	0.2

Product Composition And Boiling Point

Boiling point is another measure of constituent volatility. Because of their complex constituent compositions, petroleum products are often classified by their boiling point ranges (rather than vapor pressures). In general, nearly all petroleum-derived organic compounds are capable of biological degradation, although constituents of higher molecular weights and higher boiling points require longer periods of time to be degraded. Products with boiling points of less than about 250°C to 300°C will volatilize to some extent and can be removed by a

combination of volatilization and biodegradation in a biosparging system. The boiling point ranges for common petroleum products are shown in Exhibit VIII-13.

Exhibit VIII-13
Petroleum Product Boiling Ranges

Product	Boiling Range (°C)
Gasoline	40 to 225
Kerosene	180 to 300
Diesel fuel	200 to 338
Heating oil	> 275
Lubricating oils	Nonvolatile

Henry's Law Constant

Another method of gauging the volatility of a constituent is by noting its Henry's law constant, which quantifies the relative tendency of a dissolved constituent to transfer to the vapor phase. Henry's law states that, for ideal gases and solutions under equilibrium conditions, the ratio of the partial pressure of a constituent in the vapor phase to the concentration in the dissolved phase is constant. That is:

$$P_a = H_a X_a$$

where: P_a = partial pressure of constituent a in air
H_a = Henry's law constant (atm)
X_a = solution concentration of constituent a (mole fraction)

Henry's law constants for several common constituents found in petroleum products are shown in Exhibit VIII-14. Constituents with Henry's law constants of greater than 100 atmospheres are generally considered volatile and, hence, more likely to be volatilized rather than biodegraded.

Laboratory Treatability And Field Pilot Scale Studies

In general, remedial approaches that rely on biological processes should be subjected to laboratory treatability tests and field pilot studies to verify and quantify the potential effectiveness of the approach and provide data necessary to design the system. However, field tests of biosparging should never be conducted if free product is known to exist at the water table, if uncontrolled vapors could migrate into nearby confined spaces (e.g., sewers, basements) or if the contaminated

Exhibit VIII-14
Henry's Law Constant Of Common Petroleum Constituents

Constituent	Henry's Law Constant (atm)
Tetraethyl lead	4,700
Ethylbenzene	359
Xylenes	266
Benzene	230
Toluene	217
Naphthalene	72
Ethylene dibromide	34
Methyl t-butyl ether	27

groundwater is in a confined aquifer. The scope of laboratory studies or pilot testing should be commensurate with the size of the area to be treated, the reduction in constituent concentrations required, and the results of the initial effectiveness screening.

Some commonly used laboratory and pilot-scale studies are described below.

- *Laboratory Microbial Screening* tests are used to determine the presence of a population of naturally occurring bacteria that may be capable of degrading petroleum product constituents. Samples of soils from the aquifer are analyzed in an offsite laboratory. Microbial plate counts determine the number of colony forming units (CFU) of heterotrophic bacteria and petroleum-degrading bacteria present per unit mass of dry soil. These tests are relatively inexpensive.

- *Laboratory Biodegradation Studies* can be used to estimate the rate of oxygen delivery and to determine if the addition of inorganic nutrients is necessary. However, laboratory studies cannot duplicate field conditions, and field tests are more reliable. A common biodegradation study for biosparging is the slurry study. Slurry studies involve the preparation of numerous "soil microcosms" consisting of small samples of site soils from the aquifer mixed into a slurry with the site groundwater. The microcosms are divided into several groups which may include control groups which are sterilized to destroy any bacteria, non-nutrified test groups which have been provided oxygen but not nutrients, and nutrified test groups which are supplied both oxygen and nutrients. Microcosms from each group are analyzed periodically (usually weekly) during the test period (usually 4 to 12 weeks) for bacterial population counts and constituent concentrations. Results of slurry studies should be

considered as representing optimal conditions because slurry microcosms do not consider the effects of limited oxygen delivery or soil heterogeneity.

- *Field Biosparging Treatability Tests* determine the effectiveness of biosparging by characterizing the rate of biodegradation, the "bubble" radius, and the potential for plume migration. Data collected from the studies are used to specify design parameters such as the number and density of the wells and the sparging rate. The study usually includes sparging a single well while its effects are being measured in monitoring wells or probes spaced at various distances. Ideally, three or more monitoring wells surrounding the plume should be installed. These monitoring wells should be screened above the saturated zone and through the dissolved phase plume. They can be used to monitor both dissolved and vapor phase migration, to monitor changes in dissolved oxygen, and to measure changes in the depth to groundwater.

  If vapor extraction is to be included in the design, the pilot study should be accomplished in two parts. The first portion of the test should be conducted using vapor extraction only and evaluated as described in Chapter II (Soil Vapor Extraction) without the biosparging system being operated. This portion of the pilot test will establish the baseline vapor extraction levels, the extent of the non-sparged vapor plume, the extraction well radius of influence and intrinsic permeability of the unsaturated zone (discussed in Chapter II). The second portion of the study would involve the installation of a sparge point with several vapor extraction points in the vadose zone. Exhibit VIII-15 summarizes the parameters and data that would be useful in a biosparging pilot study.

Evaluation Of The Biosparging System Design

Once you have verified that biosparging has the potential for effectiveness at your site, you can evaluate the design of the system. The CAP should include a discussion of the rationale for the system design and the results of the pilot test(s). Detailed engineering design documents might also be included, depending on individual state requirements. Further detail about information to look for in the discussion of the biosparging design is provided at the end of this chapter. Discussion of the vapor extraction portion of the design is included in Chapter II: Soil Vapor Extraction.

Exhibit VIII-15
Pilot Test Data Objectives

Data Requirement	Source
Vapor Extraction Test Portion (if necessary)	
Extraction well radius of influence (ROI)	Monitoring point pressure gauges
Wellhead and monitoring point vacuum	Well-head pressure gauge
Initial contaminant vapor and CO_2 concentrations	Vapor extraction exhaust flame ionization detector (FID) readings and CO_2 probe (or other suitable detection device)
Initial hydraulic gradient	Water level tape at monitoring wells or pressure transducers and data logger
Biosparging Test Portion	
Air sparging bubble radius	Monitoring point pressure gauge
Sparging rate	Compressor discharge flow gauge
Sparging vapor concentrations	Monitoring well and vapor point FID readings (or other suitable detection device)
CO_2 level in the exhaust vapors	Carbon dioxide probe
Hydraulic gradient influence	Water level tape at monitoring wells or pressure transducers and data logger
Dissolved oxygen and carbon dioxide	Dissolved oxygen and carbon dioxide probes at monitoring wells
Combined Test (if necessary)	
Sparging/SVE capture rates	Pressure/flow gauges
Contaminant vapor concentrations	Blower discharge and monitoring points

Rationale For The Design

The following factors should be considered as you evaluate the design of the biosparging system in the CAP.

- *Bubble radius* for sparging wells. The bubble radius should be considered in the design of the biosparging system. The bubble radius is defined as the greatest distance from a sparging well at which sufficient sparge pressure and airflow can be induced to enhance the biodegradation of contaminants. The bubble radius will determine the number and spacing of the sparging wells.

  The bubble radius should be determined based on the results of pilot tests. One should be careful, however, when evaluating pilot test results. The measurement of air flow, increased dissolved oxygen, or the presence of air bubbles in a monitoring point can be falsely

interpreted as an air flow zone that is thoroughly permeated with injected air when these observations actually represent localized sparging around sparsely distributed air flow channels. The bubble radius depends primarily on the hydraulic conductivity of the aquifer material in which sparging takes place. Other factors that affect the bubble radius include soil heterogeneities and differences between lateral and vertical permeability of the soils. Generally, the design bubble radius can range from 5 feet for fine-grained soils to 100 feet for coarse-grained soils.

- *Sparging Air Flow Rate.* The sparging air flow rate required to provide sufficient air flow to enhance biological activity is site specific and will be determined via the pilot test. Typical air flow rates are much lower than for air sparging, ranging from 3 to 25 standard cubic feet per minute (scfm) per injection well. Pulsing of the air flow (i.e., turning the system on and off at specified intervals) may provide better distribution and mixing of the air in the contaminated saturated zone, thereby allowing for greater contact with the dissolved phase contaminants. If a vapor extraction system is used, it should have a greater flow capacity and greater area of influence than the biosparging system. Typically the SVE extraction rates range from 1.25 to 5 times greater than the biosparging rate.

- *Sparging Air Pressure* is the pressure at which air is injected below the water table. Injection of air below the water table requires pressure greater than the static water pressure (1 psig for every 2.3 ft of hydraulic head) and the head necessary to overcome capillary forces of the water in the soil pores near the injection point. A typical system will be operated at approximately 10 to 15 psig. Excessive pressure may cause fracturing of the soils and create permanent air channels that can significantly reduce biosparging effectiveness.

- *Nutrient Formulation and Delivery Rate* (if needed) will be based on the results of the laboratory tests and pilot study results. Common nutrient additions include nitrogen (in an aqueous solution containing ammonium ions) and phosphorus (in an aqueous solution containing phosphate ions). Note that state regulations may either require permits for nutrient injection or prohibit them entirely.

- *Initial Constituent Concentrations* will be measured during pilot-scale studies. They establish a baseline for estimating the constituent mass removal rate and the system operation time requirements. In addition, they will help to determine whether vapor treatment will be required.

- *Initial Concentrations of Oxygen and* CO_2 in the saturated zone will be measured during pilot studies. They are used to establish system operating requirements, to provide baseline levels of subsurface biological activity, and to allow measurement of the system's progress.

- *Required Final Dissolved Constituent Concentrations* in the saturated zone are either defined by state regulations as "remedial action levels" or determined on a site-specific basis using transport models and risk assessment calculations. They will determine which areas of the site require treatment and when biosparging system operations can be terminated.

- *Required Remedial Cleanup Time* may influence the design of the system. The designer may vary the spacing of the sparging wells to speed remediation to meet cleanup deadlines, if required.

- *Saturated Zone Volume To Be Treated* is determined by state action levels or a site-specific risk assessment using site characterization data for the groundwater.

- *Discharge Limitations and Monitoring Requirements* are usually established by state regulations but must be considered by system designers to ensure that monitoring ports are included in the system. Discharge limitations imposed by state air quality regulations will determine whether offgas treatment is required.

- *Site Construction Limitations* (e.g., building locations, utilities, buried objects, residences) must be identified and considered in the design process.

Components Of A Biosparging System

Once the design rationale is defined, the design of the biosparging system can be developed. A typical biosparging system design includes the following components and information:

- Sparging well orientation, placement, and construction details
- Manifold piping
- Compressed air equipment
- Monitoring and control equipment

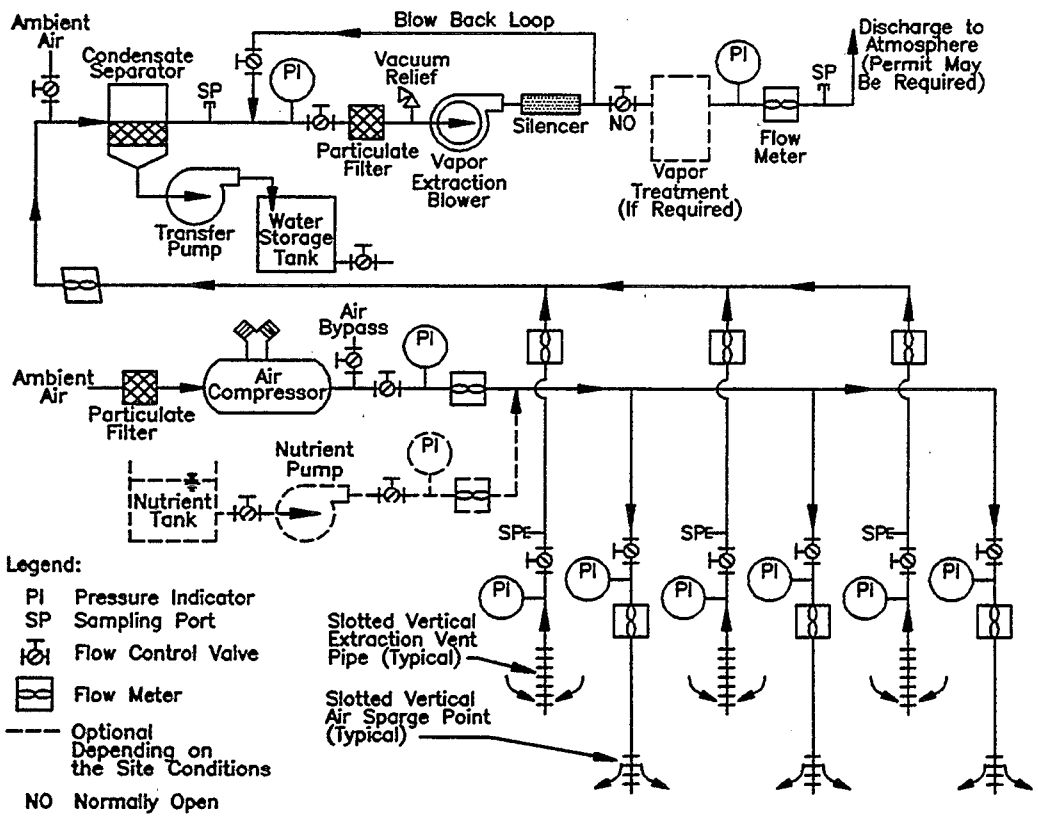
A nutrient delivery system is sometimes included in biosparging design. If nutrients are added, the design should specify the type of nutrient addition and the construction details. Note that state regulations may either require permits for nutrient injection wells or prohibit them entirely.

If an SVE system is used for vapor control, the following components and information will also be needed:

- Vapor pretreatment design
- Vapor treatment system selection
- Blower specification

Exhibit VIII-16 provides a schematic diagram of a typical biosparging system used with vapor extraction. Chapter II: Soil Vapor Extraction, should be consulted for information on the design of the vapor extraction portion of the remedial system (if necessary), including vapor pretreatment design, vapor treatment system selection, and blower specification.

Exhibit VIII-16
Schematic Of Biosparging System Used With Vapor Extraction



Sparge And Extraction Wells

Well Orientation. A biosparging system can use either vertical or horizontal sparge wells. Well orientation should be based on site-specific needs and conditions. For example, horizontal systems should be considered when evaluating sites that will require 10 or more sparge or extraction points, if the affected area is located under a surface structure, or if the thickness of the saturated zone is less than 10 feet. Exhibit VIII-17 lists site conditions and the corresponding appropriate well orientation.

Exhibit VIII-17
Well Orientation And Site Conditions

Well Orientation	Site Conditions
Vertical wells	○ Deep contamination (> 25 feet) ○ Depth to groundwater (> 10 feet) ○ Fewer than 10 wells ○ Thickness of saturated zone (> 10 feet)
Horizontal wells	○ Shallow groundwater table (< 25 feet) ○ Zone of contamination within a specific stratigraphic unit ○ System under an operational facility ○ Thickness of saturated zone (< 10 feet)

Well Placement And Number of Wells. Exhibit VIII-18, Biosparging/Vapor Extraction Well Configurations, shows various configurations that can be used in laying out biosparging systems used in conjunction with vapor extraction. The essential goals in configuring the wells and monitoring points are (1) to optimize the influence on the plume, thereby maximizing the treatment efficiency of the system, and (2) to provide optimum monitoring and vapor extraction points to ensure minimal migration of the vapor plume and no undetected migration of either the dissolved phase or vapor phase plumes. In shallow applications, in large plume areas, or in locations under buildings or pavements, horizontal vapor extraction wells are very cost effective and efficient for controlling vapor migration. Exhibit VIII-19 is a typical layout for a system that surrounds and contains a plume and includes sparging wells and vapor extraction wells.

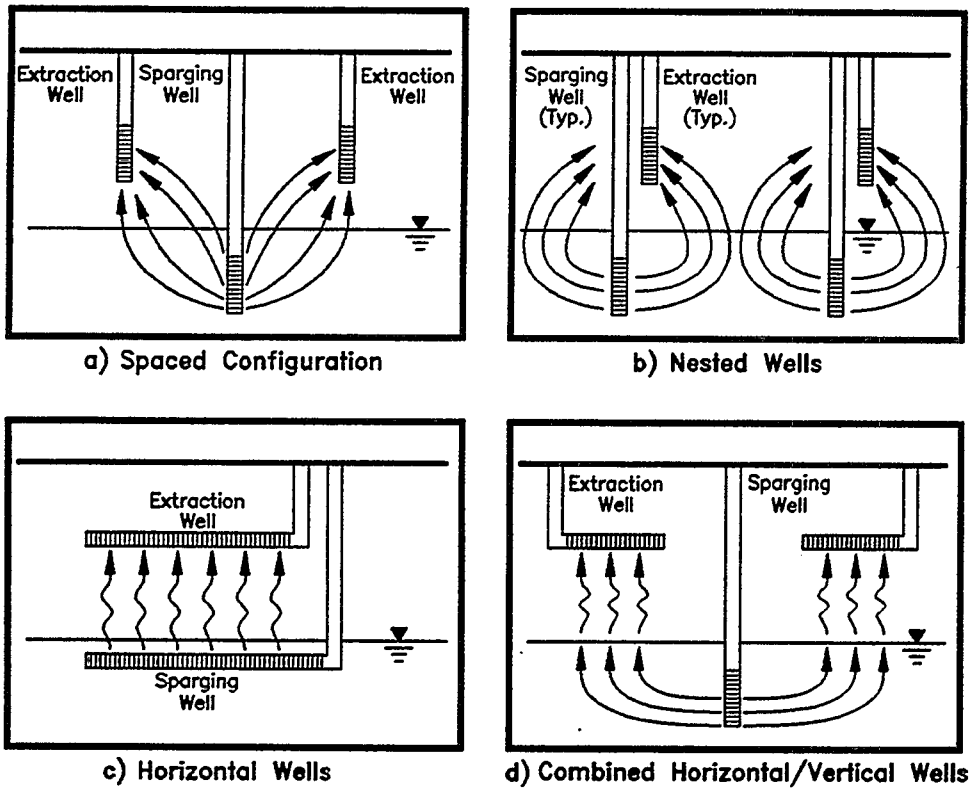
The number and location of extraction wells (if needed) can be determined by using several methods as discussed in Chapter II: Soil Vapor Extraction. However, the following general points should be considered:

- Closer well spacing is often appropriate in areas of high contaminant concentrations in order to enhance air distribution (and oxygen delivery rate), thus increasing the rate of biodegradation.

- If a surface seal exists or is planned for the design, the extraction wells can be spaced slightly farther apart. Surface seals force air to be drawn from a greater distance rather than directly from the surface.

- At sites with stratified soils, wells screened in strata with low permeabilities might require closer well spacing than wells screened in strata with higher permeabilities.

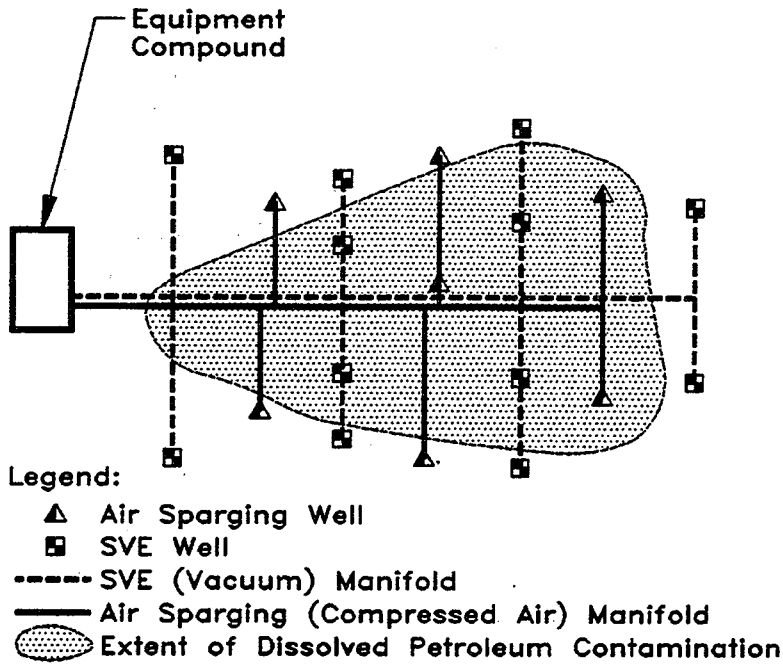
Exhibit VIII-18
Biosparging/Vapor Extraction Well Configurations



Source: "Advances in Air Sparging Design," The Hazardous Waste Consultant, Vol. 11, Issue 1, January/February 1993, p. 1-4.

Well Construction. Sparging wells are generally constructed of 1- to 5-inch PVC, galvanized steel, or stainless steel pipe. The screened interval is normally 1-3 feet in length and is generally set 5-15 feet below the deepest extent of adsorbed contaminants. Setting the screen at a deeper interval requires higher pressures on the system, but generally does not achieve higher sparge rates. Increased screen length will not improve system efficiency because air tends to exit at the top portion of the screen where hydraulic pressure head is lower. Sparge points must be properly grouted to prevent short circuiting of the air. Horizontal injection wells should be designed and installed carefully to ensure that air exits from along the entire screen length. Perforated pipe, rather than well screening, is sometimes preferred for horizontal wells. Exhibits VIII-20 and VIII-21 present typical vertical and horizontal sparging well constructions, respectively.

Exhibit VIII-19
Combined Biosparging/Vapor Extraction System Layout

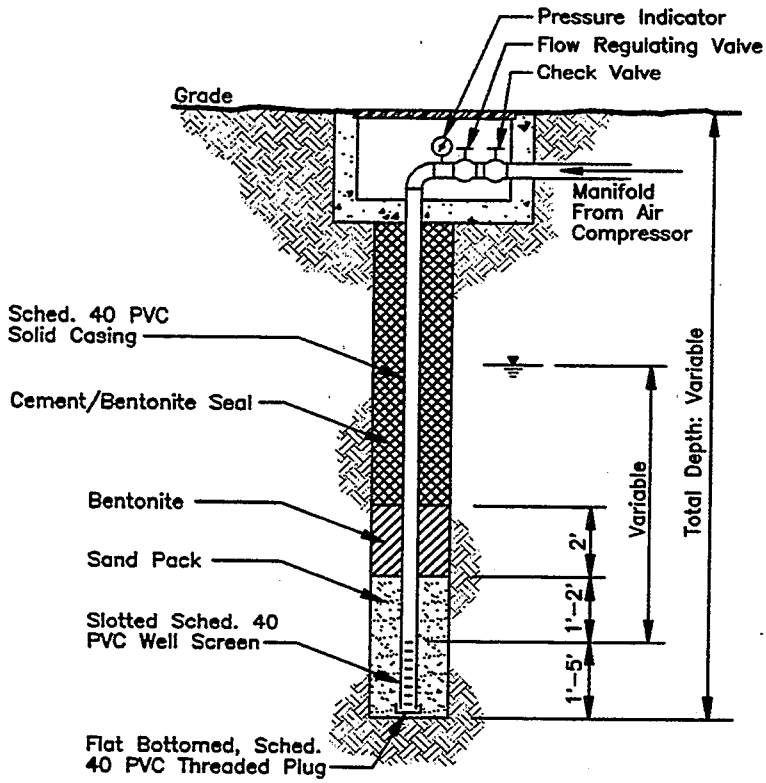


Injection wells should be fitted with check valves to prevent potential line fouling. Fouling occurs when pressure in the saturated zone forces water up the sparge point while the system is shut down. Each sparging well should also be equipped with a pressure gauge and flow regulator to enable adjustments in sparging air distribution. Refer to Chapter II: Soil Vapor Extraction for vapor extraction well details.

Manifold Piping

Manifold piping connects sparging wells to an air compressor. Piping can be placed above or below grade depending on site operations, ambient temperature, and local building codes. Below-grade piping is more common and is installed in shallow utility trenches that lead from the sparging wellhead vault(s) to a central equipment location. The piping can either be manifolded in the equipment area or connected to a common compressor main that supplies the wells in series; in this case, flow control valves are located at the wellhead. Piping to the well locations should be sloped toward the well so that condensate or entrained groundwater will flow back toward the well.

Exhibit VIII-20
Vertical Sparging Well Construction

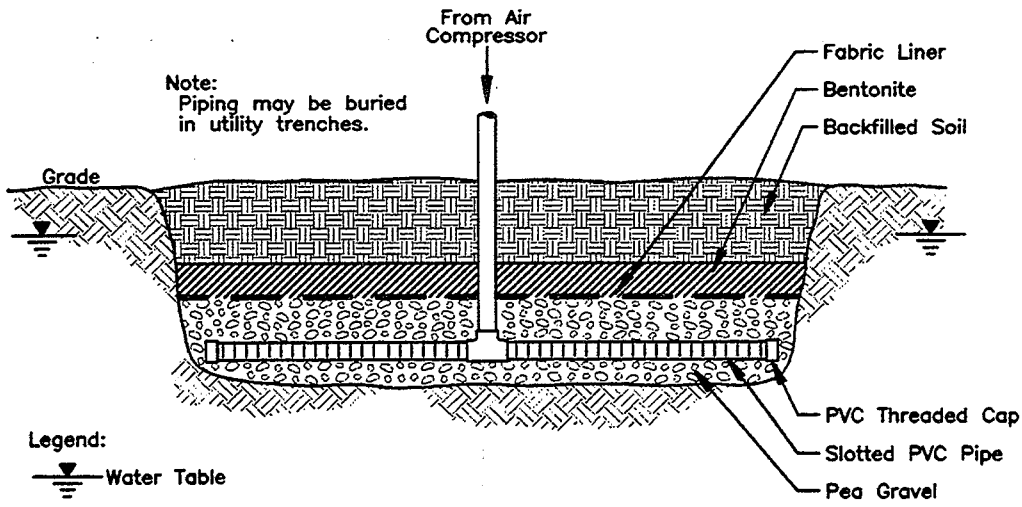


The pressurized air distribution system can be made of metal pipe or rubber-reinforced air hose. PVC pipe should not be connected directly to the compressor because of the high temperatures of air leaving the compressor which can diminish the integrity of the PVC. If pipe trenches are used for the distribution system, they must be sealed to prevent short circuiting of air flow.

Compressed Air Equipment

An oil-free compressor or a standard compressor equipped with downstream coalescing and particulate filters should be used to ensure that no contaminants are injected into the saturated zone. The compressor should be rated for continuous duty at the maximum expected flow rate and pressure to provide adequate flexibility during full operations.

Exhibit VIII-21
Horizontal Sparging Well Construction



Monitoring And Controls

The parameters typically monitored in a sparging system include:

- Pressure
- Air/vapor flow rate
- Carbon dioxide and oxygen concentration in soil vapor and groundwater
- Constituent concentrations in soil vapor and groundwater
- Nutrient delivery rate

The equipment in a sparging system used to monitor these parameters provides the information necessary to make appropriate system adjustments and track remedial progress. The control equipment in a sparging system allows the flow and sparge pressure to be adjusted at each sparging well of the system as necessary. Control equipment typically includes flow control valves or regulators. Exhibit VIII-22 lists typical monitoring and control equipment for a biosparging system, the location for each of these pieces of equipment, and the types of equipment that are available.

Exhibit VIII-22
Monitoring And Control Equipment

Monitoring Equipment	Location In System	Example Of Equipment
Flow meter	○ At each sparge and vapor extraction well head ○ Manifold to blower ○ Stack discharge ○ Nutrient manifold	○ Pitot tube ○ In-line rotameter ○ Orifice plate ○ Venturi or flow tube ○ Turbine wheel
Pressure gauge	○ At each sparge and vapor extraction well head or manifold branch ○ Before blower (before and after filters) ○ Before and after vapor treatment	○ Manometer ○ Magnehelic gauge ○ Vacuum gauge
Sampling port	○ At each vapor extraction well head or manifold branch ○ Manifold to blower ○ Blower discharge	○ Hose barb ○ Septa fitting
Control Equipment		
Flow control valves/ regulators	○ At each vapor extraction well head or manifold branch ○ Dilution or bleed valve at manifold to blower ○ At header to each sparge point	○ Ball valve ○ Gate valve ○ Dilution/ambient air bleed valve ○ Gate valve ○ Dilution/ambient air bleed valve

Evaluation Of Operation And Monitoring Plans

The system operation and monitoring plan should include both system startup and long-term operations. Operations and monitoring are necessary to ensure optimal system performance and to track the rate of contaminant mass removal/reduction.

Startup Operations

The startup phase should begin with only the SVE portion of the system (if used) as described in Chapter II. After the SVE system is adjusted, the air sparging system should be started. Generally, 7 to 10 days of manifold valving adjustments are required to adjust the air sparging system. These adjustments should balance flow to optimize the carbon dioxide production and oxygen uptake rate. Monitoring data should include sparge pressure and flows, vacuum readings for SVE, depth of groundwater, vapor concentrations, dissolved oxygen levels, CO_2 levels, and pH. During the initial start up, these parameters should be monitored hourly once the flow is stabilized. Vapor concentration should also be monitored in any nearby utility lines, basements, or other subsurface confined spaces. Other monitoring of the system should be done in accordance with the SVE requirements from Chapter II.

Long-Term Operations

To evaluate the performance of a biosparging system the following parameters should be monitored weekly to biweekly after the startup operation:

- Contaminant levels, carbon dioxide level, dissolved oxygen level, and pH in the groundwater.
- Contaminant level, oxygen, and carbon dioxide in the effluent stack and the manifold of the SVE system (if used).
- Pressures and flow rates in the sparging wells and, if SVE is used, in the extraction wells.

It should be noted that the samples from the groundwater monitoring wells that will be analyzed to track dissolved contaminant concentrations should be collected after a short period of time following system shutdown. Sampling at these times allows the subsurface environment to reach equilibrium. Samples collected during sparging operations may have lower concentrations of dissolved contaminants than does the surrounding aquifer. This result could lead to the erroneous conclusion that remediation is occurring throughout the aquifer because the monitoring wells may serve as preferential flow paths for the injected air.

Exhibit VIII-23 provides a brief synopsis of system monitoring requirements.

Exhibit VIII-23
System Monitoring Recommendations

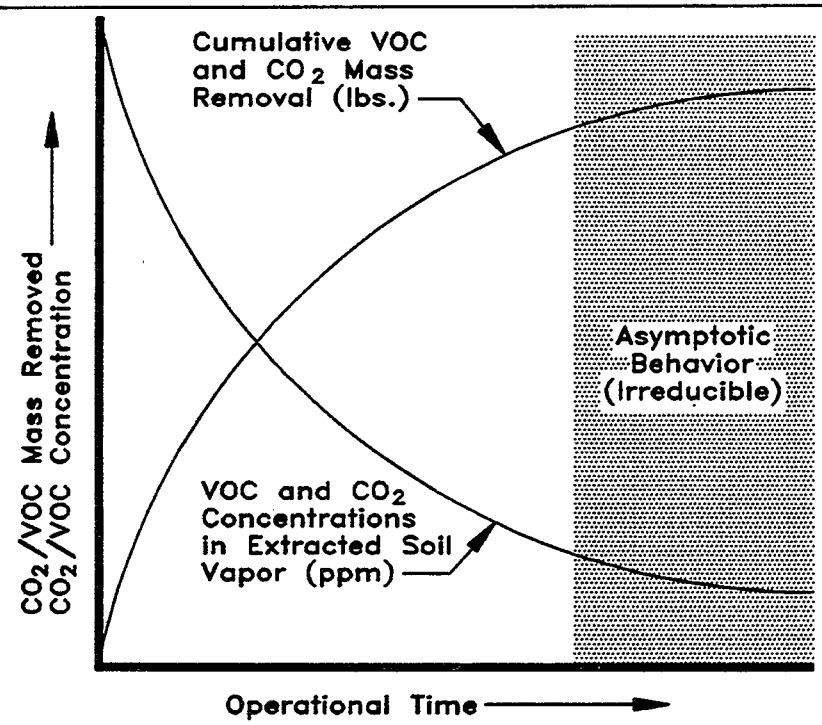
Phase	Monitoring Frequency	What To Monitor	Where To Monitor
Startup (7-10 days)	At least daily	o Sparge pressure o Flow	o Air sparging wellheads o Sparge and extraction wells (if used) o Manifold o Extraction wells (if SVE is used)
		o Vacuum readings (if SVE is used) o D.O., CO_2, pH	o Groundwater and soil vapor monitoring points
		o Depth to groundwater	o Groundwater monitoring wells
Remedial (ongoing)	Weekly to bi-weekly	o Vacuum readings	o Extraction wells (if SVE is used)
		o Vapor concentrations	o Effluent stack (if SVE is used) o Manifold (if SVE is used)
		o Sparge pressure and flow	o Air sparging wellheads
		o D.O., CO_2, pH	o Groundwater and soil vapor monitoring points
	Quarterly to annually	o Dissolved constituent concentrations	o Groundwater monitoring wells

Remedial Progress Monitoring

Monitoring the performance of the biosparging system in reducing contaminant concentrations in the saturated zone is necessary to determine if remedial progress is proceeding at a reasonable pace. A variety of methods can be used. One method includes monitoring contaminant levels in the groundwater in monitoring wells and, if vapor extraction is used, vapors in the blower exhaust. The vapor and contaminant concentrations are then each plotted against time.

The plot can be used to show the impact of the biosparging operation. As biosparging reaches the limit of its ability to biodegrade further, the reduction of dissolved constituents reaches asymptotic conditions. This effect is also reflected in the concentrations of oxygen, CO_2, and VOC in the vapors released from the system. A plot of this effect is demonstrated in Exhibit VIII-24. When asymptotic behavior begins to occur, the operator should evaluate alternatives that increase the mass transfer removal rate (e.g., pulsing, or turning off the system for a period of time and then restarting it). Other more aggressive steps to further reduce constituent concentrations can include the installation of additional sparging points or vapor extraction wells.

Exhibit VIII-24
Concentration Reduction And Mass Removal Behavior For Biosparging Systems



If asymptotic behavior is persistent for periods greater than about six months and the concentration rebound is sufficiently small following periods of temporary system shutdown, the performance of the biosparging system should be reviewed with regulatory agencies to determine whether remedial goals have been reached. If further contaminant reduction is desired, another remedial technology may need to be considered.

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Checklist: Can Biosparging Be Used At This Site?

This checklist can help you to evaluate the completeness of the CAP and to identify areas that require closer scrutiny. As you go through the CAP, answer the following questions. If the answer to several questions is no, you will want to request additional information to determine if biosparging will accomplish the cleanup goals at the site.

1. Site Factors

Yes	No	
❑	❑	Is the aquifer clear of floating free product?
❑	❑	Is the soil intrinsic permeability greater than 10^{-9} cm^2?
❑	❑	Is the soil free of impermeable layers or other conditions that would disrupt air flow?
❑	❑	Is soil temperature between 10°C and 45°C during the proposed treatment season?
❑	❑	Is the pH of groundwater between 6 and 8?
❑	❑	Is the total heterotrophic bacteria count > 1,000 CFU/gram dry soil?
❑	❑	Is the carbon:nitrogen:phosphorus ratio between 100:10:1 and 100:1:0.5?
❑	❑	Is the dissolved iron concentration at the site < 10 mg/L?
❑	❑	Is vapor migration of constituents controlled?

2. Constituent Characteristics

Yes	No	
❑	❑	Are constituents all sufficiently biodegradable?
❑	❑	Is the concentration of Total Petroleum Hydrocarbon ≤ 50,000 ppm and heavy metals ≤ 2,500 ppm?
❑		Are the constituent vapor pressures less than 0.5 mm Hg?
❑	❑	Are the Henry's law constants for the constituents present lower than 100 atm?

3. Evaluation Of The Biosparging System Design

Yes	No	
❑	❑	Examine the sparging air pressure. Will the proposed pressure be sufficient to overcome the hydraulic head and capillary forces?
❑	❑	Is the proposed well density appropriate, given the total area to be cleaned up and the radius of influence of each well?
❑	❑	Do the proposed well screen intervals account for contaminant plume location at the site?
❑	❑	Is the proposed well configuration appropriate for the site conditions present?
❑	❑	Is the air compressor selected appropriate for the desired sparge pressure?
❑	❑	If nutrient addition is needed, are nutrient formulation and delivery rates appropriate for the site, based on laboratory or field studies?
❑	❑	Have background concentrations of oxygen and CO_2 (measured in pilot studies) been taken into account in establishing operating requirements?

4. Operation And Monitoring Plans

Yes	No	
❑	❑	Are manifold valving adjustments proposed during the first 7 to 10 days of operation?
❑	❑	Are hourly recordings of injection and extraction rates, pressures, depth to groundwater, hydraulic gradient, and VOC levels proposed during the first 7 to 10 days of operation?
❑	❑	Is daily monitoring of injection rates proposed during the first 7 to 10 days of operation?
❑	❑	Are biweekly to monthly measurements of contaminant levels in groundwater, vapor wells, and blower exhausts proposed?
❑	❑	Are biweekly to monthly measurements of vapor concentration proposed?

Chapter IX

Natural Attenuation

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Chapter IX
Natural Attenuation Of Petroleum Hydrocarbons

Overview

Natural attenuation, also known as passive bioremediation, intrinsic bioremediation, or intrinsic remediation, is a passive remedial approach that depends upon natural processes to degrade and dissipate petroleum constituents in soil and groundwater. Some of the processes involved in natural attenuation of petroleum products include aerobic and anaerobic biodegradation, dispersion, volatilization, and adsorption. In general, for petroleum hydrocarbons, biodegradation is the most important natural attenuation mechanism; it is the only natural process that results in an actual reduction of petroleum constituent mass.

