United States
Environmental Protection
Agency

Solid Waste and
Emergency Response
5401G

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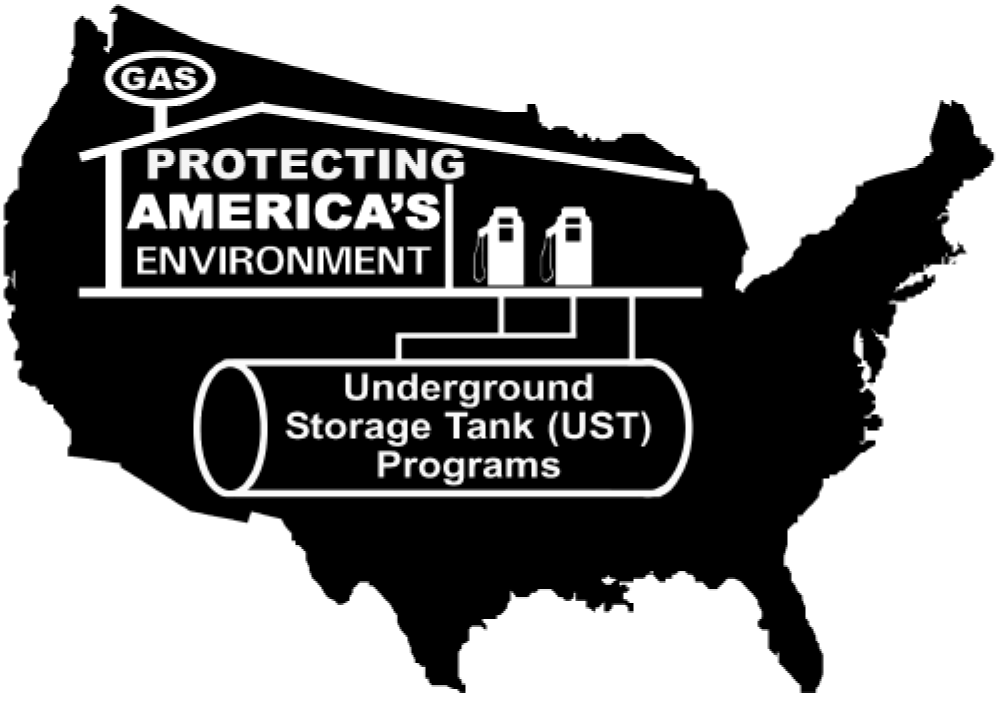
May 2004
*www.epa.gov/oust/pubs/tums.htm*

EPA

# How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites

## A Guide for Corrective Action Plan Reviewers



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# Chapter I

# Introduction

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## Background

As of September 30, 2003, more than 439,000 releases from leaking underground storage tanks (LUSTs) have been reported nationwide. Cleanups have been initiated at more than 403,000 of these sites, and more than 303,000 sites have been cleaned up. The backlog of sites still to be cleaned up is more than 136,000. In many cases, the workload for state regulators (who must oversee 50 to 400 cleanups at a time) is burdensome.

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

A primary factor in the high cost cleanups is the use of cleanup methods that are either inappropriately selected or not optimally designed and operated given the specific conditions of the site. Pump-and-treat, the most commonly used method for remediating groundwater, is often unsuccessful because either the source of contamination is not adequately addressed, or the systems are not optimized. Even when properly operated, pump-and-treat systems have inherent limitations[1]: they may not work well in complex geologic settings or heterogeneous aquifers; they often stop reducing contamination long before reaching intended cleanup levels; and in some situations they can 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 movess the problem from one location to another. In addition to being costly, 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) actively promotes faster, more effective, and less costly alternatives to traditional cleanup methods. EPA's Office of Underground Storage Tanks (OUST) continues to work with

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[1] In spite of its limitations, there may be some situations where pump-and-treat is the most appropriate remediation alternative available (*e.g.*, to remediate a small, dissolved phase plume or to contain the plume in order to prevent migration into uncontaminated areas).

state and local governments to encourage the use of the most appropriate cleanup technology for each and every site. When this manual was first published in 1994, it covered the first eight technologies listed in the table of contents (Chapters II through IX). The manual was updated in 1995 to add two additional technologies (Chapters X and XI). Back then, these ten technologies were referred to as “alternative technologies” because although they had the ability to make cleanups faster, more effective, and less costly than traditional options, they were not widely used (although they certainly are today). The current update (May 2004) adds two new technologies (chemical oxidation-Chapter XI, and enhanced aerobic bioremediation-Chapter XII) to the suite of “alternative technologies”.

## 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 sitespecific 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. Also, you can add your own notes in 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, generally 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(s), 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.

- Advantages and disadvantages of each technology, initial screening criteria, and other data specific to each technology.

## How to Obtain Additional Copies of the Manual

A limited number of single copies are available directly from OUST. Contact OUST by telephone at 703-603-9900 and ask for “publications outreach”. The entire document is also available in electronic format (PDF) from the “Publications” section of OUST’s web site at *http://www.epa.gov/oust/pubs/tums.htm*.

# Chapter II

# Soil Vapor Extraction

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# Chapter II
# Soil Vapor Extraction

## Overview

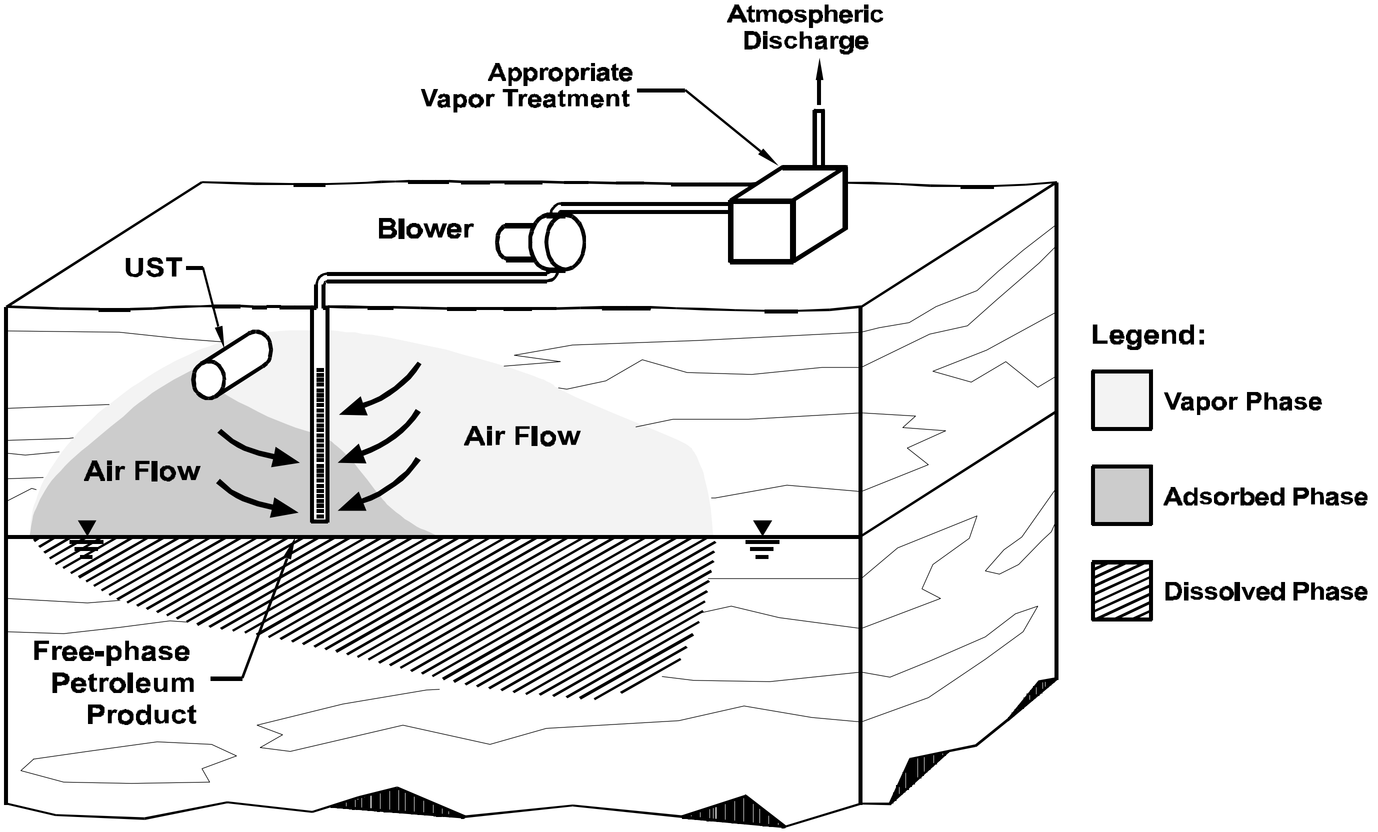
Soil vapor extraction (SVE), also known as soil venting or vacuum extraction, is an *in situ* remedial technology that reduces concentrations of volatile constituents in petroleum products adsorbed to soils in the unsaturated (vadose) zone. In this technology, a vacuum is applied to the soil matrix to 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

- Proven performance; readily available equipment; easy installation.
- Minimal disturbance to site operations.
- Short treatment times: usually 6 months to 2 years under optimal conditions.
- Cost competitive: $20-50/ton of contaminated soil.
- Easily combined with other technologies (e.g., air sparging, bioremediation, and vacuum-enhanced dual-phase extraction).
- Can be used under buildings and other locations that cannot be excavated.

### Disadvantages

- Concentration reductions greater than about 90% are difficult to achieve.
- Effectiveness less certain when applied to sites with low-permeability soil or stratified soils.
- May require costly treatment for atmospheric discharge of extracted vapors.
- Air emission permits generally required.
- Only treats unsaturated-zone soils; other methods may also be needed to treat saturated-zone soils and groundwater.

- **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.

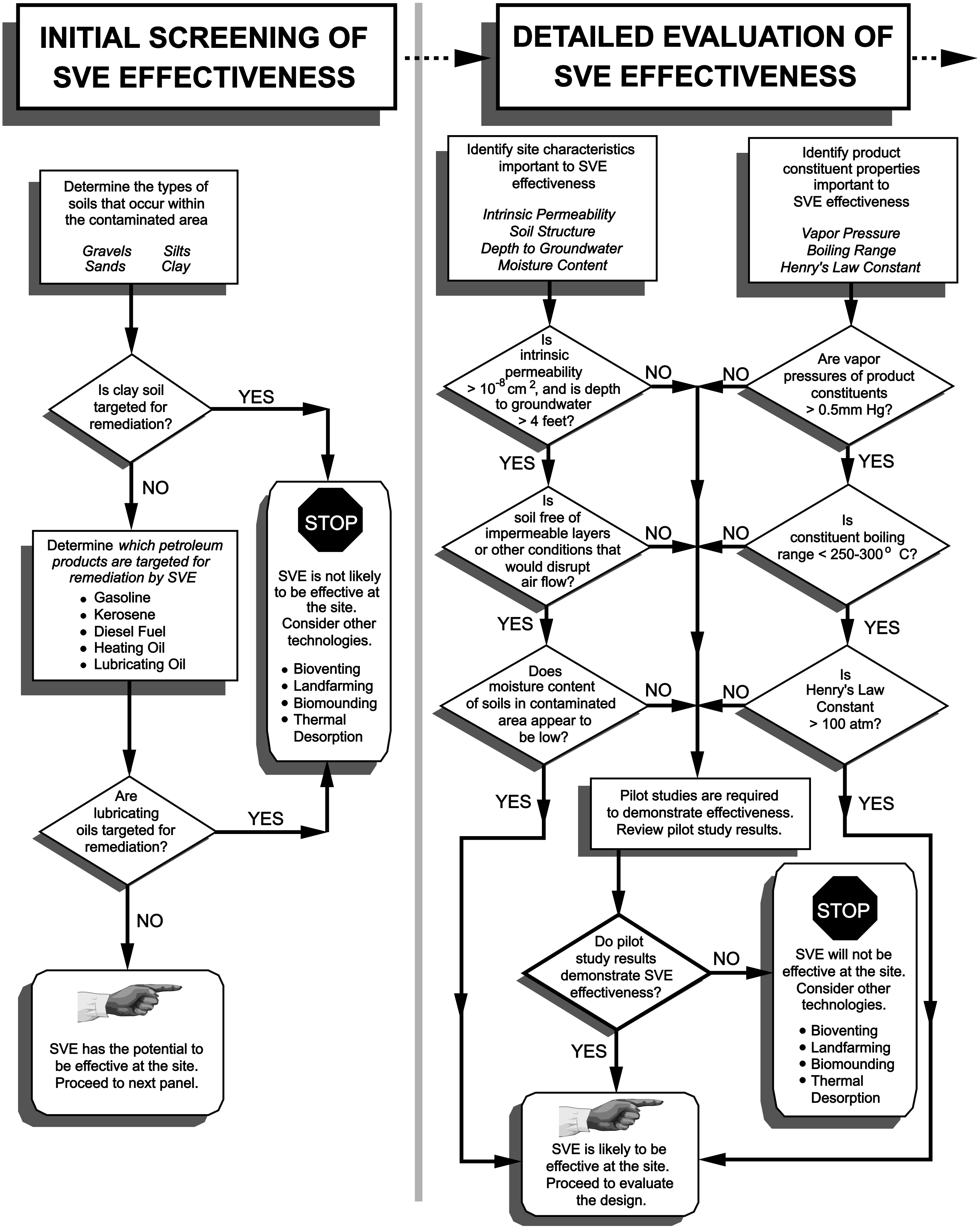
❍ *Volatility* of the petroleum constituents. Volatility determines the rate (and degree) at which petroleum constituents will vaporize from the soil-adsorbed state to the soil vapor state.

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.

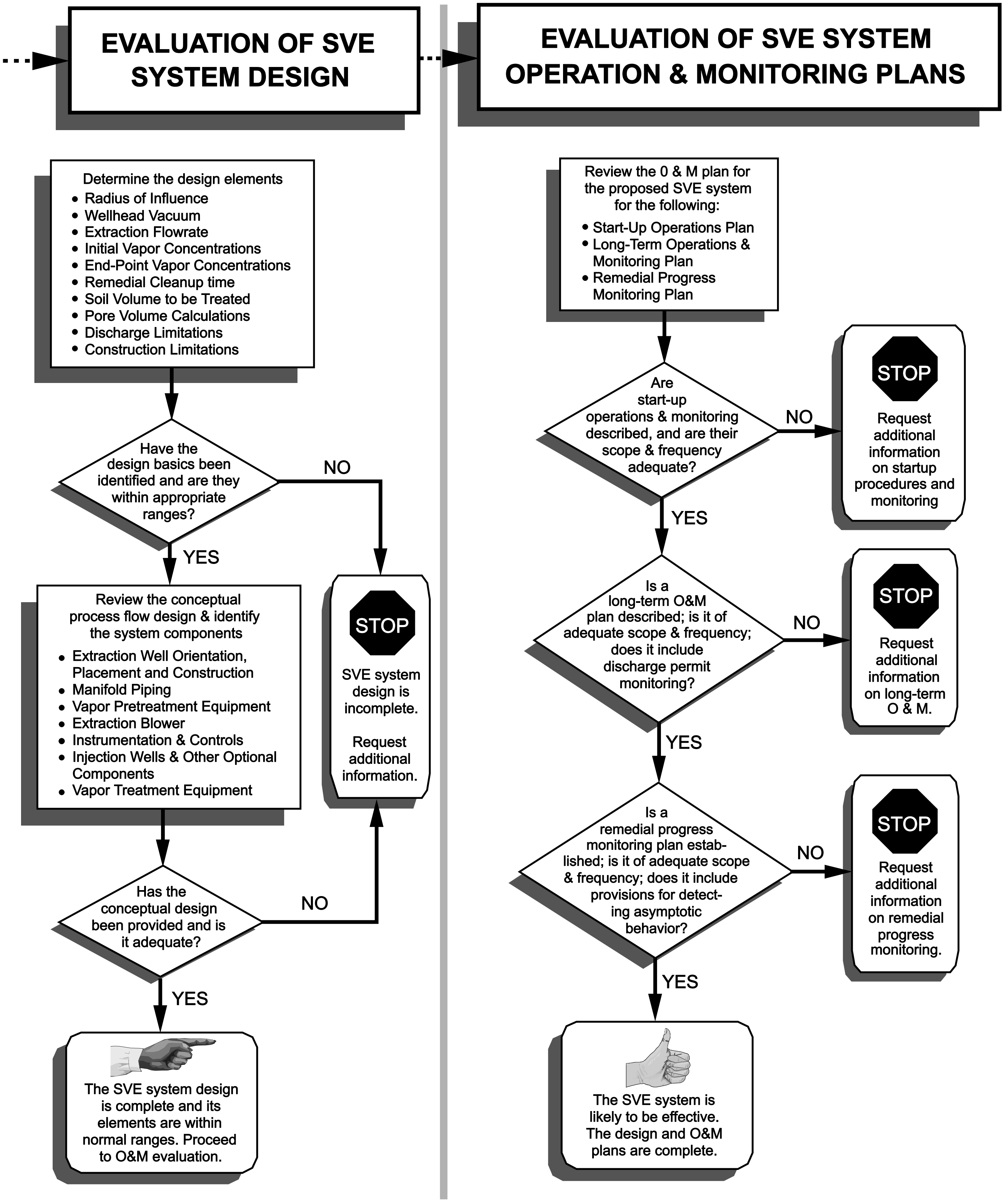
Information provided in the following section will allow a more thorough effectiveness evaluation and will identify areas that could require special design considerations.

## Exhibit II-3
## SVE Evaluation Process Flow Chart



## Exhibit II-3

## SVE Evaluation Process Flow Chart



### EVALUATION OF SVE SYSTEM DESIGN

Determine the design elements
- Radius of Influence
- Wellhead Vacuum
- Extraction Flowrate
- Initial Vapor Concentrations
- End-Point Vapor Concentrations
- Remedial Cleanup time
- Soil Volume to be Treated
- Pore Volume Calculations
- Discharge Limitations
- Construction Limitations

Have the design basics been identified and are they within appropriate ranges?

Review the conceptual process flow design & identify the system components
- Extraction Well Orientation, Placement and Construction
- Manifold Piping
- Vapor Pretreatment Equipment
- Extraction Blower
- Instrumentation & Controls
- Injection Wells & Other Optional Components
- Vapor Treatment Equipment

Has the conceptual design been provided and is it adequate?

SVE system design is incomplete.

Request additional information.

The SVE system design is complete and its elements are within normal ranges. Proceed to O&M evaluation.

### EVALUATION OF SVE SYSTEM OPERATION & MONITORING PLANS

Review the 0 & M plan for the proposed SVE system for the following:
- Start-Up Operations Plan
- Long-Term Operations & Monitoring Plan
- Remedial Progress Monitoring Plan

Are start-up operations & monitoring described, and are their scope & frequency adequate?

Request additional information on startup procedures and monitoring

Is a long-term O&M plan described; is it of adequate scope & frequency; does it include discharge permit monitoring?

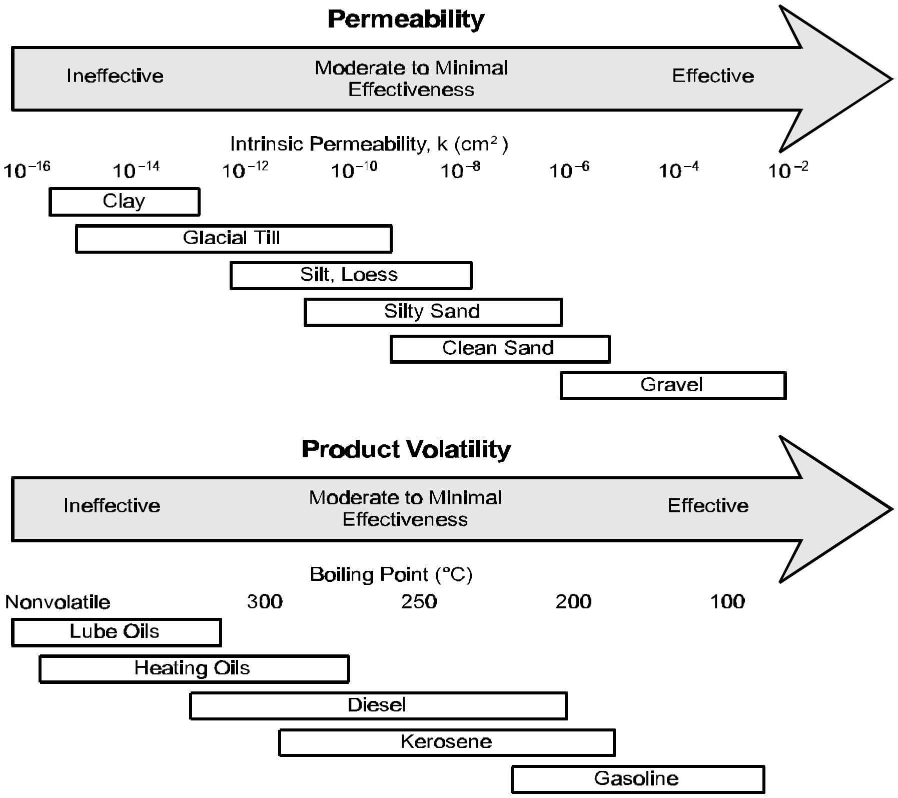
Request additional information on long-term O & M.

Is a remedial progress monitoring plan established; is it of adequate scope & frequency; does it include provisions for detecting asymptotic behavior?

Request additional information on remedial progress monitoring.

The SVE system is likely to be effective. The design and O&M plans are complete.

**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)
$\mu$ = water viscosity (g/cm $\cdot$ sec)
$\rho$ = 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 $\cdot$ 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:

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

where:
$E$ = pore volume exchange time (hr)
$\varepsilon$ = soil porosity ($\text{m}^3$ vapor/$\text{m}^3$ soil)
$V$ = volume of soil to be treated ($\text{m}^3$ soil)
$Q$ = total vapor extraction flowrate ($\text{m}^3$ 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.

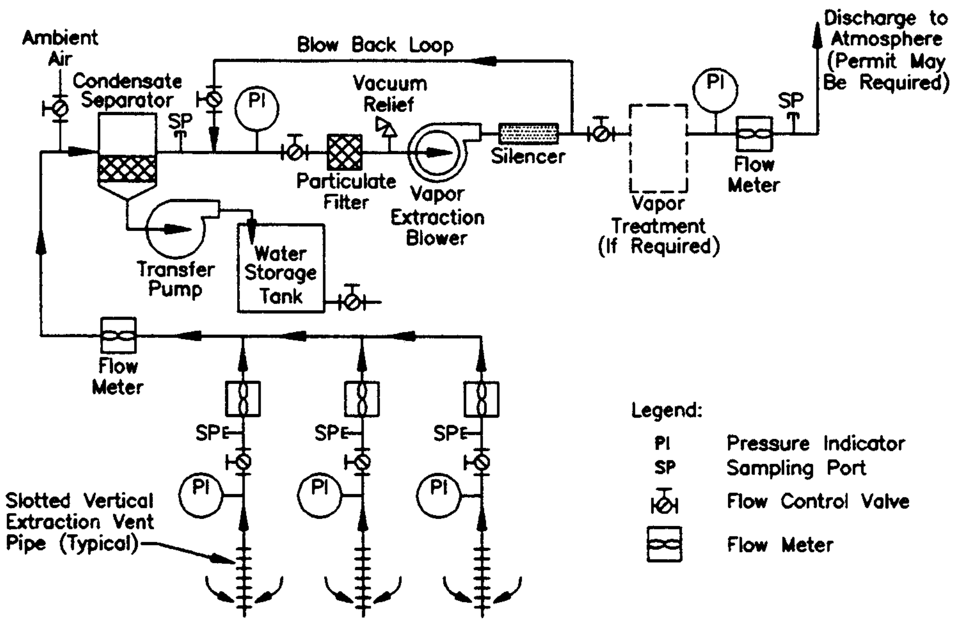
## Components Of An SVE System

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.