This chapter describes chemical and environmental factors that influence the rate of natural attenuation processes. Because of the complex interrelationship among these controlling factors, using specific numerical thresholds to determine whether natural attenuation will be effective is frequently not possible. A detailed site investigation is necessary to provide sufficient data on site conditions and hydrocarbon constituents present to evaluate the potential effectiveness of natural attenuation. In addition, site conditions will need to be monitored over time to confirm whether or not contaminants are being naturally degraded at reasonable rates to ensure protection of human health and the environment. Site data should clearly indicate whether concentrations of soil and groundwater contaminants are being adequately reduced without active remediation treatment. If not, more aggressive remedial alternatives should be considered.

Petroleum hydrocarbon constituents are generally biodegradable, regardless of their molecular weight, as long as indigenous microorganisms have an adequate supply of nutrients and biological activity is not inhibited by toxic substances. For heavier hydrocarbons, which are less volatile and less soluble than many lighter components, biodegradation will exceed volatilization as the primary removal mechanism, even though degradation is generally slower for heavier molecular weight constituents than for lighter ones.

The essential nutrients required for biodegradation are usually naturally present in the subsurface. Aerobic biodegradation consumes oxygen which, if not replenished, can limit the effectiveness of further aerobic biodegradation. When the geologic materials at a site are relatively porous and permeable, oxygen is naturally replenished through the soil and groundwater. When, however, the permeability is high, the possibility exists for greater downgradient migration of contaminants. Conversely, when the geologic materials have low porosity and are

relatively impermeable, the potential for migration is reduced but so is the rate of oxygen replenishment. In addition, less permeable materials typically are finer grained and contain higher percentages of organic carbon. Both of these features favor adsorption and retardation of contaminant movement. In this case, contaminants may remain relatively undegraded but in close proximity to the original source.

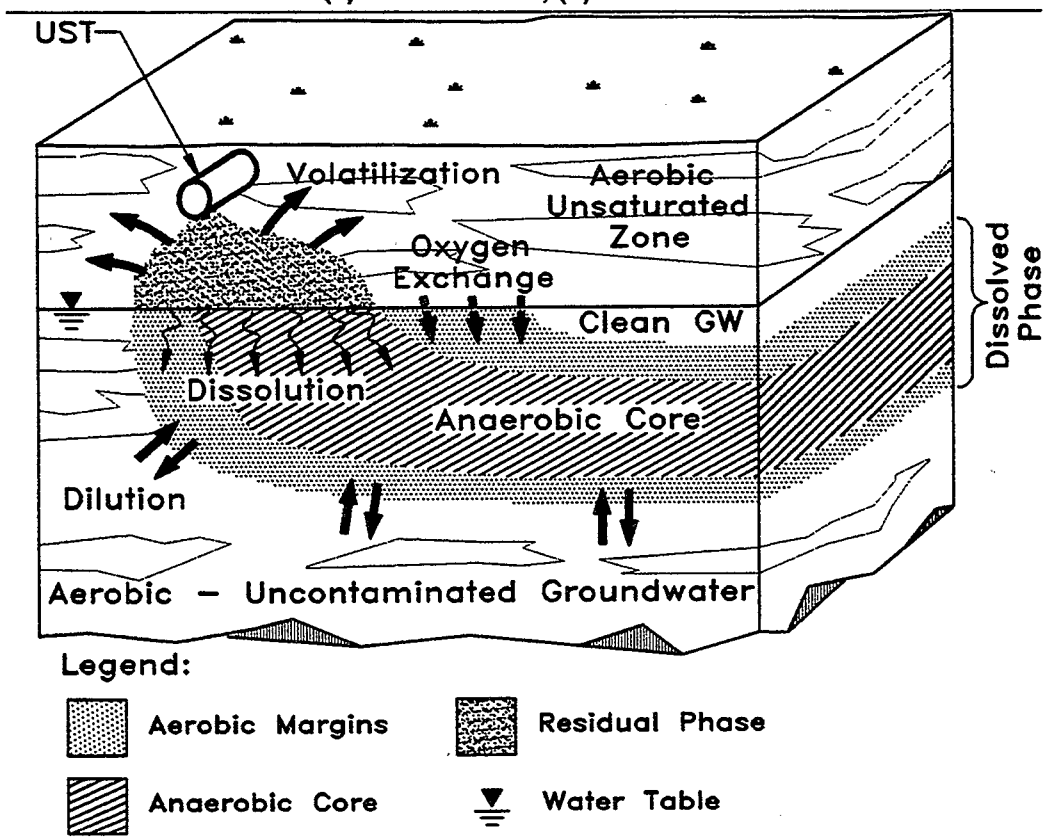
Anaerobic biodegradation is also a significant attenuation process. Oxygen depletion in the subsurface is a characteristic of biodegradation of petroleum hydrocarbons and is a consequence of the rate of metabolic oxygen utilization exceeding the natural capacity for oxygen replenishment. The core of a contaminant plume is typically under anaerobic conditions and only the margins are aerobic, as illustrated in Exhibit IX-1. Therefore, even though the rate of anaerobic biodegradation is much slower than aerobic biodegradation (often by a factor of 10 to several hundred), anaerobic processes may dominate the degradation of hydrocarbon contaminants.

Exhibit IX-2 provides a summary of the advantages and disadvantages of using natural attenuation as a remedial option for petroleum-contaminated soils and groundwater. Under the appropriate site conditions, natural attenuation can reduce the potential impact of petroleum product release either by preventing constituents from being transported to sensitive receptors or by reducing constituent concentrations to less harmful levels. Natural attenuation may also be an acceptable option for sites that have been subject to active remediation and which now have substantially reduced concentrations of contaminants. However, natural attenuation is not an appropriate option at all sites. The rates of natural processes are typically slow; contaminant levels may not be reduced to acceptable regulatory levels for years. In addition, long-term monitoring is necessary to demonstrate that contaminant concentrations are continually decreasing at a rate sufficient to ensure that potential receptors are not adversely affected.

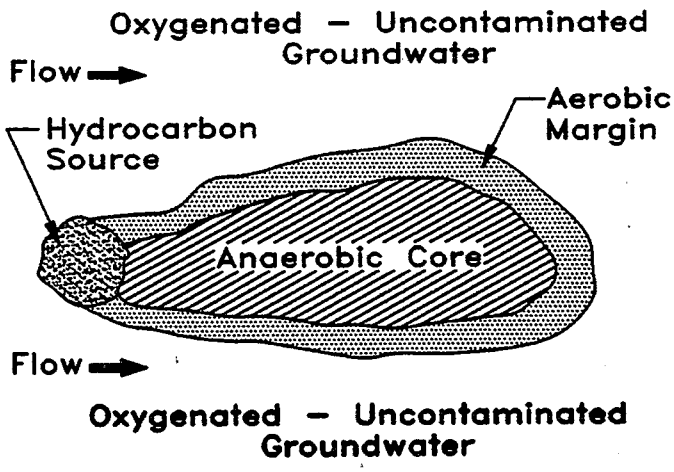
The policies and regulations of your state determine whether natural attenuation will be allowed as a treatment option. Before beginning an analysis of the potential effectiveness of natural attenuation, determine if your state restricts the use of this remedial option. For example, natural attenuation may not be allowed if groundwater is contaminated at levels exceeding drinking water standards (i.e., Maximum Contaminant Levels [MCLs]) or at concentrations that may pose risks to receptors or human health. Natural attenuation is not generally an option at sites with free product in the subsurface.

This chapter will assist you in evaluating a corrective action plan (CAP) that proposes natural attenuation as a remedial option for petroleum-contaminated soil and groundwater. The evaluation guidance is presented in the four steps described below. The evaluation process, which is summarized in a flow diagram shown in Exhibit IX-3, can serve as a roadmap for the decisions you will make during your evaluation. A

Exhibit IX-1
A Typical Hydrocarbon Plume Undergoing Natural Bioremediation;
(a) Cross-section, (b) Plan View



(a) Cross Section



(b) Plan View

Exhibit IX-2
Advantages And Disadvantages Of Natural Attenuation

Advantages	Disadvantages
O Lower costs than most active remedial alternatives.	O Not effective where constituent concentrations are high (> 20,000 to 25,000 ppm TPH).
O Minimal disturbance to the site operations.	O Not suitable under certain site conditions (e.g., impacted ground water supply, presence of free product).
O Potential use below buildings and other areas that cannot be excavated.	O Some migration of constituents may occur; not suitable if receptors might be affected.
	O Long period of time required to remediate heavier petroleum products.
	O Longer period of time may be required to mitigate contamination than for active remedial measures.
	O May not always achieve the desired cleanup levels within a reasonable length of time.

checklist has also been provided at the end of this chapter to be used as a tool to evaluate the completeness of the CAP and to help focus attention on areas where additional information may be needed.

- **Step 1:** ***Determine if state regulations permit natural attenuation as a remedial option.*** If not, an alternative remedial technology should be employed.

- **Step 2:** ***An initial screening of natural attenuation effectiveness*** allows you to quickly gauge whether natural attenuation is likely to be effective.

- **Step 3:** ***A detailed evaluation of natural attenuation effectiveness*** provides further screening criteria to confirm whether natural attenuation is likely to be effective. To complete this evaluation, you will need to review monitoring data, chemical and physical parameters of the petroleum constituents, and site conditions. You will then need to determine whether site and constituent characteristics are such that natural attenuation will likely result in adequate reductions of constituent concentrations.

Exhibit IX-3
Natural Attenuation Evaluation Process Flow Chart

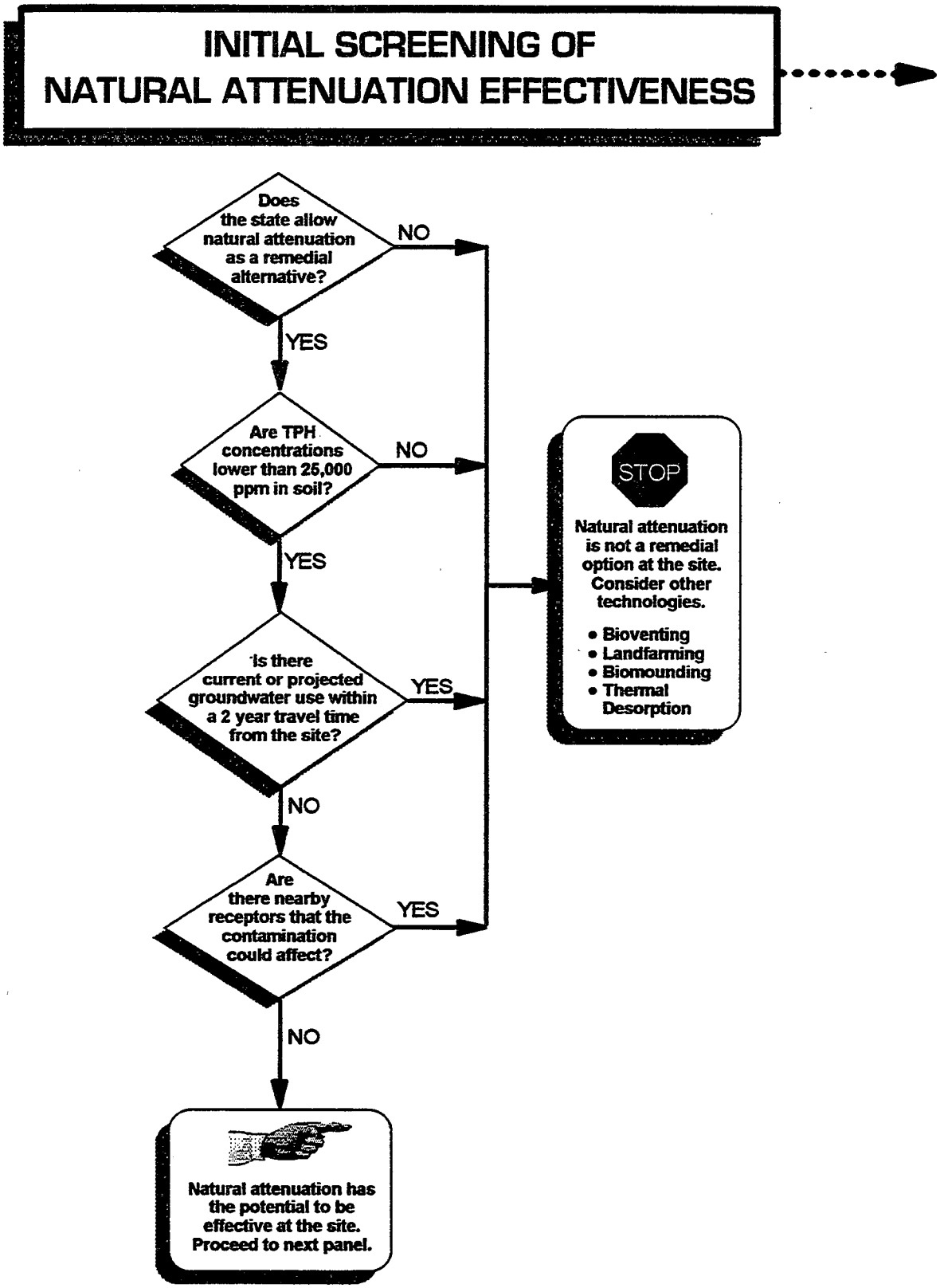
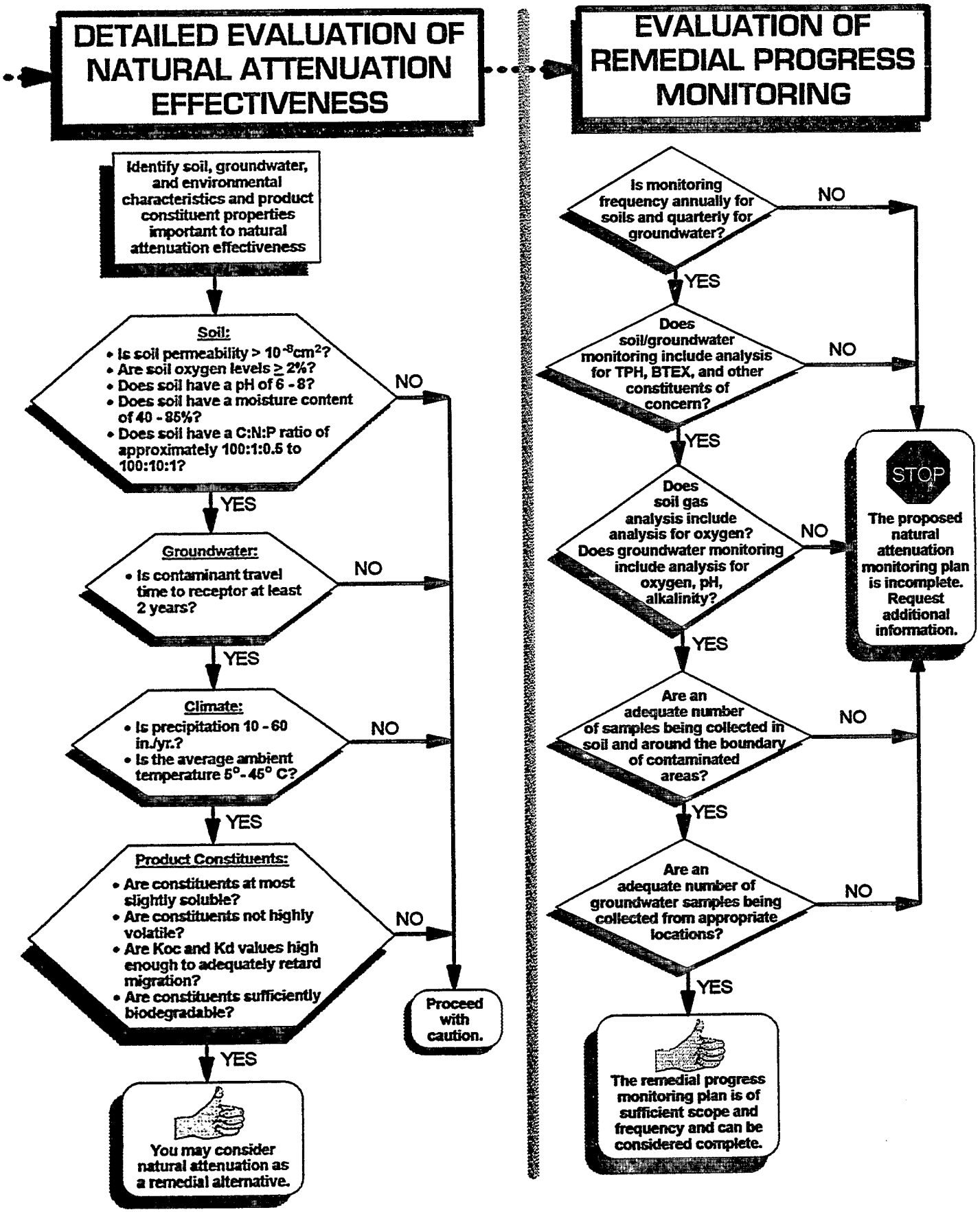


Exhibit IX-3
Natural Attenuation Evaluation Process Flow Chart



- **Step 4:** ***An evaluation of monitoring plans*** allows you to determine whether the proposed monitoring schedule will provide adequate data to evaluate the effectiveness of natural attenuation.

Initial Screening Of Natural Attenuation Effectiveness

You should consider the following two critical factors early on when evaluating the potential effectiveness of natural attenuation:

(1) Constituent concentrations--whether the petroleum hydrocarbon constituent concentrations are low enough for natural attenuation to be a viable alternative; and

(2) Nearby receptors--whether receptors located near the site could be affected by the presence of petroleum constituents during the remediation process.

Constituent Concentrations

If initial total petroleum hydrocarbon (TPH) concentrations are too high, natural attenuation will not reduce concentrations to acceptable levels within a reasonable time period (i.e., a few years). Natural attenuation should not be used at sites where free product is present. In general, natural attenuation is probably not effective at sites with soil TPH concentrations greater than about 20,000 to 25,000 ppm. At concentrations higher than this level it is probable that free phase hydrocarbons exist in the subsurface. These limits are highly variable and depend upon site-specific factors including the type and concentration of contaminants, proximity and sensitivity of receptors, and the hydrogeological conditions. These are typical values generally considered acceptable for natural attenuation at sites with simple geologic and hydrologic conditions, and minimal risk. For sites for which conditions are highly complex or the risk to receptors is greater, maximum acceptable TPH concentrations will be lower.

Nearby Receptors

Because natural attenuation generally allows constituents to migrate farther than active remedial measures, it is important to determine whether individuals or sensitive environmental areas might be affected by the release (e.g., through ingestion of contaminated soil and/or groundwater, direct contact with contaminated groundwater at discharge points (e.g., streams or marshes), direct contact with contaminated soil, or inhalation of constituent vapors (especially in a basement or other confined space).

Look for information in the CAP regarding the location of potential receptors as well as the quality of groundwater, depth to groundwater, flow rate and direction of groundwater, discharge points for groundwater, and use of groundwater in the vicinity of the site. If potential receptors are located near the site, also look for modeling and/or monitoring results that demonstrate that the constituents will not reach the receptors. Determination of whether a receptor is in close proximity to a site may be considered in terms of either contaminant travel time from the source to the receptor or distance separating the source from the receptor. Both of these will vary from site to site depending upon site specific factors. The length of time necessary for contaminants to travel from the source to a downgradient receptor can be calculated from the average hydraulic gradient, hydraulic conductivity, effective porosity, and distance between the source and the receptor. Travel times of 2 years or more should allow for an evaluation of the potential effectiveness of natural attenuation and provide sufficient time to implement active remedial measures should natural attenuation prove to be ineffective in protecting human health and the environment. For example, if the average groundwater seepage velocity at a site is 2 feet per day, it would require 2 years for a conservative contaminant to travel 1,500 feet (approximately ¼ mile). Therefore, as a rule of thumb, downgradient receptors within ¼ mile of the source should be identified and probable travel times calculated. If travel times to receptors within this radius are less than 2 years, the radius should be extended to the distance that corresponds to a travel time of 2 years. It should be noted that the presence of layers of high permeability soil or rock, fractures or faults, or utility conduits could potentially accelerate the migration of contaminants. If the groundwater is potable and future land use is expected to be residential, potential future receptors should also be considered. The most important parameters that determine water potability are listed in Exhibit IX-4. If this information is not provided in the CAP, you will need to request the missing data. If constituents are expected to reach receptors, an active remedial technology should be used instead of natural attenuation, unless the CAP demonstrates that resulting exposures would not result in significant adverse environmental or human health effects.

Exhibit IX-4
Factors Determining Groundwater Potability

Factor	Potability Parameters
Total dissolved solids	< 500 mg/L
Chemical concentrations	< MCLs
Biological characteristics	No harmful microbes (pathogens)

Under some circumstances natural attenuation might be considered a remedial option even when there is potential for groundwater contamination. For instance, active remediation to protect a groundwater resource may not be required if the affected groundwater is not currently potable (e.g., because of high salinity or other chemical or biological contamination) and it is not likely to be used as a potential source of drinking water in the future.

In addition to reviewing the water use in the area, it is important to determine whether there are receptors that could come into contact with contaminated soil or groundwater. Because soils associated with UST contamination are generally below the surface of the ground, there will usually be limited opportunity for receptors to come into contact with contaminated soils. However, if the contaminated soils might be excavated (e.g., for construction) before natural attenuation has adequately reduced constituent concentrations, receptor contact with contaminated subsurface soil could occur unless appropriate controls are implemented. If direct contact with contaminated soils is likely, controls to prevent such contact or alternative remedial methods should be implemented. If the potential for direct contact is not addressed in the CAP, request additional information.

Exposure to petroleum constituent vapors may also be a concern at some sites. Hazardous constituents can volatilize from free petroleum product and from petroleum products adsorbed to soils or dissolved in groundwater. Vapors tend to collect in underground vaults, basements, or other subsurface confined spaces, posing exposure risks from inhalation and creating the possibility of explosions. Inhalation and dermal exposure to volatile constituents can also be significant if groundwater is used for bathing (even if it is not used for drinking). If vapor migration and associated health and safety risks are not addressed in the CAP, request additional information.

Detailed Evaluation Of Natural Attenuation Effectiveness

Once you have completed the initial screen and determined that natural attenuation could potentially be effective at the site, review the CAP further to confirm that natural attenuation will be effective. A thorough understanding of natural attenuation processes, the site conditions, and the constituents present will be necessary to make this determination.

Natural Attenuation Mechanisms

In order to assess site conditions to determine whether natural attenuation is an acceptable alternative to active treatment, it is important to understand the mechanisms that degrade petroleum products in soil and groundwater. Mechanisms may be classified as either destructive (i.e., result in a net decrease in contaminant mass) or

non-destructive (i.e., result in decrease in equilibrium concentrations but no net decrease in mass). Destructive mechanisms are primarily biological. The primary non-destructive mechanisms are abiotic, physical phenomena. Chemical processes are important for many compounds (including some gasoline additives such as ethylene dibromide [EDB]), but relatively insignificant for the hydrocarbon fuels themselves. For this reason chemical processes will not be considered in the following discussion.

Also, although it is not likely that all environmental conditions will be within optimal ranges under natural field conditions, natural attenuation processes will still be occurring. The natural attenuation mechanisms discussed in the following section are:

- *Biological Processes*--aerobic (requires oxygen), anaerobic (must occur in the absence of oxygen), and hypoxic (can occur under conditions of low oxygen content); and
- *Physical Phenomena*--volatilization, dispersion (mechanical mixing and molecular diffusion), and sorption.

Both of these mechanisms and how they contribute to natural attenuation effectiveness are described below and summarized in Exhibit IX-5.

Exhibit IX-5
Potential Natural Attenuation Mechanisms

Mechanism	Description	Potential For BTEX Attenuation
Biological		
Aerobic	Microbes utilize oxygen as an electron acceptor to convert contaminant to CO_2, water, and biomass.	Most significant attenuation mechanism if sufficient oxygen is present. Soil air (0_2) $\geq$ 2 percent. Groundwater D.O. $\geq$ 1 to 2 mg/L.
Anaerobic Denitrification Sulfate reducing Methanogenic Fe reducing	Alternative electron acceptors (e.g., NO_3^-, SO_4^{2-}, Fe^{3+}, CO_2) are utilized by microbes to degrade contaminants.	Rates are typically much slower than for aerobic biodegradation: toluene is the only component of BTEX that has been shown to consistently degrade.
Hypoxic	Secondary electron acceptor required at low oxygen content for biodegradation of contaminants.	Has not been demonstrated in the field for BTEX.
Physical		
Volatilization	Contaminants are removed from groundwater by volatilization to the vapor phase in the unsaturated zone.	Normally minor contribution relative to biodegradation. More significant for shallow or highly fluctuating water table.
Dispersion	Mechanical mixing and molecular diffusion processes reduce concentrations.	Decreases concentrations, but does not result in a net loss of mass.
Sorption	Contaminants partition between the aqueous phase and the soil matrix. Sorption is controlled by the organic carbon content of the soil, soil mineralogy and grain size.	Sorption retards plume migration, but does not permanently remove BTEX from soil or groundwater as desorption may occur.

Source: Adapted from McAllister and Chiang, 1994.

Biological Processes

Aerobic biodegradation of BTEX by naturally occurring microorganisms is more rapid than anaerobic biodegradation, but both are important. The rate of oxygen depletion due to microbial metabolism typically exceeds the rate at which oxygen is naturally replenished to the subsurface. This is especially true in the core region of the hydrocarbon plume dissolved in groundwater. The result is that anaerobic processes can become predominant. When oxygen is depleted, an alternative electron acceptor (e.g., NO_3^-, SO_4^{2-}, Fe^{3+}) and a microorganism capable of using the alternative electron acceptor must be available for biodegradation to occur. Toluene is the only BTEX component that has been shown to degrade under anaerobic conditions in the field. Conditions where oxygen is partially depleted are referred to as hypoxic (about 0.1 to 2 ppm oxygen). Biodegradation of BTEX under hypoxic conditions may be possible, but it has not been demonstrated.

Anaerobic biodegradation is also a significant attenuation process. Oxygen depletion in the subsurface is a characteristic of biodegradation of petroleum hydrocarbons and is a consequence of the rate of metabolic oxygen utilization exceeding the natural capacity for oxygen replenishment. The core of a contaminant plume is typically under anaerobic conditions and only the margins are aerobic (Exhibit IX-1). Therefore, even though the rate of anaerobic biodegradation is much slower than aerobic biodegradation (often by a factor of 10 to several hundred), anaerobic processes may dominate the degradation of hydrocarbon contaminants. Because a variety of models are available and their appropriate use requires a high degree of technical expertise, a more detailed discussion of modeling is beyond the scope of this manual.

Physical Phenomena

Physical processes such as volatilization, dispersion, and sorption also contribute to natural attenuation. Volatilization removes constituents from the groundwater or soil by transfer to the gaseous phase. In general, volatilization accounts for about 5 to 10 percent of the total mass loss of benzene at a typical site, with most of the remaining mass loss due to biodegradation (McAllister, 1994). For less volatile constituents, the expected mass loss due to volatilization is even lower. Dispersion ("spreading out" of constituents through the soil profile or groundwater unit) results in lower concentrations of constituents, but no reduction in contaminant mass. In soil, hydrocarbons disperse due to the effects of gravity and capillary forces (suction). In groundwater, hydrocarbons disperse by advection and hydrodynamic dispersion. Advection is the movement of dissolved components in flowing groundwater. Hydrodynamic dispersion is the result of mechanical mixing and molecular diffusion. If groundwater velocities are relatively high, mechanical mixing is the dominant process and diffusion is insignificant. At low velocity, these effects are reversed. Sorption (the

process by which particles such as clay and organic matter "hold onto" liquids or solids) retards migration of some hydrocarbon constituents (thereby allowing more time for biodegradation before the constituents reach a receptor). Although none of these three processes results in a loss of mass, they can help to improve the rate at which natural attenuation occurs.

Evaluation Of Site And Constituent Factors

At most sites, monitoring data collected during the site characterization (prior to submission of the CAP) will not cover a sufficient time span to demonstrate that natural attenuation is occurring. In this case, fate and transport models can be used to predict the effectiveness of natural attenuation. Even with historical data showing reductions in a constituent plume, modeling may be useful in evaluating the mechanism responsible for the observed concentration reductions (e.g., are constituents simply being diluted?). Modeling is especially appropriate for sites with nearby receptors.

Fate and transport models typically account for attenuation factors such as biodegradation, adsorption/retardation, and dispersion/ dilution. Model calibration involves comparison of simulation results with field measurements collected over time. Predictive simulations of contaminant movement and degradation should only be made using a properly calibrated model. After the model is calibrated, model predictions may be used to evaluate potential risks associated with the attenuated contaminants. Not every site will require sophisticated modeling. Often there are not enough data available to construct a representative model. In some cases, other techniques such as statistical regression analysis or analytical solutions may be adequate to demonstrate the effectiveness of natural attenuation.

Even without modeling results, an evaluation of site and chemical constituent factors can help you determine whether natural attenuation is likely to be effective. For example, calculation of contaminant travel times using conservative assumptions can be made if the hydraulic gradient, hydraulic conductivity, and effective porosity are known.

Site Factors Affecting Constituent Migration

The potential for natural attenuation to result in reduction of BTEX concentrations can be determined by evaluation of the site factors listed in Exhibit IX-6. Each of these site factors is discussed in detail below.

Exhibit IX-6
Potential For Natural Attenuation: Site Factors

Factor	Potential For Natural Attenuation
Soil texture	Coarse-grained soils provide the greatest drainage and aeration, but may also promote contaminant migration.
Soil structure	Layered soils inhibit vertical migration and dispersion of constituents, but may promote lateral spreading.
Adsorption potential	Higher organic carbon content and smaller grain size in soil results in greater adsorption of chemicals and retards migration.
Groundwater flow rate	Greater groundwater flow rate will enhance constituent dispersion.
Soil and groundwater aeration	Greatest when soil $O_2 \geq 2\%$, and groundwater D.O. $\geq$ 1 to 2 mg/L.
Soil moisture content	Greatest between 40 to 85 percent of field capacity.
Soil pH	Greatest between soil pH values of 6 to 8.
Microbial community	Greatest with soil/groundwater conditions that allow O_2 flow and in the absence of toxic levels of constituents.
Precipitation	Most favorable at 10 to 60 inches of rain per year.
Temperature	Most active microbial activity occurs at ambient temperatures of 5° to 45°C. Activity typically doubles for every 10°C rise in temperature.
Soil nutrient concentration	Greatest when the C:N:P ratio is about 100:10:1.

Soil Texture

Soil texture refers to the size of mineral particles. It is a qualitative measure of the soil permeability to both air and water. Fine-grained soils (e.g., clays and silts), have lower permeabilities than coarse-grained soils (e.g., sand and gravel). Thus, sandy soils (which have an intrinsic permeability of about 10^{-8} cm^2 or greater) promote drainage and aeration, which is favorable to both the dispersion and biodegradation of constituents. However, high permeability also promotes faster and farther downgradient migration of contaminants, which could adversely impact potential receptors. Because of their high sorptive capacities (owing to both small particle size and higher organic matter content), clays and silts are associated with a slower migration (i.e., retardation) of contaminants and less dilution than those of sands and gravels. But, at the same time, the potential for downgradient migration is also reduced. Thus, even though biodegradation may take longer, there may be little or no risk to potential downgradient receptors.

Also consider the amount of precipitation in the region, as precipitation can increase leaching rates to groundwater. If the soil at the site has a high permeability and there is moderate to heavy precipitation in the area, aeration, dilution, and dispersion will be enhanced, thereby reducing constituent concentrations. However, these conditions also favor migration of constituents (especially lighter, more soluble products) from soils to groundwater. Whether this migration is acceptable depends on your state's policies and the presence of receptors near the site.

Soil Structure

Soil structure refers to the arrangement of soil particles into groups. Soil structure can enhance or inhibit constituent migration. Layered soils tend to hinder the vertical migration of constituents, but may promote lateral migration. Naturally occurring fissures, cracks, or channels (or those created by roots or burrowing animals), however, can facilitate the migration of constituents from soil to either the atmosphere or groundwater. Low-permeability layers can also reduce aeration of the soils, slowing aerobic biodegradation. The soil types and structures may be identified by reviewing soil boring logs.

Adsorption Potential

Adsorption is the affinity of a chemical substance for particulate surfaces and is an important factor that retards a constituent's movement in the environment. Constituents that adsorb tightly may be less subject to transport in the gaseous phase or in solution, whereas constituents that are not tightly adsorbed can be transported through soils, aquatic systems, and the atmosphere. With respect to the impact on natural attenuation, the higher the adsorption potential, the greater the retardation of contaminant migration. Increased adsorption can increase the time required for constituents to reach receptors, allowing greater time for biodegradation to occur.

Adsorption potential is closely associated with soil type and soil organic matter content. Finer-grained soils typically have a higher organic carbon content than coarser-grained soils, and the higher the organic content, the greater the tendency to adsorb (retard) organic compounds. The fraction of organic carbon (f_{oc}) in surficial soils typically ranges from 1 to 3.5 percent. The organic matter content in subsurface soils is typically an order of magnitude lower because most organic residues are incorporated or deposited on the surface.

Adsorption is also influenced by:

- Hydrophobicity of the compound--the more hydrophobic (i.e., insoluble in water), the greater its tendency to adsorb onto particulate matter, while the more hydrophilic (i.e., soluble in water), the less of a tendency it has to adsorb onto particulate matter; and

- Sorption to mineral surfaces--this may be more important than sorption to organic carbon, if f_{oc} is low and soil particles have a large surface area to volume ratio (e.g., small clay particles).

Fine-grained soils have more binding sites that can immobilize hydrocarbon compounds in the soil matrix, and soils with a high organic carbon content (i.e., > 2 percent) also have greater capacities for holding fluids, which retards downward migration and facilitates biodegradation.

Groundwater Flow Rate

Dispersion and migration of constituents increases with increasing groundwater flow rate. True groundwater velocity is referred to as the seepage velocity. Seepage velocity is equal to the product of the hydraulic conductivity and the gradient divided by the effective porosity. For a given hydraulic gradient, the higher the hydraulic conductivity the higher the seepage velocity. High hydraulic conductivity (i.e., > 10^{-4} cm/sec) will contribute significantly to the dispersion of constituent concentrations, while low hydraulic conductivity (i.e., < 10^{-7} cm/sec) will generally result in concentrations remaining more or less localized. Of course, a higher flow rate also increases migration of dissolved constituents, which, at many sites, may not be desirable. Rapid infiltration and groundwater flow can also promote reoxygenation in the subsurface by transporting higher levels of dissolved oxygen.

Soil And Groundwater Aeration

Aerobic biodegradation is substantially faster than anaerobic biodegradation. Aerobic biodegradation requires that soils are relatively permeable (with an intrinsic permeability about 10^{-8} cm^2 or greater) to allow transfer of oxygen to subsurface soils where the microorganisms are degrading the petroleum constituents. Soils with a low oxygen content can hinder aerobic biodegradation. Oxygen levels greater than or equal to 2 percent are optimal for aerobic biodegradation in the unsaturated zone. Another indication of well-aerated soils is the presence of chemicals in their oxidized state (e.g., ferric iron [Fe^{3+}], manganic manganese [Mn^{4+}], nitrate [NO_3^-], and sulfate [SO_4^{2-}]); the presence of the reduced forms of these elements indicates restricted drainage and poor aeration.

If constituents are present in groundwater, it is important that the groundwater have sufficient dissolved oxygen for aerobic biodegradation to occur. Generally, aerobic biodegradation of BTEX constituents will occur with dissolved oxygen concentrations greater than 1 to 2 mg/L. Natural groundwater flow into the contaminated area may provide a continuous supply of dissolved oxygen, which will continue to encourage aerobic biodegradation.

Dissolved hydrocarbon plumes typically have three zones defined by the concentration of dissolved oxygen: (1) anaerobic core, (2) aerobic margins, and (3) hypoxic interface between the aerobic and anaerobic zones (Exhibit IX-1). For many subsurface hydrocarbon releases, anaerobic biodegradation predominates over aerobic biodegradation because oxygen becomes depleted by microbial metabolism and remains depleted.

Soil Moisture Content

Moisture is necessary for microbial growth. Microbes can only utilize petroleum hydrocarbons when the hydrocarbons are in the dissolved phase. In addition, water facilitates the movement of bacteria to other parts of the soil, where these bacteria can continue to degrade petroleum constituents. In the unsaturated zone, soil moisture content of between 40 and 85 percent of the total water-holding capacity (field capacity), or about 12 to 30 percent by weight, is considered optimal for aerobic microbial activity.

Soil pH

Ssoils that have a pH of 6 to 8 generally promote bacterial growth. Soils with a pH significantly above or below these values generally result in limited microbial activity.

Microbial Community

Because microbes capable of degrading petroleum products are present in almost all subsurface environments. However, it may be important in some situations to analyze soil samples with the intent of confirming the presence of hydrocarbon degrading microorganisms. The exercise of collecting soil samples and conducting laboratory microcosm studies is generally not necessary. If microcosm studies are conducted, the collection of soil material, the procedures used to set up, monitor, and analyze the study, and the interpretation of the results should be based on established procedures. Degradation rate constants determined in the laboratory may not correspond to rates that occur under field conditions. Therefore, it is best to determine these rate constants from *in situ* field measurements. Soil samples should be analyzed for toxic levels

of chemicals (e.g., heavy metals, corrosive materials, and pesticides) that would inhibit the effectiveness of the microbial community.

Precipitation

Moderate to heavy precipitation (i.e., 10 to 60 inches/year) is favorable for maintaining soil moisture necessary to support microbial populations. Precipitation also transports oxygen and nutrients as it percolates downward through the subsurface soils, enhancing microbial metabolic activity. As mentioned above, microbial activity is generally greatest when the moisture content in the soils is 40 to 85 percent of the water-holding capacity of the soils.

Temperature

Effective biodegradation can generally occur within a temperature range of 5°C to 45°C; ideally, temperatures should be above 15°C for optimum biological activity. Extreme temperatures (either hot or cold) prohibit microbial growth. In most areas of the U.S., subsurface soils generally have a fairly constant temperature of about 13°C throughout the year. Surficial soil temperature at sites in colder states, especially Alaska, are likely to be lower, reducing the rate of microbial activity. The rate of microbial activity typically doubles for every 10°C rise in temperature.