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

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

### Exhibit II-12
### Well Orientation And Site Conditions

| Well Orientation | Site Conditions |
|---|---|
| Vertical extraction well | ❍ Shallow to deep contamination (5 to 100+ feet).<br>❍ 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.<br>❍ 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:
$\varepsilon$ = 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.

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

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.

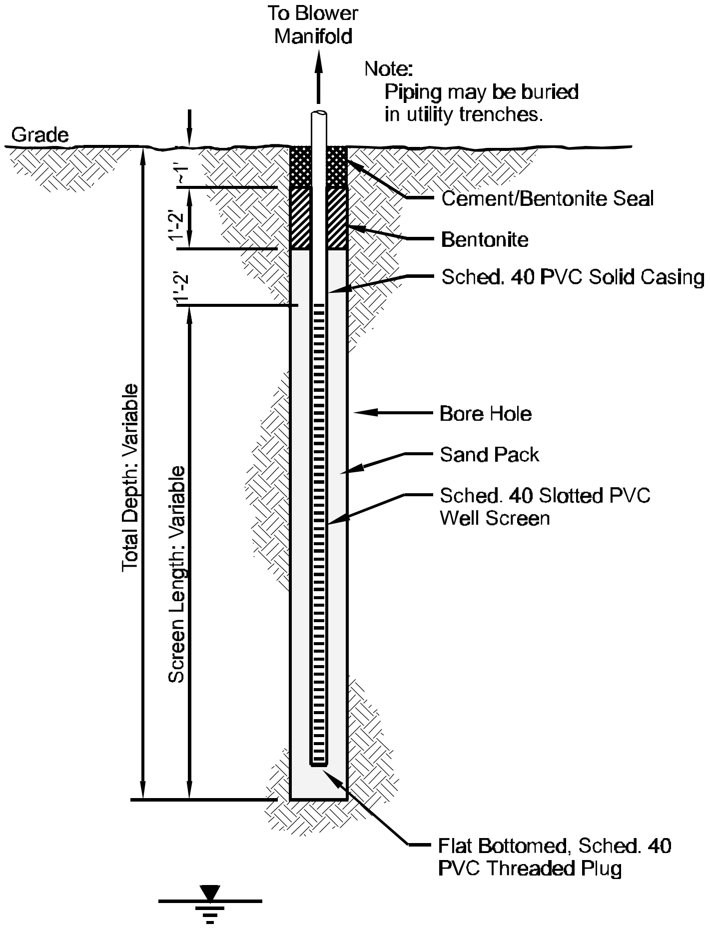
Exhibit II-13 depicts a typical vertical extraction well. Vertical extraction wells are constructed by placing the casing and screen in the center of a borehole. Filter pack material is placed in the annular space between the casing/screen and the walls of the borehole. The filter pack material extends 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**

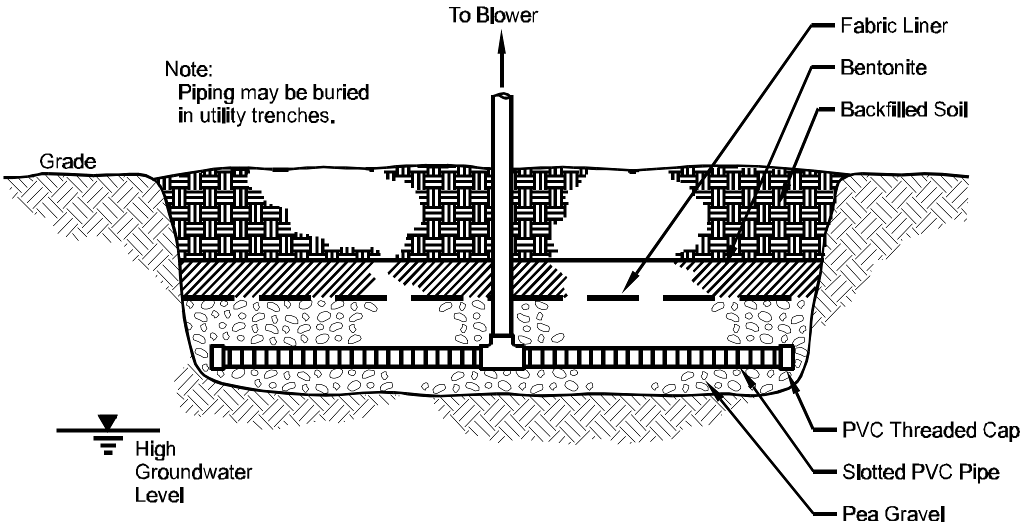


*Horizontal Well Construction*. Look for horizontal extraction wells or trench systems in shallow groundwater conditions. Exhibit II-14 shows a typical shallow horizontal well construction detail. Horizontal extraction wells are constructed by placing slotted (PVC) piping near the bottom of an excavated 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*

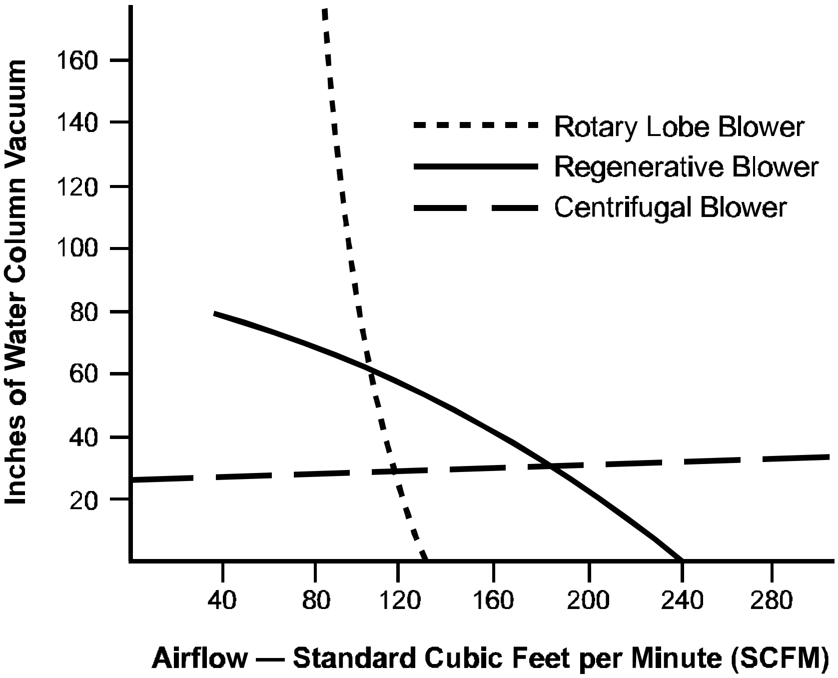
Extracted vapor can contain condensate, entrained groundwater, and particulates that can damage blower parts and inhibit the effectiveness of downstream treatment systems. In order to minimize the potential for damage to blowers, vapors are usually passed through a moisture separator and a particulate 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<br>❍ Manifold to blower<br>❍ Blower discharge | ❍ Pitot tube<br>❍ In-line rotameter<br>❍ Orifice plate<br>❍ Venturi or flow tube |
| Vacuum gauge | ❍ At each well head or manifold branch<br>❍ Before and after filters upstream of blower<br>❍ Before and after vapor treatment | ❍ Manometer<br>❍ Magnehelic gauge<br>❍ Vacuum gauge |
| Vapor temperature sensor | ❍ Manifold to blower<br>❍ Blower discharge (prior to vapor treatment) | ❍ Bi-metal dial-type thermometer |
| Sampling port | ❍ At each well head or manifold branch<br>❍ Manifold to blower<br>❍ Blower discharge | ❍ Hose barb<br>❍ Septa fitting |
| Vapor sample collection equipment (used through a sampling port) | ❍ At each well head or manifold branch<br>❍ Manifold to blower<br>❍ Blower discharge | ❍ Tedlar bags<br>❍ Sorbent tubes<br>❍ Sorbent canisters<br>❍ Polypropylene tubing for direct GC injection |
| **Control Equipment** | | |
| Flow control valves | ❍ At each well head or manifold branch<br>❍ Dilution or bleed valve at manifold to blower | ❍ Ball valve<br>❍ Gate/globe valve<br>❍ 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 | ❍ Flow<br>❍ Vacuum<br>❍ Vapor concentrations | ❍ Extraction vents<br>❍ Manifold<br>❍ Effluent stack |
| Remedial (ongoing) | Biweekly to monthly | ❍ Flow<br>❍ Vacuum<br>❍ Vapor concentrations | ❍ Extraction vents<br>❍ Manifold<br>❍ 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.

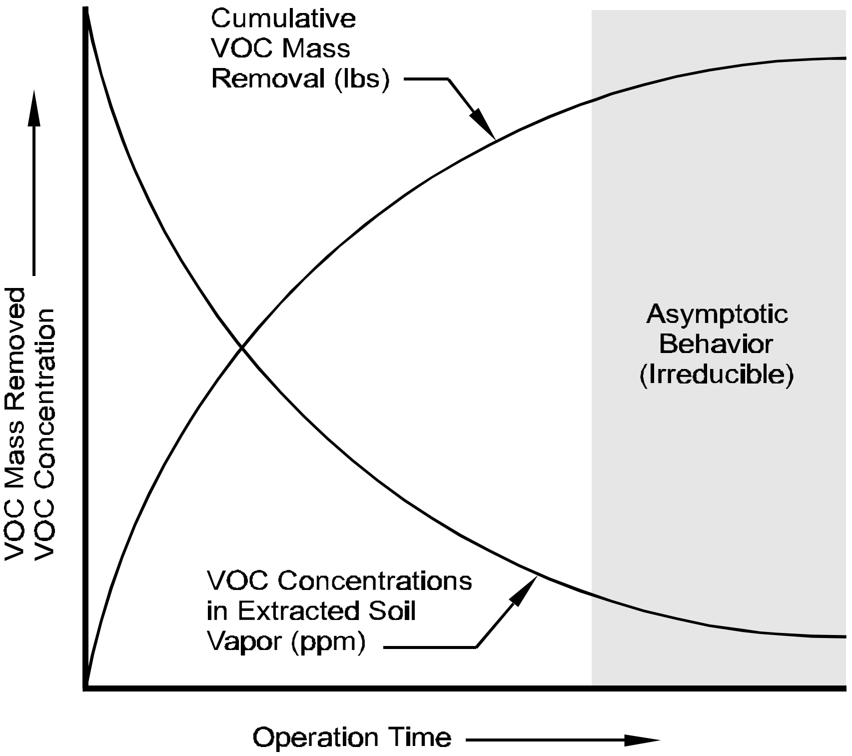
$$M = C \cdot Q \cdot t$$

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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Johnson, P.C., Stanley, C.C., Kemblowski, M.W., Byers, D.L., and J.D. Colthart. "A Practical Approach to the Design, Operation and Monitoring of In Situ Soil-Venting Systems." *Ground Water Monitoring Review*, Vol. 10, No. 2, pp. 159-178, 1990.