Soil Nutrient Concentration

In addition to requiring sufficient organic (carbon-rich) material (i.e., petroleum constituents) for consumption as a food source, adequate levels of nitrogen and phosphorus also are necessary for bacterial growth. For optimal microbial growth, the carbon to nitrogen to phosphorus (C:N:P) ratio should be between 100:10:1 and 100:1:0.5.

Chemical Constituent Factors

The most commonly encountered petroleum products from UST releases are gasoline, diesel fuel, kerosene, heating oils, and lubricating oils. Each of these petroleum products is a complex mixture often containing more than 100 separate compounds. Individual constituents will be attenuated to a varying degree, based on its chemical and physical properties. This chapter focuses on the chemical properties of the BTEX constituents, because regulatory clean-up levels are typically established for BTEX. Tables in this section present the chemical properties of the BTEX constituents and may be used to establish the magnitude of dispersion or degradation of the individual constituents.

The chemical factors discussed below largely determine the partitioning of constituents among the dissolved, gaseous, and adsorbed

phases. Exhibit IX-7 shows the relative environmental partitioning of the

Exhibit IX-7
Relative Environmental Partitioning Of BTEX Constituents

Petroleum Constituent	Adsorption On Soil Particles (%)	Volatilization (%)	Soluble Portion In Groundwater And Soil Moisture (%)
Benzene	3	62	35
Ethylbenzene	21	59	20
Toluene	3	77	20
o-Xylene	15	54	31

Source: Adapted from McLearn et al. 1988, *The International Journal of Air Pollution Control and Waste Management.*

BTEX constituents based on soil modeling (SESOIL) results. Each BTEX constituent will migrate via multiple pathways depending on its chemical and physical characteristics. Consequently, different chemicals prefer different migration pathways. For example, benzene tends to partition between the vapor phase, the adsorbed phase, and the dissolved phase. As shown in Exhibit IX-7, the majority of the benzene mass will either volatilize or dissolve in either soil moisture or groundwater. Only a relatively small percentage will adsorb to soil particles. For example, if the soil contains a higher percentage of organic carbon, a higher percentage of benzene will potentially be adsorbed. In contrast to benzene's behavior, ethylbenzene will more likely adsorb to soil particles and would not be as soluble in water. Exhibit IX-7 is an illustrative example and partitioning may not represent equilibrium conditions. Also, partitioning depends upon many site-specific parameters and may not be the same at other sites.

While reviewing the CAP, it should be noted that fate and transport characteristics are much different for the heavier petroleum hydrocarbon molecules, which do not tend to disperse as readily. The heavier constituents should, therefore, be considered separately. Lighter hydrocarbon constituents (e.g., the BTEX constituents) tend to have greater mobility (e.g., via volatilization and leaching), whereas heavier constituents have a greater adsorption and lower volatilization potential. Thus, there is greater potential for lighter constituents to migrate and disperse.

The lighter constituents of petroleum hydrocarbon fuels (e.g., benzene) tend to be more toxic than the heavier constituents. Although natural attenuation is slower for heavier constituents than for lighter constituents, it may still be an acceptable remedial approach for heavier constituents, as long as there are no nearby receptors and an indeterminate time frame is permitted for attaining cleanup levels. After the free product (if any) has been recovered from the subsurface, natural attenuation may be the most appropriate remedial approach for heavier petroleum constituents because they are less soluble and less volatile (hence less mobile) than lighter fuels and they contain only small

fractions of toxic constituents (e.g., benzene). In fact, after moderate degradation or weathering, almost all of the lighter (more mobile and more toxic) compounds have been stripped away, leaving the residue enriched with the heavier, constituents that generally do not pose a significant threat to distant receptors.

With the exception of lead, inorganic chemicals are not typically of concern at sites with petroleum releases. Soils that are contaminated with older gasoline products may contain relatively high concentrations of lead, which can cause serious health and environmental effects. Many organic lead compounds are volatile and toxic. Lead may also be leached into the groundwater where it can be transported downgradient. The presence of lead in site soils may require active remediation to eliminate potential risk.

This section examines the most important factors that contribute to a constituent's partitioning into the soil (adsorbed), groundwater (dissolved), and air (gaseous) phases. The potential for natural attenuation to be effective and for constituent concentration reduction to occur as a result of chemical factors is shown in Exhibit IX-8. Each of these factors is discussed below in more detail.

Exhibit IX-8
Potential For Natural Attenuation: Chemical Constituent Factors

Factor	Description	Potential For Natural Attenuation
Solubility	The extent to which a constituent will dissolve in another substance (e.g., water).	The greater the constituent's solubility, the greater the dispersion in groundwater and the greater the migration in soil.
Vapor pressure	A measure of a constituent's tendency to evaporate.	The higher the vapor pressure, the more likely that the constituent will volatilize.
Henry's law constant	A measure of a constituent's tendency to partition between the aqueous phase and gaseous phase.	The higher the Henry's law constant, the greater the tendency to volatilize.
Boiling point	A measure of a constituent's tendency to volatilize.	The lower the boiling point, the greater the tendency for volatilization.
K_{oc}, K_d,	The tendency of a constituent to adsorb onto organic matter in the soil.	The lower the K_{oc} and K_d, the less the adsorption potential.
Molecular weight	The mass of a chemical constituent.	In general, the lighter the constituent the more likely that it will solubilize.

Solubility

Solubility is the amount of a substance (e.g., hydrocarbon) that will dissolve in a given amount of another substance (e.g., water). Therefore, a constituent's solubility provides insight to its fate and transport in the aqueous phase. Constituents that are highly soluble have a tendency to dissolve into the groundwater and are not likely to remain in the

adsorbed phase. They are also less likely to volatilize from groundwater and are more easily biodegraded. Conversely, chemicals that have low water solubilities tend to remain in the adsorbed phase or are likely to volatilize more readily, but they are less likely to biodegrade. In general, lower molecular weight constituents tend to be more soluble and, therefore, migrate and disperse much more readily in groundwater or soil moisture than do heavier constituents.

In the field, aqueous concentrations rarely approach the solubility of a substance because dissolved concentrations tend to be reduced through processes such as biodegradation, dilution, and adsorption. Nevertheless, the mobility of a constituent is largely determined by its water solubility. Exhibit IX-9 lists the solubility of the BTEX constituents. Note that these values are for pure components and mixtures tend to result in lower aqueous concentrations for individual constituents. The higher the solubility, the more likely it is that the constituent will be transported with flowing groundwater. Less soluble components may also be transported, although the aqueous concentration will be lower. More soluble gasoline additives (e.g., MTBE) are transported farther and faster than hydrocarbons. Often these additives can be detected in distant wells long before hydrocarbons arrive.

Exhibit IX-9
Solubilities of BTEX Constituents

Petroleum Constituent	Typical Percentage in Gasoline	Pure Compound Solubility (mg/L) (20°C)	Solubility of Compound in Typical Gasoline (%)
Ethylbenzene	2 to 8	152	4 to 8
o-Xylene	5 to 20	175	10 to 20
Toluene	2 to 10	515	30 to 80
Benzene	1 to 4	1,780	30 to 60

As shown in the exhibit, benzene is relatively more soluble than the other BTEX constituents and will therefore preferentially dissolve into the aqueous phase. As a result, benzene is the most likely BTEX constituent to be mobile and disperse in the aqueous phase. Ethylbenzene has a much lower solubility, therefore its concentration in the aqueous phase will be lower than the concentration of benzene.

Vapor Pressure

The vapor pressure of a constituent is a measure of its tendency to evaporate. More precisely, it is the pressure that a vapor exerts when in equilibrium with its pure liquid or solid form. Constituents with higher

vapor pressures (i.e., those constituents that readily evaporate at room temperature) more readily disperse, as they have a greater tendency to partition into the vapor phase and are, therefore, more mobile in soil vapor. Alternatively, constituents with relatively low vapor pressures are less likely to vaporize and become airborne. Volatilization from soil or groundwater is highest for constituents with higher vapor pressures.

Exhibit IX-10 presents vapor pressures of the BTEX constituents. As shown in the Exhibit, benzene is the BTEX constituent with the highest vapor pressure, and is therefore the constituent most likely to volatilize and disperse. Alternatively, xylenes will more readily adsorb to soil than enter the vapor phase. If the constituents of concern have high vapor pressures, they will likely volatilize and disperse readily, constituents with low vapor pressures are more likely to remain in soil and groundwater.

Exhibit IX-10
Vapor Pressures Of BTEX Constituents

Constituent	Vapor Pressure (mm Hg at 20°C)
Xylenes	6
Ethylbenzene	7
Toluene	22
Benzene	76

Henry's Law Constant

The Henry's law constant is a measure of a constituent's tendency to preferentially partition between the aqueous phase and the gaseous phase. The Henry's law constant provides a qualitative indication of the importance of volatilization: for constituents with Henry's law constants greater than about 100 atmospheres (atm), volatilization from the aqueous phase tends to be rapid.

As shown by the Henry's law constant values in Exhibit IX-11, each of the BTEX constituents has a value greater than 200, indicating that each will volatilize from water fairly readily, resulting in constituent migration from the aqueous phase. In the field, however, volatilization is generally limited by mass transfer (i.e., from the groundwater, through the capillary fringe and the unsaturated zone, and finally to the atmosphere), decreasing the importance of volatilization as a natural attenuation mechanism.

Exhibit IX-11 Henry's Law Constant Of BTEX Constituents	
Constituent	Henry's Law Constant (atm)
Ethylbenzene	359
Xylenes	266
Benzene	230
Toluene	217

Boiling Point

Petroleum products are often classified by their boiling point range because the boiling point is a measure of volatility. As shown in Exhibit IX-12, the boiling point for benzene is the lowest for the constituents in BTEX, implying that benzene will tend to volatilize most readily and be quite mobile in the soil vapor. Comparing the BTEX constituents, dissipation via volatilization is most important for benzene and least important for xylenes.

Boiling point ranges for heavier petroleum products are higher than those of the BTEX constituents (e.g., 40 to 225°C for gasoline, 180 to 300°C for kerosene, and > 275°C for heating oil), indicating that these constituents will volatilize less readily than the BTEX chemicals in gasoline.

Exhibit IX-12 Boiling Points Of BTEX Constituents	
Constituent	Boiling Point (°C)
Benzene	80.1
Toluene	110.8
Ethylbenzene	136.2
Xylenes	144.4

Organic Carbon Partition Coefficient (K_{oc}), Adsorption Potential (K_d)

The organic carbon partition coefficient (K_{oc}) is an approximation of the propensity of a compound to adsorb to organic matter found in the soil. The adsorption coefficient (K_d) value is an expression of the tendency of a constituent to remain adsorbed on soil and is the product

of K_{oc} and the fraction organic carbon (f_{oc}) in the soil. Compounds that have higher K_{oc} and K_d values tend to remain sorbed on soil and not migrate and dissipate as readily as those with lower K_{oc} and K_d values. K_{oc} values can range from 1 to 10^7. The K_{oc}s of BTEX constituents are all low, indicating relatively weak adsorption potential, as shown in Exhibit IX-13. None of the BTEX constituents will remain strongly sorbed to soils; rather, other factors such as volatilization and solubility will be more important to their degradation because these factors increase the likelihood that constituents will dissipate. Heavier petroleum constituents tend to have greater K_{oc} values and will thus sorb more strongly to soils, retarding constituent migration.

Exhibit IX-13
K_{oc} Values For BTEX Constituents

Constituent	K_{oc} Value (cm^3/g)
Benzene	65
Toluene	120
Ethylbenzene	220
Xylenes	237

Molecular Weight

Aromatic constituents with lighter molecular weights (i.e., the more soluble fractions, $\leq C_7$) tend to dissipate and degrade more readily than aromatic hydrocarbons with heavier molecular weights. Of the BTEX constituents, benzene and toluene have the lightest molecular weights (i.e., molecular weights of 78 g/mole for benzene and 92 g/mole for toluene).

Remedial Progress Monitoring

Monitoring the progress of natural attenuation is necessary to confirm whether petroleum constituents are being degraded or dissipated at acceptable rates and that potential receptors are not likely to be adversely affected.

Indicators Of Natural Attenuation

Site characterization data can provide numerous indicators to demonstrate that natural attenuation is occurring (McAllister, 1994). Some of the necessary data may be collected as part of a standard site characterization, while other data would likely be collected specifically for the purpose of evaluating natural attenuation effectiveness. Site

assessment data useful in evaluating natural attenuation effectiveness are listed in Exhibit IX-14. Note that sampling and analytical methods

Exhibit IX-14
Site Characterization Data Used To Evaluate Effectiveness Of Natural Attenuation

Site Characterization Data	Application
Direction and gradient of groundwater flow	Estimate expected rate of plume migration.
Hydraulic conductivity	Estimate expected rate of plume migration.
Definition of lithology	Understand preferential flow paths.
Aquifer thickness	Estimate volatilization rates and model groundwater flow.
Depth to groundwater	Estimate volatilization rates.
Range of water table fluctuations	Evaluate potential source smearing, influence of fluctuations on groundwater concentrations, and variation in flow direction.
Delineation of contaminant source and soluble plume	Compare expected extent without natural attenuation to actual extent.
Date of contaminant release	Estimate expected extent of plume migration.
Historical concentrations along the primary flow path from the source to the leading edge	Evaluate status of plume (i.e., steady state, decreasing, migrating).
Background D.O. levels upgradient of the source and plume	Determine if sufficient D.O. is present for aerobic biodegradation ($\geq$ 1 to 2 mg/L).
D.O. levels inside and outside the contaminant plume	Identify inverse correlation indicative of aerobic biodegradation.
Alkalinity, hardness, pH, and soluble Fe inside and outside the contaminant plume	Evaluate geochemical indicators of natural attenuation.
Redox potential	Determine nature of biologically mediated degradation of contaminants.
Locations of nearest groundwater recharge areas (e.g., canals, retention ponds, catch basins, and ditches)	Identify areas of natural groundwater aeration.

Source: Adapted from McAllister and Chiang, 1994.

must be consistent and appropriate, and well and screen placement must be appropriate to the site conditions, or the monitoring data might not accurately reflect the rate at which natural attenuation is occurring.

A thorough evaluation of constituent mass balance can be used to demonstrate the extent and rate of natural attenuation, but this approach requires extensive monitoring data that completely define the horizontal and vertical extent of the contaminant plume. This approach has been used to investigate natural attenuation, but it is generally

practical only for research. Several other indicators of natural attenuation with less extensive data requirements are described below.

Constituent Plume Characteristics

In the absence of natural attenuation mechanisms, constituent concentrations would remain relatively constant within the plume, and then decrease rapidly at the edge of the plume. If natural attenuation is occurring, constituent concentrations will decrease with distance from the source along the flow path of the plume as a result of dispersion. If other natural attenuation mechanisms are occurring, the rate at which concentrations of constituents are reduced will be accelerated.

Monitoring of constituent concentrations in the groundwater over time will give the best indication of whether natural attenuation is occurring. If natural attenuation is occurring, the contaminant plume will migrate more slowly than expected based on the average groundwater velocity. Receding plumes typically occur when the source has been eliminated. Natural attenuation may also be occurring in plumes that are expanding, but at a slower than expected rate. For example, in sandy soils with relatively low organic carbon content (about 0.1 percent), BTEX constituents are expected to migrate at one-third to two-thirds of the average groundwater speed velocity (McAllister, 1994). Higher organic carbon content would further retard constituent migration. If constituents are migrating more slowly than expected based on groundwater flow rates and retardation factors, then other natural attenuation mechanisms (primarily biodegradation) are likely reducing constituent concentrations. For stable plumes, the rate at which contaminants are being added to the system at the source is equal to the rate of attenuation. A plume may be stable for a long period of time before it begins to recede, and in some cases, if the source is not eliminated, the plume may not recede.

Occurrence of biodegradation might also be deduced by comparison of the relative migration of individual constituents. The relative migration rates of BTEX constituents, based on the chemical properties, are expected to be in the following order:

benzene > toluene, o-xylene > ethylbenzene, m-xylene, p-xylene.

If the actual migration rates do not follow this pattern, biodegradation may be responsible.

Dissolved Oxygen Indicators

The rate of biodegradation will depend, in part, on the supply of oxygen to the contaminated area. At levels of dissolved oxygen (D.O.) below 1 to 2 mg/L in the groundwater, aerobic biodegradation rates are very slow. If background D.O. levels (upgradient of the contaminant

source) equal or exceed 1 to 2 mg/L, the flow of groundwater will supply D.O. to the contaminated area, and aerobic degradation is possible.

Where aerobic biodegradation is occurring, an inverse relationship between D.O. concentration and constituent concentrations can be expected (i.e., D.O. levels increase as constituent levels decrease). Thus, if D.O. is significantly below background within the plume, aerobic biodegradation is probably occurring at the perimeter of the plume.

Geochemical Indicators

Certain geochemical characteristics can also serve as indicators that natural attenuation, particularly aerobic biodegradation, is occurring. Aerobic biodegradation of petroleum products produces carbon dioxide and organic acids, both of which tend to cause a region of lower pH and increased alkalinity within the constituent plume.

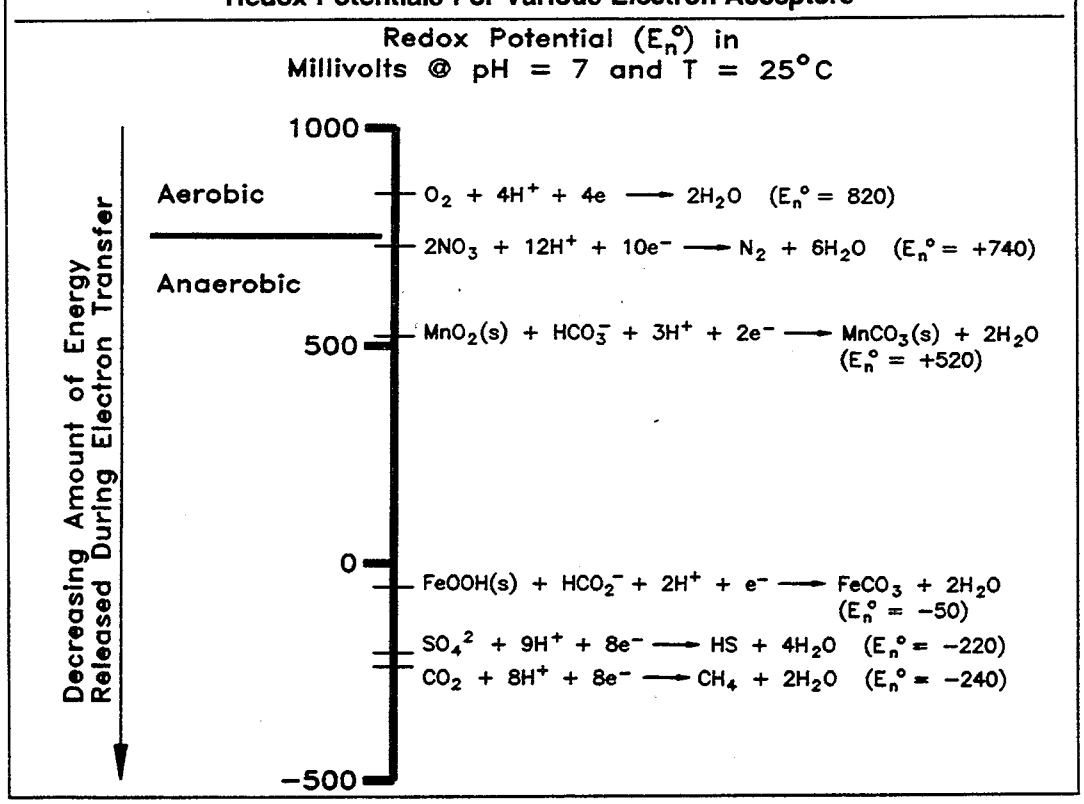
Anaerobic biodegradation may result in different geochemical changes, such as increased pH. Under anaerobic conditions, biodegradation of aromatic hydrocarbons typically causes reduction of Fe^{3+} [insoluble] to Fe^{2+} [soluble], because iron is commonly used as an electron acceptor under anaerobic conditions. Thus, soluble iron concentrations in the groundwater tend to increase immediately downgradient of a petroleum source as the D.O. is depleted, and conditions change to become anaerobic (i.e., reduced). The concentration of methane increases, another indication that anaerobic biodegradation is occurring.

Oxidation/Reduction Potential

The oxidation/reduction (redox) potential of groundwater is a measure of electron activity and is an indicator of the relative tendency of a solution to accept or transfer electrons. Because redox reactions in groundwater are biologically mediated, the rates of biodegradation both influence and depend on redox potential. Many biological processes operate only within a prescribed range of redox conditions. Redox potential also can be used as an indicator of certain geochemical activities (e.g., reduction of sulfate, nitrate, or iron). The redox potential of groundwater generally ranges from 800 millivolts to about -400 millivolts (Exhibit IX-15). The lower the redox potential, the more reducing and anaerobic the environment.

Measurement of redox potential of groundwater also allows for approximate delineation of the extent of the contaminant plume. Redox potential values taken from within the contaminant plume will be lower than background (upgradient) redox values and values from outside the plume. This is due in part to the anaerobic conditions that typically exist within the core of the dissolved hydrocarbon plume.

Exhibit IX-15
Redox Potentials For Various Electron Acceptors



Source: Modified from Norris et al., (1994).

Ongoing Monitoring

If the indicators described above suggest that natural attenuation is occurring, it is important for ongoing monitoring to be conducted to confirm effectiveness and estimate the rate. As with the active remediation technologies also described in this manual, if natural attenuation does not appear to be effective in remediating the contamination at the site within a reasonable time frame, then an alternative active remedial technology will be required. Alternatively, if permissible under state regulations, a risk assessment (using fate and transport modeling and/or exposure models) may be acceptable to determine if an aggressive remedial alternative is necessary.

A table summarizing the constituents to monitor and the suggested monitoring frequency is presented as Exhibit IX-16, while more specific details are discussed below.

Exhibit IX-16
Ongoing Progress Monitoring

Medium	Monitoring Frequency	What To Monitor	Where/Number Of Samples To Monitor
Soil	Annually	BTEX; TPH; any other constituents of concern; O_2, CO_2, temperature, pH.	Several representative samples located throughout the area of contamination.
Groundwater	Quarterly for the first year, then annually thereafter.	BTEX; TPH; any other constituents of concern; D.O., CO_2, pH, alkalinity, hardness, soluble Fe, redox potential.	Minimum of 4 wells: 1 upgradient, 3 downgradient. Wells along the plume centerline and outside the plume boundaries.

Soils

Soil samples should be collected from the unsaturated zone and should be analyzed for the BTEX constituents, TPH, and any other constituents of concern at the site. Sampling should take place annually to demonstrate reductions in constituent concentrations.

At a minimum, samples should be collected in locations where the contamination is known to be greatest (e.g., where the LUST was initially located), to determine whether concentrations are being reduced. Any other affected areas also should be sampled. Samples should also be collected from the boundary of the contaminated soil area to evaluate whether the extent of contamination in the soils is increasing or decreasing. If the primary constituents of concern at the site are volatile organic chemicals (VOCs), monitoring of soil gas may be substituted for direct soil measurements at some locations.

In addition, analyses for O_2, CO_2, and methane may be conducted to determine the microbial activity in the soils. As described above, reduced O_2 concentrations in the plume area (relative to background) and elevated CO_2 concentrations are a good indication that aerobic biodegradation is occurring. These measurements are best collected from permanent gas probes.

Groundwater

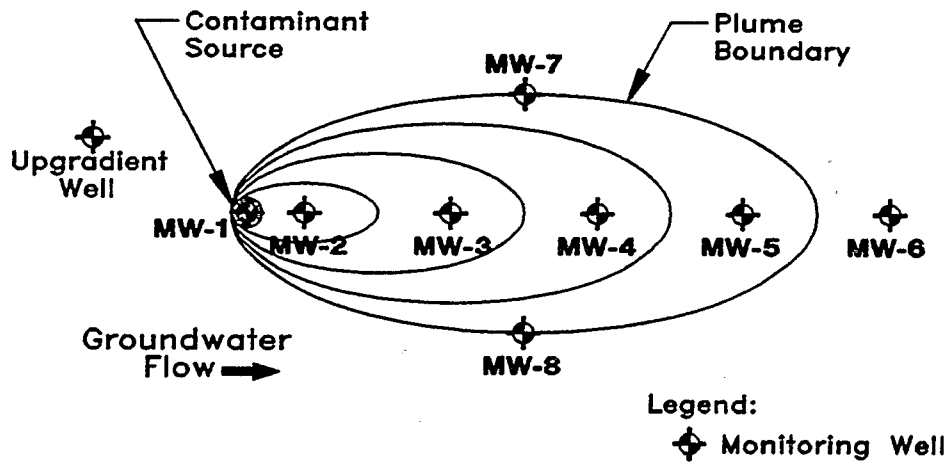
Groundwater monitoring should be designed to ensure that the vertical and lateral extent of constituents in groundwater is evaluated. At a minimum, the groundwater should be analyzed for VOCs and other constituents of concern, TPH, dissolved oxygen (D.O.), pH, redox potential, alkalinity, and hardness. Groundwater monitoring should be

conducted quarterly during the first year. Sampling frequency can then be reduced depending upon contaminant travel times and other site-specific factors (e.g., distance to nearest receptor).

In order to demonstrate that natural attenuation is occurring, a sufficient number of monitoring wells that are appropriately located are necessary. A typical site characterization may involve installation of one upgradient well and three downgradient wells. Appropriate monitoring of natural attenuation requires additional wells; at least 1 close to the original source and several along the centerline of the dissolved plume and around the outer boundary of the plume as illustrated in Exhibit IX-17. The number of wells required must be determined based on site-specific considerations. If natural attenuation is occurring, concentrations in these wells should decrease with distance from the source area. Optimally, some of these additional wells will be placed so that they are outside the plume. Another type of well, a sentinel well, is located between the leading downgradient edge of the dissolved plume and a receptor (e.g., a drinking water supply well). Such wells provide early warning to the well user should the plume continue to migrate. Detection of contamination in sentinel wells or wells outside the plume indicate that natural attenuation is not occurring at an acceptable rate and more aggressive remedial alternatives should be considered.

If the potential exists for constituents in shallow groundwater to discharge into surface water bodies such as streams or rivers, these water bodies should be sampled for the same characteristics (e.g., VOCs, TPH, D.O.) at the same frequency as groundwater. However, dilution and biodegradation will potentially be of such magnitude that the presence of the constituent, parameter, or characteristic of interest may be completely masked.

Exhibit IX-17
Recommended Groundwater Monitoring Well Network For Demonstrating Natural Attenuation



Source: Adapted from McAllister and Chiang, 1994.

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Checklist: Can Natural Attenuation Be Used At This Site?

This checklist can help you to evaluate the completeness of the CAP and to identify areas that require closer scrutiny. As you go through the CAP, answer the following questions. If the answer to several of the questions below is no, you may want to request additional information to determine if natural attenuation will accomplish the cleanup goals at the site.

1. Initial Screening

Yes	No	
❑	❑	Are there no nearby human or sensitive ecological receptors near the site that could be exposed to the petroleum contamination in soil?
❑	❑	If potential receptors are present, are they located at a distance that represents a minimum 2 year travel time?
❑	❑	Are maximum total constituent concentrations less than 20,000 to 25,000 ppm TPH?
❑	❑	Are there potential receptors who could be exposed to contaminated groundwater, soil, or vapors?

2. Detailed Evaluation -- Site Factors Affecting Constituent Degradation

Yes	No	
❑	❑	Are the soils well aerated, allowing for transfer of oxygen to subsurface soils?
❑	❑	Is the adsorption potential of the constituent/soil combination high enough to adequately retard constituent migration?
❑	❑	Is the seepage velocity low enough to prevent rapid migration of constituents?
❑	❑	Is soil oxygen content $\geq$ 2 percent and dissolved oxygen content $\geq$ 1 to 2 mg/L?
❑	❑	Is moisture available for transport of microorganisms (soil moisture of 40 to 85 percent of field capacity)?
❑	❑	Is the pH of the soil between 6 and 8?

2. Detailed Evaluation -- Site Factors Affecting Constituent Degradation (continued)

Yes	No	
❑	❑	Are concentrations of heavy metals and other toxic compounds below levels that could inhibit microbial activity?
❑	❑	Is rainfall moderate to heavy (i.e., 10 to 60 inches/year)?
❑	❑	Is the climate moderate to warm (i.e., 5° to 45°C)?
❑	❑	Does the soil have a C:N:P ratio of about 100:1:0.5 to 100:10:1?

3. Detailed Evaluation -- Chemical Constituent Factors Affecting Migration For Those Constituents Requiring The Most Significant Concentration Reduction

Yes	No	
❑	❑	Are the majority of the hydrocarbon constituents at most slightly soluble in water?
❑	❑	Are the majority of the hydrocarbon constituents not highly volatile (as measured by vapor pressure, Henry's law constant, and boiling point)?
❑	❑	Are the K_{oc} and K_d values of constituents high enough to adequately retard migration?
❑	❑	Are the constituents sufficiently biodegradable?

4. Remedial Monitoring

Yes	No	
❑	❑	Will soil samples be collected?
❑	❑	Will a minimum of 4 groundwater wells be sampled?
❑	❑	Is the groundwater monitoring frequency at least quarterly during the first year?
❑	❑	Are the groundwater wells placed to detect the reductions of constituent concentrations in the plume and potential migration of constituents?

Chapter X

In-Situ Groundwater Bioremediation

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Chapter X
In-Situ Groundwater Bioremediation

Overview

In-situ groundwater bioremediation is a technology that encourages growth and reproduction of indigenous microorganisms to enhance biodegradation of organic constituents in the saturated zone. In-situ groundwater bioremediation can effectively degrade organic constituents which are dissolved in groundwater and adsorbed onto the aquifer matrix.

Bioremediation generally requires a mechanism for stimulating and maintaining the activity of these microorganisms. This mechanism is usually a delivery system for providing one or more of the following: An electron acceptor (oxygen, nitrate); nutrients (nitrogen, phosphorus); and an energy source (carbon). Generally, electron acceptors and nutrients are the two most critical components of any delivery system.

In a typical in-situ bioremediation system, groundwater is extracted using one or more wells and, if necessary, treated to remove residual dissolved constituents. The treated groundwater is then mixed with an electron acceptor and nutrients, and other constituents if required, and re-injected upgradient of or within the contaminant source. Infiltration galleries or injection wells may be used to re-inject treated water, as illustrated in Exhibits X-1 and X-2, respectively. In an ideal configuration, a "closed-loop" system would be established. All water extracted would be reinjected without treatment and all remediation would occur in situ. This ideal system would continually recirculate the water until cleanup levels had been achieved. If your state does not allow re-injection of extracted groundwater, it may be feasible to mix the electron acceptor and nutrients with fresh water instead. Extracted water that is not re-injected must be discharged, typically to surface water or to publicly owned treatment works (POTW).

In-situ bioremediation can be implemented in a number of treatment modes, including: Aerobic (oxygen respiration); anoxic (nitrate respiration); anaerobic (non-oxygen respiration); and co-metabolic (see Abbreviations and Definitions). The aerobic mode has been proven most effective in reducing contaminant levels of aliphatic (e.g., hexane) and aromatic petroleum hydrocarbons (e.g., benzene, naphthalene) typically present in gasoline and diesel fuel. In the aerobic treatment mode, groundwater is oxygenated by one of three methods: Direct sparging of air or oxygen through an injection well; saturation of water with air or oxygen prior to re-injection; or addition of hydrogen peroxide directly

Exhibit X-1
Schematic Diagram Of Typical In-Situ Groundwater Bioremediation System Using Infiltration Gallery

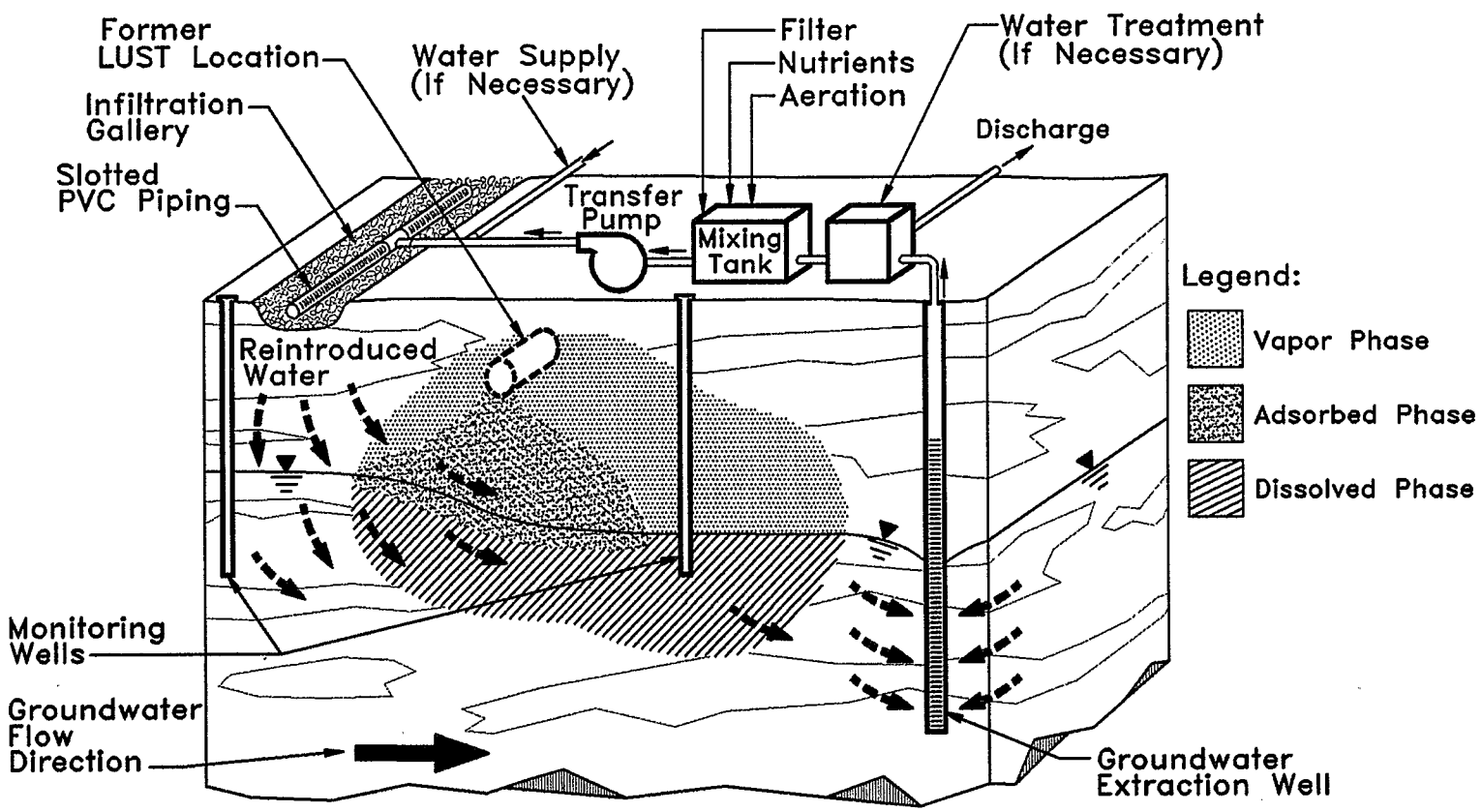
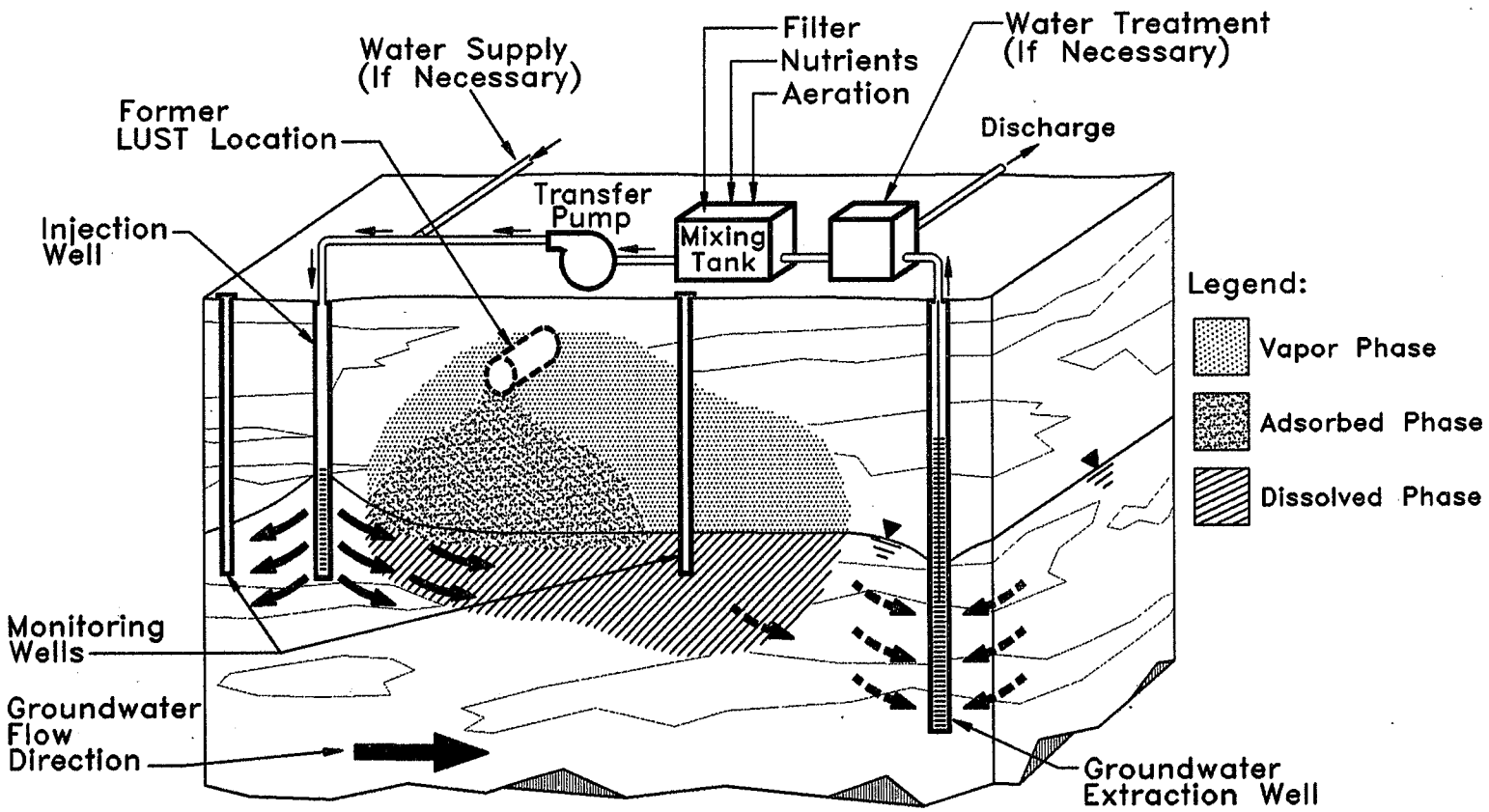


Exhibit X-2
Schematic Diagram Of Typical In-Situ Groundwater Bioremediation System Using Injection Wells



into an injection well or into reinjected water. Whichever method of oxygenation is used, it is important to ensure that oxygen is being distributed throughout the area of contamination. Anoxic, anaerobic, and co-metabolic modes are sometimes used for remediation of other compounds, such as chlorinated solvents, but are generally slower than aerobic respiration in breaking down petroleum hydrocarbons.

In-situ groundwater bioremediation can be effective for the full range of petroleum hydrocarbons. While there are some notable exceptions, such as MTBE, the short-chain, low-molecular-weight, more water soluble constituents are degraded more rapidly and to lower residual levels than are long-chain, high-molecular-weight, less soluble constituents. Recoverable free product should be removed from the subsurface prior to operation of the in-situ groundwater bioremediation system. This will mitigate the major source of contaminants as well as reduce the potential for smearing or spreading high concentrations of contaminants. A summary of the advantages and disadvantages of in-situ bioremediation of the saturated zone is shown in Exhibit X-3.

In-situ bioremediation of groundwater can be combined with other saturated zone remedial technologies (e.g., air sparging) and vadose zone remedial operations (e.g., soil vapor extraction, bioventing).

This chapter will assist you in evaluating a corrective action plan (CAP) that proposes in-situ groundwater bioremediation for a petroleum-contaminated aquifer. The evaluation process, which is summarized in a flow diagram shown in Exhibit X-4, will serve as a roadmap for the decisions you will make during your evaluation. You can use the checklist at the end of this chapter as a tool to evaluate the completeness of the CAP and to help focus attention on areas where additional information may be needed. The evaluation process can be divided into the following steps:

- **Step 1:** ***An initial screening of in-situ groundwater bioremediation effectiveness***, which will allow you to quickly gauge whether this technology is likely to be effective, moderately effective, or ineffective.

- **Step 2:** ***A detailed evaluation of in-situ groundwater bioremediation effectiveness***, which provides further screening criteria to confirm the effectiveness of this technology and develop design standards and operating conditions. To complete the detailed evaluation, you will need to identify specific soil and constituent characteristics and properties, compare them to ranges where in-situ groundwater bioremediation is potentially effective, decide whether

Exhibit X-3
Advantages And Disadvantages Of In-Situ Groundwater Bioremediation

Advantages	Disadvantages
○ Remediates contaminants that are adsorbed onto or trapped within the geologic materials of which the aquifer is composed along with contaminants dissolved in the groundwater.	○ Injection wells and/or infiltration galleries may become plugged by microbial growth or mineral precipitation.
○ Application involves equipment that is widely available and easy to install.	○ High concentrations (TPH > 50,000 ppm) of low solubility constituents may be toxic and/or not bioavailable.
○ Creates minimal disruption and/or disturbance to on-going site activities.	○ Difficult to implement in low-permeability aquifers ($<10^{-4}$ cm/sec).
○ Time required for subsurface remediation may be shorter than other approaches (e.g., pump and treat).	○ Re-injection wells or infiltration galleries may require permits or may be prohibited. Some states require permit for air injection.
○ Is generally recognized as being less costly than other remedial options (e.g., pump and treat, excavation).	○ May require continuous monitoring and maintenance.
○ Can be combined with other technologies (e.g., bioventing, soil vapor extraction) to enhance site remediation.	○ Remediation may only occur in more permeable layer or channels within the aquifer.
○ In many cases, this technique does not produce waste products that must be disposed of.	

treatability studies are necessary to determine effectiveness, and conclude whether this technology is likely to be effective at a site.

○ **Step 3:** ***An evaluation of the in-situ groundwater bioremediation system design***, which will allow you to determine if the rationale for the design has been appropriately defined based on treatability study data, whether the necessary design components have been specified, and whether the construction process flow designs are consistent with standard practice.

○ **Step 4:** ***An evaluation of the operation and monitoring plans***, which will allow you to determine whether plans for start-up and long-term system operation monitoring are of sufficient scope and frequency, and whether remedial progress monitoring plans are appropriate.

Exhibit X-4
In-situ Groundwater Bioremediation Evaluation Process Flow Chart

INITIAL SCREENING OF IN-SITU GROUNDWATER BIOREMEDIATION EFFECTIVENESS

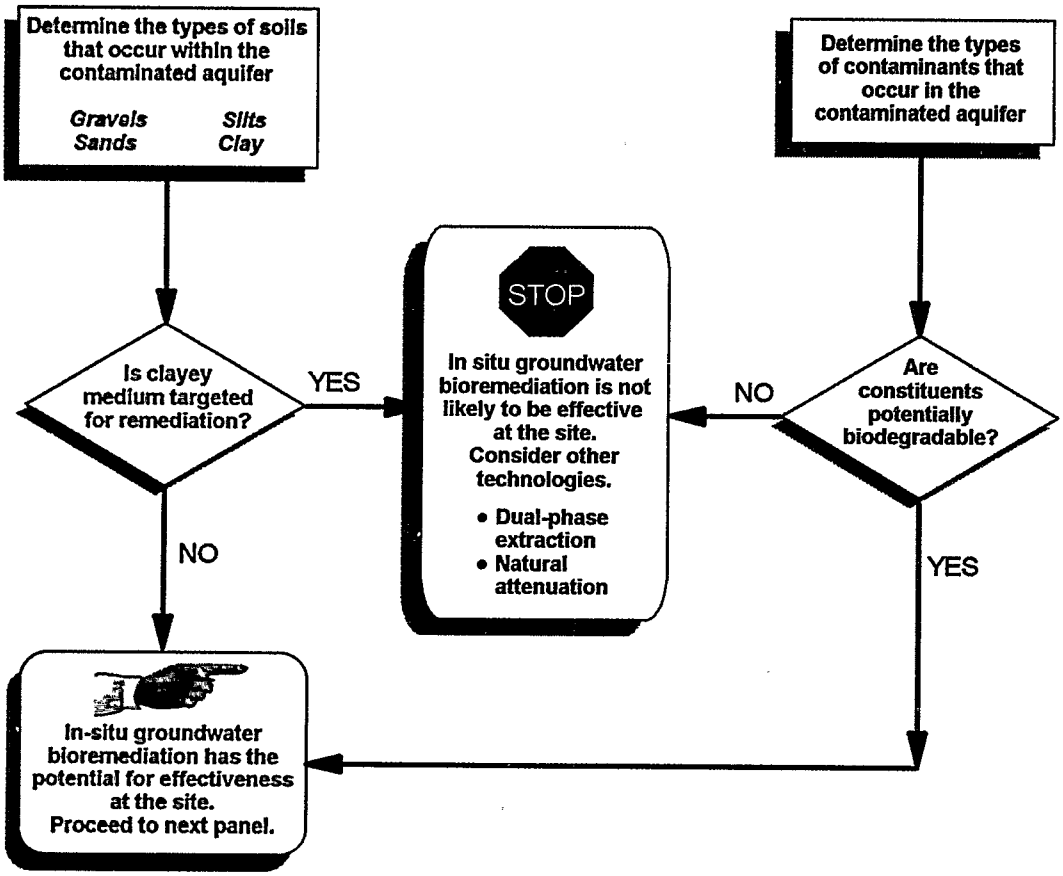


Exhibit X-4
In-situ Groundwater Bioremediation Evaluation Process Flow Chart

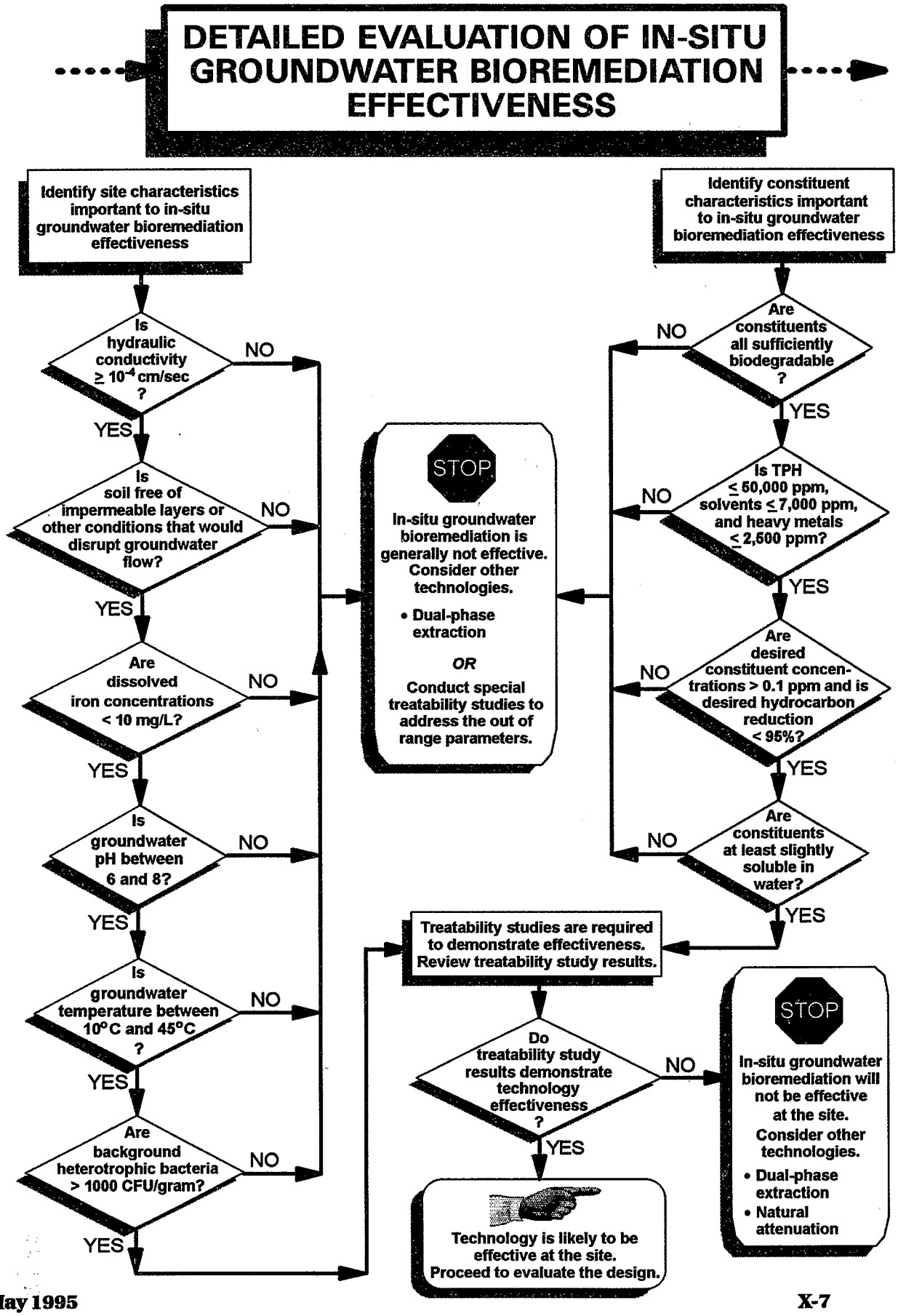
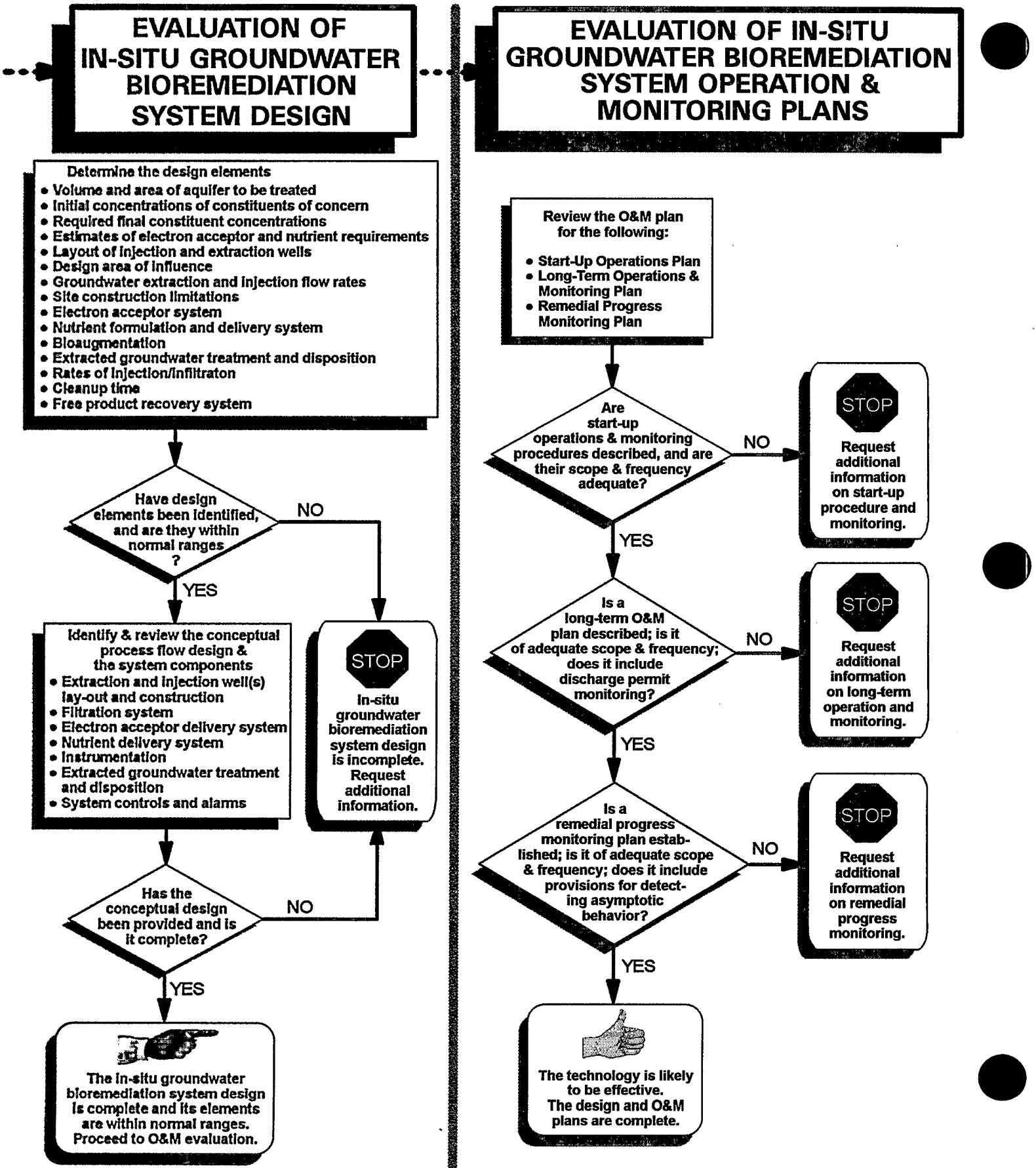


Exhibit X-4
In-situ Groundwater Bioremediation Evaluation Process Flow Chart



Initial Screening Of In-Situ Groundwater Bioremediation

This section allows you to quickly assess whether in-situ groundwater bioremediation is likely to be effective at a site. The key parameters that determine the effectiveness of this technology are:

- The *hydraulic conductivity* of the aquifer, which controls the distribution of electron acceptors and nutrients in the subsurface;
- The *biodegradability* of the petroleum constituents, which determines both the rate and degree to which constituents will be degraded by microorganisms; and
- The *location of petroleum contamination* in the subsurface. Contaminants must be dissolved in groundwater or adsorbed onto more permeable sediments within the aquifer.

In general, the aquifer medium will determine *hydraulic conductivity.* Fine-grained media (e.g., clays, silts) have lower intrinsic permeability than coarse-grained media (e.g., sands, gravels).

Bioremediation is generally effective in permeable (e.g., sandy, gravelly) aquifer media. However, depending on the extent of contamination, bioremediation also can be effective in less permeable silty or clayey media. In general, an aquifer medium of lower permeability will require longer to clean up than a more permeable medium.

The *biodegradability* of a petroleum constituent is a measure of its ability to be metabolized (or co-metabolized) by hydrocarbon-degrading bacteria or other microorganisms.

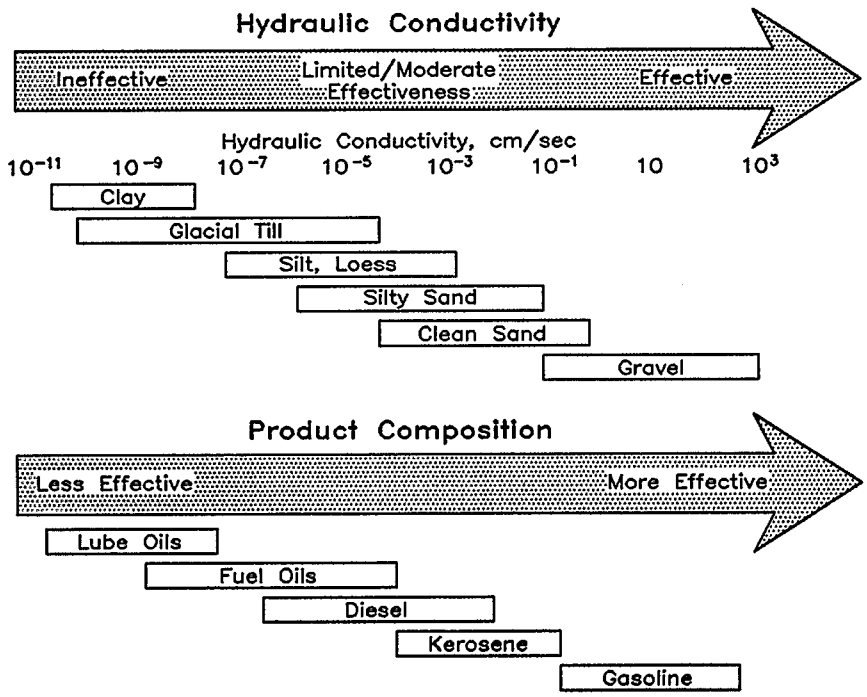
The chemical characteristics of the contaminants will dictate their biodegradability. For example, heavy metals are not degraded by bioremediation. The biodegradability of organic constituents depends on their chemical structures and physical/chemical properties (e.g., water solubility, water/octanol partition coefficient). Highly soluble organic compounds with low molecular weights will tend to be more rapidly degraded than slightly soluble compounds with high molecular weights. The low water solubilities of the more complex compounds render them less bioavailable to petroleum-degrading organisms. Consequently, the larger, more complex chemical compounds may be slow to degrade or may even be recalcitrant to biological degradation (e.g., asphaltenes in No. 6 fuel oil).

The location, distribution, and disposition of petroleum contamination in the subsurface can significantly influence the likelihood of success for

bioremediation. This technology generally works well for dissolved contaminants and contamination adsorbed onto higher permeability sediments (sands and gravels). However, if the majority of contamination is (1) in the unsaturated zone; (2) trapped in lower permeability sediments, or (3) outside the "flow path" for nutrients and electron acceptors, this technology will have reduced impact or no impact.

Exhibit X-5 is an initial screening tool that you can use to help assess the potential effectiveness of in-situ groundwater bioremediation. To use this tool, you must first determine the type of aquifer medium present and the type of petroleum product released at the site. Information provided in the following section will allow a more thorough evaluation of

Exhibit X-5
Initial Screening For In-Situ Groundwater Bioremediation Effectiveness



Note:
All petroleum products listed are amenable to in-situ groundwater bioremediation.

effectiveness and will identify areas that could require special design considerations.

Detailed Evaluation Of In-Situ Groundwater Bioremediation Effectiveness

Once you have completed the initial screening and determined that in-situ groundwater bioremediation may be effective for the aquifer media and petroleum product present, evaluate the CAP further to confirm that the technology will be effective.

While the initial screening focused on hydraulic conductivity and constituent biodegradability, the detailed evaluation should consider a broader range of site and constituent characteristics, which are listed in Exhibit X-6.

Exhibit X-6
Key Parameters Used To Evaluate The Effectiveness Of In-Situ Groundwater Bioremediation

Site Characteristics	Constituent Characteristics
Hydraulic conductivity	Chemical structure
Soil structure and stratification	Concentration and toxicity
Groundwater mineral content	Solubility
Groundwater pH	
Groundwater temperature	
Microbial presence	
Terminal electron acceptors	
Nutrient concentrations	

The remainder of this section describes each parameter, why it is important to in-situ groundwater bioremediation, how it can be determined, and a range of values over which in-situ groundwater bioremediation is generally effective.

Site Characteristics That Affect In-Situ Groundwater Bioremediation

Site characteristics that influence the potential effectiveness of in-situ groundwater bioremediation are described below.

Hydraulic Conductivity

Hydraulic conductivity, which is a measure of water's ability to move through the aquifer medium, is one of the important factors in determining the potential effectiveness of in-situ groundwater bioremediation. This characteristic controls the rate and the distribution of electron acceptors and nutrients delivered to the bacteria in the aquifer. Hydraulic conductivity can be determined from aquifer tests, including slug tests and pumping tests. These tests must be designed carefully to ensure that contaminants are not forced to spread further in the aquifer and that a large volume of contaminated groundwater is not generated which then requires expensive treatment or disposal. The hydraulic conductivity of aquifer media varies over a wide range depending on the constituent materials (e.g., sand, gravel, silt, clay). In general, fine-grained soils composed of clays or silts offer resistance to water flow. Soils that are highly fractured, however, may have sufficient permeability to use in-situ bioremediation. For aquifers with hydraulic conductivity greater than 10^{-4} cm/sec, in-situ groundwater bioremediation is effective. For sites with lower hydraulic conductivities (e.g., 10^{-4} to 10^{-6} cm/sec), the technology also could be effective, but it must be carefully evaluated, designed, and controlled.

Intrinsic permeability, which is a measure of the ability of soils to transmit fluids, is sometimes reported instead of hydraulic conductivity. If intrinsic permeability is given, you calculate the hydraulic conductivity from the following equation:

$$K = \frac{k(\rho g)}{\mu}$$

where

K = hydraulic conductivity (cm/sec),

k = intrinsic permeability (cm^2),

μ = water viscosity ($g/cm \cdot sec$),

ρ = water density (g/cm^3),

g = acceleration of gravity (cm/sec^2).

At 20°C: $(\rho g/\mu) = 9.8 \times 10^4\ (cm \cdot sec)^{-1}$. To convert k from cm^2 to darcy, multiply by 10^8.

Soil Structure and Stratification

Soil structure and stratification are important to in-situ groundwater bioremediation because they affect groundwater flowrates and patterns when water is extracted or injected. Structural characteristics such as microfracturing can result in higher permeabilities than expected for certain soils (e.g., clays). In this case, however, flow will increase in the fractured media but not in the unfractured media. The stratification of soils with different permeabilities can dramatically increase the lateral flow of groundwater in the more permeable strata while reducing the flow through less permeable strata. This preferential flow behavior can lead to reduced effectiveness and extended remedial times for less-permeable strata.

The intergranular structure and stratification of aquifer media can be determined by reviewing soil logs from wells or borings and by examining geologic cross-sections. It will be necessary to verify that soil types have been properly identified, that visual observations of soil structure have been documented, and that boring logs are of sufficient detail to define soil stratification. Stratified soils may require special design consideration (e.g., special injection well(s)) to ensure that these less-permeable strata are adequately handled.

Fluctuations in the groundwater table should also be determined. Significant seasonal or daily (e.g., tidal, precipitation-related) fluctuations will submerge some of the soil in the unsaturated zone, which should be considered during design of the system.

Groundwater Mineral Content

Excessive calcium, magnesium, or iron in groundwater can react with phosphate, which is typically supplied as a nutrient in the form of tripolyphosphate, or with carbon dioxide, which is produced by microorganisms as a by-product of aerobic respiration. The products of these reactions can adversely affect the operation of an in-situ bioremediation system. When calcium, magnesium, or iron reacts with phosphate or carbon dioxide, crystalline precipitates or "scale" is formed. Scale can constrict flow channels and can also damage equipment, such as injection wells and sparge points. In addition, the precipitation of calcium or magnesium phosphates ties up phosphorus compounds, making them unavailable to microorganisms for use as nutrients. This effect can be minimized by using tripolyphosphates in a mole ratio of greater than 1:1 tripolyphosphates to total minerals (i.e., magnesium

and calcium). At these concentrations, the tripolyphosphate acts as a sequestering agent to keep the magnesium and calcium in solution (i.e., prevent the metal ions from precipitating and forming scale).

When oxygen is introduced to the subsurface as a terminal electron acceptor, it can react with dissolved iron (Fe^{+2}) to form an insoluble iron precipitate, ferric oxide. This precipitate can be deposited in aquifer flow channels, reducing permeability. The effects of iron precipitation tend to be most noticeable around injection wells, where oxygen concentration in groundwater is highest and can render injection wells inoperable. Exhibit X-7 provides a guide to assessing the potential impact of dissolved iron in groundwater.

Exhibit X-7
Dissolved Iron And In-Situ Bioremediation Effectiveness

Dissolved Iron Concentration (mg/L)	Effectiveness
$Fe^{+2} < 10$	Probably effective
$10 \leq Fe^{+2} \leq 20$	Injection wells require periodic testing and may need periodic cleaning or replacement
$Fe^{+2} > 20$	Not recommended

Other parameters that could be good indicators of potential groundwater scaling are hardness, alkalinity, and pH. In particular, very hard water (i.e., $\geq$ 400-500 mg/L carbonate hardness) tends to promote scaling. The potential adverse effects caused by excessive mineral content (e.g., calcium, magnesium, iron, total carbonates) in the groundwater warrants careful attention during site characterization activities.

Groundwater pH

Extreme pH values (i.e., less than 5 or greater than 10) are generally unfavorable for microbial activity. Typically, optimal microbial activity occurs under neutral pH conditions (i.e., in the range of 6–8). The optimal pH is site specific. For example, aggressive microbial activity has been observed at lower pH conditions outside of this range (e.g., 4.5 to 5) in natural systems. Because indigenous microorganisms have adapted to the natural conditions where they are found, pH adjustment, even toward neutral, can inhibit microbial activity. If man-made

conditions (e.g., releases of petroleum) have altered the pH outside the neutral range, pH adjustment may be needed. If the pH of the groundwater is too low (too acid), lime or sodium hydroxide can be added to increase the pH. If the pH is too high (too alkaline), then a suitable acid (e.g., hydrochloric, muriatic) can be added to reduce the pH. Changes to pH should be closely monitored because rapid changes of more than 1 or 2 units can inhibit microbial activity and may require an extended acclimation period before the microbes resume their activity.

Groundwater Temperature

Bacterial growth rate is a function of temperature. Subsurface microbial activity has been shown to decrease significantly at temperatures below 10°C and essentially to cease below 5°C. Microbial activity of most bacterial species important to petroleum hydrocarbon biodegradation also diminishes at temperatures greater than 45°C. Within the range of 10°C to 45°C, the rate of microbial activity typically doubles for every 10°C rise in temperature. In most cases, for in-situ groundwater bioremediation, the bacteria living in an aquifer system are likely to experience relatively stable temperatures with only slight seasonal variations. In most areas of the U.S., the average groundwater temperature is about 13°C, but groundwater temperatures may be somewhat lower or higher in the extreme northern and southern states.

Microbial Presence

Soil normally contains large numbers of diverse microorganisms, including bacteria, algae, fungi, protozoa, and actinomycetes. Of these organisms, the bacteria are the most numerous and biochemically active group, particularly at low oxygen levels, and they contribute significantly to in-situ groundwater bioremediation.

At a contaminated site, the natural microbial population undergoes a selection process. First, there is an acclimation period, during which microbes adjust to their new environment and new source of food. Second, those organisms that adapt most quickly tend to grow fastest and can use up nutrients that other microbes would need. Third, as the environmental conditions change and the nature of the food supply changes, the microorganism populations change as well. Organisms capable of withstanding the stress of their changing environment will generally be those that will contribute to the bioremediation of the site.

To determine the presence and population density of naturally occurring bacteria that will contribute to degradation of petroleum constituents, laboratory analysis of soil samples from the site should be completed. These analyses, at a minimum, should include plate counts

for total heterotrophic bacteria (i.e., bacteria that use organic compounds as an energy source) and hydrocarbon-degrading bacteria. Although heterotrophic bacteria are normally present in all soil environments, plate counts of less than 1,000 colony-forming units (CFU)/gram of soil could indicate depletion of oxygen or other essential nutrients or the presence of toxic constituents. However, concentrations as low as 100 CFU per gram of soil can be stimulated to acceptable levels, assuming toxic conditions (e.g., exceptionally high concentrations of heavy metals) are not present. These conditions are summarized in Exhibit X-8.

Exhibit X-8
Heterotrophic Bacteria And In-Situ Groundwater Bioremediation Effectiveness

Total Heterotrophic Bacteria	Effectiveness
> 1,000 CFU/gram dry soil	Generally effective.
100 - 1,000 CFU/gram dry soil	May be effective; needs further evaluation to determine whether toxic conditions are present and/or whether population responds to stimulation (e.g., increased supply of electron acceptor and/or nutrients).
< 100	Not generally effective.

Some CAPs propose the addition of microorganisms (bioaugmentation) into the aquifer environment when colony plate counts are low. However, research has shown that most in-situ bioremediation projects have been successfully completed without microbial augmentation. Experience with microbial augmentation shows that it varies in effectiveness. Except in coarse-grained, highly permeable material, microbes tend not to move very far past the point of injection, therefore, their effectiveness is limited in extent. In general, microbial augmentation does not adversely affected bioremediation, but it could be an unnecessary cost.

Terminal Electron Acceptors

Microorganisms require carbon as an energy source to sustain their metabolic functions, which include growth and reproduction. The metabolic process used by bacteria to produce energy requires a terminal electron acceptor (TEA) to enzymatically oxidize the carbon source (organic matter) to carbon dioxide.

$$\text{Organic Matter} + O_2 + \text{Biomass} \rightarrow CO_2 + H_2O + \Delta H_f$$

where ΔH_f is energy generated by the reaction to fuel other metabolic processes including growth and reproduction. In this example, oxygen serves as the TEA.

Microorganisms are classified by the carbon and TEA sources they use to carry out metabolic processes. Bacteria that use organic compounds as their source of carbon are called *heterotrophs*; those that use inorganic carbon compounds such as carbon dioxide are called *autotrophs*. Bacteria that use oxygen as their TEA are called *aerobes*; those that use a compound other than oxygen (e.g., nitrate, sulfate) are called *anaerobes*; and those that can utilize both oxygen and other compounds as TEAs are called *facultative*. For in-situ groundwater bioremediation applications directed at petroleum products, bacteria that are both *aerobic* (or *facultative*) and *heterotrophic* are most important in the degradation process.

Nutrient Concentrations

Microorganims require inorganic nutrients such as nitrogen and phosphate to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in the aquifer but, more frequently, nutrients need to be added to maintain adequate bacterial populations.

A rough approximation of maximum nutrient requirements can be based on the stoichiometry of the overall biodegradation process:

$$\text{C-source} + \text{N-source} + O_2 + \text{Minerals} + \text{Nutrients} \text{ --->}$$
$$\text{Cell mass} + CO_2 + H_2O + \text{other metabolic by-products}$$

Different empirical formulas of bacterial cell mass have been proposed; the most widely accepted are $C_5H_7NO_2$ and $C_{60}H_{87}O_{32}N_{12}P$. Using the empirical formulas for cell biomass and other assumptions, the carbon:nitrogen:phosphorus ratios necessary to enhance biodegradation fall in the range of 100:10:1 to 100:1:0.5, depending on the constituents and bacteria involved in the biodegradation process.

Chemical analyses of soil samples (collected from below the water table) and groundwater samples should be completed to determine the available concentrations of nitrogen (expressed as ammonia) and phosphate. Soil analyses are routinely conducted in agronomic laboratories that test soil fertility for farmers. These concentrations can be compared to the nitrogen and phosphorus requirements calculated

from the stoichiometric ratios of the biodegradation process. Some microbes can use nitrate as a nitrogen source. The drinking water standard for nitrate is 40 mg/L and there may be regulatory prohibitions against injecting nitrate into groundwater. If nitrogen addition is necessary, slow release sources should be used and addition of these materials should be monitored throughout the project to prevent degradation of water quality. In addition, excessive nitrogen additions can lower soil pH, depending on the amount and type of nitrogen added.

Because of water quality and soil chemistry considerations, in situ groundwater bioremediation should be operated at near nutrient-limited conditions.

Constituent Characteristics That Affect In-Situ Groundwater Bioremediation

Chemical Structure

The chemical structures of the constituents to be treated by in-situ groundwater bioremediation are important for determining the rate at which biodegradation will occur. Although nearly all constituents in petroleum products typically found at UST sites are biodegradable, the more complex the molecular structure of the constituent, the more difficult the product is to treat and the greater the time required for treatment. Most low-molecular-weight (nine carbon atoms or less) aliphatic and monoaromatic constituents are more easily biodegraded than higher-molecular-weight aliphatic or polyaromatic organic constituents. Straight chain, aliphatic (i.e., alkanes, alkenes, and alkynes) hydrocarbon compounds are more readily degraded than their branched isomers, and mono-aromatic compounds (e.g., benzene, ethyl benzene, toluene, xylenes) are more rapidly degraded than the two-ring compounds (e.g., naphthalene), which in turn are more rapidly degraded than the larger multi-ringed compounds (i.e., polyaromatic hydrocarbons or polynuclear aromatic hydrocarbons). The larger, more complex chemical structures may be slow to degrade or be essentially resistant to biological degradation (e.g., asphaltenes in No. 6 fuel oil). Exhibit X-9 lists, in order of decreasing rate of potential biodegradability, some common constituents found at petroleum UST sites.

Petroleum hydrocarbon contamination is sometimes accompanied by other organic contaminants, including both non-chlorinated solvents (e.g., alcohols, ketones, esters, acids) and chlorinated compounds (e.g., trichloroethane, chlorinated phenols, polychlorinated biphenyls (PCBs)). The non-chlorinated solvents tend to be readily biodegradable but can exert toxic effects at high concentrations. Lightly chlorinated compounds (e.g., chlorobenzene, dichlorobenzene, chlorinated phenols,

Exhibit X-9
Chemical Structure And Biodegradability

Biodegradability	Example Constituents	Products In Which Constituent Is Typically Found
More degradable	n-butane, l-pentane, n-octane	○ Gasoline
	Nonane	○ Diesel fuel
	Methyl butane, dimethylpentenes, methyloctanes	○ Gasoline
	Benzene, toluene, ethylbenzene, xylenes	○ Gasoline
	Propylbenzenes	○ Diesel, kerosene
	Decanes Dodecanes Tridecanes Tetradecanes	○ Diesel ○ Kerosene ○ Heating fuels ○ Lubricating oils
Less degradable	Naphthalenes Fluoranthenes Pyrenes Acenaphthenes	○ Diesel ○ Kerosene ○ Heating oil ○ Lubricating oils
Resistant	Asphaltenes MTBE	○ Fuel oil no. 6 ○ Gasoline

lightly chlorinated PCBs) are typically degradable under aerobic conditions. The more highly chlorinated compounds tend to be more resistant to aerobic degradation, but they can be degraded by dechlorination under anaerobic conditions. Several common chlorinated solvents (e.g., chlorinated ethanes, ethenes) can be degraded under aerobic conditions if they exist in the presence of another contaminant that can behave as a co-metabolite (e.g., methane, toluene, phenol).

Evaluation of the chemical structure of the constituents proposed for reduction by in-situ groundwater bioremediation at the site will allow you to determine which constituents will be the most difficult to degrade. You should verify that remedial time estimates, treatability studies, and operation and monitoring plans are based on the constituents that are the most difficult to degrade in the biodegradation process.

Concentration And Toxicity

High concentrations of petroleum organics or heavy metals in site soils can be toxic to or inhibit the growth and reproduction of bacteria responsible for biodegradation. In addition, very low concentrations of organic material will result in diminished levels of bacterial activity.

In general, concentrations of petroleum hydrocarbons (measured as total petroleum hydrocarbons) in excess of 50,000 ppm, organic solvent concentrations in excess of 7,000 ppm, or heavy metals in excess of 2,500 ppm in the groundwater or aquifer medium are considered inhibitory and/or toxic to aerobic bacteria. Review the CAP to verify that the average concentrations of petroleum hydrocarbons and heavy metals in the soils and groundwater to be treated are below these levels. Exhibit X-10 provides the general criteria for constituent concentration and bioremediation effectiveness.