# 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? |

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[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

# Contents

# List Of Exhibits

# Chapter III
# Bioventing

## Overview

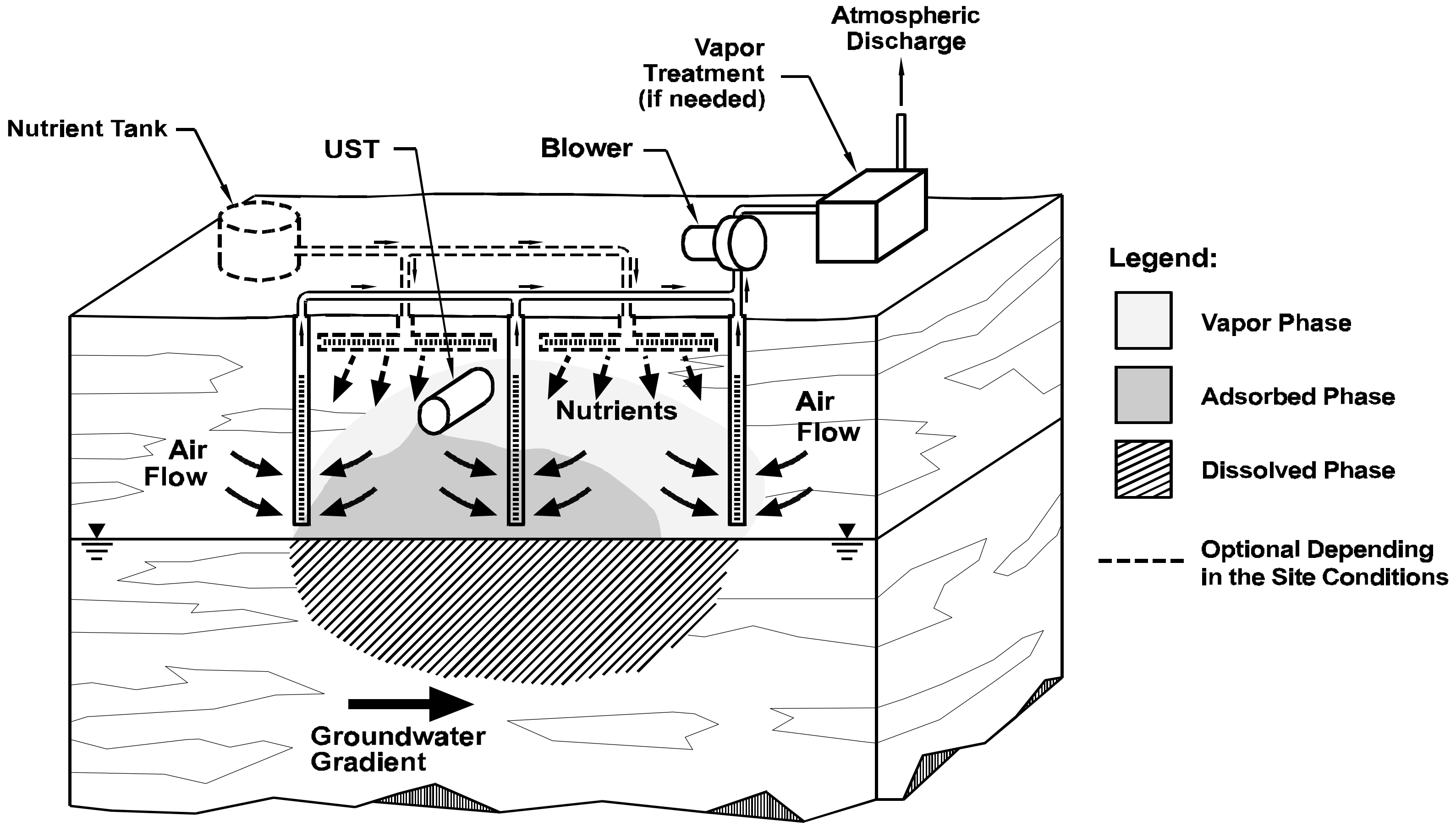
Bioventing is an in-situ remediation technology that uses indigenous microorganisms to biodegrade organic constituents adsorbed to soils in the unsaturated zone. Soils in the capillary fringe and the saturated zone are not affected. In bioventing, the activity of the indigenous bacteria is enhanced by 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

- Uses readily available equipment; easy to install.
- Creates minimal disturbance to site operations. Can be used to address inaccessible areas (e.g., under buildings).
- Requires short treatment times: usually 6 months to 2 years under optimal conditions.
- Is cost competitive: $45-140/ton of contaminated soil.
- Easily combinable with other technologies (e.g., air sparging, groundwater extraction).
- May not require costly offgas treatment.

### Disadvantages

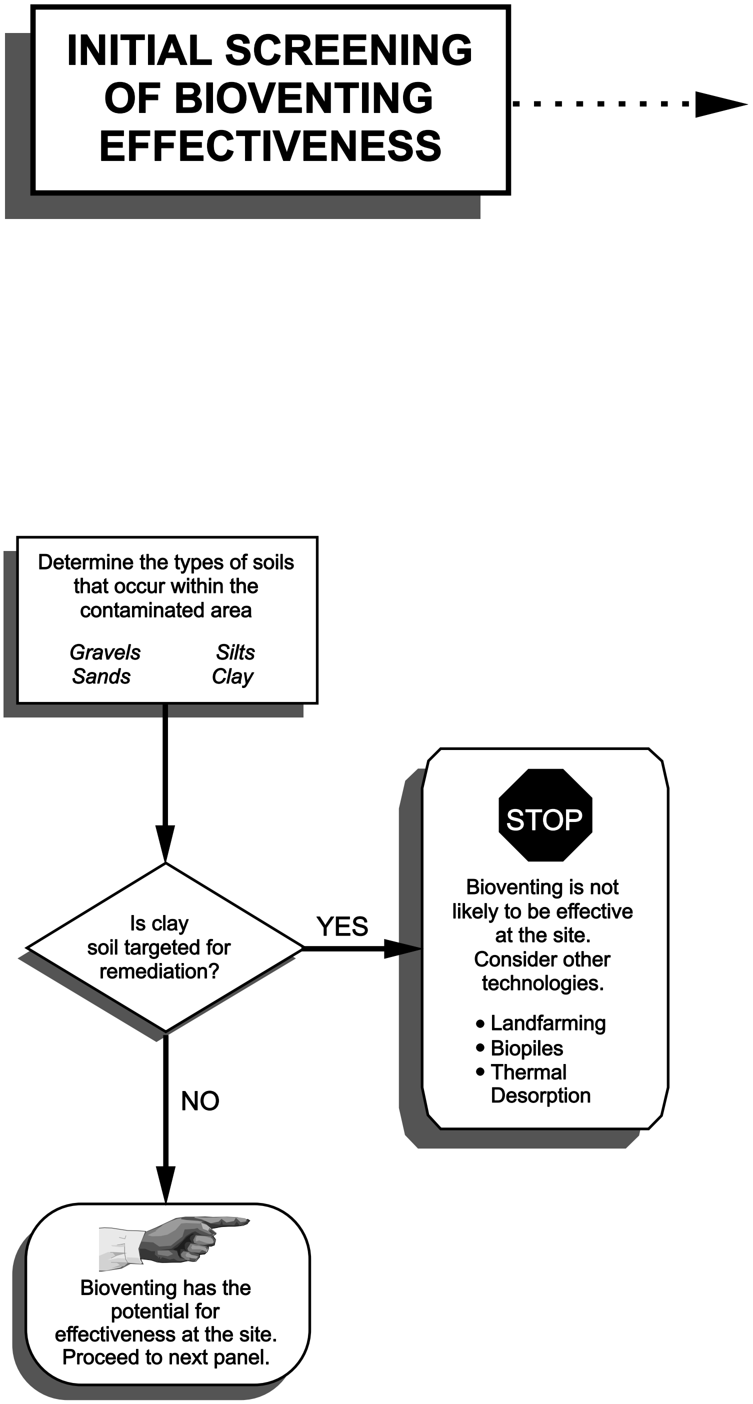
- High constituent concentrations may initially be toxic to microorganisms.
- Not applicable for certain site conditions (e.g., low soil permeabilities, high clay content, insufficient delineation of subsurface conditions).
- Cannot always achieve very low cleanup standards.
- Permits generally required for nutrient injection wells (if used). (A few states also require permits for air injection.)

- **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

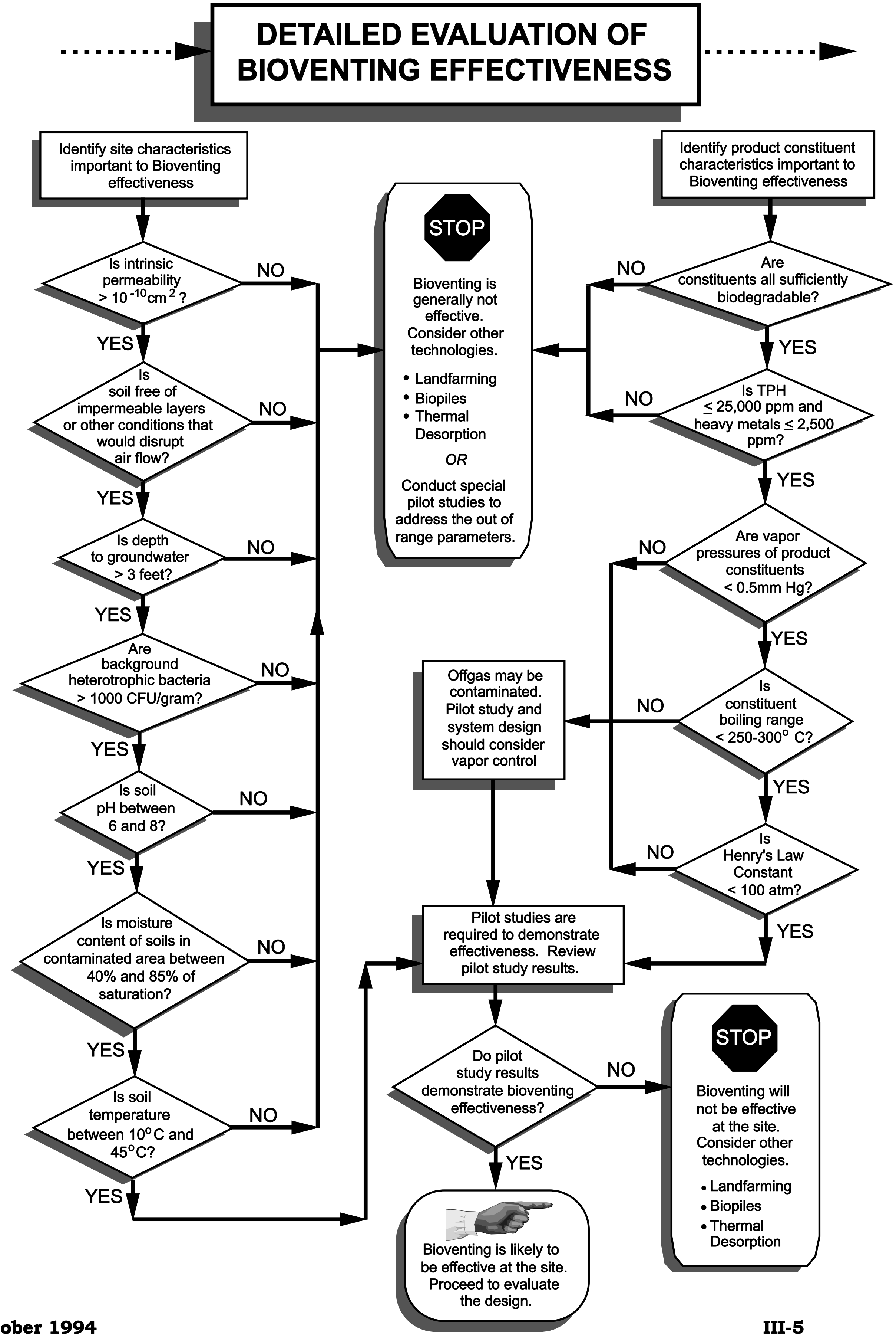
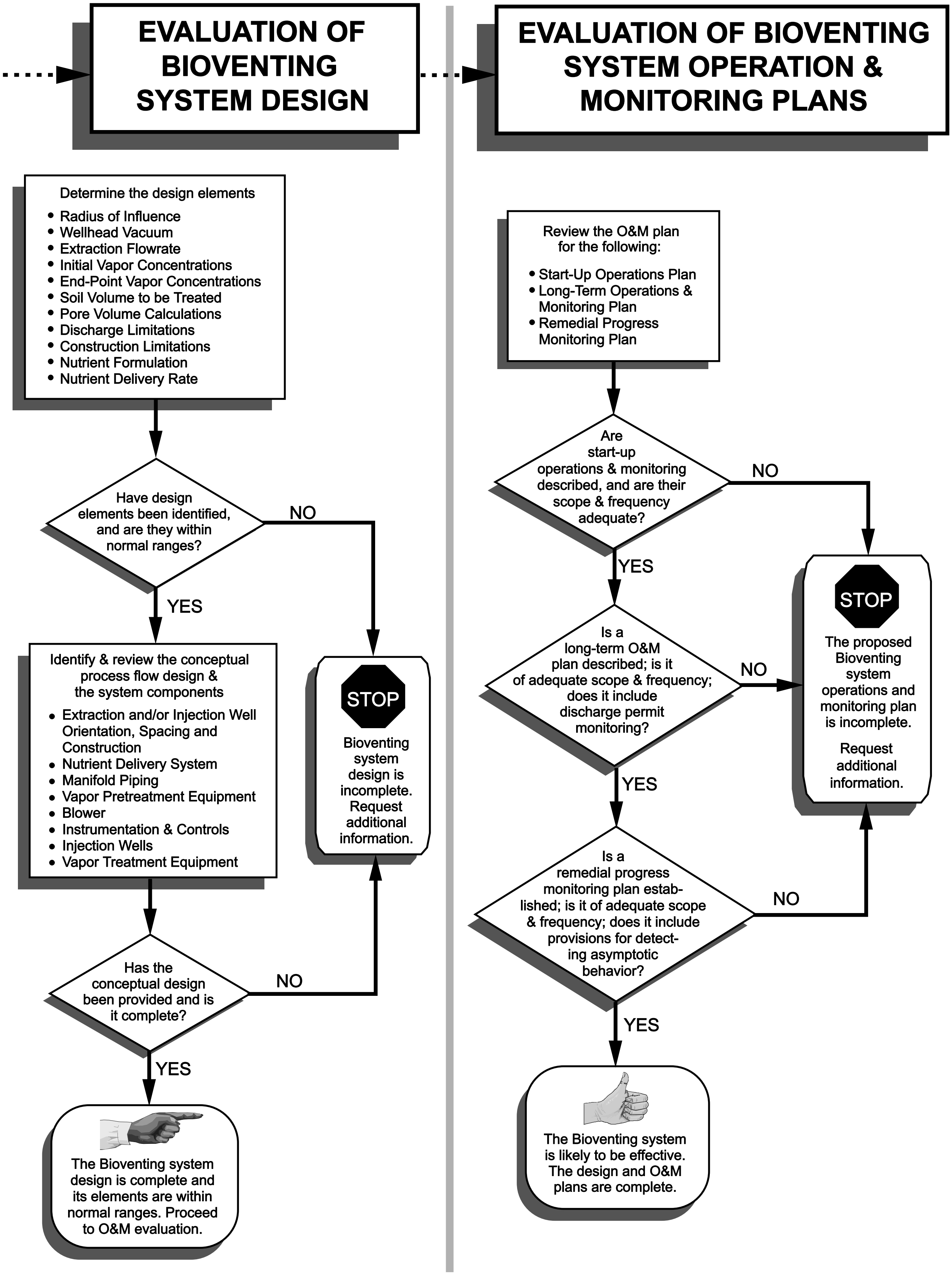


**Exhibit III-3**
**Bioventing Evaluation Process Flow Chart**



- **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.

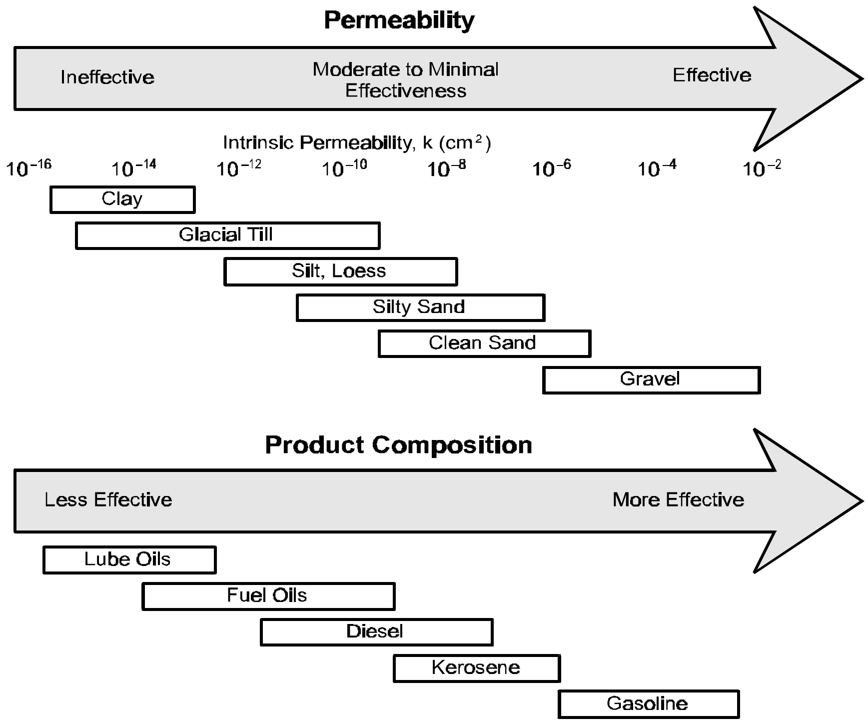
In general, the type of soil will determine its *permeability*. Fine-grained soils (e.g., clays and silts) have lower permeabilities than coarse-grained soils (e.g., sands and gravels). The *biodegradability* of a petroleum product constituent is a measure of its ability to be metabolized by hydrocarbon-degrading 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)
$\mu$ = water viscosity (g/cm $\cdot$ sec)
$\rho$ = 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:

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

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:l 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 | ❍ 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 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 ≤ 25,000 ppm<br>and<br>Heavy metals ≤ 2,500 ppm | Effective. |
| Petroleum constituents > 25,000 ppm<br>or<br>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<br>and<br>TPH reduction < 95% | Effective. |
| Constituent concentration ≤ 0.1 ppm<br>or<br>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)
$\varepsilon$ = 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

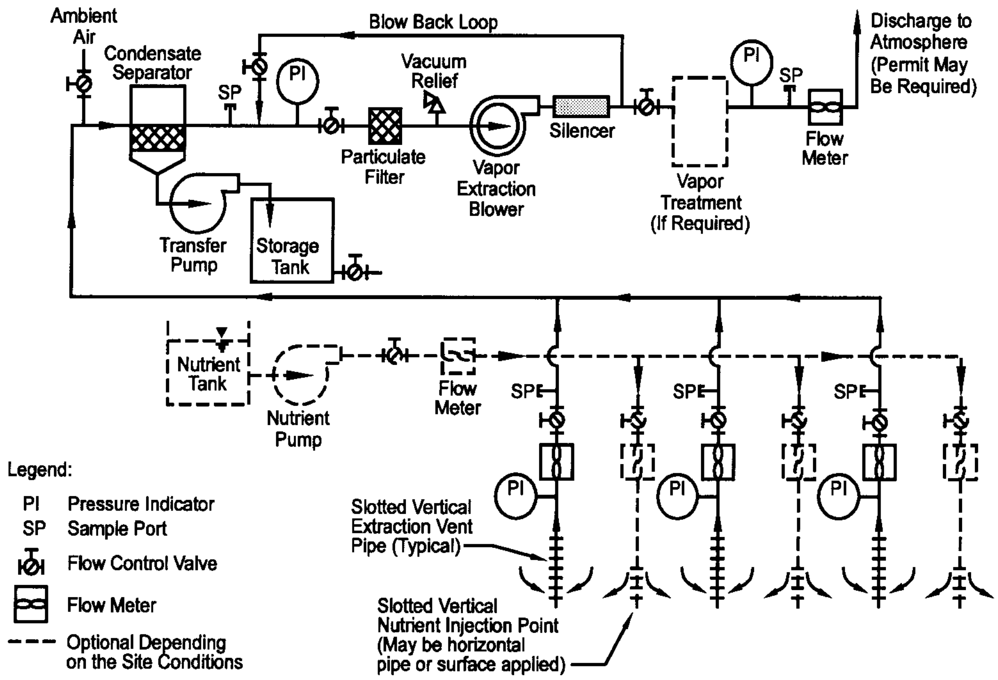
Nutrient additions are sometimes included in bioventing designs. If nutrients are added, the design should specify the nutrient addition well orientation, placement, and construction details. Note that state regulations may either require permits for nutrient injection wells or prohibit them entirely. 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).<br>❍ 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.<br>❍ 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.

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

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.

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

where: $\varepsilon$ = 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.

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

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.

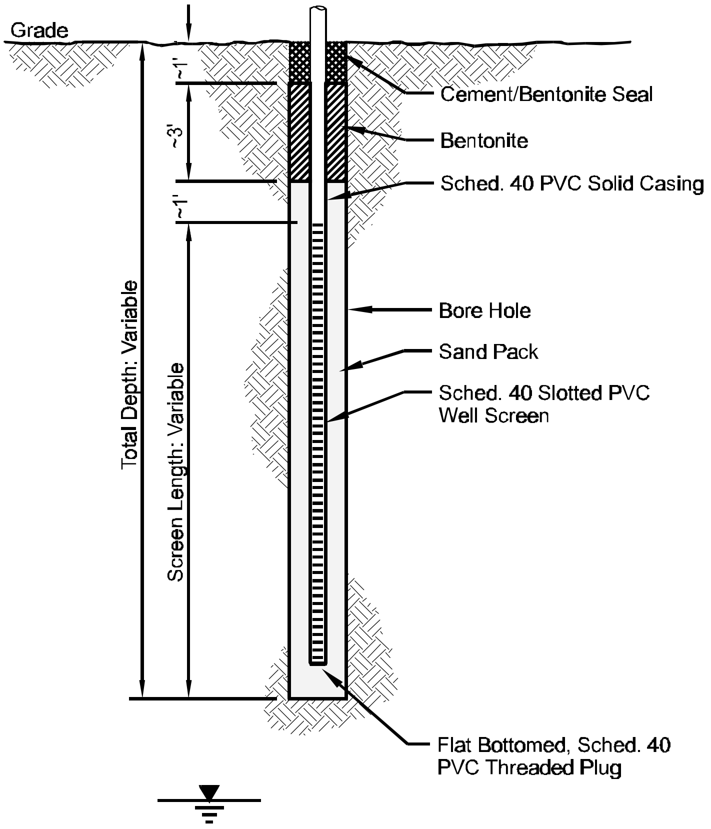
○ In stratified or structured soils, well spacings may be irregular. Wells screened in zones of lower intrinsic permeability must be spaced closer together than wells screened in zones of higher intrinsic permeability.

**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.

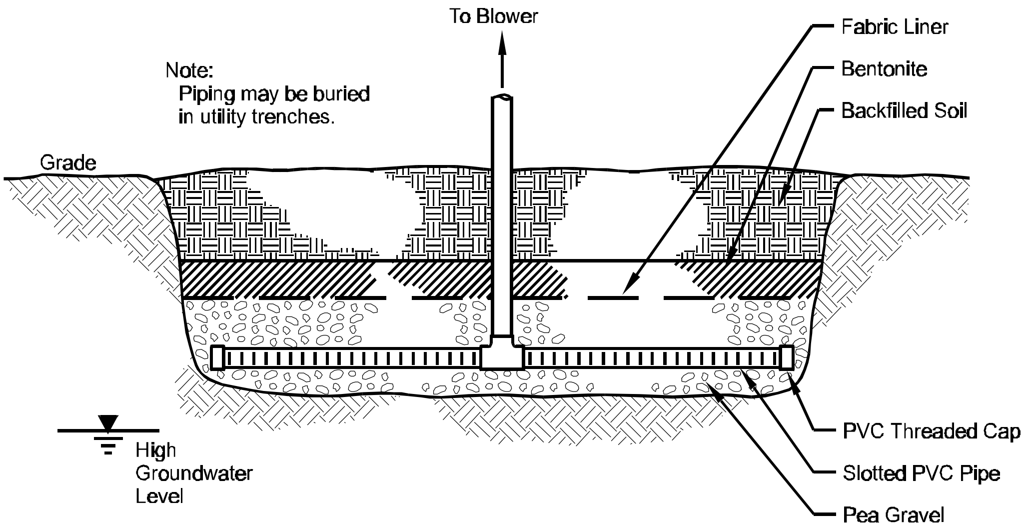
The location and length of the well screen in vertical extraction or injection wells can vary and should be based on the depth to groundwater, the stratification of the soil, and the location and distribution of contaminants. In general, the length of the screen has little effect on the ROI of an extraction 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.