Exhibit X-10
Constituent Concentration And In-Situ Groundwater Bioremediation Effectiveness

Constituent Concentration	In-Situ Groundwater Bioremediation Effectiveness
Petroleum constituents $\leq$ 50,000 ppm, Solvent constituents $\leq$ 7,000 ppm, and Heavy metals $\leq$ 2,500 ppm	Effective.
Petroleum constituents > 50,000 ppm, Solvent constituents > 7,000 ppm, or Heavy metals > 2,500 ppm	Ineffective; toxic or inhibitory conditions to bacterial growth exist. Long remediation times likely.

In addition to maximum concentrations, you should consider the cleanup concentrations proposed for the treated soils. Below a certain "threshold" constituent concentration, the bacteria cannot obtain sufficient carbon from degradation of the constituents to maintain adequate biological activity. The threshold level determined from treatability studies conducted in the laboratory is likely to be much lower than what is achievable in the field under less than optimal conditions. Although the threshold limit varies greatly depending on bacteria-specific and constituent-specific features, constituent concentrations below 0.1 ppm in the total aquifer matrix may be difficult to achieve. However, concentrations in the groundwater for these

specific constituents may be below detection levels. Experience has shown that reductions in petroleum hydrocarbon concentrations greater than 95 percent can be very difficult to achieve because of the presence of "resistant" or nondegradable petroleum constituents. Identify the average starting concentrations and the desired cleanup concentrations in the CAP. If a cleanup level lower than 0.1 ppm is required for any individual constituent or a reduction in petroleum hydrocarbon concentration of greater than 95 percent is required to reach the cleanup level, either a treatability study should be required to demonstrate the ability of bioremediation to achieve these reductions at the site, or another technology should be considered. Another option is to combine one or more technologies to achieve cleanup goals. These conditions are summarized in Exhibit X-11.

Exhibit X-11
Cleanup Concentrations And In-Situ Groundwater Bioremediation Effectiveness

Cleanup Requirement	In-Situ Groundwater Bioremediation Effectiveness
Constituent concentration > 0.1 ppm and Petroleum hydrocarbon reduction < 95%	Effective.
Constituent concentration ≤ 0.1 ppm or Petroleum hydrocarbon reduction ≥ 95%	Potentially effective; pilot studies are required to demonstrate reductions.

Solubility

Solubility is the amount of a substance (e.g., hydrocarbon) that will dissolve in a given amount of another substance (e.g., water). Therefore, a constituent's solubility provides insight to its fate and transport in the aqueous phase. Constituents that are highly soluble have a tendency to dissolve into the groundwater and are more available for biodegradation. Conversely, chemicals that have low water solubilities tend to remain in the adsorbed phase and will biodegrade more slowly. In general, lower molecular weight constituents tend to be more soluble and biodegrade more readily than do higher molecular weight or heavier constituents.

In the field, aqueous concentrations rarely approach the solubility of a substance because dissolved concentrations tend to be reduced through competitive dissolution of other constituents and degradation processes such as biodegradation, dilution, and adsorption.

Treatability Testing

To implement an in-situ groundwater bioremediation system at a site contaminated with compounds other than BTEX, treatability testing should be performed to verify applicability of the proposed remedial approach and to develop site specific design criteria and operating conditions. Treatability testing is probably not necessary at typical gasoline station sites. This is because the microbes capable of degrading BTEX compounds are ubiquitous and the contaminants are known to be degradable. This treatability testing can be accomplished in two phases – bench-scale and pilot-scale testing. Bench-scale tests are conducted in the laboratory (using apparatus sufficiently small to be placed on a laboratory bench) to evaluate the feasibility of a process, while pilot-scale tests simulate full-scale operations and are often conducted in the field. The extent and scope of the treatability testing will depend greatly on the volume of groundwater to be remediated.

For a relatively small volume of water with fairly well defined site and constituent characteristics, bench-scale testing may suffice. However, for large, more complex sites, it is recommended that both bench- and pilot-scale treatability testing be performed.

Bench-Scale Treatability Testing

The purposes of a bench-scale treatability study are to determine the following treatability characteristics:

- Presence of a responsive microbial population;
- Biodegradability of the groundwater contaminants;
- Degradation rate;
- Oxygen and nutrients required to sustain the biodegradation;
- Likely interactions between the introduced and generated compounds and the aquifer media (plugging potential); and
- Achievable cleanup levels.

There are two basic types of bench-scale studies, the flask (slurry) study and the column study. For flask studies, samples of aquifer material and contaminated groundwater are analyzed to determine the presence of organic, inorganic, and heavy metal compounds, and to estimate the numbers of microbes present. A minimum of three treatment conditions are generally tested – some combination of nutrients, a supply of

electron acceptors, and possibly an introduction of commercially available microorganisms. Tests are conducted over a 4- to 12-week period (most commonly 8 to 10 weeks) in both sterile and unamended control conditions. During this time, analyses are periodically performed to determine the rate of biodegradation. Results of flask studies should be considered as representing optimal conditions because the flask microcosm does not consider the effects of variables such as limited oxygen and nutrient delivery or soil heterogeneity. At the completion of the study, a preliminary treatment design is prepared that specifies the anticipated rate of contaminant reduction (cleanup time) and the quantities of oxygen and nutrients required.

Column studies employ the same approach as flask studies. Glass columns are filled with aquifer material, and contaminated groundwater is percolated through the columns; sterile and nutrient-amended columns are also evaluated as controls. While the columns do not accurately re-create actual in-situ conditions, they do provide an indication of the likely effects of adsorption and precipitation within the aquifer medium.

Pilot-Scale Treatability Testing

Pilot-scale treatability testing is a simulation of the full scale operation. The objective of this type of treatability testing is to verify treatability of constituents of concern under actual field conditions and to generate data to design the full-scale system. At small, typical gasoline stations, the pilot-scale system will be the same as the full-scale system. This pilot testing could extend from a few weeks to several months depending on the data generation requirements. Longer study times are required to track contaminant reduction to project the time required to attain clean-up goals.

A pilot testing program could also include the following:

- Pumping test to determine sustained groundwater extraction rate and general aquifer response;
- Aquifer recharge response tests (tracer test);
- Microbial response to injection of electron acceptor and nutrients; and
- Long-term operability of the system (aquifer and/or injection well fouling).

Information from these tests will be generated from measurements collected from a network of monitoring wells. The results of these tests will enable determination of (1) groundwater flow velocities and flow

paths in the vicinity of the injection well or infiltration gallery and extraction well, (2) potential zones of anisotropy within the aquifer (i.e., areas where properties, such as hydraulic conductivity, vary depending on the direction in which they are measured), (3) the distribution and concentrations of electron acceptors and nutrients, and (4) site specific remediation rates. Long-term operation of the pilot system also will provide information on potential fouling/plugging of the aquifer matrix in the vicinity of injection and extraction wells. Monitoring wells should be sampled at a frequency which will allow statistical validation of data generated.

Groundwater Modeling

For large, complex sites and even for some smaller sites, groundwater modeling can be a valuable tool to develop a more accurate conceptualization of the site and analyze the impacts of varying the locations and pumping rates of injection and extraction wells. This can be very important in determining whether the system can achieve and maintain hydraulic containment of the contaminant plume. The complexity and sophistication of the model used will depend on the site characteristics and the amount of data available to develop the model. The cost of groundwater modeling needs to be evaluated against the total remediation costs of the site. The data generated in the site characterization and pilot testing can be incorporated into a model that provides projections and predictions of aquifer conditions with time. Typical factors that can be determined by modeling include:

- Aquifer conditions, including flow rates and direction, water levels, extraction/injection points, aquifer sensitivity;
- Numbers, locations, and configurations of injection, extraction, and monitoring wells that will maximize system efficiency; and
- Fate and transport of contaminants, including concentration, distribution, and degradation with time.

Evaluations Of In-Situ Groundwater Bioremediation System Design

Once you have verified that in-situ groundwater bioremediation has the potential to be effective, you can evaluate the design of the proposed remedial system. The CAP should include a discussion of the rationale for the design and present the conceptual engineering design. Detailed engineering design documents might also be included, depending on state requirements.

Rationale For The Design

The following design elements are presented in the order in which design information might typically be collected.

- *Volume and area of aquifer to be treated* is generally determined by site characterization combined with regulatory action levels or a site-specific risk assessment.

- *Initial concentration of constituents of concern* can be measured during initial site characterization and during treatability studies. These concentrations will be used to predict likely toxic effects of the contaminants on indigenous microorganisms and to estimate electron acceptor and nutrient requirements, and the extent of treatment required.

- *Required Final Constituent Concentrations* are generally defined by your state as remediation action levels or determined on a site-specific basis using transport models and/or risk assessment calculations. These limits will define the areal extent of the aquifer to be remediated.

- *Estimates of electron acceptor and nutrient requirements.* As a rule of thumb, 3 lbs of oxygen are added per pound of hydrocarbon as an electron acceptor. For nutrients, a maximum ratio of 100:10:1 for C:N:P is typically used (assume 1 pound of hydrocarbon is equal to 1 pound of carbon). Often systems require substantially less, on the order of 100:1:0.5, especially if plugging of injection wells/galleries is a problem.

- *Layout of injection and extraction wells.* Probably the most critical factor is ensuring that the contaminant plume is hydraulically controlled. This will prevent it from spreading and concentrate bioremediation efforts on the contaminants. For large complex sites, designing this layout can be facilitated by groundwater modeling. Injection wells/infiltration galleries can be located upgradient of the contaminant source, with extraction wells located downgradient of the source. Alternatively, injection points can be located along the centerline of the plume axis, with extraction wells located on the edges of the plume. The latter arrangement can typically achieve shorter remediation times, but at greater expense.

- *Design Area of Influence.* (AOI) is an estimate of the volume/area of aquifer to which an adequate amount of electron acceptor and nutrient can be supplied to sustain microbial activity. Establishing the design AOI is not a trivial task because it depends on many

factors including intrinsic permeability of the soil, soil chemistry, moisture content, and desired remediation time. Although the AOI should usually be determined through field pilot studies, it can be estimated from groundwater modeling or other empirical methods. For sites with stratified geology, the area of influence should be defined for each soil type. The AOI is important in determining the appropriate number and spacing of extraction or injection wells or infiltration galleries.

- *Groundwater extraction and injection flow rates* can vary from a few to a few hundred gallons per minute, depending primarily on the hydraulic conductivity of the aquifer. Although flow rates can be estimated by groundwater modeling, they are best determined by pilot studies. In general, only about 75 percent of extracted water can be readily re-injected using either injection wells or infiltration galleries.

- *Site Construction Limitations.* Locations of buildings, utilities, buried objects, etc. must be identified and considered in the design process.

- *Electron Acceptor System.* For aerobic processing, air, oxygen or hydrogen peroxide can be used; for anaerobic processing, alternative electron acceptors (e.g., nitrate, sulfate, or ferric iron) can be used. The electron acceptors may be introduced using a direct air/oxygen sparge system into the injection well (air sparging) or a water injection system.

- *Nutrient Formulation and Delivery System.* Site characterization and bench-scale treatability studies will determine if nutrients are required. The nutrients selected should be compatible with aquifer chemistry to minimize precipitation and flow-channel fouling.

- *Bioaugmentation.* Microorganisms can be added to the injected or infiltrated water to increase microbial activity. However, as discussed earlier, bioaugmentation is usually not necessary.

- *Extracted Groundwater Treatment and Disposition.* The above ground treatment system for extracted groundwater should be of sufficient size to process the volume of water extracted. Disposition of treated groundwater will depend on specific state policies. Some states discourage reinjection, although in most instances, re-injection makes good technical sense without causing adverse impacts on the receiving groundwater. Groundwater treatment systems could entail biological, chemical, and/or physical treatment. The selection of the appropriate extracted groundwater treatment technology will depend on the proposed duration of operation, size of treatment system, and cost.

- *Remedial Cleanup Time.* Imposed remedial cleanup time could affect the design of the remedial system. Ultimately, the duration of the cleanup will depend on the rate of biological activity attainable, the bio-availability of the contaminants of concern, and the locations and spacings of the injection/extraction wells.

- *Ratio of Injection/Infiltration to Extraction.* The percentage of the treated water that is reinjected or reinfiltrated should be based on hydraulic control. Because dispersion and diffusion at the boundary of the AOI is likely to allow some migration of contaminated groundwater, less groundwater is generally injected or recharged to the aquifer than is extracted. This provides for better hydraulic containment of the contamination.

- *Free Product Recovery System.* A system designed to recover free product should be used to reduce "source" input effects to the groundwater and generally optimize saturated zone remediation.

Components Of An In-Situ Groundwater Bioremediation System

Once the design rationale is defined, the design of the in-situ groundwater bioremediation system can be developed. Exhibit X-12 is a schematic diagram of a typical in-situ groundwater bioremediation system using injection wells. A typical in-situ groundwater bioremediation system design includes the following components and information:

- Extraction well(s) orientation, placement, and construction details;

- Injection well(s) or infiltration gallery(ies) orientation, placement, and construction details;

- Filtration system to remove biomass and particulates that could promote clogging of injection wells or galleries;

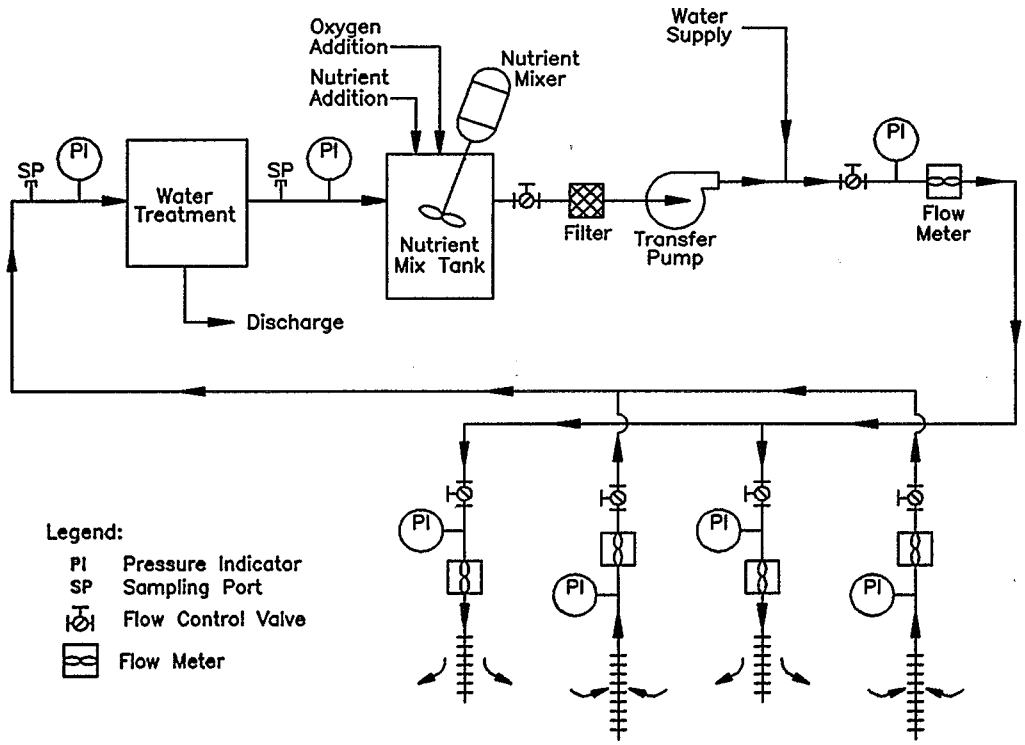
- Extracted groundwater treatment system (e.g., biological, chemical oxidation, granular carbon adsorption) and methods for disposal or re-use of treated groundwater (surface discharge, discharge to a sewer, re-injection);

- Nutrient solution preparation system and storage;

- Microorganism addition system (if required);

- Electron acceptor system (e.g., air, oxygen, hydrogen peroxide);

Exhibit X-12
Schematic Diagram Of Typical In-Situ Groundwater Bioremediation System Using Injection Wells



- Monitoring well(s) orientation, placement, and construction details; and

- System controls and alarms.

Extraction wells are generally necessary to achieve hydraulic control over the plume to ensure that it does not spread contaminants into areas where contamination does not exist or accelerate the movement toward receptors. Placement of extraction wells is critical, especially in systems that also use nutrient injection wells or infiltration galleries. These additional sources of water can alter the natural groundwater flow patterns which can cause the contaminant plume to move in an unintended direction or rate. Without adequate hydraulic control, this

situation can lead to worsening of the original condition and complicate the cleanup or extend it.

Nutrient injection systems may not be necessary at all, if the groundwater contains adequate amounts of nutrients, such as nitrogen and phosphorus.

The following sections provide more detailed descriptions of the electron acceptor and nutrient addition systems and system control alarms. For a detailed explanation of suggested well construction guidelines, see Chapters VII and VIII, "Air Sparging" and "Biosparging." In some cases, electron acceptor and nutrient supply systems are combined rather than discrete systems (i.e., both the electron acceptor and nutrients are added to the same stream for injection into the aquifer).

Well Placement

Location of extraction wells, injection wells (or infiltration galleries), and monitoring wells can vary substantially depending on site-specific conditions. However, the essential goals in configuring these wells are as follows:

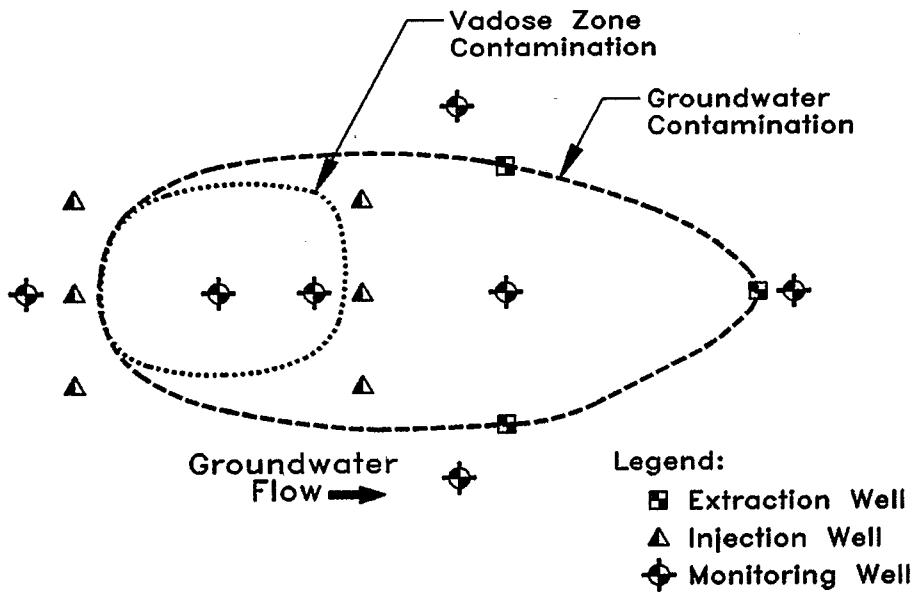
- Extraction wells should be located such that hydraulic control is achieved at the outer limits of the contaminant plume. In other words, the cones of depression created by the pumping wells should intersect so that hydraulic gradients throughout the plume are inward in the direction of the pumping wells;

- Injection wells (and/or infiltration galleries) should be located to provide distribution of the electron acceptor and nutrients throughout the area targeted for remediation; the impacts on water table gradients caused by injection well location and rate of liquid injection should be considered carefully. Excessive mounding of the water table could induce migration of contaminants in unintended directions, or alter the effectiveness of the extraction well in achieving hydraulic control; and

- Monitoring wells should be located outside the plume in each direction and within the plume to track remedial progress and to ensure that the extraction wells are achieving the desired hydraulic control and preventing further migration.

One possible configuration of extraction, injection, and monitoring wells is shown in Exhibit X-13.

Exhibit X-13
Idealized Layout Of Extraction, Injection, And Monitoring Wells For In-Situ Groundwater Bioremediation



The design area of influence of extraction and injection wells will determine the number of wells needed. The area of influence of neighboring extraction wells should overlap to achieve hydraulic control.

Electron Acceptor and Nutrient Addition System

For a given site, selection of an appropriate electron acceptor will depend on the results of the treatability studies. The most widely used electron acceptor in the remediation of petroleum hydrocarbons is oxygen, which enhances the aerobic biological process. Oxygen can be delivered by either a "carrier stream" of water which has been enriched with atmospheric air or pure oxygen or by air or oxygen sparging. Air sparging is covered in Chapter VII. Water saturated with atmospheric air (20 percent oxygen) contains dissolved oxygen concentrations of 8-10 mg/l. Water saturated with pure oxygen can attain dissolved oxygen concentrations of approximately 40 mg/l.

Higher dissolved oxygen concentrations in groundwater are attainable with hydrogen peroxide. However, at levels greater than 500 to 1,000 mg/l, hydrogen peroxide behaves like a biocide; therefore, it should be used with caution. Hydrogen peroxide degrades relatively rapidly and is very difficult to disperse through the aquifer. Also, hydrogen peroxide is very expensive, and its use may not be cost-effective.

A typical electron acceptor addition system would include:

- Oxygen Enriched Stream, including an air blower or pure oxygen source and contacting chamber;
- Injection Well Sparging System, including an air blower or pure oxygen source; or
- Hydrogen Peroxide System, including a hydrogen peroxide supply, storage, and metering pump system.

A typical nutrient addition system could include the following components:

- Reagent (e.g., hydrogen peroxide, ammonium salt, phosphate) storage facilities
- Mixing tanks for reagent solutions (i.e., solutions of ammonium or urea and phosphorus salt solutions)
- Meters to measure rate of introduction of nutrient solutions into carrier streams
- Control system for metering systems

System Controls and Alarms

In many cases, remediation sites are remote and have minimal operation and maintenance staff. In these cases, equipment is fitted with control devices to shut down the system in the event of failure or unusual conditions (e.g., high water levels in injection wells because of plugging). When these systems shut down, alarms are triggered. These alarms can notify personnel on-site, or can be relayed to a remote station from which control personnel can be summoned.

Evaluation Of Operation And Monitoring Plans

Monitoring operations of the in-situ groundwater bioremediation system is necessary to ensure that equipment functions according to

specification, that nutrients and electron acceptors are being effectively supplied and distributed, and that contaminant removal is proceeding according to projections. A system operating and monitoring plan which covers both start-up and normal operations must be developed.

Start-up Operation

Initial start-up should entail hydraulic balancing of rates of extraction and injection of water. Depending on the system size and complexity, this hydraulic balancing can take 1 to 3 days. Once the extraction and injection flows are balanced and stabilized, addition of nutrients and the electron acceptor should be initiated. After about two or three days, the groundwater electron acceptor levels should be checked. In highly contaminated areas, the electron acceptor concentration will be depressed. Start-up adjustments are generally needed for the first 1 to 2 weeks of operation. Concentrations of the electron acceptor should be measured daily; water levels across the site should be measured every two to three days.

At the end of this start-up period, a set of samples (groundwater and soils) should be collected for detailed analysis for constituents of concern.

Normal Operation

The normal operation of the system should consist of weekly routine checking of (a) the operation and maintenance of equipment (e.g., pumps, blowers, mixers and controllers); (b) groundwater levels; (c) extraction and injection flow rates; (d) groundwater electron acceptor concentrations; (e) nutrient levels (ammonium, phosphate, nitrate); (f) pH; and (g) conductivity. System monitoring parameters can be measured using field test kits. Nutrient addition can be an intermittent operation and can be scheduled to coincide with routine operation checks. Exhibit X-14 provides a brief synopsis of system monitoring requirements.

Remedial Progress Monitoring

It is assumed that the objective of in-situ groundwater bioremediation processing is remediation of the saturated zone. To monitor remedial progress, samples of both groundwater and aquifer media (soil) should be collected on a routine basis and analyzed for parameters of concern. Groundwater samples should be collected and analyzed monthly to quarterly. Soil samples should be collected prior to site closure to demonstrate that cleanup objectives have been achieved.

Exhibit X-14
System Monitoring Recommendations

Phase	Monitoring Frequency	What To Monitor	Where To Monitor
Start-up (1-2 weeks)	At least daily	○ Extraction volume ○ Injection volume ○ Electron acceptor concentration	○ Extraction and injection well heads or manifolds ○ Monitoring wells
	Every 2-3 days	○ Groundwater levels	○ Monitoring wells
Remedial (ongoing)	Weekly	○ Groundwater levels ○ Extraction and injection flow rates ○ Concentration of electron acceptor, ammonia, phosphate, nitrate, pH, and conductivity	○ Monitoring wells ○ Extraction and injection wellheads or manifolds ○ Monitoring wells
	Monthly to quarterly	○ Constituent concentrations in soil and groundwater	○ Extraction, injection, and monitoring wells ○ Soil borings

In developing the monitoring plan, it will be necessary to identify potential monitoring points. Sampling points could be extraction, injection and monitoring wells. In sampling at the injection wells, the injection system should be shut down for approximately 24 hours to allow ambient conditions to be re-established. This delay will help ensure that the samples are representative of conditions in the aquifer without the effects of dilution.

Groundwater sampling and analysis can be scheduled about once every 1 to 3 months. Procedures for the collection of groundwater samples should be described in a sampling and analysis plan provided in the CAP. Analyses must be conducted according to prescribed or approved procedures as required by state regulations. In addition, water table maps can be useful in assessing whether injected water is flowing toward extraction wells as predicted. These maps should be prepared on a monthly to quarterly basis.

During remediation, contaminant levels decrease until they reach an asymptotic level. Once asymptotic conditions are reached for several successive sampling periods, continuing remediation activities generally

results in little further decrease of contaminant concentrations. However, frequently when active remediation is ceased, levels of dissolved contaminants abruptly increase. This increase is caused by the diffusion into solution of contaminants that were previously adsorbed onto the surfaces of individual grains that comprise the aquifer media. When asymptotic behavior begins, the operator should evaluate alternatives that will facilitate aquifer biodegradation. Alternatively, you may need to re-evaluate the rates and concentrations of nutrients and electron acceptors being injected, examine other remedial alternatives, or consider changing from active to passive (natural attenuation) remediation.

If asymptotic behavior is persistent for periods greater than about 6 months and the concentration rebound is sufficiently small following periods of pulsing (i.e., varying the extraction rate or turning the system off and on), the performance of the in-situ groundwater bioremediation system should be reviewed to determine whether remedial goals have been reached. If further contaminant reduction is necessary, another remedial technology may need to be considered.

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Checklist: Can In-Situ Groundwater Bioremediation Be Used At This Site?

This checklist can help you evaluate the completeness of the CAP and identify areas that require closer scrutiny. As you go through the CAP, answer the following questions. If the answer to several questions is no, you should request additional information to determine if in-situ groundwater bioremediation will accomplish cleanup goals at the site.

1. Site Characteristics

Yes	No	
❑	❑	Is the aquifer hydraulic conductivity greater than 10^{-4} cm/sec?
❑	❑	Have impermeable layers or other conditions that would disrupt groundwater flow been considered in the design of the remediation system?
❑	❑	Has the groundwater mineral content been quantified and taken into consideration?
❑	❑	Are dissolved iron concentrations < 10 mg/l?
❑	❑	Is the groundwater pH between 6 and 8?
❑	❑	Is the groundwater temperature been 10°C and 45°C?
❑	❑	Is the total heterotrophic bacteria count > 1,000 CFU/gram in dry soil?
❑	❑	Is the carbon:nitrogen:phosphorus ratio between 100:10:1 and 100:1:0.5?

2. Constituent Characteristics

Yes	No	
❑	❑	Have all constituents of concern been identified?
❑	❑	Are constituents all sufficiently biodegradable?
❑	❑	Is the concentration of total petroleum hydrocarbon $\leq$ 50,000 ppm and heavy metals $\leq$ 2,500 ppm?
❑	❑	Are organic solvent concentrations $\leq$ 7,000 ppm?

❑	❑	Are desired constituent concentrations > 0.1 ppm and is the desired hydrocarbon reduction < 95%?
❑	❑	Are the constituents present soluble in groundwater?

3. Evaluation Of The In-situ Groundwater Bioremediation System Design

Yes	No	
❑	❑	Has treatability testing been performed?
❑	❑	Has groundwater modelling been used to calculate aquifer conditions over time?
❑	❑	If not, has some other method been used to calculate cleanup times?
❑	❑	Will the processing rates achieve cleanup in the time allotted for remediation in the CAP?
❑	❑	Have remediation rates been established for the project?
❑	❑	Has the area of influence for the proposed extraction or injection wells been determined?
❑	❑	Is the proposed well placement appropriate, given the total area to be cleaned up and the area of influence of each injection/extraction well system?
❑	❑	Has the amount of the contaminant to be remediated been determined?
❑	❑	Has the quantity and type of electron acceptors required for the remediation been determined?
❑	❑	If an electron acceptor system will be needed, is a design for that system provided?
❑	❑	Will aboveground treatment of groundwater be required?
❑	❑	Has the quantity of nutrients required for remediation been determined?
❑	❑	If nutrient delivery systems will be needed, are designs for those systems provided?
❑	❑	Is bioaugmentation addressed, if needed, in the design?

❑	❑	Have groundwater extraction rates been determined?
❑	❑	Is a system control/alarm system included in the design?
❑	❑	Is a free product recovery system needed?

4. Operating and Monitoring Plans

Yes	No	
❑	❑	Is hydraulic balancing proposed as the first activity in start-up?
❑	❑	Is routine system operation and monitoring proposed?
❑	❑	Is subsurface soil and groundwater sampling proposed for tracking constituent reduction and biodegradation conditions?
❑	❑	Is a schedule for tracking constituent reduction proposed?
❑	❑	Is nutrient addition (if necessary) proposed to be controlled on a periodic rather than continuous basis?

Chapter XI

Dual-Phase Extraction

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Chapter XI
Dual-Phase Extraction

Overview

Dual-phase extraction, also known as multi-phase extraction, vacuum-enhanced extraction, or bioslurping, is an in-situ technology that uses pumps to remove various combinations of contaminated groundwater, separate-phase petroleum product, and hydrocarbon vapor from the subsurface. Extracted liquids and vapor are treated and collected for disposal, or re-injected to the subsurface (where permissible). Dual-phase extraction systems can be effective in removing separate-phase product from the subsurface, thereby reducing concentrations of petroleum hydrocarbons in both the saturated and unsaturated zones of the subsurface. Dual-phase extraction systems are typically designed to maximize extraction rates; however, the technology also stimulates biodegradation of petroleum constituents in the unsaturated zone by increasing the supply of oxygen, in a manner similar to bioventing (see Chapter III for more information on bioventing).

Although the general class of technologies presented in this chapter is referred to as dual-phase extraction (DPE), significant variations in the technology exist. DPE systems often apply relatively high vacuums to the subsurface. Thus, the adjective "high-vacuum" is sometimes used to describe DPE technologies, even though all DPE systems are not high-vacuum systems. DPE technologies can be divided into two general categories, depending on whether subsurface liquid(s) and soil vapor are extracted together as a high-velocity dual-phase (liquid(s) and vapor) stream using a single pump or whether the subsurface liquid(s) and soil vapor are extracted separately using two or more pumps. Exhibits XI-1 and XI-2 display typical single- and dual-pump DPE systems, respectively.

Single-pump systems rely on high-velocity airflow to lift suspended liquid droplets upwards by frictional drag through an extraction tube to the land surface. Single-pump vacuum extraction systems can be used to extract groundwater or combinations of separate-phase product and groundwater. The somewhat more conventional dual-pump systems use one pump to extract liquids from the well and a surface blower (the second pump) to extract soil vapor. A third DPE configuration uses a total of three pumps, including the surface blower together with one pump to extract floating product and one to extract groundwater. Because both double- and triple-pump DPE systems extract the well liquids separately from the soil vapor and are similar in operation and

Exhibit XI-1
Typical Single-Pump DPE System

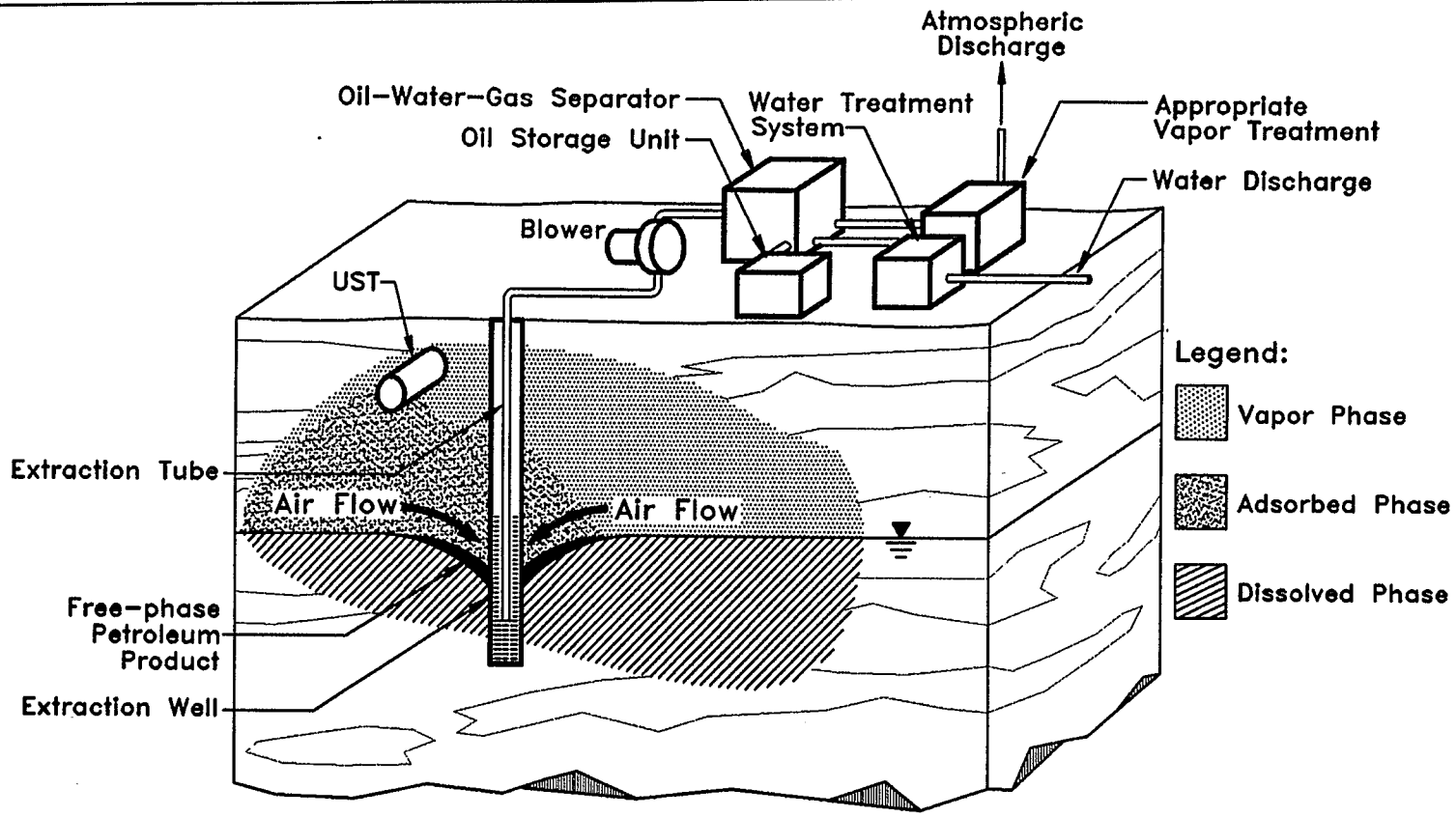
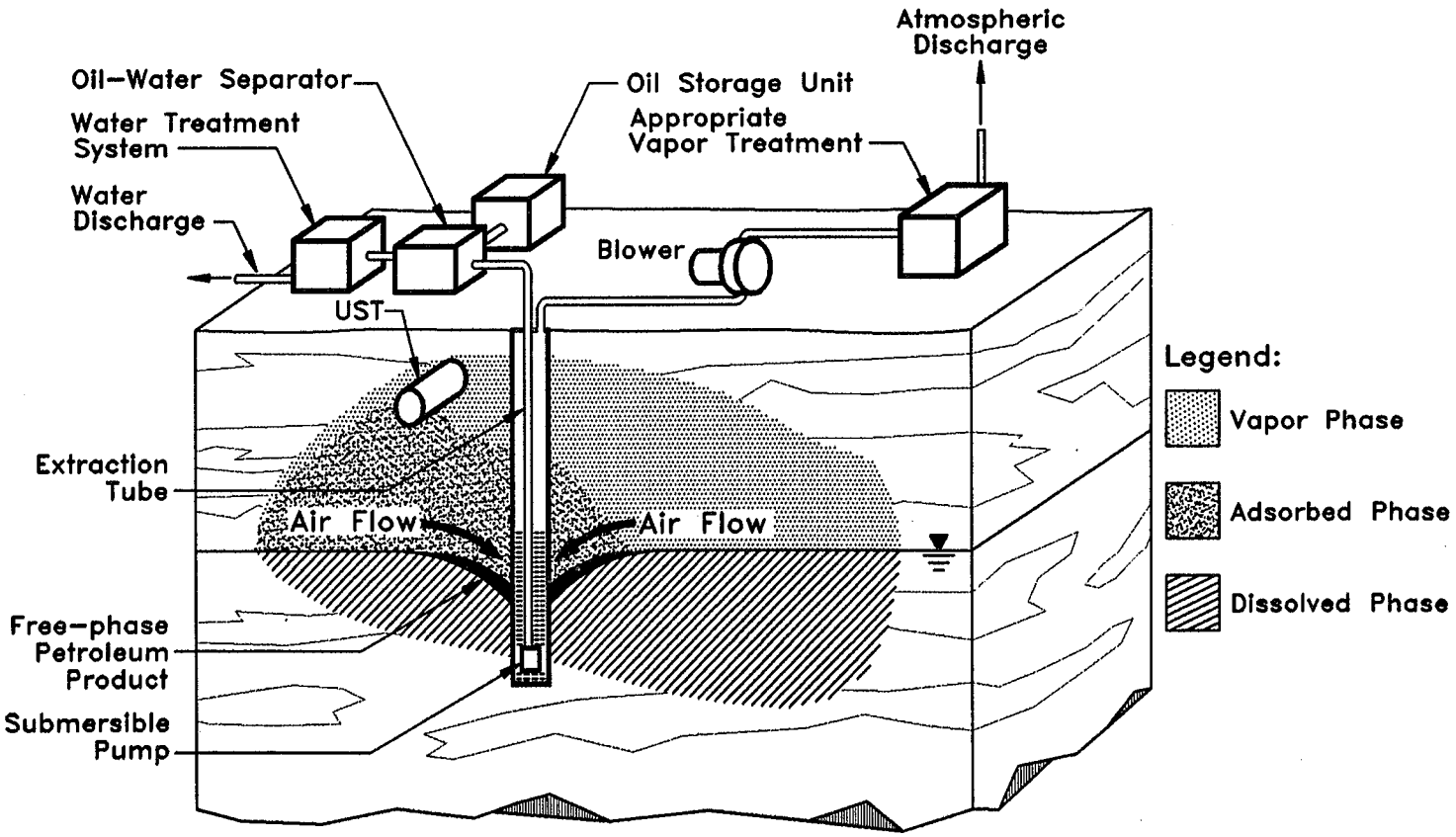


Exhibit XI-2
Typical Multi-Pump DPE System



application, these systems will be discussed together under the heading of "dual-pump DPE systems" in the remainder of this chapter. Exhibits XI-3 and XI-4 are diagrams of typical single-pump and dual-pump DPE extraction wells, respectively.