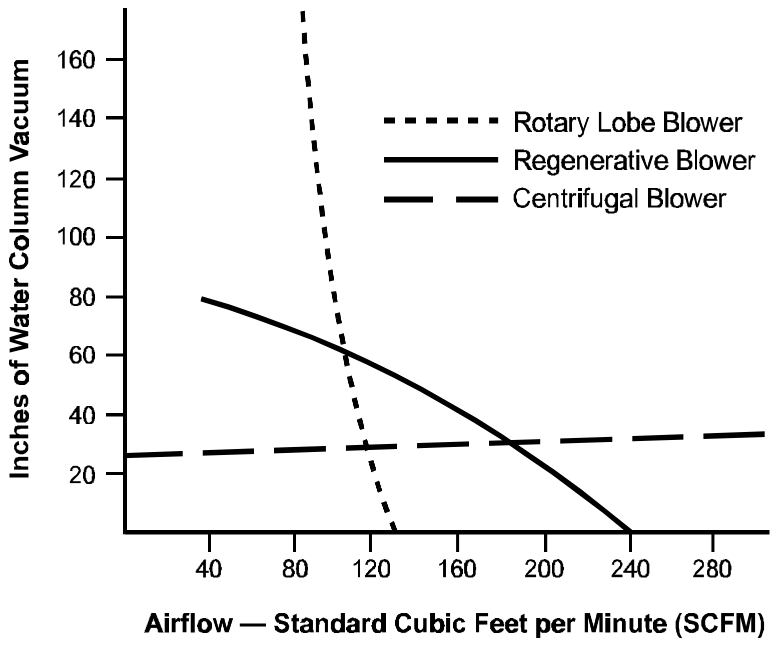
### *Instrumentation and Controls*

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<br>❍ Manifold to blower<br>❍ Blower discharge<br>❍ Nutrient manifold | ❍ Pitot tube<br>❍ In-line rotameter<br>❍ Orifice plate<br>❍ Turbine wheel<br>❍ Venturi or flow tube |
| Vacuum/Pressure gauge | ❍ At each well head or manifold branch<br>❍ Before and after filters before blower<br>❍ Before and after vapor treatment | ❍ Manometer<br>❍ Magnehelic gauge<br>❍ Vacuum gauge |
| Sampling port | ❍ At each well head or manifold branch<br>❍ Manifold to blower<br>❍ Blower discharge | ❍ Hose barb<br>❍ Septa fitting |
| Flow control valves | ❍ At each well head or manifold branch<br>❍ Dilution or bleed valve at manifold to blower | ❍ Ball valve<br>❍ Gate valve<br>❍ Dilution/ambient air bleed valve |
| Vapor temperature sensor | ❍ Manifold to blower<br>❍ 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<br>❍ Manifold to blower<br>❍ Blower discharge | ❍ Tedlar bags<br>❍ Sorbent tubes<br>❍ Sorbent canisters<br>❍ Polypropylene tubing for direct GC injection |
| **Control Equipment** | | |
| Flow control valves | ❍ At each well head or manifold branch<br>❍ Dilution or bleed valve at manifold to blower | ❍ Ball valve<br>❍ Gate/globe valve<br>❍ 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 | ❍ Flow<br>❍ Vacuum readings<br>❍ VOCs<br>❍ Carbon dioxide<br>❍ Oxygen | ❍ Extraction vents<br>❍ Manifold<br>❍ Effluent stack |
| Remedial | Weekly to bi-weekly | ❍ Flow<br>❍ Vacuum<br>❍ VOCs<br>❍ Carbon dioxide<br>❍ Oxygen | ❍ Extraction vents<br>❍ Manifold<br>❍ 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.

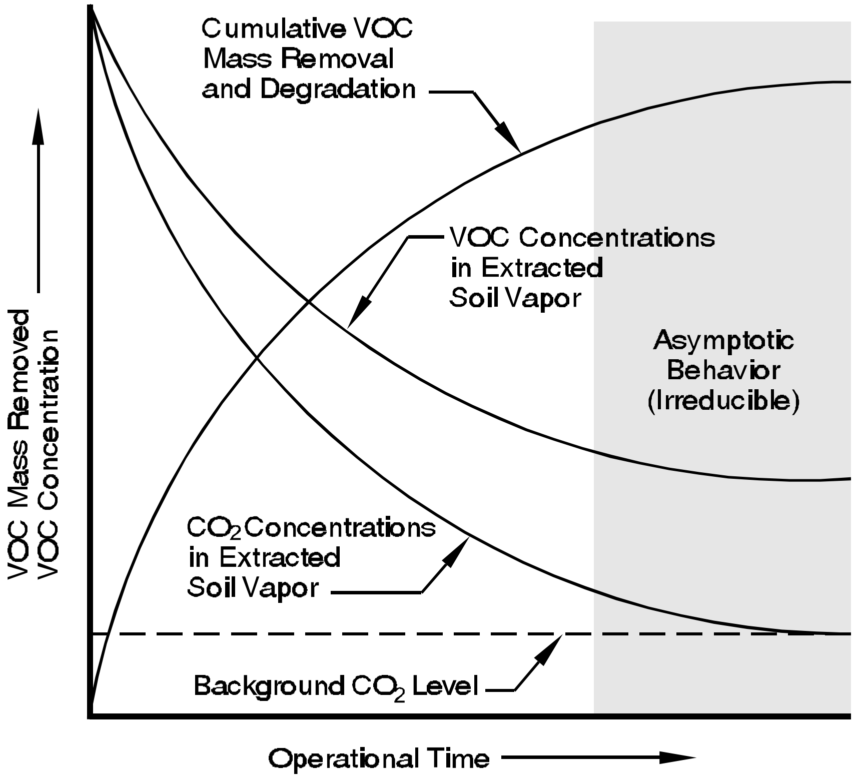
Since concentrations of petroleum constituents may be reduced due to both volatilization and biodegradation, both processes should be monitored in order to track the cumulative effect. The constituent mass extraction component can be tracked and calculated using the VOC concentrations measured in the 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? |

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[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

# Contents

# List Of Exhibits

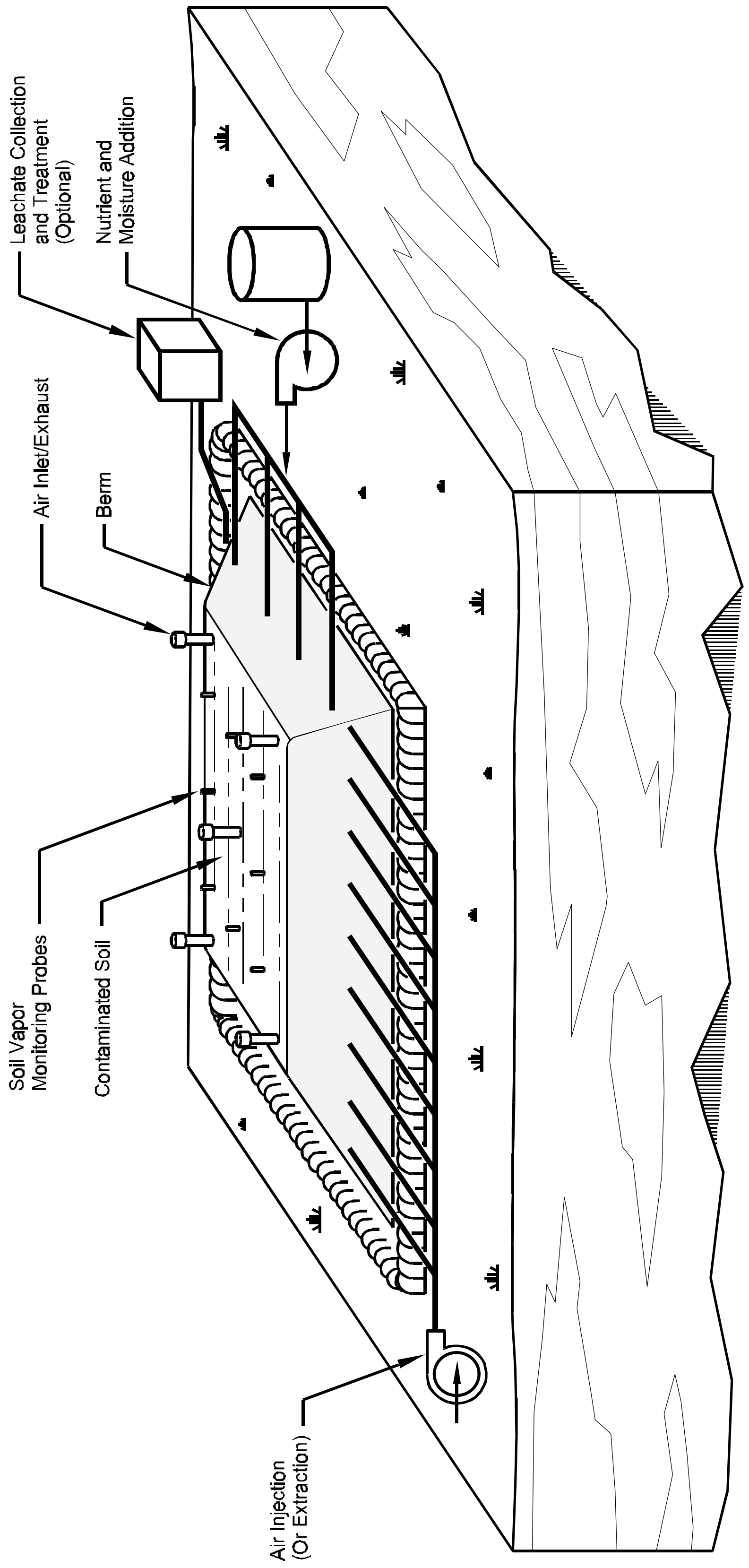
# Chapter IV
# Biopiles

## 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

- Relatively simple to design and implement.
- Short treatment times: usually 6 months to 2 years under optimal conditions.
- Cost competitive: $30-90/ton of contaminated soil.
- Effective on organic constituents with slow biodegradation rates.
- Requires less land area than landfarms.
- Can be designed to be a closed system; vapor emissions can be controlled.
- Can be engineered to be potentially effective for any combination of site conditions and petroleum products.

### Disadvantages

- Concentration reductions > 95% and constituent concentrations < 0.1 ppm are very difficult to achieve.
- May not be effective for high constituent concentrations (> 50,000 ppm total petroleum hydrocarbons).
- Presence of significant heavy metal concentrations (> 2,500 ppm) may inhibit microbial growth.
- Volatile constituents tend to evaporate rather than biodegrade during treatment.
- Requires a large land area for treatment, although less than landfarming.
- Vapor generation during aeration may require treatment prior to discharge.
- 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**

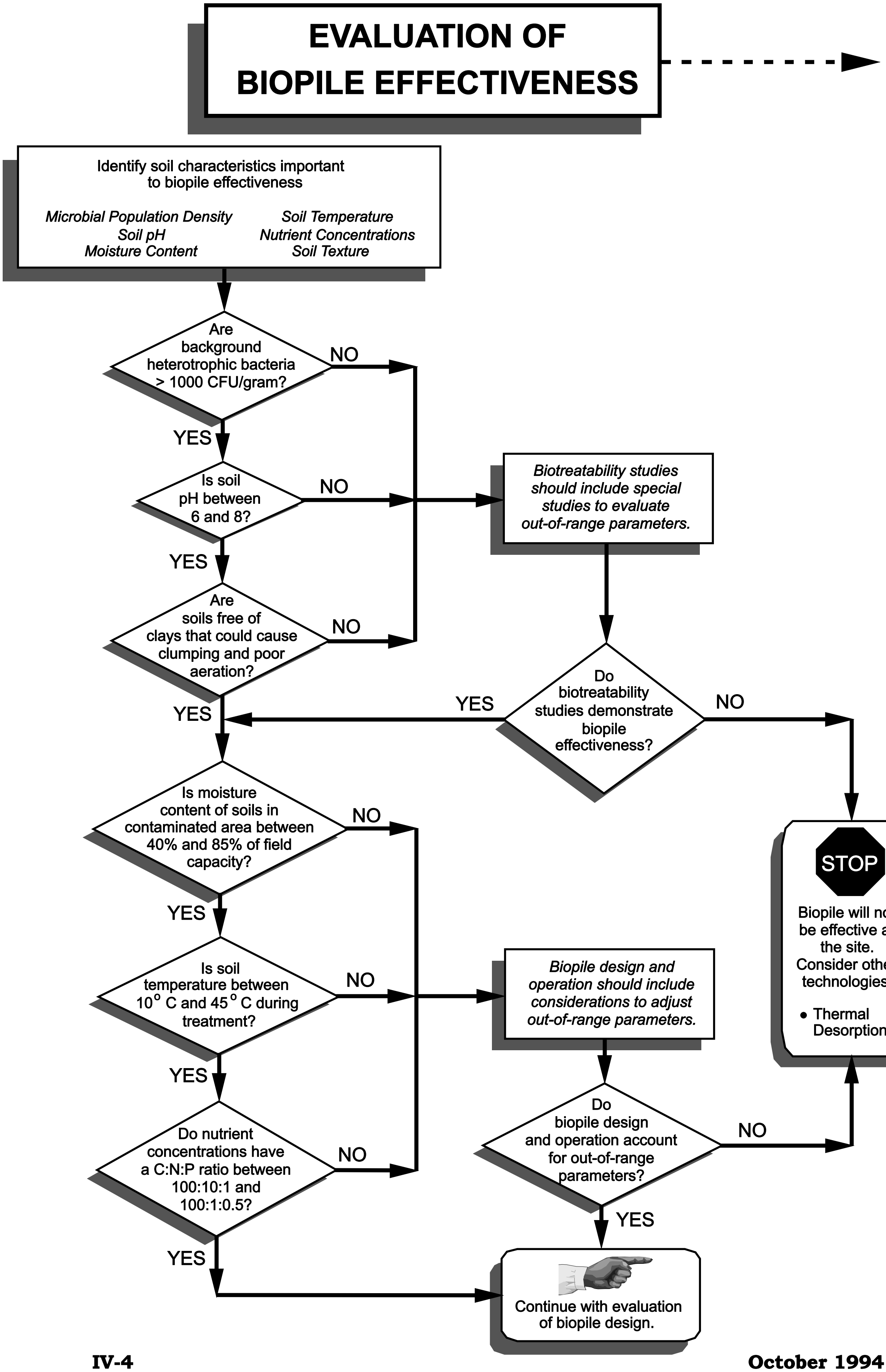
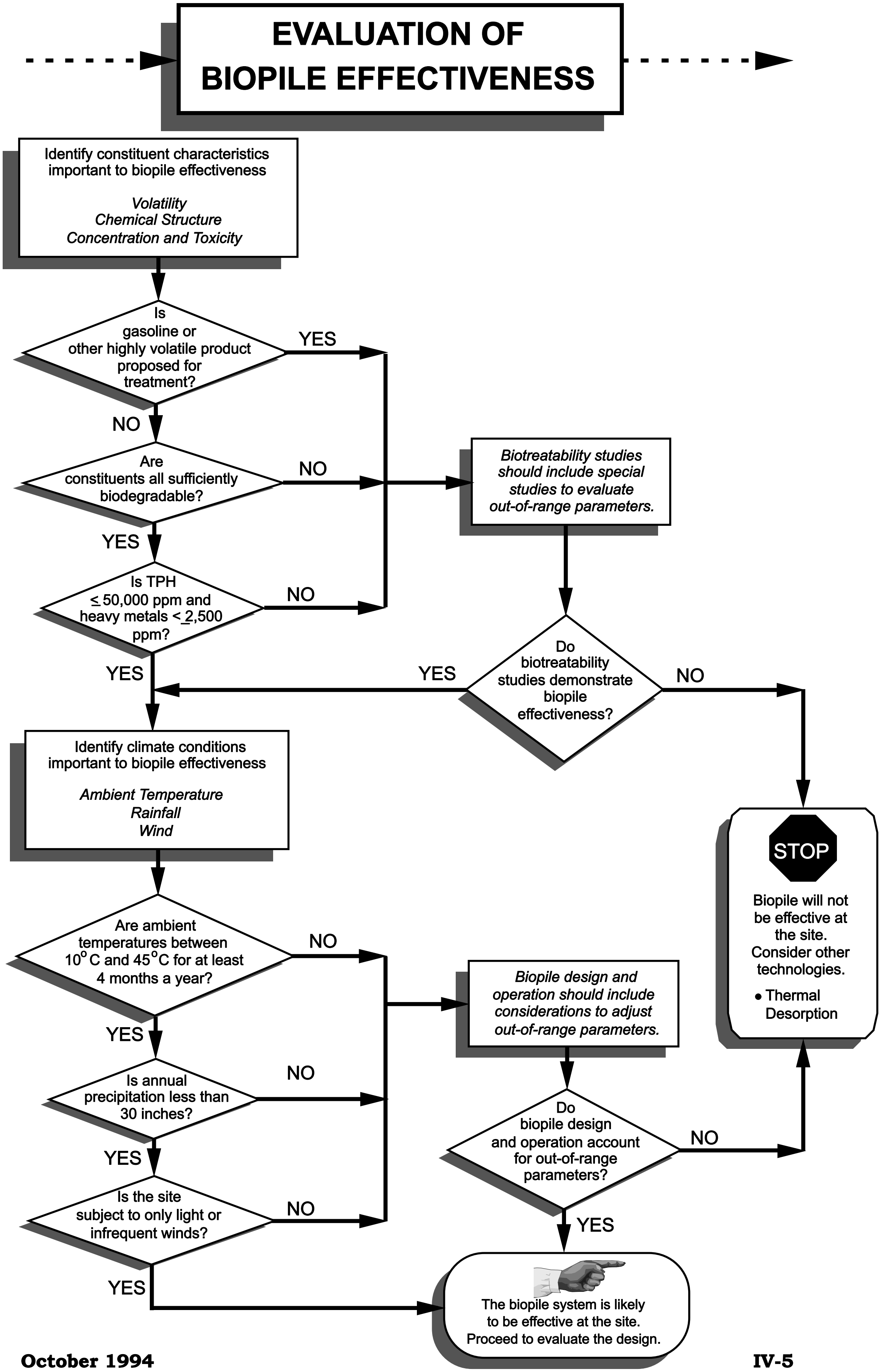
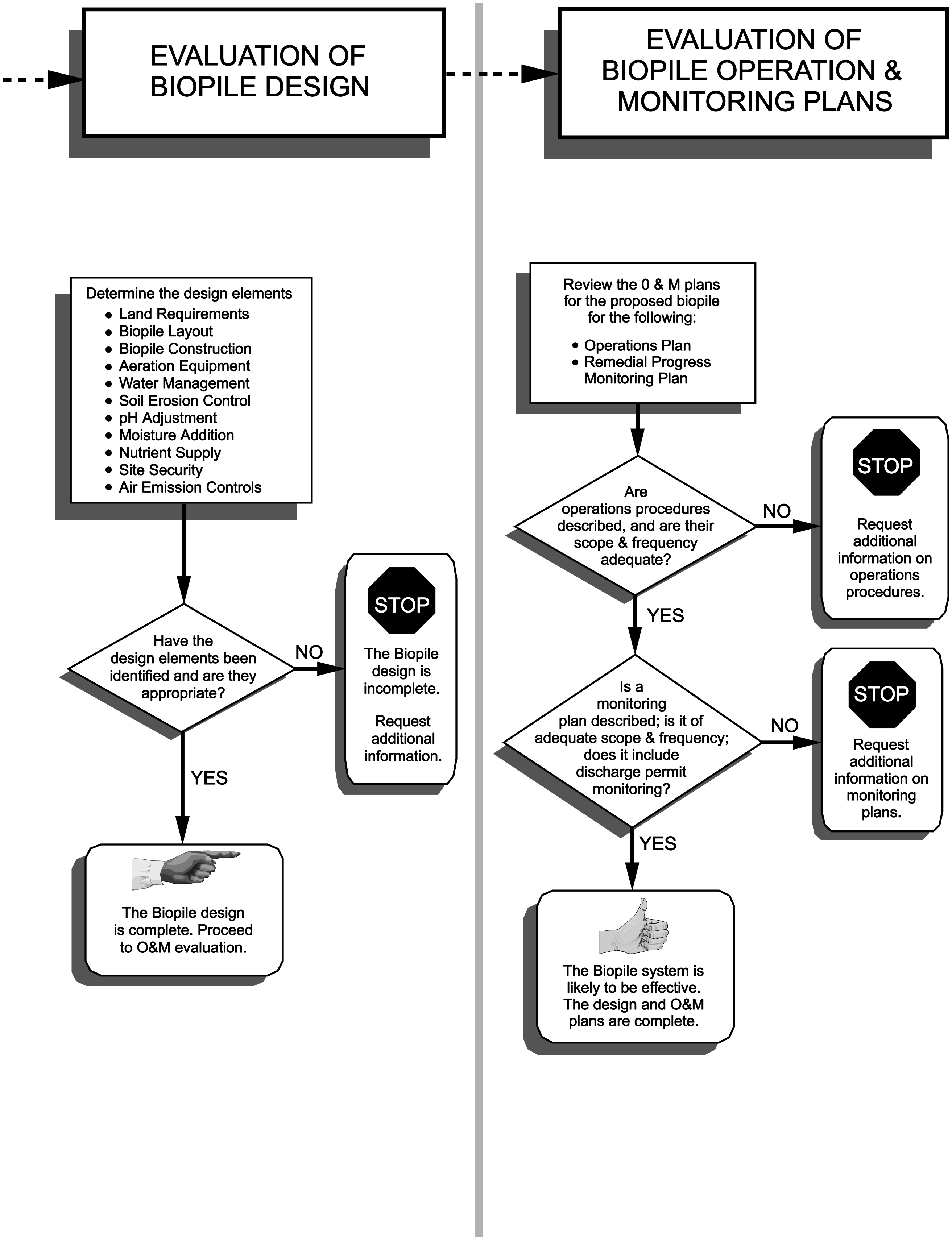


**Exhibit IV-3**
**Biopile Evaluation Process Flow Chart**



## 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. 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.

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 ≤ pH ≤ 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% ≤ field capacity ≤ 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:

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

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:

$$\text{contaminant mass} =$$

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

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 ≤ 50,000 ppm<br>and<br>Heavy metals ≤ 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<br>or<br>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<br>and<br>TPH reduction < 95% | Effective. |
| Constituent concentration ≤ 0.1 ppm<br>or<br>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.