Vacuum groundwater extraction has been used for many decades as a standard method for extracting groundwater to control seepage or effect dewatering during construction and mining activities (Powers, 1981). Single-pump DPE systems represent a recent adaptation of this long-established technology to the task of subsurface remediation. Single-pump DPE systems are generally better suited to low-permeability conditions, and they are difficult to implement at sites where natural fluctuations in groundwater levels are substantial. United States patents exist on certain applications of single-pump DPE systems (Hess et al., 1991; Hajali et al., 1992; Hess et al., 1993). Single-pump DPE technology is sometimes referred to as bioslurping (U.S. Air Force, 1994).

Dual-pump DPE systems are simply a combination of traditional soil vapor extraction (SVE) and groundwater (and/or floating product) recovery systems. Dual-pump systems tend to be more flexible than single-pump systems, making dual-pump systems easier to apply over a wider range of site conditions (e.g., fluctuating water tables, wide permeability ranges); however, equipment costs are higher.

The vacuum applied to the subsurface with DPE systems creates vapor-phase pressure gradients toward the vacuum well. These vapor-phase pressure gradients are also transmitted directly to the subsurface liquids present, and those liquids existing in a continuous phase (e.g., water and "free" petroleum product) will flow toward the vacuum well in response to the imposed gradients (the term "free" product is a commonly used, though imprecise term because a greater fraction of resident petroleum product may be recovered using vacuum-enhanced DPE compared to the fraction of product recoverable using gravity drainage alone). The higher the applied vacuum, the larger the hydraulic gradients that can be achieved in both vapor and liquid phases, and thus the greater the vapor and liquid recovery rates.

Dramatic enhancements in both water and petroleum product recovery rates resulting from the large hydraulic gradients attainable with DPE systems have been reported in the literature (Blake and Gates, 1986; Blake, et al., 1990; Bruce, et al., 1992). The depressed groundwater table that results from these high recovery rates serves both to hydraulically control groundwater migration and to increase the efficiency of vapor extraction. The remedial effectiveness of DPE within the zone of dewatering that commonly develops during DPE application

Exhibit XI-3
Typical Single-Pump, DPE Extraction Well

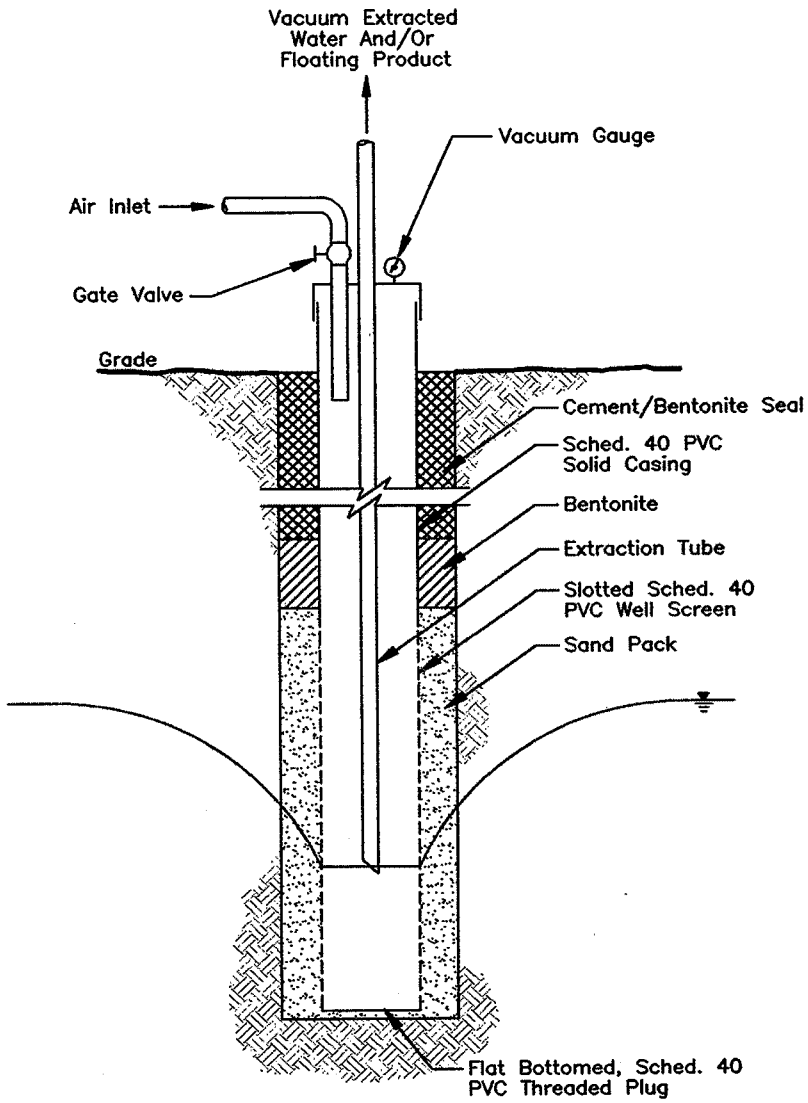
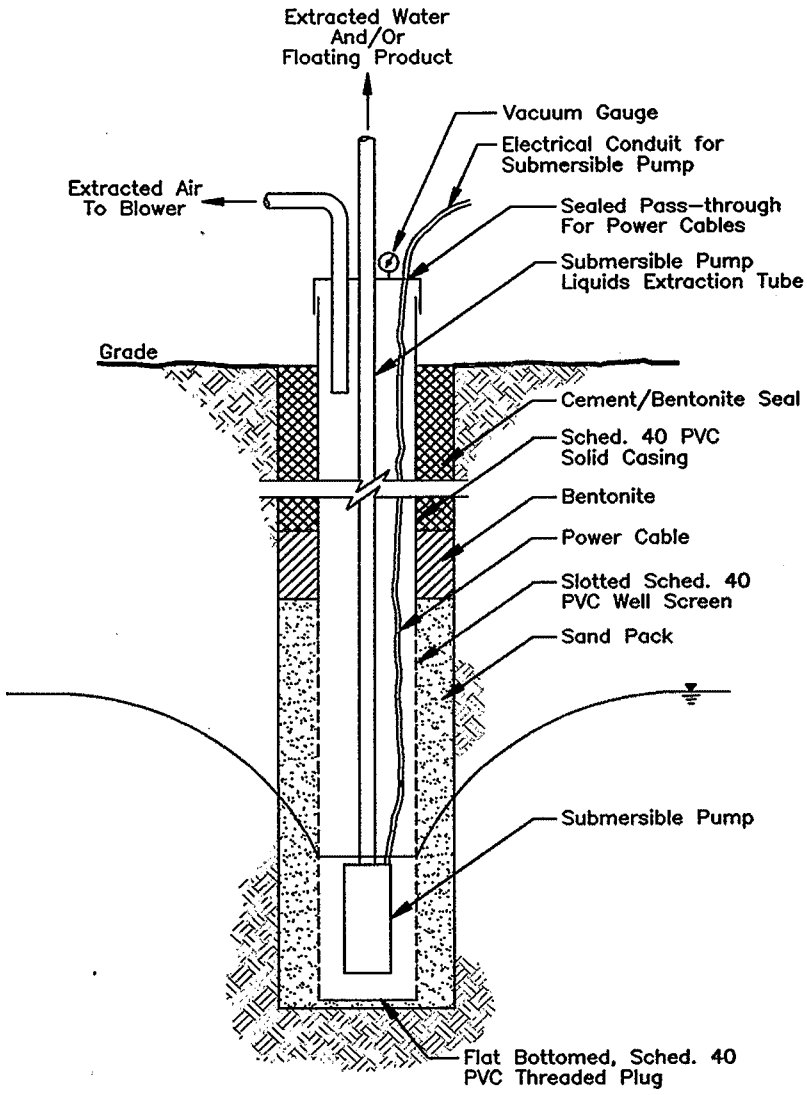


Exhibit XI-4
Typical Multi-Pump, DPE Extraction Well



should be greater than that of air sparging due to the more uniform air flow developed using DPE (Johnson, et al., 1992).

Because of the varied nature of DPE systems, the conceptual design objectives for DPE can vary widely. DPE is often selected because it enhances groundwater and/or product recovery rates, especially in layered, fine-grained soils. The application of DPE also maximizes the effectiveness of SVE by lowering the water table and therefore increasing air-phase permeabilities in the vadose zone. Finally, DPE can enhance biodegradation by substantially increasing the supply of oxygen to the vadose zone. Exhibits XI-5 and XI-6 list the advantages and disadvantages of single-pump and dual-pump DPE systems, respectively.

Exhibit XI-5
Advantages and Disadvantages of Single-Pump DPE

Advantages	Disadvantages
○ Proven performance in low-permeability soils. Requires no downhole pumps.	○ Expensive to implement at sites with medium to high-permeability soils.
○ Minimal disturbance to site operations.	○ Difficult to apply to sites where the water table fluctuates.
○ Short treatment times (usually 6 months to 2 years under optimal conditions).	○ Treatment may be expensive for extracted vapors and for oil-water separation
○ Substantially increases groundwater extraction rates.	○ Can extract a large volume of groundwater that may require treatment.
○ Can be applied at sites with floating product, and can be combined with other technologies, such as air sparging and bioremediation.	○ Requires specialized equipment with sophisticated control capability.
○ Can be used under buildings and other locations that cannot be excavated.	○ Requires complex monitoring and control during operation.
○ Can reduce the cost of groundwater treatment through air stripping within the vacuum extraction tube.	

This chapter will assist you in evaluating a corrective action plan (CAP) that proposes DPE as a remedy for petroleum-contaminated soil and groundwater. The evaluation process, which is summarized in the flow diagram shown in Exhibit XI-7, will serve as a roadmap for the

Exhibit XI-6 Advantages and Disadvantages of Multi-Pump DPE	
Advantages	**Disadvantages**
○ Proven performance under a wide range of conditions; readily available equipment.	○ Effectiveness less certain when applied to soils with very low permeabilities or when applied with lack of sufficient information of subsurface conditions.
○ Minimal disturbance to site operations.	○ May require costly treatment for atmospheric discharge of extracted vapors.
○ Short treatment times (usually 6 months to 2 years under optimal conditions).	○ May require costly oil/water separation and groundwater treatment.
○ Substantially increases groundwater extraction rates.	○ Requires complex monitoring and control during operation.
○ Flexible applications to sites with water-table fluctuations or widely ranging permeabilities.	
○ Can be applied to sites with floating product, and can be combined with other technologies, such as air sparging and bioremediation.	
○ Can be used under buildings and other locations that cannot be excavated.	

decisions you will make during your evaluation. The evaluation can be divided into the following steps.

- **Step 1: An *initial screening of DPE effectiveness*,** which will allow you to quickly gauge whether DPE is likely to be effective, moderately effective, or ineffective for a given site-specific application.
- **Step 2: A *detailed evaluation of DPE effectiveness*,** which provides further screening criteria to confirm whether DPE is likely to be effective at a given site. To complete the detailed evaluation, you will need to identify key site characteristics and soil properties in the CAP, compare them with conditions under which DPE is typically effective, decide whether pilot studies are needed, and conclude whether DPE is likely to be effective for the site-specific application.
- **Step 3: An *evaluation of the DPE system design*,** which will allow you to determine whether the rationale for the design has been appropriately defined based on pilot study data or other studies, whether the necessary design components have been specified, and

Exhibit XI-7
DPE Evaluation Process Flow Chart

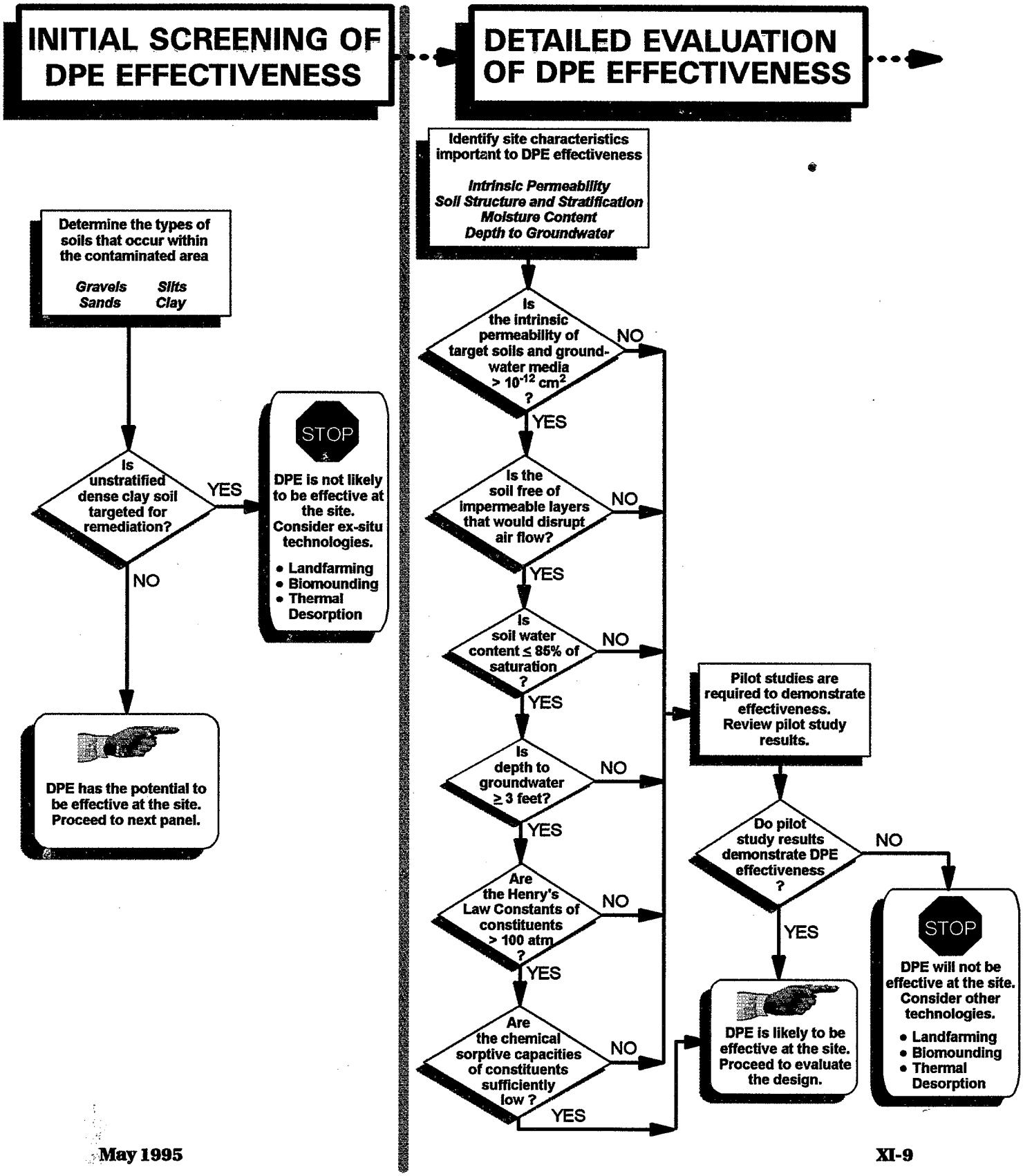
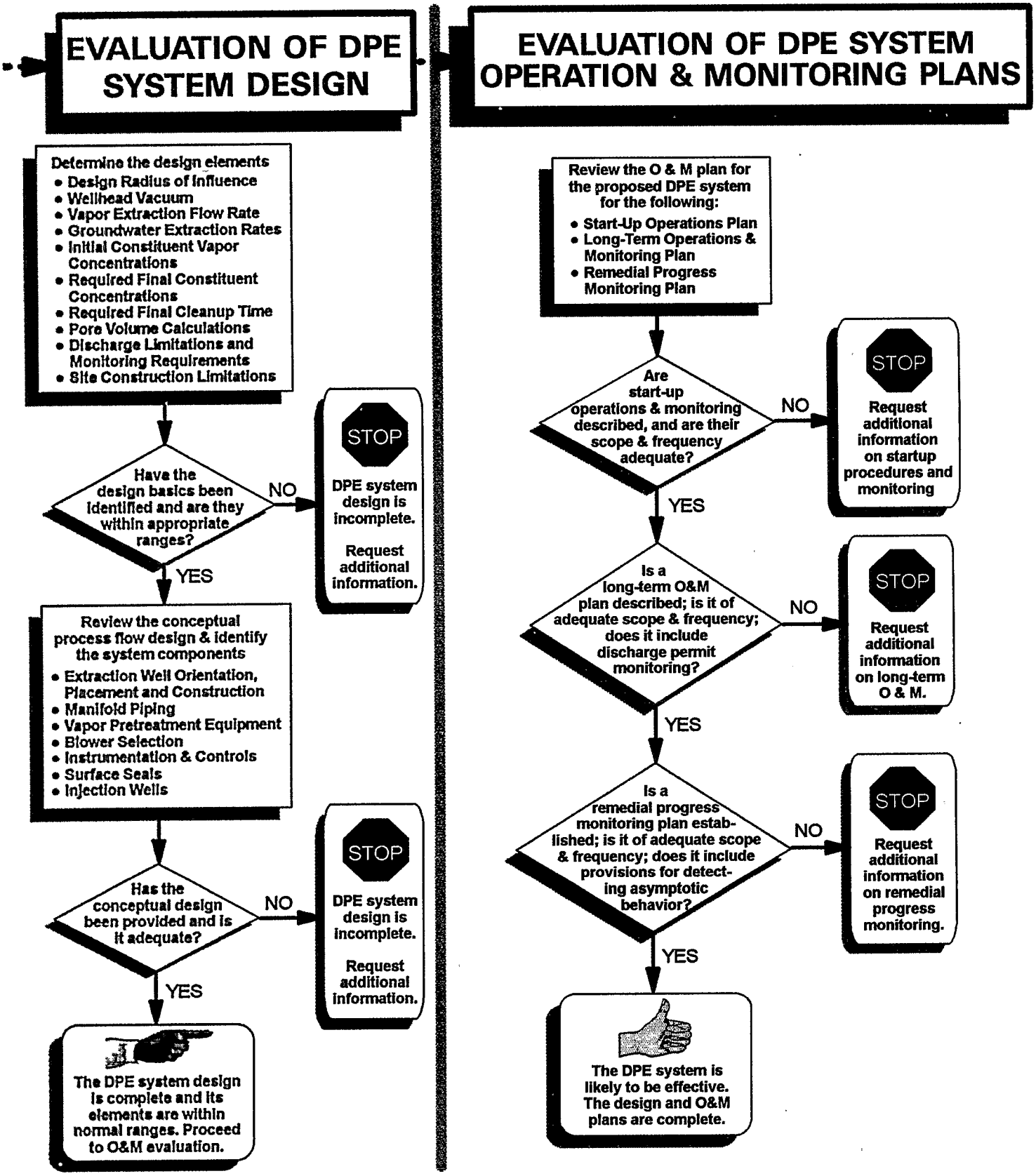


Exhibit XI-7
DPE Evaluation Process Flow Chart



whether the construction process flow designs are consistent with standard practice.

- **Step 4: An *evaluation of the operation and monitoring plans,*** which will allow you to determine whether plans for start-up and long-term monitoring of the system are of sufficient scope and frequency and whether remedial progress monitoring plans are appropriate.

Initial Screening Of DPE Effectiveness

Because of the differences in application of various types of DPE systems and the complexity of DPE, determining whether DPE will work effectively at a given site is complex. This section discusses the key site parameters that should be evaluated in deciding whether DPE will be a viable remedy for a particular site. The key site parameters include:

- *Permeability* of the petroleum-contaminated soils and aquifer media. Permeability affects the rates at which groundwater and soil vapors can be extracted and controls the pore volume exchange rate.

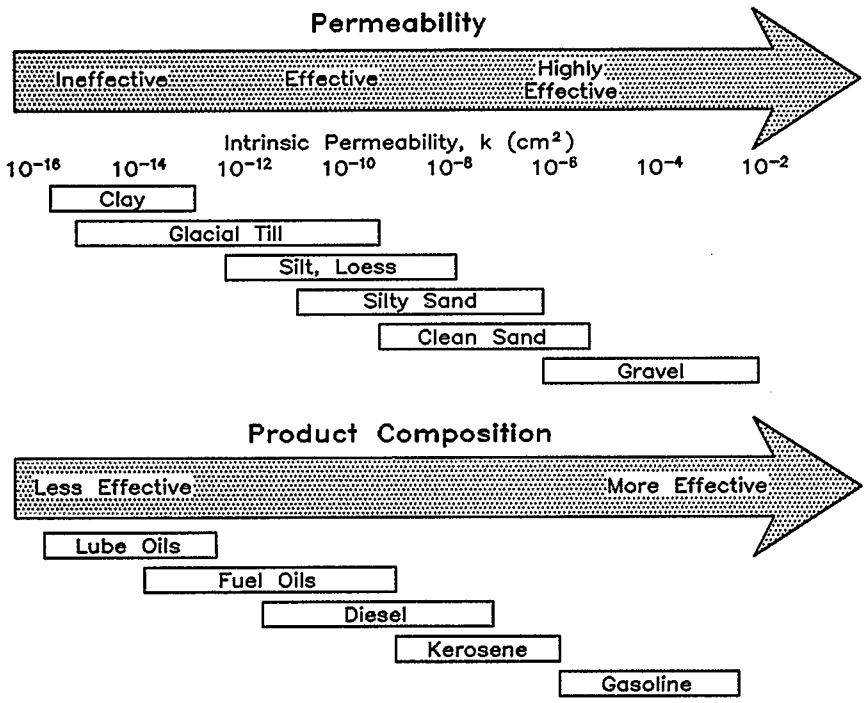
- *Volatility* of the petroleum constituents. Volatility determines the rate at and degree to which petroleum constituents will vaporize to the soil vapor state.

In general, the type of soil (e.g., clay, silt, sand) will determine its *permeability*. Fine-grained soils (e.g., clays and silts) have lower permeability than coarse-grained soils (e.g., sands and gravels). Permeability usually varies significantly with depth; for screening purposes, consider the effects of the most permeable soil that is found areally continuous through a significant portion of the chemically-affected soil profile. Permeability affects remediation in both the vadose and groundwater zones.

The *volatility* of a petroleum product or its constituents is a measure of its ability to vaporize and can be measured in several ways. Because petroleum products are highly complex mixtures of chemical constituents, the volatility of the product mixture can be gauged most easily by its boiling point. If the boiling point is low, the volatility of the product will be high. Conversely, petroleum products with higher boiling points are less volatile. If product volatility is low, DPE will be less effective in removing petroleum constituents in the vapor phase from the unsaturated zone.

Exhibit XI-8 is an initial screening tool that can be used to help assess the potential effectiveness of DPE for a given site. It provides a

Exhibit XI-8
Initial Screening for DPE Effectiveness



Note:
All petroleum products listed are amenable for the DPE remediation alternative.

range of soil permeabilities for typical soil types as well as ranges in composition for typical petroleum products. Use this screening tool to make an initial assessment of the potential effectiveness of DPE. To use this tool, you should scan the CAP to determine the soil type present and the type of petroleum product released to assess the potential remedial effectiveness of DPE at the site.

Information provided in the following section will allow a more thorough effectiveness evaluation and will identify issues that could require special design considerations.

Detailed Evaluation Of DPE Effectiveness

Once you have completed the initial screening and determined that DPE is potentially effective for the soil permeability and petroleum product composition present, you need to further evaluate the CAP to

confirm that DPE will be effective. While the initial screen focused on permeability and constituent volatility, the detailed evaluation should consider a broader range of site and constituent characteristics, which are listed in Exhibit XI-9.

The factors listed on Exhibit XI-9 largely control the initial contaminant mass extraction rate, which will decrease during DPE operation as concentrations of volatile organics in the soil (and soil vapor) are reduced. However, based on the total contaminant mass present in soils and a reasonable remediation time frame, acceptable ranges for the site-specific factors can be determined.

Exhibit XI-9
Key Parameters Used To Evaluate Site Characteristics And Chemical Properties

Site Characteristics	Chemical Properties
Intrinsic permeability	Effective volatility
Soil structure and stratification	Chemical sorptive capacity
Moisture content in the unsaturated zone	
Depth to groundwater	

The remainder of this section describes these parameters, why each is important to DPE, how they can be determined, and the range of each parameter considered appropriate for DPE. Keep in mind that the site-specific factors that govern the effectiveness of DPE are generally the same as those that govern the effectiveness of both SVE and bioventing.

Site Characteristics

Intrinsic Permeability

Intrinsic permeability is a measure of the ability of soil to transmit fluids and is the most important factor in determining the effectiveness of DPE because it controls the pore volume rates of groundwater and soil vapor extraction. In addition, intrinsic permeability influences the amount of oxygen supply that can be delivered to the unsaturated zone bacteria and it controls the groundwater drawdown associated with given extraction rates.

Intrinsic permeability varies over 13 orders of magnitude (from 10^{-16} to 10^{-3} cm^2) for the full range of earth materials, although a more limited range applies for most soil types (10^{-13} to 10^{-5} cm^2). Intrinsic permeability is best determined from field or laboratory tests, but it can

be estimated within one or two orders of magnitude from soil boring log data and laboratory tests. Coarse-grained soils (e.g., sands) have higher intrinsic permeability than fine-grained soils (e.g., clays, silts). Note that the ability of a soil to transmit air, which is of great importance in DPE, is reduced by the presence of soil water, which can block the soil pores and reduce air flow. The presence of soil water is especially important in fine-grained soils, which tend to retain pore water.

The relatively high vacuum achievable with DPE systems is generally effective in extracting liquids from relatively uniform soils with permeabilities as low as 10^{-11} cm^2. Single-pump DPE technology is best suited to sites with intrinsic permeabilities ranging from 10^{-9} to 10^{-11} cm^2, although it can be effective at sites with permeabilities as low as 10^{-12} cm^2. Single-pump DPE systems are generally not economical at sites with permeabilities greater than 10^{-9} cm^2 because of the large air flow required to maintain an adequate vacuum. There is no maximum permeability limit for application of dual-pump DPE systems, provided sufficient air confinement exists above the soils targeted for remediation (see Depth to Groundwater, below). However, the added cost of vacuum enhanced extraction is not warranted strictly to enhance groundwater recovery rates in more permeable soils, and DPE should only be considered for highly permeable soils in cases where soil and groundwater remediation is required.

At most sites, intrinsic permeability varies significantly with depth, and therefore the effectiveness of DPE systems depends on the soil stratification. This relationship is further discussed in the "Soil Structure and Stratification" section on page XI-15. Soils with very low intrinsic permeabilities (i.e., $< 10^{-11}$ cm^2) can be dewatered if they are interbedded with coarser-grained sediments. The coarser-grained sediments are dewatered first, then the fine-grained sediments drain to the dewatered layers, which are under high vacuum.

Hydraulic conductivity is a measure of the ability of soils to transmit water. Hydraulic conductivity can be determined from aquifer tests, including slug tests and pumping tests. You can convert hydraulic conductivity to intrinsic permeability using the following equation:

$$k = K\,(\mu/\rho g)$$

where: k = intrinsic permeability (cm^2)
K = hydraulic conductivity (cm/sec)
μ = water dynamic viscosity (g/cm · sec)
ρ = water density (g/cm^3)

g = acceleration due to gravity (cm/sec^2)

At 20°C: $\mu/\rho g = 1.02 \times 10^{-5}$ cm · sec

To convert k from cm^2 to darcy, multiply by 10^8.

The *effective air-phase permeability* of the petroleum-contaminated vadose-zone soils, along with the supply of air to the subsurface, controls the air-flow rates achievable using DPE. The extracted air-flow rate largely determines both the efficiency of vapor extraction and the rates at which oxygen can be supplied to hydrocarbon-degrading microorganisms in the subsurface. The effective air-phase permeability is the product of the intrinsic soil permeability and the relative permeability of the soil to the air phase *in situ*. The relative permeability to air is greatest at low volumetric contents (or saturations) of soil-water and petroleum product, and decreases as the liquid content increases owing to the blockage of soil pores by the liquid(s).

Soil Structure And Stratification

Soil structure and stratification are important to DPE because they affect how and where soil vapors will flow within the soil matrix during extraction. Structural characteristics such as microfracturing and secondary porosity features (e.g., root holes, mole holes, and worm holes) can result in higher permeabilities than expected for certain soils (e.g., clays). Increased flow will occur in the fractured but not in the unfractured media. Stratification of soils with different permeabilities can dramatically increase the lateral flow of soil vapors in more permeable strata while reducing the soil vapor flow through less permeable strata. Consequently, a significant volume of contaminated soil can remain untreated, and the remaining residual contamination can act as a future source of groundwater contamination.

You can determine soil structure and stratification by reviewing soil boring logs for wells or borings and by examining geologic cross-sections. Verify that soil types have been identified, that visual observations of soil structure have been documented, and that boring logs are of sufficient detail to define soil stratification. Special design provisions may be necessary for stratified soils to ensure that less-permeable strata are adequately vented.

Moisture Content In The Unsaturated Zone

High moisture content in the unsaturated zone soils can reduce soil permeability and, therefore, the effectiveness of DPE in removing hydrocarbons from the unsaturated zone. Generally, with water

saturation levels equal to or greater than 85 percent of field capacity, air flow is blocked because the effective air permeability is essentially zero.

Airflow is particularly important for soils within the capillary fringe, where a significant portion of petroleum constituents often accumulate. Fine-grained soils create a thicker capillary fringe than coarse-grained soils. The thickness of the capillary fringe can usually be determined from soil boring logs (i.e., in the capillary fringe, soils are usually described as moist or wet). By lowering the groundwater table, DPE can effectively vent soils within the capillary fringe.

Depth To Groundwater

DPE is difficult to apply at sites where the water table is located less than 3 feet below the land surface. This difficulty is due primarily to the high potential for air-flow short circuiting due to large vertical air-flow rates in the immediate vicinity of extraction wells within highly permeable soils. Vertical short circuiting of air flow prevents more uniform and lateral air flow through the affected soils. If a natural barrier (e.g., shallow moist clay layer or sealed building slab) does not exist to provide the necessary air confinement near the ground surface, then an engineered surface seal must be installed to prevent the undesirable air-flow short circuiting at sites with shallow groundwater.

Groundwater upwelling that can occur within SVE wells under vacuum pressures generally does not pose a problem for DPE systems because of the concurrent groundwater extraction that offsets potential upwelling in the vicinity of DPE wells. Groundwater extraction with DPE can be used to lower the water table and significantly expand the thickness of unsaturated soil through which air can be circulated, thus enhancing remedial effectiveness in shallow soils.

If water-table elevations fluctuate significantly at the site, special design provisions must be made to accommodate them. Knowledge of water table elevation fluctuations is especially critical if a single-pump DPE system is in use because the inlet ends of the downhole extraction tubes must be kept at or very near the liquid-gas interface in the wells to maintain the entrainment of suspended liquid droplets within the extracted air stream. As groundwater levels fluctuate, the liquid-gas interface will move accordingly, making it difficult to keep the vacuum extraction tubes in the optimal position for extraction of the air/droplet stream.

Chemical Properties

Effective Volatility

Effective volatility controls the rate at and degree to which constituents will vaporize from the adsorbed and aqueous phases in the unsaturated zone to the soil-vapor phase. The effective volatility of petroleum constituents in the subsurface depends on whether mobile free-phase product is present. If free-phase product is not present, the effective volatility of petroleum constituents is characterized by their Henry's law constants. In general, Henry's law constants increase as the boiling points of the constituents decreases. When free petroleum product exists in the subsurface, the product directly contacts soil vapor, and the effective volatility is given by the constituent's saturation vapor concentration times the mole fraction of the constituent in the product mixture (Raoult's Law).

Vapor pressure of a constituent is the pressure that a vapor exerts when in equilibrium with its pure liquid or solid form. This is an approximate measure of its tendency to evaporate. Constituents with higher vapor pressures (> 0.5 mm Hg) are generally volatilized efficiently by the induced air stream of DPE systems. Constituents with vapor pressures less than 0.5 mm Hg will not volatilize to a significant degree and are primarily remediated by in-situ biodegradation by microorganisms.

As previously discussed, petroleum products contain many different chemical constituents. Depending on its vapor pressure, each constituent will be volatilized to different degrees by a DPE system. If concentrations of volatile constituents are significant, treatment of extracted vapors may be needed. Exhibit XI-10 lists the vapor pressures of common petroleum constituents.

Boiling point is another measure of constituent volatility. Because of their complex constituent compositions, petroleum products are often classified by their boiling point ranges rather than their vapor pressures. Products with boiling points of less than about 250°C to 300°C are sufficiently volatile to be amenable to physical removal from the unsaturated zone by volatilization in a DPE system. Nearly all gasoline constituents, a portion of kerosene and diesel fuel constituents, and a lesser portion of heating oil constituents can be removed by volatilization. Biodegradation will also contribute to removal of the these constituents and will be a primary mechanism for removal of heavier, less volatile constituents. If the petroleum product at the site comprises predominantly low-volatility constituents, the DPE system should be designed to maximize biodegradation, in a manner similar to bioventing

Exhibit XI-10 Vapor Pressures Of Common Petroleum Constituents	
Constituent	**Vapor Pressure (mm Hg at 20°C)**
Methyl t-butyl ether	245
Benzene	76
Toluene	22
Ethylene dibromide	11
Ethylbenzene	7
Xylenes	6
Naphthalene	0.5
Tetraethyl lead	0.2

(see Chapter III), or bioventing could be used in lieu of DPE. If, however, the constituents are primarily volatile (e.g., gasoline), then higher air flow, similar to that used in conventional SVE systems, would be appropriate (see Chapter II). The boiling point ranges for common petroleum products are shown in Exhibit XI-11.

Exhibit XI-11 Petroleum Product Boiling Ranges	
Product	**Boiling Range (°C)**
Gasoline	40 to 205
Kerosene	180 to 300
Diesel fuel	200 to 338
Heating oil	> 275
Lubricating oils	Nonvolatile

Henry's law constant is the partition coefficient that relates the concentration of a constituent dissolved in water to its partial vapor pressure under equilibrium conditions. In other words, it describes the relative tendency for a dissolved constituent to exist in the vapor phase. Henry's law constant is a measure of the degree to which constituents that are dissolved in soil moisture or groundwater will volatilize for physical removal by DPE. Henry's law constants for several common constituents found in petroleum products are shown in Exhibit XI-12. Constituents with Henry's law constants of greater than 100 atmospheres are considered sufficiently volatile to be physically removed with extracted soil vapor.

Exhibit XI-12 Henry's Law Constant Of Common Petroleum Constituents	
Constituent	**Henry's Law Constant (atm)**
Tetraethyl lead	4,700
Ethylbenzene	359
Xylenes	266
Benzene	230
Toluene	217
Naphthalene	72
Ethylene dibromide	34
Methyl t-butyl ether	27

Chemical Sorptive Capacity

The chemical sorptive capacity determines the amount and degree of adsorption of constituents onto the soils and aquifer media. The higher the sorptive capacity of the soil, the more difficult the removal of constituents from the subsurface. The sorptive capacity is described by the soil-water partition coefficient, K_d, which is primarily a function of the organic carbon-water partition coefficient, K_{oc} (a chemical-specific parameter) and the fractional content of soil organic carbon, f_{oc} (a soil-specific parameter). For a given petroleum constituent, the sorptive capacity (and thus the difficulty of remediation) tends to increase as the soil becomes finer grained. The sorptive capacity affects the remedial effectiveness in both the vadose and groundwater zones. Although higher sorption decreases remedial effectiveness, it also reduces the risk of hydrocarbon transport from affected soil to underlying groundwater or to the atmosphere, thus decreasing the need for thorough remediation (i.e., increasing the residual chemical concentrations) that may be safely left behind in the targeted soils.

Pilot Scale Studies

After you have examined the data in the CAP to gauge the potential effectiveness of DPE, you will be in a position to decide if DPE is likely to be highly effective, somewhat effective, or ineffective given the site conditions. If the site shows marginal to moderate potential for effectiveness to DPE, you should evaluate the design closely and verify that adequate DPE pilot studies have been completed at the site and that the test results indicate DPE should be effective.

While pilot studies are valuable to any DPE evaluation and design, they are critical in cases where the screening-level assessment of the site conditions indicates only moderate to marginal applicability to DPE. Ideally, a small-scale pilot version of the actual DPE system intended for use at the site should be tested. For small sites, where the volume of soil requiring remediation is less than roughly 2000 cubic yards, it may not be economically attractive to conduct thorough DPE pilot tests in the field. Nevertheless, it is advisable to at least conduct a simple soil vapor extraction (SVE) test to verify that soil vapor can be extracted at achievable vacuum pressures. Also, aquifer testing is recommended to gather information needed to design the groundwater extraction portion of the DPE system.

For SVE testing, different extraction rates and wellhead vacuums are applied to the well to determine optimal operating conditions. The vacuum influence is measured at increasing distances from the extraction well using vapor probes or existing wells to establish the pressure field induced in the subsurface by the extraction system. The pressure field measurements can be used to define the radius of vacuum influence for the vadose-zone portion of the DPE system. Vapor concentrations should also be measured two or more times during the pilot testing to estimate the initial vapor concentrations that might be expected of a full-scale system at the site. This information serves as the basis for the vapor treatment system design. If an extended pilot test is conducted, long-term changes in soil-vapor concentrations can be used to assess how concentrations will vary over time, and to estimate the time required for full remediation.

Mistakes in the SVE field test commonly lead to erroneous conclusions regarding the potential effectiveness of DPE. Sometimes, the applied vacuum is too great, and the water level within the well casing rises rapidly to a level above the slotted portion of the well casing. When the applied vacuum is too high, no air can be extracted from the subsurface, leading to the erroneous conclusion that DPE cannot be applied at the site. Similarly, DPE is erroneously thought to be infeasible because the results from a simple pumping aquifer test (using conventional pumps) indicate that insufficient production of groundwater and/or petroleum product is obtained. In such cases, the high vacuum achievable with DPE systems can greatly enhance groundwater and/or product recovery, and DPE could still be a potentially effective remedy for low permeability sites. This illustrates the importance of actual DPE pilot testing.

To assess the groundwater flow parameters necessary to design the groundwater extraction portion of the DPE system, aquifer testing should be conducted. The use of DPE equipment for vacuum-assisted

aquifer testing is desirable, because such testing yields information that is directly relevant to the potential effectiveness of a full-scale DPE system at the site. However, this approach may be prohibitively expensive for smaller sites; in such cases, traditional aquifer testing (using groundwater extraction alone) may be used. Aquifer pumping tests are preferred over slug tests because slug tests only yield information regarding the local transmissivity (hydraulic conductivity times the thickness of the groundwater flow zone) in the immediate vicinity of the tested well, whereas pumping tests yield information regarding the transmissivity over a relatively wide area surrounding the pumped well. When properly conducted and analyzed, aquifer tests will yield reliable estimates of the relevant hydraulic parameters (transmissivity and storage coefficients) of the tested groundwater flow zone(s) that are targeted for remediation. These values should then be used in an appropriate groundwater model to simulate the potential groundwater extraction effectiveness under the applied vacuums achievable with a DPE system. In this way, the feasibility of the groundwater extraction portion of the DPE system can be properly assessed.

If the success of the DPE application is particularly dependent on biodegradation, relevant field and/or laboratory testing should be conducted. Chapter III on Bioventing describes several types of pilot-scale tests that can be performed to confirm the potential effectiveness of biodegradation.

Evaluation Of The DPE System Design

Once you have verified that DPE is generally applicable to the site, you can scrutinize the design of the system. A pilot study that provides data used to design the full-scale DPE system is highly recommended. The CAP should include a discussion of the rationale for the design and a presentation of the conceptual engineering design. Detailed engineering design documents might also be included, depending on state requirements. Further detail about information to look for in the discussion of the design is provided below.

Rationale For The Design

The primary basis for any subsurface remedial design is a definition of the volume of the subsurface targeted for active remediation (volume of attainment) and the cleanup levels or concentrations of constituents that must be achieved within the volume of attainment to protect human health and the environment. The cleanup levels may either be defined by state regulated "remedial action levels" or be determined on a site-

specific basis using transport modeling and risk assessment. Site characterization data must be used to determine what volumes of site soils and/or groundwater exceed the state action levels or site-specific, health-based cleanup levels. The CAP should clearly describe how the proposed DPE system is designed to meet the remedial action objectives. In addition, information such as the following should be included:

- The *Design Radius of Influence* (ROI) is the maximum distance from a vapor extraction well at which sufficient air flow can be induced to sustain acceptable rates of remediation (as dictated by the desired or required remediation time). The usefulness of the simple ROI concept is limited to certain site conditions (e.g., a single extraction well operating without air inlets or air-injection wells), and even when applicable, the task of establishing a meaningful ROI is not trivial. The ROI depends on many factors including the geometric configuration of extraction and injection wells, intrinsic permeability of the soil, soil moisture content, and desired remediation time. The ROI is best determined through field pilot studies, but it can be estimated from air flow modeling or other empirical methods. Generally, the design ROI can range from 5 feet (for fine-grained soils) to 100 feet (for coarse-grained soils) for a single well operating alone. For sites with stratified geology, radii of influence should be defined for each major soil type that occupies a significant portion of the chemically affected soil profile.

  For applications where the groundwater is shallow, ambient air is supplied readily through the land surface to the soils requiring treatment. In this case, the ROI can be used in a simple manner to determine the appropriate number and spacing of extraction wells. For applications in deeper treatment intervals, or treatment intervals that are effectively isolated from surface air supply, air inlet wells are required for effective remediation, and the simple ROI concept is not directly applicable. In such cases, subsurface air-flow stimulation is recommended to aid in properly designing a system of extraction and injection wells (or passive air inlets) that provides reasonably uniform air circulation throughout the targeted regions of the vadose zone.

- *Wellhead Vacuum* is the vacuum pressure that is required at the top of the vent well to produce the desired radius of vacuum influence in the soils. Required wellhead vacuums are usually determined with the aid of field pilot studies, and they typically range from 3 to 100 inches of water vacuum. Less permeable soils generally require higher wellhead vacuum pressures to produce reasonable influence radii of influence. It should be noted, however, that high vacuums can cause upwelling of the water table and occlusion of all or part of the extraction well screens.

- *Vapor Extraction Flow Rate* is the volumetric flow rate of soil vapor that will be extracted from each extraction well. Vapor extraction rate, radius of influence, and wellhead vacuum are all interdependent, (i.e., a change in the extraction rate will cause a change in wellhead vacuum and radius of influence). Appropriate vapor extraction flow rates are best determined from pilot studies, but they can be estimated using mathematical models and estimated values of the air-flow parameters such as effective air permeability and flow-zone thickness. The flow rate will contribute to the operational time requirements of the DPE system. Typical extraction rates range from 2 to 50 cubic feet per minute (cfm) per well.

- *Groundwater Extraction Rates* should, at a minimum, be sufficient to capture groundwater that has constituent concentrations that exceed applicable standards or that pose a threat to human health or the environment. Higher groundwater extraction rates may also be specified to produce greater water-table drawdowns and enhance the effectiveness of vadose zone remediation. The design of the groundwater extraction portion of the DPE system should be based on the results of aquifer testing and groundwater flow modeling. This is especially true when groundwater extraction is proposed from multiple groundwater flow zones, or when the objectives of the groundwater extraction include lowering the water table (dewatering).

- *Initial Constituent Vapor Concentrations* can be measured during pilot studies or estimated from soil gas samples or soil samples. They are used to estimate constituent mass removal rate and DPE operational time requirements, and to determine whether treatment of extracted vapors will be required prior to atmospheric discharge or reinjection (if allowed).

  The concentration of constituents in the extracted vapor is typically much higher during system start up than during sustained, long-term operations. The higher initial vapor concentrations usually last only a few hours or days before dropping off significantly. Vapor treatment requirements may be greater during this early phase of remediation, compared to the long-term requirements.

- *Required Final Constituent Concentrations* in soils, or soil cleanup levels, may be defined by state regulations as "remedial action levels," or they may be determined on a site-specific basis using fate and transport modeling and risk assessment. The required soil cleanup levels will determine what areas of the site require treatment and when DPE operation can be terminated.

- *Required Remedial Cleanup Time* may also influence the design of the system. The designer may reduce the spacing of the extraction wells to increase the rate of remediation to meet cleanup deadlines or client preferences, as required.

- *Soil Volume To Be Treated* is determined by state action levels or a site-specific risk assessment using site characterization data for the soils.

- *Pore Volume Calculations* are used along with extraction flow rate to determine the pore volume exchange rate. The exchange rate is calculated by dividing the pore space within the treatment zone by the design extraction rate (for vapor and groundwater separately). The pore space within the treatment zone is calculated by multiplying the soil porosity by the volume of soil to be treated. Some literature suggests that one pore volume of soil vapor be extracted at least daily for effective remedial progress if volatilization is intended to be the primary removal mechanism.

You can calculate the time required to exchange one pore volume of soil vapor using the following equation:

$$E = \frac{\varepsilon V}{Q}$$

where: E = pore volume exchange time (hr)
ε = soil porosity (m^3 vapor / m^3 soil)
V = volume of soil to be treated (m^3 soil)
Q = total vapor extraction flow rate (m^3 vapor / hr)

- *Discharge Limitations And Monitoring Requirements* are usually established by state regulations, but they must be considered by designers of a DPE system to ensure that monitoring ports are included in the system hardware. Discharge limitations imposed by state air quality regulations will determine the offgas treatment requirements.

- *Site Construction Limitations*, such as building locations, utilities, buried objects, and residences must be identified and considered in the design process.

Components Of A DPE System

Once the design basis is defined, the design of the DPE system can be developed. A typical DPE system design will include the following components and information:

- Extraction well orientation, placement, and construction details
- Manifold piping
- Vapor pretreatment (if necessary)
- Vapor treatment (if necessary)
- Blower selection
- Instrumentation and control design
- Optional DPE components
- Surface seals
- Injection wells

Exhibits XI-13 and XI-14 are schematic diagrams of single-pump and dual-pump DPE systems, respectively.

The following subsections provide guidance for selecting the appropriate system configuration, standard system components, and additional system components to adequately address petroleum contaminated soils at a particular UST site.

Extraction Wells

Well Orientation. DPE systems generally use vertical extraction wells, although horizontal wells can be used for air injection and/or for nutrient addition to enhance biodegradation, if needed.

Well Placement And Number Of Wells. This design element is critical to the effectiveness of a DPE system. For complex sites, numerical modeling should be used to simulate subsurface vapor flow and groundwater flow. For simpler, shallow groundwater sites, you can determine the number and location of extraction wells by using several methods. In the first method, divide the area of the site requiring treatment by the area of influence for a single well to obtain the total number of wells needed.

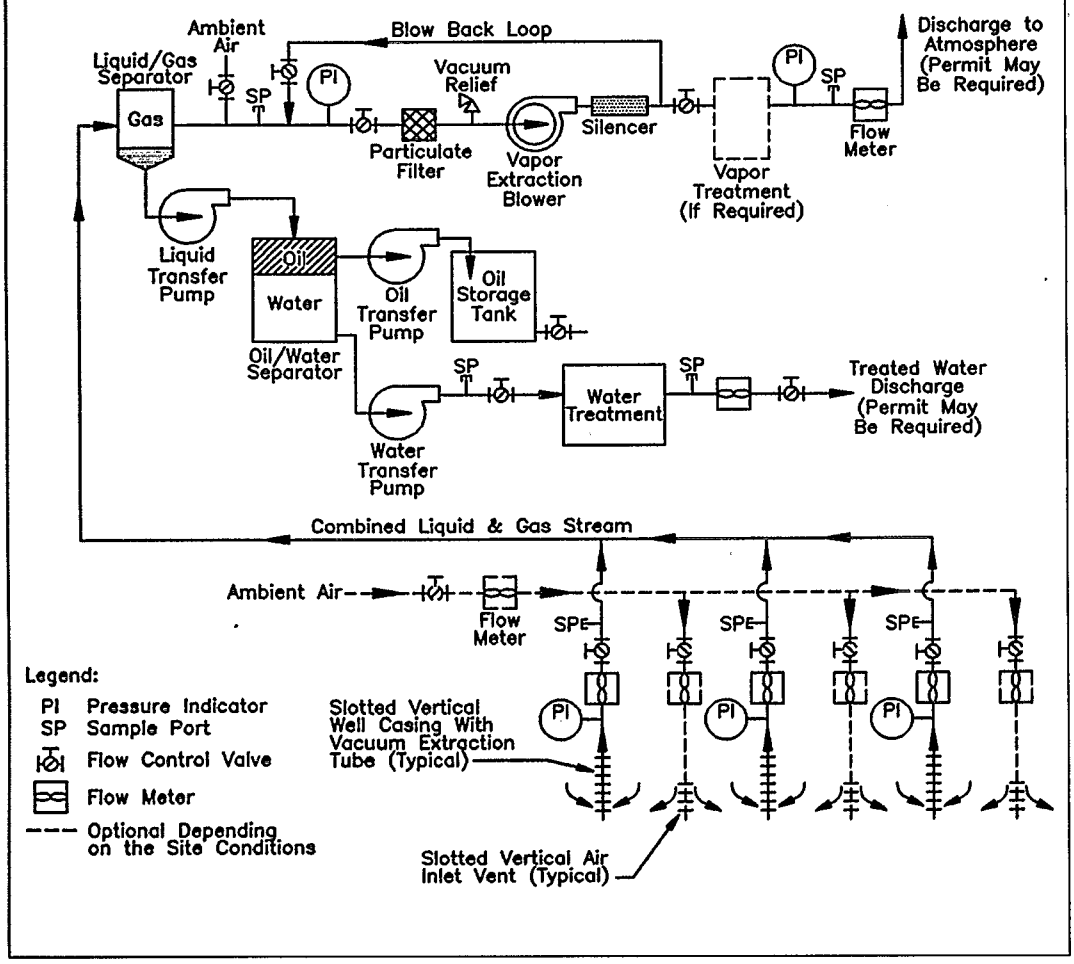
Then, space the wells evenly within the treatment area to provide areal coverage so that the areas of influence cover the entire area of contamination.

$$\text{Area of influence for a single well} = \pi \cdot (\text{ROI})^2$$

$$\text{Number of wells needed} = \frac{\text{Treatment area } (m^2)}{\text{Area of influence for single extraction well } (m^2/\text{well})}$$

This approximation method will work reasonably well in cases where ambient air is readily supplied to the extraction wells through the affected soils from the land surface. When there is no significant airflow from the land surface downward through the treatment zone,

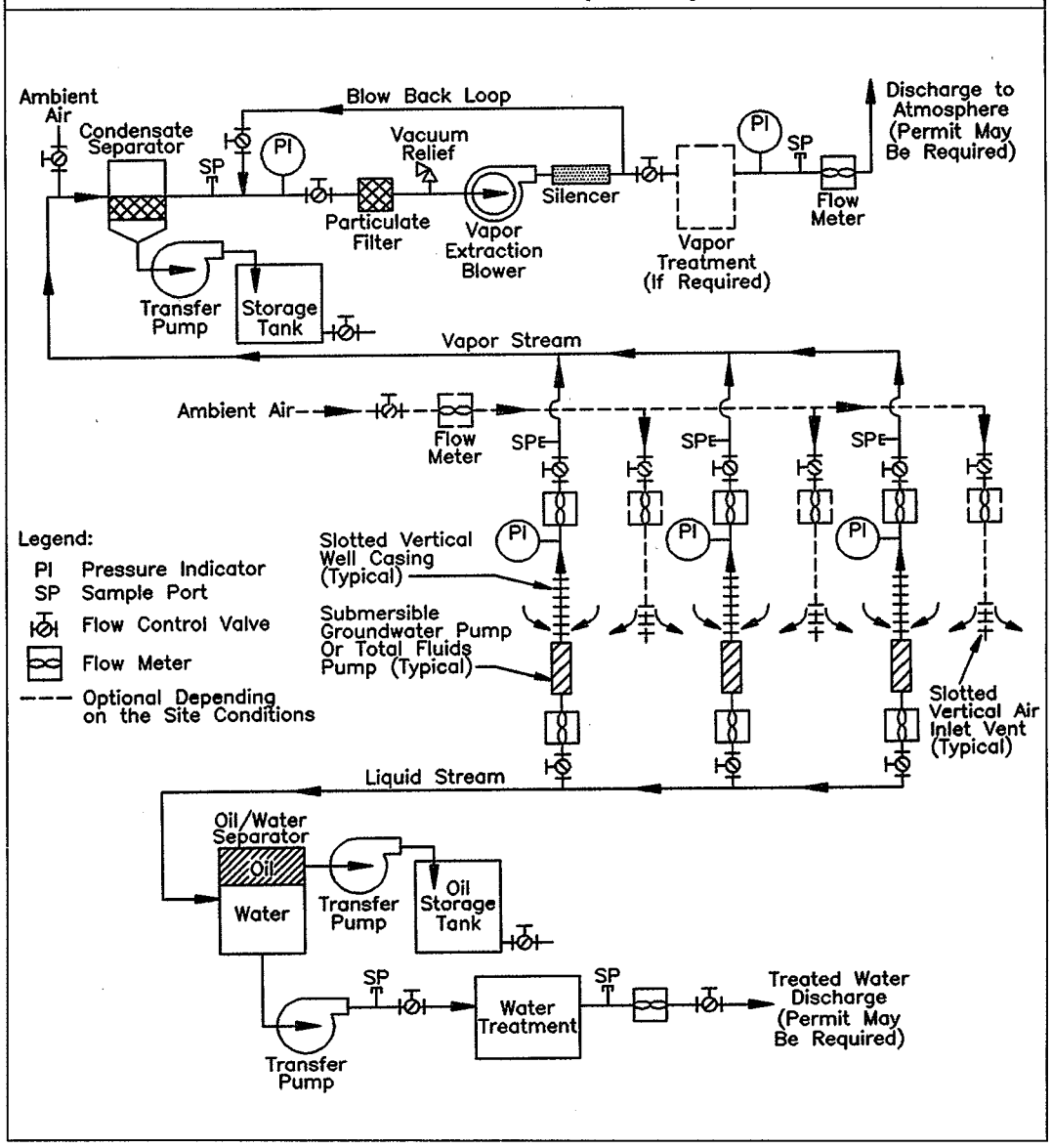
Exhibit XI-13
Schematic of Single Pump DPE System



approximately half of the evenly spaced wells specified should be air injection wells or passive air inlets.

It is important to note the potential for "short circuiting" of vertical air flow downward from the land surface in the immediate vicinity of an extraction well. Such short circuiting leads to ineffective remediation because the resulting air-flow circulation pattern only affects a small volume of soil surrounding the extraction well. Short circuiting may occur at system startup, or it may begin to occur after a DPE system has been in operation for some time. Short circuiting at initial system startup usually results from placing screened intervals at shallow depths in media with high effective vertical air permeabilities. This allows a relatively large volume of air to enter near the extraction well, reducing the well's effective radius of influence. The potential for this problem can

Exhibit XI-14
Schematic of Multi-Pump DPE System



usually be assessed by conducting field testing, as previously discussed, and engineered surface seals may be used to overcome this type of problem. Short circuiting can likewise be caused by improper sealing of the well boring annulus during the well construction. In such cases, the well must be carefully sealed or replaced with a well of more air-tight design.

The potential for short circuiting after a period of sustained operations can be difficult to predict based on the results of a short field test. Short circuiting that develops after a period of system operation is

usually caused by a significant increase in effective vertical air-flow permeability due to the drainage of water and/or product from the soil pores, which increases the air-filled porosity of the aquifer matrix and hence the effective air permeability. Adequate monitoring systems are therefore required to detect changes in the system vacuum and/or air-flow rates over time.

In the second method used to estimate the number of wells needed, determine the total extraction flow rate required to exchange the soil pore volume within the treatment area in 1 to 7 days. Determine the number of wells required by dividing the total extraction flow rate needed by the flow rate achievable with a single well.

$$\text{Number of wells needed} = \frac{\varepsilon V/t}{q}$$

where:
- ε = soil porosity (m^3 vapor / m^3 soil)
- V = volume of soil in treatment area (m^3 soil)
- q = vapor extraction rate from single extraction well (m^3 vapor/hr)
- t = pore volume exchange time (hours)

Similar calculations can be used for evaluating groundwater extraction. Consider the following additional factors in determining well spacing.

- Use closer well spacing in areas of high contaminant concentrations to increase mass removal rates.

- If a surface seal exists or is planned for the design, space the wells slightly farther apart because air is drawn from a greater lateral distance and not directly from the surface. However, be aware that the presence of a surface seal and the increase in extraction well spacing increases the need for air injection wells.

- At sites with stratified soils, wells that are screened in strata with low intrinsic permeabilities should be spaced more closely than wells that are screened in strata with higher intrinsic permeabilities. Well spacing may be irregular.

Well Construction. Typical single-pump and dual-pump DPE extraction wells are shown in Exhibits XI-3 and XI-4, presented earlier. Extraction wells are similar in construction to monitoring wells and are drilled using the same techniques. Extraction wells are usually constructed of polyvinyl chloride (PVC) casing and screening. Extraction well diameters typically range from 2 to 8 inches, depending on flow rates and depth; a 4-inch diameter is most common.

Extraction wells are constructed by placing the casing and screen in the center of a borehole. Filter pack material is placed in the annular space between the casing/screen and the walls of the borehole. The filter pack material extends 1 to 2 feet above the top of the well screen; a 1 to 2 foot thick bentonite seal is placed above the filter pack. Cement-bentonite grout seals the remaining space up to the land surface. Filter pack material and screen slot size must be consistent with the grain size of the surrounding soils.

The location and length of the well screen in vertical extraction wells can vary and should be based on the depth to groundwater, the stratification of the soil, and the location and distribution of contaminants. The bottom of the screened interval must be sufficiently deep to allow for the maximum anticipated groundwater drawdown.

- At a site with homogeneous soil conditions, ensure that the well is screened throughout the contaminated zone. A deeper well helps to ensure remediation of the greatest amount of soil during seasonal low groundwater conditions.

- At a site with stratified soils or lithology, check to see that an adequate number of wells have been screened within the lower permeability zones, as well as the higher permeability zones, because these zones are generally more difficult to remediate.

Manifold Piping

Manifold piping connects the extraction wells to the surface blower. Piping can either be placed above or below grade depending on site operations, ambient temperature, and local building codes. Below-grade piping is most common and is installed in shallow utility trenches that lead from the extraction wellhead vault(s) to a central equipment location. The piping can either be manifolded in the equipment area or connected to a common vacuum main that supplies the wells in series, in which case flow control valves are sited at the wellheads. Piping to the well locations should be sloped toward the well so that condensate or groundwater that is entrained with the air flow stream will flow back toward the well.

Vapor Pretreatment

Extracted vapor can contain condensate, entrained groundwater, and particulates that can damage blower parts and inhibit the effectiveness of downstream treatment systems. In order to minimize damage, vapors are usually passed through a moisture separator and a particulate filter

prior to entering the blower. Check the CAP to verify that these elements have been included in the design.

Vapor Treatment

Look for vapor treatment systems in the DPE design if pilot study data indicate that extracted vapors will contain VOC concentrations in excess of established air quality limits. Available options for vapor treatment include granular activated carbon (GAC), catalytic oxidation, or thermal oxidation.

GAC is a popular choice because of its simplicity and effectiveness. Catalytic oxidation is often used, however, when the contaminant mass loading rate is expected to be too high to make GAC economical, and when concentrations are at or below 20 percent of their lower explosive limit (LEL). A thermal oxidizer may be employed when concentrations of chemical constituents are expected to be sustained at levels greater than 20 percent of their LELs.

Blower Selection

The type and size of blower selected should be based on (1) the vacuum required to achieve design vacuum pressure at the vent wellheads (including upstream and downstream piping losses) and (2) the total flow rate required. The flow rate requirement should be based on the sum of the flow rates from the contributing vapor extraction wells. In applications where explosive concentrations of hydrocarbon vapors can collect, be sure the CAP specifies blowers with explosion-proof motors, starters, and electrical systems. Exhibit XI-15 depicts the performance curves for the three basic types of blowers that can be used in a DPE system.

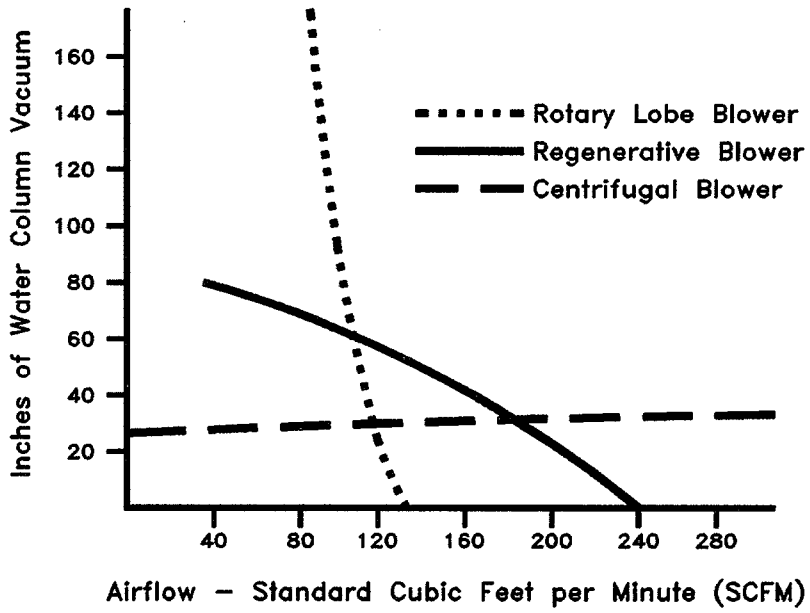
- *Centrifugal* blowers (such as squirrel-cage fans) should be used for high-flow, low-vacuum applications. Centrifugal blowers are only applicable for dual-pump DPE systems, because higher vacuums are required for single-pump DPE systems.

- *Regenerative and turbine* blowers should be used when a moderately high vacuum is needed.

- *Rotary lobe* and other positive displacement blowers should be used when a very high vacuum is needed.

Liquid ring vacuum pumps are also commonly used for DPE applications in very low permeability environments where high vacuums are required.

Exhibit XI-15
Performance Curves For Three Types Of Blowers



Notes: Centrifugal blower type shown is a New York model 2004A at 3500 rpm. Regenerative blower type shown is a Rotron model DR707. Rotary lobe blower type shown is a M-D Pneumatics model 3204 at 3000 rpm.

From "Guidance for Design, Installation and Operation of Soil Venting Systems." Wisconsin Department of Natural Resources, Emergency and Remedial Response Section, PUBL-SW185-93, July 1993.

Instrumentation and Controls

The parameters typically monitored in an DPE system include:

- Pressure (or vacuum)
- Air/vapor flow rate
- Groundwater extraction rates
- Carbon dioxide and/or oxygen concentrations in extracted air (to monitor biodegradation)
- Contaminant mass removal rates
- Temperature

The equipment in a DPE system used to monitor these parameters provides the information necessary to make appropriate system adjustments and track remedial progress. The monitoring equipment in a DPE system enables you to control each component of the system. Exhibit XI-16 lists typical monitoring and control equipment for a DPE

system, where each of these pieces of monitoring equipment should be placed, and the types of equipment that are available.

Exhibit XI-16
Monitoring And Control Equipment

Monitoring Equipment	Location In System	Example Of Equipment
Flow meter	○ At each wellhead ○ Manifold to blower ○ Blower discharge	○ Pitot tube ○ In-line rotameter ○ Orifice plate ○ Venturi or flow tube
Vacuum gauge	○ At each well head or manifold branch ○ Before and after filters upstream of blower ○ Before and after vapor treatment	○ Manometer ○ Magnehelic gauge ○ Vacuum gauge
Vapor temperature sensor	○ Manifold to blower ○ Blower discharge (prior to vapor treatment)	○ Bi-metal dial-type thermometer
Sampling port	○ At each well head or manifold branch ○ Manifold to blower ○ Blower discharge	○ Hose barb ○ Septa fitting
Vapor sample collection equipment (used through a sampling port)	○ At each well head or manifold branch ○ Manifold to blower ○ Blower discharge	○ Tedlar bags ○ Sorbent tubes ○ Sorbent canisters ○ Polypropylene tubing for direct GC injection
Control Equipment		
Flow control valves	○ At each well head or manifold branch ○ Dilution or bleed valve at manifold to blower	○ Ball valve ○ Gate/globe valve ○ Butterfly valve

Optional DPE Components

Additional DPE system components might be required when certain site conditions exist or pilot studies dictate they are necessary. These components include land surface seals and injection wells. Each of these system components is discussed on the following pages.

Land Surface Seals

Land surface seals might be included in an DPE system design in order to prevent surface water infiltration that can reduce air flow rates, reduce fugitive emissions, and increase the lateral extent of air flow to increase the volume of soil being treated. These results are accomplished because surface seals force fresh air to be drawn from a greater distance from the extraction well. If a surface seal is used, lower pressure gradients may exist and decreased flow velocities will result unless a higher vacuum is applied to the extraction well, or additional air injection wells are used.

Surface seals or caps should be selected to match the site conditions and regular business activities at the site. Options include high density polyethylene (HDPE) liners (similar to landfill liners), clay or bentonite seals, or concrete or asphalt paving. Existing covers (e.g., pavement or concrete slabs) might not be effective as an air-flow barrier if they are constructed with a porous subgrade material.

Injection Wells

Air injection wells are used to enhance air flow rates from the extraction wells by providing an active or passive air source to the subsurface. These wells are often used at sites that are covered with an impermeable cap (e.g., pavement or buildings) because the cap restricts direct air flow to the subsurface. They may also be used to help reduce short-circuiting of air flow in the subsurface. In addition, air injection is used to eliminate potential stagnation zones (areas of no flow) which can exist between extraction wells.

Air injection wells are similar in construction to extraction wells, and they may be operated in either passive or active mode. Active injection wells force compressed air into soils. Passive injection wells, or inlets, simply provide a pathway that helps extraction wells draw ambient air into the subsurface. Air injection wells should be placed to eliminate stagnation zones, but should not force contaminants toward areas from which they cannot be recovered (i.e., away from the influence areas of the systems' extraction wells).

Evaluation Of Operation And Monitoring Plans

Make sure that a system operation and monitoring plan has been developed for both the system start-up phase and for long-term operations. Operations and monitoring are necessary to ensure that system performance is optimized and contaminant mass removal is tracked. When significant biodegradation occurs in the subsurface, mass

removal cannot be directly measured by simply monitoring extracted liquid and vapors. Both constituent concentrations and carbon dioxide concentrations (to measure microbial respiration) should be monitored in the extracted vapor stream. Dissolved constituent concentrations in the extracted groundwater and the quantity of petroleum product collected must be monitored to assess constituent mass removal.

Start-Up Operations

The start-up phase of operations for single-pump DPE systems will include about 7 to 10 days of adjustments in the vacuum pump settings and the depth of the extraction tube inlet. Multi-pump systems will require a similar period of adjusting the valves and pumps for the separate groundwater and air extraction systems. The start-up phase should also include manifold valving adjustments. These adjustments should balance flow between the wells within the system. To optimize DPE effectiveness, flow measurements, pressure or vacuum readings, carbon dioxide concentrations, oxygen concentrations, and volatile organic compound (VOC) concentrations should be recorded daily from each extraction well, from the manifold, and from the effluent stack during the start up adjustment period. These measurement can be used to decide how to best operate the system. Nutrient delivery (if needed to enhance biodegradation) should not be performed until after start-up operations are complete.

Long-Term Operations

Long-term monitoring should consist of flow-balancing, flow and pressure measurements, and vapor concentration readings. Measurements are commonly made at weekly or biweekly intervals for the duration of the system operational period.

Exhibit XI-17 provides a brief synopsis of system monitoring requirements.

Remediation Progress Monitoring

Monitoring the performance of the DPE system in reducing contaminant concentrations in soils is necessary to track the progress of remediation. Since concentrations of petroleum constituents may be reduced due to both volatilization and biodegradation, both processes should be monitored in order to track their cumulative effect. Constituent mass extraction can be tracked and calculated by multiplying the vapor concentrations measured in the extraction manifold by the extraction air flow rate and adding the rate of petroleum

Exhibit XI-17
System Monitoring Recommendations

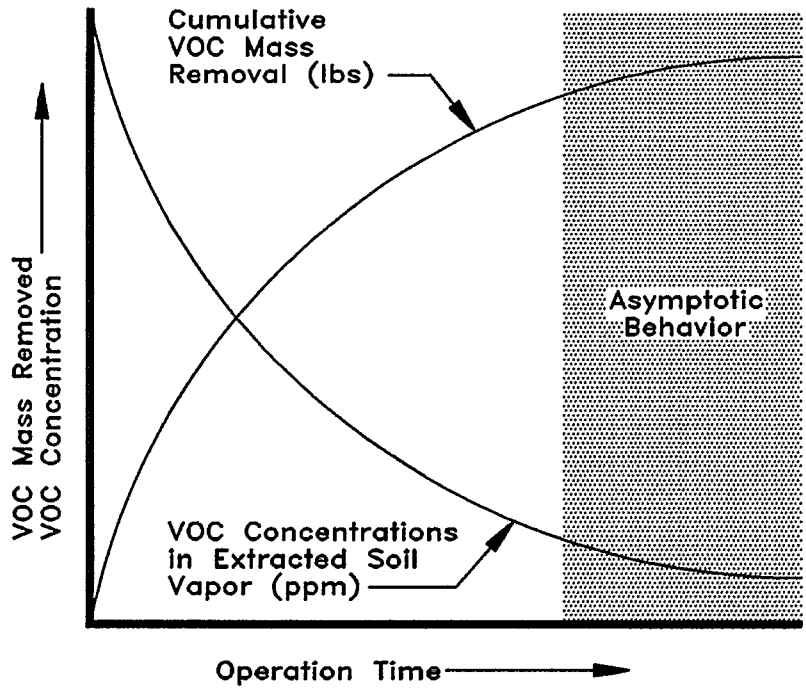
Phase	Monitoring Frequency	What To Monitor	Where To Monitor
Start-up (7-10 days)	At least daily	○ Flow ○ Vacuum readings ○ Vapor concentrations ○ Carbon dioxide ○ Oxygen	○ Extraction vents ○ Manifold ○ Effluent stack
Remedial (ongoing)	Weekly to bi-weekly	○ Flow-balancing ○ Flow ○ Vacuum ○ Vapor concentrations ○ Carbon dioxide ○ Oxygen	○ Extraction vents ○ Manifold ○ Effluent stack

product recovery and dissolved aqueous phase recovery. The constituent mass that is biodegraded is more difficult to quantify but can be estimated from monitoring data on carbon dioxide and oxygen concentrations in the extracted air stream. The quantities of petroleum hydrocarbons degraded can then be estimated stoichiometrically (see Chapter III, Bioventing).

Remediation progress of DPE systems typically exhibits asymptotic behavior with respect to the rates of recovery of free product and groundwater, and a reduction in vapor concentration and the overall rate of mass removed. (See Exhibit XI-18.) When asymptotic behavior begins to occur, the operator should evaluate alternatives that may increase DPE effectiveness (e.g., altering the subsurface airflow patterns by changing airflow rates). Other more aggressive steps to renew remediation effectiveness can include installing additional injection wells or extraction wells. If very low effluent concentrations persist, extraction flow rates may be reduced significantly, or the system may be operated in a pulsed mode (although pulsed operation is generally less efficient than operating at a very low, sustained extraction rate). Pulsing involves the periodic shutdown and startup of extraction wells to allow the subsurface environment to come to equilibrium (shutdown) before beginning to extract vapors again.

If asymptotic behavior persists for periods greater than about 6 months, the concentration rebound remains small following periods of system shutdown, and residual contamination levels are at or below regulatory limits, termination of operations may be appropriate. If not,

Exhibit XI-18
Relationship Between Concentration Reduction And Mass Removal



operation of the system as a bioventing system with reduced vacuum and air flow may be an effective way to complete remediation.

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Checklist: Can Dual-Phase Extraction Be Used At This Site?

This checklist can help you evaluate the completeness of the CAP and to identify areas that require closer scrutiny. As you go through the CAP, answer the following questions. If the answer to several questions is no, you should request additional information to determine if DPE will accomplish cleanup goals at the site:

1. Site Characteristics

Yes	No	
❑	❑	Are the soil and aquifer media intrinsic permeabilities greater than 10^{-12} cm^2?
❑	❑	Is the soil free of impermeable layers or other conditions that would disrupt air flow?
❑	❑	Is the soil moisture in the unsaturated zone less than or equal to 85 percent of saturation?
❑	❑	Is depth to groundwater at least three feet?

2. Constituent Characteristics

Yes	No	
❑	❑	Are constituent vapor pressures greater than 0.5 mm Hg, boiling points less than 300°C, and Henry's law constants greater than 100 atm?
❑	❑	Are the chemical sorptive capacities of the constituents present sufficiently low?

3. Evaluation Of The DPE System Design

Yes	No	
❑	❑	Does the radius of influence (ROI) for the proposed extraction wells fall within the range of 5 to 100 feet?
❑	❑	Has the ROI been calculated for each soil type at the site?

- ❑ ❑ For more complex sites with multiple treatment depth intervals and/or the need for multiple extraction wells, was subsurface airflow modeling conducted to determine well placement?
- ❑ ❑ Is wellhead vacuum determined from field pilot studies and between 3 and 100 inches of water?
- ❑ ❑ Is vapor extraction flow rate between 2 and 50 cfm per well?
- ❑ ❑ Are groundwater extraction rates sufficient to capture groundwater with constituent concentrations above cleanup goals?
- ❑ ❑ Will initial constituent vapor concentrations be monitored?
- ❑ ❑ Are required final constituent concentrations specified?
- ❑ ❑ Is a specified cleanup time required?
- ❑ ❑ Is soil volume to be treated estimated?
- ❑ ❑ Is the pore volume exchange rate calculated?
- ❑ ❑ Are discharge limits specified?
- ❑ ❑ Were site construction limitations considered?
- ❑ ❑ Is the well density appropriate, given the total area to be cleaned up and the radius of influence of each well?
- ❑ ❑ Is manifold piping design addressed and do extraction pipes slope toward the wells?
- ❑ ❑ Is vapor pretreatment specified?
- ❑ ❑ Is vapor treatment included, if warranted based on treatability study?
- ❑ ❑ Is the blower selected appropriate for the desired vacuum conditions?

❑	❑	Are appropriate instrumentation and controls specified, including means to monitor pressure (or vacuum), air/vapor flow rate, groundwater extraction rates, carbon dioxide and/or oxygen concentrations in extracted air, contaminant concentrations in extracted air, and temperature.

4. Optional DPE Components

Yes	No	
❑	❑	Are land surface seals proposed?
❑	❑	Are air injection or passive inlet wells proposed and are they appropriate to the site?

5. Operation And Monitoring Plans

Yes	No	
❑	❑	Does the CAP propose daily monitoring for at least 1 week of flow measurements, constituent concentrations, vacuum readings, and carbon dioxide and oxygen concentrations?
❑	❑	Does the CAP propose weekly to biweekly ongoing monitoring of these same parameters?

Chapter XII

Abbreviations and Definitions

Chapter XII
Abbreviations and Definitions

Abbreviations

AS	Air Sparging
ASTM	American Society of Testing and Materials
atm	atmosphere (pressure)
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
Btu	British thermal unit
CAP	Corrective Action Plan
CFU	Colony Forming Units
DNAPL	Dense Non-Aqueous Phase Liquid
DO	Dissolved Oxygen
DPE	Dual-Phase Extraction
FID	Flame Ionization Detector
GAC	Granular Activated Carbon
GC	Gas Chromatograph
HDPE	High Density Polyethylene
Hg	Mercury, elemental
LEL	Lower Explosive Limit
LNAPL	Light Non-Aqueous Phase Liquid
LTTD	Low Temperature Thermal Desorption
LUST	Leaking Underground Storage Tank
MS	Mass Spectrometer
NAPL	Non-Aqueous Phase Liquid
NPDES	National Pollutant Discharge Elimination System
OUST	Office of Underground Storage Tanks (USEPA, Washington, DC)
PAH	Polyaromatic Hydrocarbon
PID	Photoionization Detector
PNA	Polynuclear Aromatic Hydrocarbon
ppb	parts per billion
ppm	parts per million
psi	pounds per square inch (pressure)
PVC	Polyvinyl Chloride
QA	Quality Assurance
QC	Quality Control
ROI	Radius of Influence
SVE	Soil Vapor Extraction
TCLP	Toxicity Characteristic Leaching Procedure (EPA Method 1311)
TEA	Terminal Electron Acceptor
TPH	Total Petroleum Hydrocarbons
TRPH	Total Recoverable Petroleum Hydrocarbons (EPA Method 418.1)
UEL	Upper Explosive Limit

UST	Underground Storage Tank
VOC	Volatile Organic Compound

Definitions

abiotic: not biotic; not formed by biologic processes.

absorption: the penetration of atoms, ions, or molecules into the bulk mass of a substance.

Actinomycetes: any of numerous, generally filamentous, and often pathogenic, microorganisms resembling both bacteria and fungi.

adsorption: the retention of atoms, ions, or molecules onto the surface of another substance.

advection: the process of transfer of fluids (vapors or liquid) through a geologic formation in response to a pressure gradient that may be caused by changes in barometric pressure, water table levels, wind fluctuations, or infiltration.

aeration: the process of bringing air into contact with a liquid (typically water), usually by bubbling air through the liquid, spraying the liquid into the air, allowing the liquid to cascade down a waterfall, or by mechanical agitation. Aeration serves to (1) strip dissolved gases from solution, and/or (2) oxygenate the liquid. The rate at which a gas transfers into solution can be described by Fick's First Law.

aerobic: able to live, grow, or take place only when free oxygen is present.

afterburner: an off-gas posttreatment unit for control of organic compounds by thermal oxidation. A typical afterburner is a refractory-lined shell providing enough residence time at a sufficiently high temperature to destroy organic compounds in the off-gas stream.

aggregate: coarse mineral material (e.g., sand, gravel) that is mixed with either cement to form concrete or tarry hydrocarbons to form asphalt.

algae: chiefly aquatic, eucaryotic one-celled or multicellular plants without true stems, roots and leaves, that are typically autotrophic, photosynthetic, and contain chlorophyll. Algae are not typically found in groundwater.

aliphatic: of or pertaining to a broad category of carbon compounds distinguished by a straight, or branched, open chain arrangement of the constituent carbon atoms. The carbon-carbon bonds may be either

saturated or unsaturated. Alkanes, alkenes, and alkynes are aliphatic hydrocarbons.

alkanes: the homologous group of linear saturated aliphatic hydrocarbons having the general formula C_nH_{2n+2}. Alkanes can be straight chains, branched chains, or ring structures. Also referred to as paraffins.

alkenes: the group of unsaturated hydrocarbons having the general formula C_nH_{2n} and characterized by being highly chemically reactive. Also referred to as olefins.

alkynes: the group of unsaturated hydrocarbons with a triple Carbon-Carbon bond having the general formula C_nH_{2n-2}.

ambient: surrounding.

anaerobic: able to live, grow, or take place where free oxygen is not present.

analog: in chemistry, a structural derivative of a parent compound.

anisotropic: the condition in which hydraulic properties of an aquifer are not equal when measured in all directions.

anoxic: total deprivation of oxygen.

aqueous solubility: the extent to which a compound will dissolve in water. The log of solubility is generally inversely related to molecular weight.

aquifer: a geologic formation capable of transmitting significant quantities of groundwater under normal hydraulic gradients.

aquitard: a geologic formation that may contain groundwater but is not capable of transmitting significant quantities of groundwater under normal hydraulic gradients. In some situations aquitards may function as confining beds.

aromatic: of or relating to organic compounds that resemble benzene in chemical behavior. These compounds are unsaturated and characterized by containing at least one 6-carbon benzene ring.

asymptote: a line that is considered to be the limit to a curve. As the curve approaches the asymptote, the distance separating the curve and the asymptote continues to decrease, but the curve never actually intersects the asymptote.

attenuation: the reduction or lessening in amount (e.g., a reduction in the amount of contaminants in a plume as it migrates away from the source).

Atterberg limits: the moisture contents which define a soil's liquid limit, plastic limit, and sticky limit.

auger: a tool for drilling/boring into unconsolidated earth materials (soil) consisting of a spiral blade wound around a central stem or shaft that is commonly hollow (hollow-stem auger). Augers commonly are available in flights (sections) that are connected together to advance the depth of the borehole.

autoignition temperature: the temperature at which a substance will spontaneously ignite. Autoignition temperature is an indicator of thermal stability for petroleum hydrocarbons.

autotrophic: designating or typical of organisms that derive carbon for the manufacture of cell mass from inorganic carbon (carbon dioxide).

bacteria: unicellular microorganisms that exist either as free-living organisms or as parasites and have a broad range of biochemical, and often pathogenic, properties. Bacteria can be grouped by form into five general categories: cocci (spherical), bacilli (rod-shaped), vibrio (curved rod-shaped), spirilla (spiral), and filamentous (thread-like).

baghouse: a dust-collection chamber containing numerous permeable fabric filters through which the exhaust gases pass. Finer particulates entrained in the exhaust gas stream are collected in the filters for subsequent treatment/disposal.

ball valve: a valve regulated by the position of a free-floating ball that moves in response to fluid or mechanical pressure.

Bentonite: a colloidal clay, largely made up of the mineral sodium montmorillonite, a hydrated aluminum silicate. Because of its expansive property, bentonite is commonly used to provide a tight seal around a well casing.

berm: a sloped wall or embankment (typically constructed of earth, hay bales, or timber framing) used to prevent inflow or outflow of material into/from an area.

bioassay: a method used to determine the toxicity of specific chemical contaminants. A number of individuals of a sensitive species are placed in water containing specific concentrations of the contaminant for a specified period of time.

bioaugmentation: the introduction of cultured microorganisms into the subsurface environment for the purpose of enhancing bioremediation of organic contaminants. Generally the microorganisms are selected for their ability to degrade the organic compounds present at the remediation site. The culture can be either an isolated genus or a mix of more than one genera. Nutrients are usually also blended with the aqueous solution containing the microbes to serve as a carrier and dispersant. The liquid is introduced into the subsurface under natural conditions (gravity fed) or injected under pressure.

bioavailability: the availability of a compound for biodegradation, influenced by the compound's location relative to microorganisms and its ability to dissolve in water.

biocide: a substance capable of destroying (killing) living organisms.

biodegradability (or biodegradation potential): the relative ease with which petroleum hydrocarbons will degrade as the result of biological metabolism. Although virtually all petroleum hydrocarbons are biodegradable, biodegradability is highly variable and dependent somewhat on the type of hydrocarbon. In general, biodegradability increases with increasing solubility; solubility is inversely proportional to molecular weight.

biodegradation: a process by which microbial organisms transform or alter (through metabolic or enzymatic action) the structure of chemicals introduced into the environment.

biomass: the amount of living matter in a given area or volume.

boiling point: the temperature at which a component's vapor pressure equals atmospheric pressure. Boiling point is a relative indicator of volatility and generally increases with increasing molecular weight.

Btu: the quantity of heat required to raise the temperature of one pound of water one degree Fahrenheit at 39°F; used as the standard for the comparison of heating values of fuels.

bubble radius: the maximum radial distance away from a biosparging well where the effects of sparging are observable. Analogous to radius of influence of an air sparging well.

bulk density: the amount of mass of a soil per unit volume of soil; where mass is measured after all water has been extracted and total volume includes the volume of the soil itself and the volume of air space (voids) between the soil grains.

butterfly valve: a shut-off valve usually found in larger pipe sizes (4 inches or greater). This type of valve can be used for non-critical flow control.

capillary fringe: the zone of a porous medium above the water table within which the porous medium is saturated by water under pressure that is less than atmospheric pressure.

capillary suction: the process whereby water rises above the water table into the void spaces of a soil due to tension between the water and soil particles.

catalytic oxidizer: an off-gas posttreatment unit for control of organic compounds. Gas enters the unit and passes over a support material coated with a catalyst (commonly a noble metal such as platinum or rhodium) that promotes oxidation of the organics. Catalytic oxidizers can also be very effective in controlling odors. High moisture content and the presence of chlorine or sulfur compounds can adversely affect the performance of the catalytic oxidizer.

chemotrophs: organisms that obtain energy from oxidation or reduction of inorganic or organic matter.

coefficient of permeability: see hydraulic conductivity.

cometabolism: the simultaneous metabolism of two compounds, in which the degradation of the second compound (the secondary substrate) depends on the presence of the first compound (the primary substrate). For example, in the process of degrading methane, some bacteria can degrade hazardous chlorinated solvents that they would otherwise be unable to attack.

complexation: a reaction in which a metal ion and one or more anionic ligands chemically bond. Complexes often prevent the precipitation of metals.

condensate: the liquid that separates from a vapor during condensation.

conductivity: a coefficient of proportionality describing the rate at which a fluid (e.g., water or gas) can move through a permeable medium. Conductivity is a function of both the intrinsic permeability of the porous medium and the kinematic viscosity of the fluid which flows through it.

cone of depression: the area around a discharging well where the hydraulic head (potentiometric surface) in the aquifer has been lowered by pumping. In an unconfined aquifer, the cone of depression is a cone-shaped depression in the water table where the media has actually been dewatered.

confined aquifer: a fully saturated aquifer overlain by a confining layer. The potentiometric surface (hydraulic head) of the water in a confined aquifer is at an elevation that is equal to or higher than the base of the overlying confining layer. Discharging wells in a confined aquifer lower the potentiometric surface which forms a cone of depression, but the saturated media is not dewatered.

confining layer: a geologic formation characterized by low permeability that inhibits the flow of water (see also aquitard).

conservative: (a) in the case of a contaminant, one that does not degrade and the movement of which is not retarded; is unreactive. (b) in the case of an assumption, one that leads to a worst-case scenario, one that is most protective of human health and the environment.

constituent: an essential part or component of a system or group (e.g., an ingredient of a chemical mixture). For instance, benzene is one constituent of gasoline.

cyclone: a type of separator for removal of larger particles from an exhaust gas stream. Gas laden with particulates enters the cyclone and is directed to flow in a spiral causing the entrained particulates to fall out and collect at the bottom. The gas exits near the top of the cyclone.

Darcy's Law: an empirical relationship between hydraulic gradient and the viscous flow of water in the saturated zone of a porous medium under conditions of laminar flow. The flux of vapors through the voids of the vadose zone can be related to a pressure gradient through the air permeability by Darcy's Law.

degradation potential: the degree to which a substance is likely to be reduced to a simpler form by bacterial activity.

denitrification: bacterial reduction of nitrite to gaseous nitrogen under anaerobic conditions.

density: the amount of mass per unit volume.

diffusion: the process by which molecules in a single phase equilibrate to a zero concentration gradient by random molecular motion (Brownian motion). The flux of molecules is from regions of high concentration to low concentration and is governed by Fick's Second Law.

dispersion: the process by which a substance or chemical spreads and dilutes in flowing groundwater or soil gas.

dissolution: dissolving of a substance in a liquid solvent (e.g., water).

downgradient: in the direction of decreasing static head (potential).

drawdown: lowering the water table due to withdrawal of groundwater as from a well.

dynamic viscosity: a measure of a fluid's resistance to tangential or shear stress.

effective porosity: the amount of interconnected pore space in a soil or rock through which fluids can pass, expressed as a percent of bulk volume. Some of the voids and pores in a rock or soil will be filled with static fluid or other material, so that effective porosity is always less than total porosity.

effluent: something that flows out, especially a liquid or gaseous waste stream.

electron acceptor: a chemical entity that accepts electrons transferred to it from another compound. It is an oxidizing agent that, by virtue of its accepting electrons, is itself reduced in the process. See also terminal electron acceptor and oxidation-reduction.

electron donor: a chemical entity that donates electrons to another compound. It is a reducing agent that, by virtue of its donating electrons, is itself oxidized in the process. See also electron acceptor and oxidation-reduction.

empirical: relying upon or gained from experiment or observation.

entrained: particulates or vapor transported along with flowing gas or liquid.

enzyme: a protein that a living organism uses in the process of degrading a specific compound. The protein serves as a catalyst in the compound's biochemical transformation.

enzyme: any of numerous proteins or conjugated proteins produced by living organisms and functioning as biochemical catalysts.

eucaryotes: an organism having one or more cells with well-defined nuclei.

evaporation: the process by which a liquid enters the vapor (gas) phase.

***ex situ*:** moved from its original place; excavated; removed or recovered from the subsurface.

extraction well: a well employed to extract fluids (either water, gas, free product, or a combination of these) from the subsurface. Extraction is usually accomplished by either a pump located within the well or suction created by a vacuum pump at the ground surface.

facultative anaerobes: microorganisms that can grow in either the presence or the absence of molecular oxygen. In the absence of oxygen these microorganism can utilize another compound (e.g., sulfate or nitrate) as a terminal electron acceptor.

facultative: used to describe organisms that are able to grow in either the presence or absence of a specific environmental factor (e.g., oxygen). See also facultative anaerobe.

Fick's First Law: an equation describing the rate at which a gas transfers into solution. The change in concentration of gas in solution is proportional to the product of an overall mass transfer coefficient and the concentration gradient.

Fick's Second Law: an equation relating the change of concentration with time due to diffusion to the change in concentration gradient with distance from the source of concentration.

field capacity: the maximum amount of water that a soil can retain after excess water from saturated conditions has been drained by the force of gravity.

flow tube: a calibrated flow measuring device made for a specific range of flow velocities and fluids.

flux: the rate of movement of mass through a unit cross-sectional area per unit time in response to a concentration gradient or some advective force.

free product: a petroleum hydrocarbon in the liquid ("free" or non-aqueous) phase (see also non-aqueous phase liquid, NAPL).

friable: easily crumbled, not cohesive or sticky.

fungi: aerobic, multicellular, nonphotosynthetic, heterotrophic microorganisms. The fungi include mushrooms, yeast, molds, and smuts. Most fungi are saprophytes, obtaining their nourishment from dead organic matter. Along with bacteria, fungi are the principal organisms responsible for the decomposition of carbon in the biosphere. Fungi have two ecological advantages over bacteria: (1) they can grow in low moisture areas, and (2) they can grow in low pH environments.

gate valve: a valve regulated by the position of a circular plate.

globe valve: a type of stemmed valve that is used for flow control. The valve has a globe shaped plug that rises or falls vertically when the stem handwheel is rotated.

gradient: the rate of change in value of a physical or chemical parameter per unit change in position. For example, hydraulic gradient is equal to the difference in head measured at two points (usually wells) divided by the distance separating the two points. The dimensions of head and distance are both lengths, therefore the gradient is expressed as a dimensionless ratio (L/L).

groundwater: the water contained in the pore spaces of saturated geologic media.

grout: a watery mixture of cement (and commonly bentonite) without aggregate that is used to seal the annular space around well casings to prevent infiltration of water or short-circuiting of vapor flow.

heat capacity: the quantity of energy that must be supplied to raise the temperature of a substance. For contaminated soils heat capacity is the quantity of energy that must be added to the soil to volatilize organic components. The typical range of heat capacity of soils is relatively narrow, therefore variations are not likely to have a major impact on application of a thermal desorption process.

Henry's law constant: the ratio of the concentration of a compound in air (or vapor) to the concentration of the compound in water under equilibrium conditions.

Henry's law: the relationship between the partial pressure of a compound and the equilibrium concentration in the liquid through a proportionality constant known as the Henry's law constant.

heterogeneous: varying in structure or composition at different locations in space.

heterotrophic: designating or typical of organisms that derive carbon for the manufacture of cell mass from organic matter.

homogeneous: uniform in structure or composition at all locations in space.

hose barb: a twist-type connector used for connecting a small diameter hose to a valve or faucet.

hydraulic conductivity: a coefficient of proportionality describing the rate at which water can move through a permeable medium. Hydraulic conductivity is a function of both the intrinsic permeability of the porous medium and the kinematic viscosity of the water which flows through it. Also referred to as the coefficient of permeability.

hydraulic gradient: the change in total potentiometric (or piezometric) head between two points divided by the horizontal distance separating the two points.

hydrocarbon: chemical compounds composed only of carbon and hydrogen.

hydrogen peroxide: H_2O_2. Hydrogen peroxide is used to increase the dissolved oxygen content of groundwater to stimulate aerobic biodegradation of organic contaminants. Hydrogen peroxide is infinitely soluble in water, but rapidly dissociates to form a molecule of water (H_2O) and one-half molecule of oxygen (O). Dissolved oxygen concentrations of greater than 1,000 mg/L are possible using hydrogen peroxide, but high levels of D.O. can be toxic to microorganisms.

hydrophilic: having an affinity for water, or capable of dissolving in water; soluble or miscible in water.

hydrophobic: tending not to combine with water, or incapable of dissolving in water; insoluble or immiscible in water. A property exhibited by non-polar organic compounds, including the petroleum hydrocarbons.

hypoxic: a condition of low oxygen concentration, below that considered aerobic.

***in situ*:** in its original place; unmoved; unexcavated; remaining in the subsurface.

in-line rotameter: a flow measurement device for liquids and gases that uses a flow tube and specialized float. The float device is supported by the flowing fluid in the clear glass or plastic flow tube. The vertical scaled flow tube is calibrated for the desired flow volumes/time.

indigenous: living or occurring naturally in a specific area or environment; native.

infiltration gallery: an engineered structure that facilitates infiltration of water into the subsurface. Infiltration galleries may consist of one or more horizontal or vertical perforated pipes, a single gravel-filled trench or a network of such trenches, or a combination of these.

infiltration: the downward movement of water through a soil in response to gravity and capillary suction.

injection well: a well used to inject under pressure a fluid (liquid or gas) into the subsurface.

inlet well: a well through which a fluid (liquid or gas) is allowed to enter the subsurface under natural pressure.

inoculate: to implant microorganisms onto or into a culture medium.

intergranular: between the individual grains in a rock or sediment.

intrinsic permeability: a measure of the relative ease with which a permeable medium can transmit a fluid (liquid or gas). Intrinsic permeability is a property only of the medium and is independent of the nature of the fluid.

isotropic: the condition in which hydraulic properties of an aquifer are equal when measured in any direction.

kinematic viscosity: the ratio of dynamic viscosity to mass density. Kinematic viscosity is a measure of a fluid's resistance to gravity flow: the lower the kinematic viscosity, the easier and faster the fluid will flow.

liquid limit (LL): the lower limit for viscous flow of a soil.

liquidity index (LI): quantitative value used to assess whether a soil will behave as a brittle solid, semisolid, plastic, or liquid. LI is equal to the difference between the natural moisture content of the soil and the plastic limit (PL) divided by the plasticity index (PI).

lithology: the gross physical character of a rock or rock types in a stratigraphic section.

lower explosive limit (LEL): the concentration of a gas below which the concentration of vapors is insufficient to support an explosion. LELs for most organics are generally 1 to 5 percent by volume.

magnehelic gauge: a sensitive differential pressure or vacuum gauge manufactured by Dwyer Instrument Co. that uses a precision diaphragm to measure pressure differences. This gauge is manufactured in specific pressure or vacuum ranges such as 0 to 2 inches of water column. Magnehelic gauges are typically used to measure SVE system vacuums.

manifold: a pipe with several apertures for making multiple connections.

manometer: an instrument for measuring fluid pressure. Typically a U-shaped tube in which opposing fluid pressures reach an equilibrium. The pressure is equal to the differences in the levels of the fluid on either side of the tube.

metabolism: a term that encompasses all of the diverse reactions by which a cell processes food material to obtain energy and the compounds from which new cell components are made.

methanogenic: referring to the formation of methane by certain anaerobic bacteria during the process of anaerobic fermentation.

microaerophilic: obligate aerobes that function best under conditions of low oxygen concentration.

microcosm: a diminutive, representative system analogous to a larger system in composition, development, or configuration. As used in biodegradation treatability studies, microcosms are typically constructed in glass bottles or jars.

microorganisms: microscopic organisms including bacteria, protozoans, yeast, fungi, mold, viruses, and algae.

mineralization: the release of inorganic chemicals from organic matter in the process of aerobic or anaerobic decay.

moisture content: the amount of water lost from a soil upon drying to a constant weight, expressed as the weight per unit weight of dry soil or as the volume of water per unit bulk volume of the soil. For a fully saturated medium, moisture content equals the porosity.

molecular diffusion: process whereby molecules of various gases tend to intermingle and eventually become uniformly dispersed.

molecular weight: the amount of mass in one mole of molecules of a substance as determined by summing the masses of the individual atoms which make up the molecule.

monoaromatic: aromatic hydrocarbons containing a single benzene ring.

non-aqueous phase liquid (NAPL): contaminants that remain as the original bulk liquid in the subsurface (see also free product).

nutrients: major elements (e.g., nitrogen and phosphorus) and trace elements (including sulfur, potassium, calcium, and magnesium) that are essential for the growth of organisms.

obligate aerobes: organisms that require the presence of molecular oxygen (O_2) for their metabolism.

obligate anaerobes: organisms for which the presence of molecular oxygen is toxic. These organisms derive the oxygen needed for cell synthesis from chemical compounds.

occlude: to cause to become obstructed or closed and thus prevent passage either into or from.

octanol/water partition coefficient (K_{ow}): a coefficient representing the ratio of the solubility of a compound in octanol (a non-polar solvent) to its solubility in water (a polar solvent). The higher the K_{ow}, the more non-polar the compound. Log K_{ow} is generally used as a relative indicator of the tendency of an organic compound to adsorb to soil. Log K_{ow} values are generally inversely related to aqueous solubility and directly proportional to molecular weight.

off-gas treatment system: refers to the unit operations used to treat (i.e. condense, collect, or destroy) contaminants in the purge gas from the thermal desorber.

olefins: see alkenes.

orifice plate: a flow measurement device for liquids or gases that uses a restrictive orifice plate consisting of a machined hole that produces a jet effect. Typically the orifice meter consists of a thin plate with a square edged, concentric, and circular orifice. The pressure drop of the jet effect across the orifice is proportional to the flow rate. The pressure drop can be measured with a manometer or differential pressure gauge.

oxidation-reduction (redox): a chemical reaction consisting of an oxidation reaction in which a substance loses or donates electrons, and a reduction reaction in which a substance gains or accepts electrons. Redox reactions are always coupled because free electrons cannot exist in solution and electrons must be conserved.

paraffins: see alkanes.

partial pressure: the portion of total vapor pressure in a system due to one or more constituents in the vapor mixture.

permeability: a qualitative description of the relative ease with which rock, soil, or sediment will transmit a fluid (liquid or gas). Often used as a synonym for hydraulic conductivity or coefficient of permeability.

pH: a measure of the acidity of a solution. pH is equal to the negative logarithm of the concentration of hydrogen ions in a solution. A pH of 7 is neutral. Values less than 7 are acidic, and values greater than 7 are basic.

phototrophs: organisms that use light to generate energy (by photosynthesis) for cellular activity, growth, and reproduction.

pilot test: operation of a small-scale version of a larger system to gain information relating to the anticipated performance of the larger system. Pilot test results are typically used to design and optimize the larger system.

pitot tube: a device used to measure the total pressure of a fluid stream that is essentially a tube attached to a manometer at one end and pointed upstream at the other.

plastic limit (PL): the lower limit of the plastic state of a soil.

plastic soil: one that will deform without shearing (typically silts or clays). Plasticity characteristics are measured using a set of parameters known as Atterberg Limits.

plasticity index (PI): the range of water content in which soil is in a plastic state. PI is calculated as the difference between the percent liquid limit and percent plastic limit.

polyaromatic hydrocarbon: aromatic hydrocarbons containing more than one fused benzene ring. Polyaromatic hydrocarbons are commonly designated PAH.

polynuclear aromatic hydrocarbon: synonymous with polyaromatic hydrocarbon. Designated PNA.

pore volume: the total volume of pore space in a given volume of rock or sediment. Pore volume usually relates to the volume of air or water that must be moved through contaminated material in order to flush the contaminants.

pore volume: the volume of water (or air) that will completely fill all of the void space in a given volume of porous matrix. Pore volume is equivalent to the total porosity. The rate of decrease in the concentration of contaminants in a given volume of contaminated porous media is directly proportional to the number of pore volumes that can be exchanged (circulated) through the same given volume of porous media.

porosity: the volume fraction of a rock or unconsolidated sediment not occupied by solid material but usually occupied by water and/or air.

pressure gradient: a pressure differential in a given medium (e.g., water or air) which tends to induce movement from areas of higher pressure to areas of lower pressure.

procaryotes: a cellular organism in which the nucleus has no limiting membrane.

protozoa: single-celled, eucaryotic microorganisms without cell walls. Most protozoa are free-living although many are parasitic. The majority of protozoa are aerobic or facultatively anaerobic heterotrophs.

psi (pounds per square inch): a unit of pressure or pressure drop across a flow resistance. One psi is equivalent to the pressure exerted by 2.31 feet of water column.

psig (pounds per square inch (gauge)): 0 psig = 14.696 psia (psi absolute) = 1.0 atmosphere.

pugmill: a chamber in which water and soil are mixed together. Typically mixing is aided by an internal mechanical stirring/kneading device.

radius of influence: the maximum distance away from an air injection or extraction source that is significantly affected by a change in pressure and induced movement of air.

reagent: a substance or solution used in a chemical reaction, especially those used in laboratory work to detect, measure, or produce other substances.

recalcitrant: unreactive, nondegradable; refractory.

redox: short for oxidation-reduction.

refractory index: a measure of the ability of a substance to be biodegraded by bacterial activity. The lower the refractory index, the greater the biodegradability.

retardation: preferential retention of contaminant movement in the subsurface resulting from adsorptive processes or solubility differences.

saturated zone: the zone in which all the voids in the rock or soil are filled with water at greater than atmospheric pressure. The water table is the top of the saturated zone in an unconfined aquifer.

sentinel well: a groundwater monitoring well situated between a sensitive receptor downgradient and the source of a contaminant plume upgradient. Contamination should be first detected in the sentinel well which serves as a warning that contamination may be moving closer to the receptor. The sentinel well should be located far enough upgradient of the receptor to allow enough time before the contamination arrives at the receptor to initiate other measures to prevent contamination from reaching the receptor, or in the case of a supply well, provide for an alternative water source.

septa fitting: a special fitting used to seal vials (a liner for a threaded cap) or gas chromatographs (GCs) to provide closure. Septas can be manufactured in single, double, or triple layers of silicone rubber and other plastic materials. A syringe with a measured quantity of

contaminant can be injected through a septa closure and into a GC column for separation analysis.

sequester: to undergo sequestration.

sequestration: the inhibition or stoppage of normal ion behavior by combination with added materials, especially the prevention of metallic ion precipitation from solution by formation of a coordination complex with a phosphate.

SESOIL: a one-dimensional model for estimating pollutant distribution in an unsaturated soil column. SESOIL results are commonly used to estimate the source term for groundwater transport modeling of the saturated zone.

short circuiting: the entry of ambient air into an extraction well without first passing through the contaminated zone. Short circuiting may occur through utility trenches, incoherent well or surface seals, or layers of high permeability geologic materials.

short circuiting: as it applies to SVE and bioventing, the entry of ambient air into the extraction well without first passing through the contaminated zone. Short circuiting may occur through utility trenches, incoherent well or surface seals, or layers of high permeability geologic materials.

soil moisture: the water contained in the pore spaces in the unsaturated zone.

solubility: the amount of mass of a compound that will dissolve in a unit volume of solution.

sorbent canisters: gas-tight canisters typically filled with activated carbon (charcoal) for collection and transport of vapor samples. In the laboratory the vapors are desorbed and analyzed to identify the organic compounds and quantify their concentration.

sorbent tubes: glass tubes filled with a sorbent material that reacts chemically with specific organic compounds. Based on the nature of the sorbent and the extent of the chemical reaction, organic compounds can be identified and their concentration quantified.

sorption: a general term used to encompass the processes of absorption, adsorption, ion exchange, and chemisorption.

sparge: injection of air below the water table to strip dissolved volatile organic compounds and/or oxygenate the groundwater to facilitate aerobic biodegradation of organic compounds.

specific gravity: the dimensionless ratio of the density of a substance with respect to the density of water. The specific gravity of water is equal to 1.0 by definition. Most petroleum products have a specific gravity less than 1.0, generally between 0.6 and 0.9. As such, they will float on water--these are also referred to as LNAPLs, or light non-aqueous phase liquids. Substances with a specific gravity greater than 1.0 will sink through water--these are referred to as DNAPLs, or dense non-aqueous phase liquids.

sticky limit: the limit at which a soil loses its ability to adhere to a metal blade.

stratification: layering or bedding of geologic materials (e.g., rock or sediments).

stratum: a horizontal layer of geologic material of similar composition, especially one of several parallel layers arranged one on top of another.

sump: a pit or depression where liquids drain, collect, or are stored.

Tedlar bags: gas-tight bags constructed of non-reactive material (Tedlar) for the collection and transport of gas/vapor samples.

terminal electron acceptor (TEA): a compound or molecule that accepts an electron (is reduced) during metabolism (oxidation) of a carbon source. Under aerobic conditions molecular oxygen is the terminal electron acceptor. Under anaerobic conditions a variety of terminal electron acceptors may be used. In order of decreasing redox potential, these TEAs include nitrate, manganic manganese, ferric iron, sulfate, and carbon dioxide. Microorganisms preferentially utilize electron acceptors that provide the maximum free energy during respiration. Of the common terminal electron acceptors listed above, oxygen has the highest redox potential and provides the most free energy during electron transfer.

thermal desorber: describes the primary treatment unit that heats petroleum-contaminated materials and desorbs the organic materials into a purge gas or off-gas.

thermal desorption system: refers to a thermal desorber and associated systems for handling materials and treated soils and treating offgases and residuals.

total petroleum hydrocarbons (TPH): a measure of the concentration or mass of petroleum hydrocarbon constituents present in a given amount of air, soil, or water. The term total is a misnomer, in that few, if any, of the procedures for quantifying hydrocarbons are capable of measuring all fractions of petroleum hydrocarbons present in the sample. Volatile hydrocarbons are usually lost in the process and not quantified.

Additionally, some non-petroleum hydrocarbons may be included in the analysis.

total recoverable petroleum hydrocarbons (TRPH): an EPA method (418.1) for measuring total petroleum hydrocarbons in samples of soil or water. Hydrocarbons are extracted from the sample using a chlorofluorocarbon solvent (typically Freon-113) and quantified by infrared spectrophotometry. The method specifies that the extract be passed through silica gel to remove the non-petroleum fraction of the hydrocarbons.

travel time: the time it takes a contaminant to travel from the source to a particular point downgradient.

tripolyphosphates: Salts with $P_3O^{-5}{}_{10}$ anion. Most common is sodium tripolyphosphate ($Na_5P_3O_{10}$).

turbine wheel: a rotor designed to convert fluid energy into rotational energy. Hydraulic turbines are used to extract energy from water as the water velocity increases due to a change in head or kinetic energy at the expense of the potential energy as the water flows from a higher elevation to a lower elevation. The fluid velocity tangential component contributes to the rotation of the rotor in a turbomachine.

unconfined aquifer: an aquifer in which there are no confining beds between the capillary fringe and land surface, and where the top of the saturated zone (the water table) is at atmospheric pressure.

unsaturated: the characteristic of a carbon atom in a hydrocarbon molecule that shares a double bond with another carbon atom.

unsaturated zone: the zone between land surface and the capillary fringe within which the moisture content is less than saturation and pressure is less than atmospheric. Soil pore spaces also typically contain air or other gases. The capillary fringe is not included in the unsaturated zone.

upgradient: it the direction of increasing potentiometric (piezometric) head.

vacuum draft tube: a narrow tube lowered into an extraction well through which a strong vacuum is pulled via a suction pump at ground surface. Fluids (gas, water, and/or free product) are drawn into the draft tube and conveyed to the surface for treatment or disposal. Depending upon the configuration of the extraction system, the inlet of the draft tube may be either above or below the static level of the liquid in the well.

vadose zone: the zone between land surface and the water table within which the moisture content is less than saturation (except in the capillary fringe) and pressure is less than atmospheric. Soil pore spaces also typically contain air or other gases. The capillary fringe is included in the vadose zone.

vapor density: the amount of mass of a vapor per unit volume of the vapor.

vapor pressure: the force per unit area exerted by a vapor in an equilibrium state with its pure solid, liquid, or solution at a given temperature. Vapor pressure is a measure of a substance's propensity to evaporate. Vapor pressure increases exponentially with an increase in temperature.

venturi: a short tube with a constricted throat for determining fluid pressures and velocities by measuring differential pressures generated at the throat as a fluid traverses the tube.

viscosity: a measure of the internal friction of a fluid that provides resistance to shear within the fluid. The greater the forces of internal friction (i.e. the greater the viscosity), the less easily the fluid will flow.

volatilization: the process of transfer of a chemical from the aqueous or liquid phase to the gas phase. Solubility, molecular weight, and vapor pressure of the liquid and the nature of the gas-liquid interface affect the rate of volatilization.

water table: the water surface in an unconfined aquifer at which the fluid pressure in the pore spaces is at atmospheric pressure.

weathering: the process during which a complex compound is reduced to its simpler component parts, transported via physical processes, or biodegraded over time.

wellhead: the area immediately surrounding the top of a well, or the top of the well casing.

windrow: a low, elongated row of material left uncovered to dry. Windrows are typically arranged in parallel.

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CORRECTION

Please substitute new page IX-19/IX-20 for the page with the same number in the shrink-wrapped package.

We would like your reactions to ***"How To Evaluate Alternative Cleanup Technologies For Underground Storage Tank Sites: A Guide For Corrective Action Plan Reviewers."***

Please take a few moments to respond to the statements below. Completion of this form is entirely voluntary. Your responses will help us to improve any revisions to this ***Guide.***

Public reporting burden for this collection of information is estimated to average 1 hour and 5 minutes per response. This includes the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Chief, Information Policy Branch, PM-223Y, U.S. Environmental Protection Agency, 401 M St. S.W., Washington, D.C. 20460; and to Office for Management and Budget, Washington, D.C. 20503. OMB ICR 2010-0023, expiration 7/31/95.

Using a scale of 1 to 5, with 1 representing "strongly disagree" and 5 representing "strongly agree", respond to each of the following statements.

		Strongly Disagree	Somewhat Disagree	Neutral	Mostly Agree	Strongly Agree	
1	The manual helps me determine when an appropriate cleanup technology has been proposed.	1	2	3	4	5	1
2	The manual is organized in a way that makes it easy for me to evaluate a CAP.	1	2	3	4	5	2
3	The manual helps me determine if the CAP proposes a technically sound approach to the cleanup.	1	2	3	4	5	3
4	The language used in the manual is easy to understand.	1	2	3	4	5	4
5	The individual Tables of Contents make it easy to find the information I'm looking for.	1	2	3	4	5	5
6	The individual flowcharts help me plan the progress of a cleanup before I start reviewing the CAP.	1	2	3	4	5	6
7	The Checklists help me focus on the most important information in the CAP.	1	2	3	4	5	7
8	The references help me find the information I need.	1	2	3	4	5	8
9	The definitions (provided in Chapter X) are useful.	1	2	3	4	5	9

Pull Off and Drop in Mail

If you responded with "**1**" or "**2**" to any of the statements above, please explain why, and feel free to offer suggestions for improvement.

Would additional chapters on other technologies be useful? If so, please list technologies you would like to see addressed in the comment space provided.

Place
Stamp
Here

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