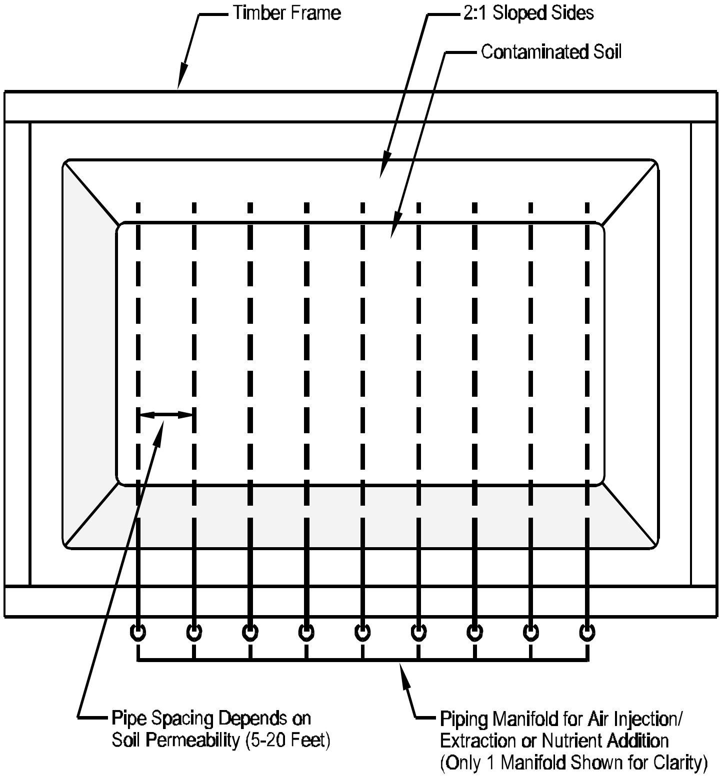
- *Land Requirements* can be determined by dividing the amount of soil to be treated by the height of the proposed biopile(s). The typical height of biopiles varies between 3 and 10 feet. Additional land area around the biopile(s) will be required for sloping the sides of the pile, for containment berms, 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.

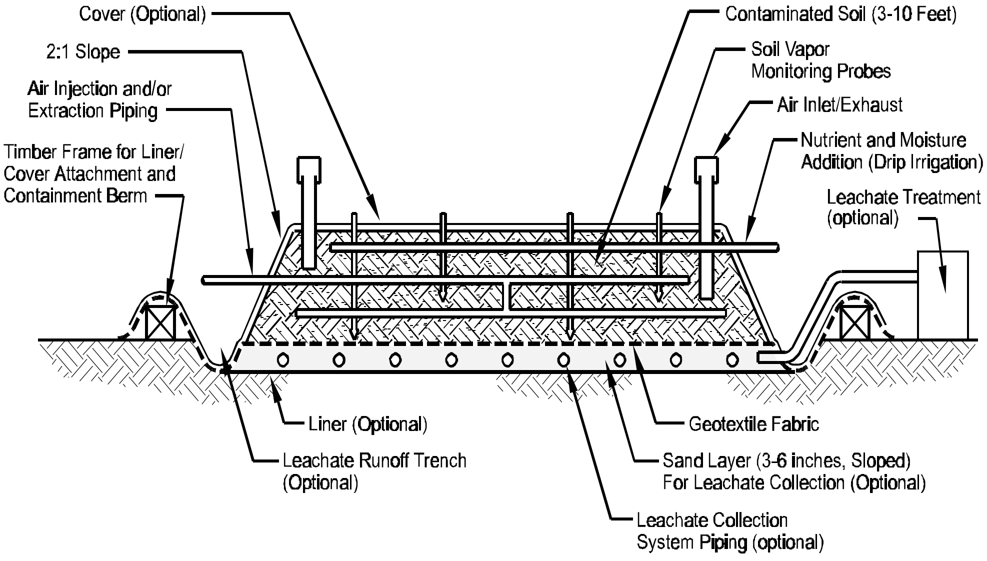
- *Aeration Equipment* usually includes blowers or fans which will be attached to the aeration piping manifold unless aeration is to be accomplished by manually turning the soil.

## 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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Norris, R.D., Hinchee, R.E., Brown, R.A., McCarty, P.L., Semprini, L., Wilson, J.T., Kampbell, D.H., Reinhard, M., Bower, E.J., Borden, R.C., Vogel, T.M., Thomas, J.M., and C.H. Ward. *Handbook of Bioremediation*. Boca Raton, FL:CRC Press, 1994.

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Pope, Daniel F., and J.E. Matthews. *Environmental Regulations and Technology: Bioremediation Using the Land Treatment Concept*. Ada, OK: U.S. Environmental Protection Agency, Environmental Research Laboratory. EPA/600/R-93/164, 1993.

# 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

# Contents

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# Chapter V
# Landfarming

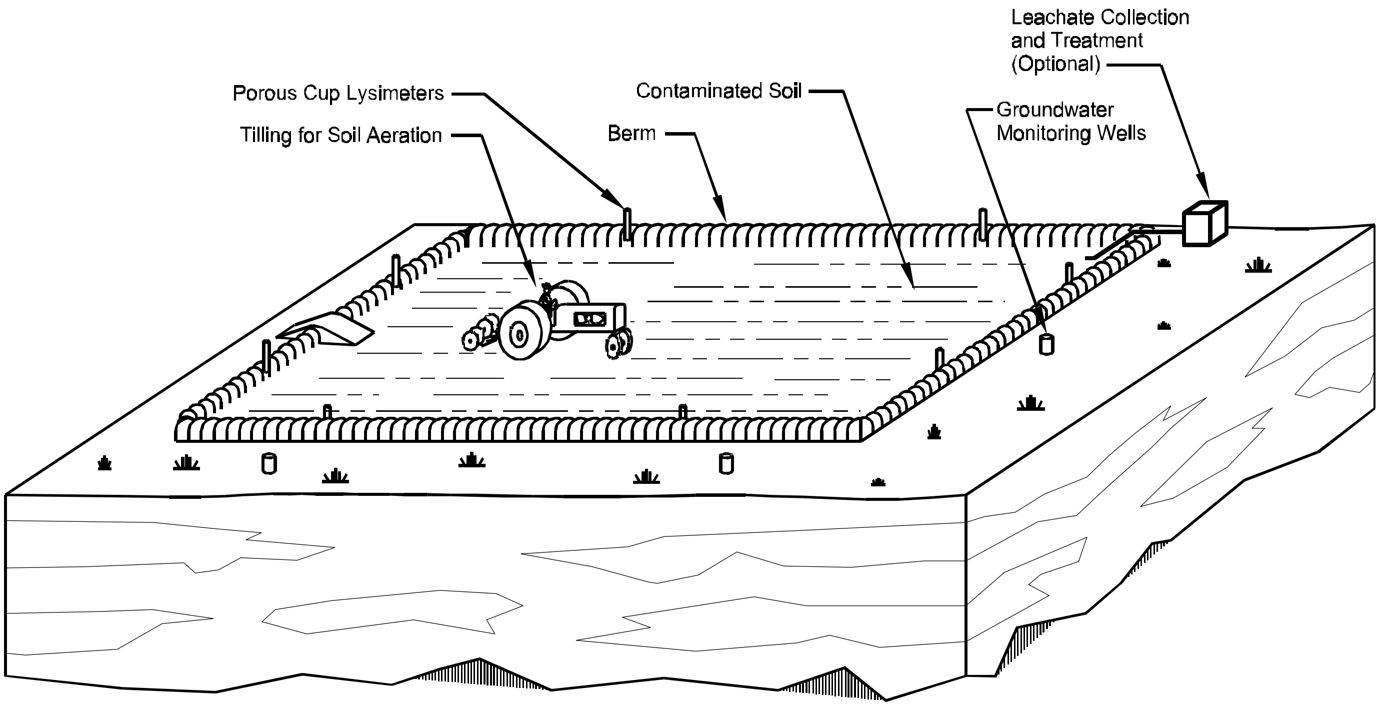
## Overview

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

- Relatively simple to design and implement.
- Short treatment times: usually 6 months to 2 years under optimal conditions.
- Cost competitive: $30-60/ton of contaminated soil.
- Effective on organic constituents with slow biodegradation rates.

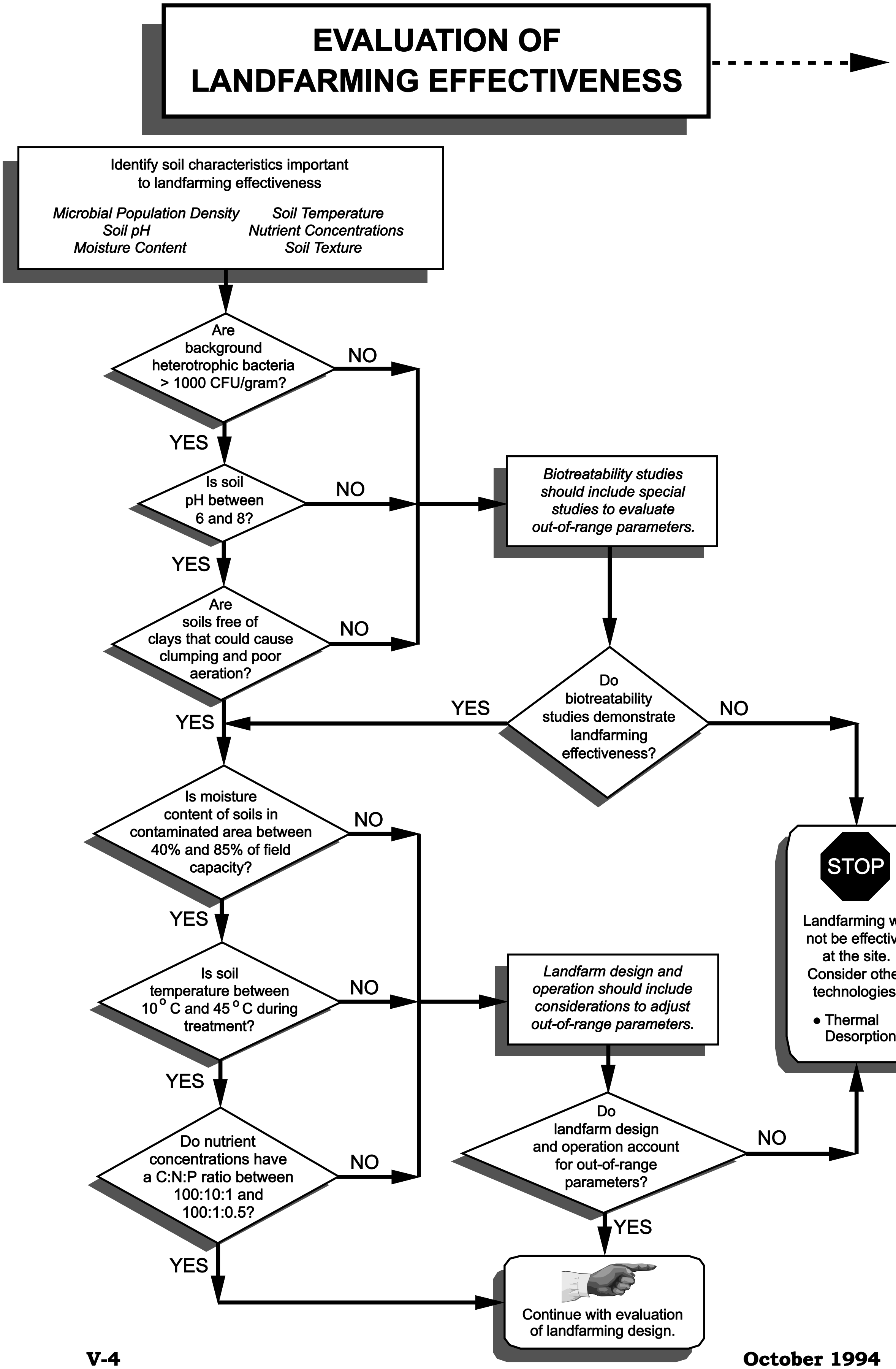
### Disadvantages

- Concentration reductions > 95% and constituent concentrations < 0.1 ppm are very difficult to achieve.
- May not be effective for high constituent concentrations (> 50,000 ppm total petroleum hydrocarbons).
- Presence of significant heavy metal concentrations (> 2,500 ppm) may inhibit microbial growth.
- 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.

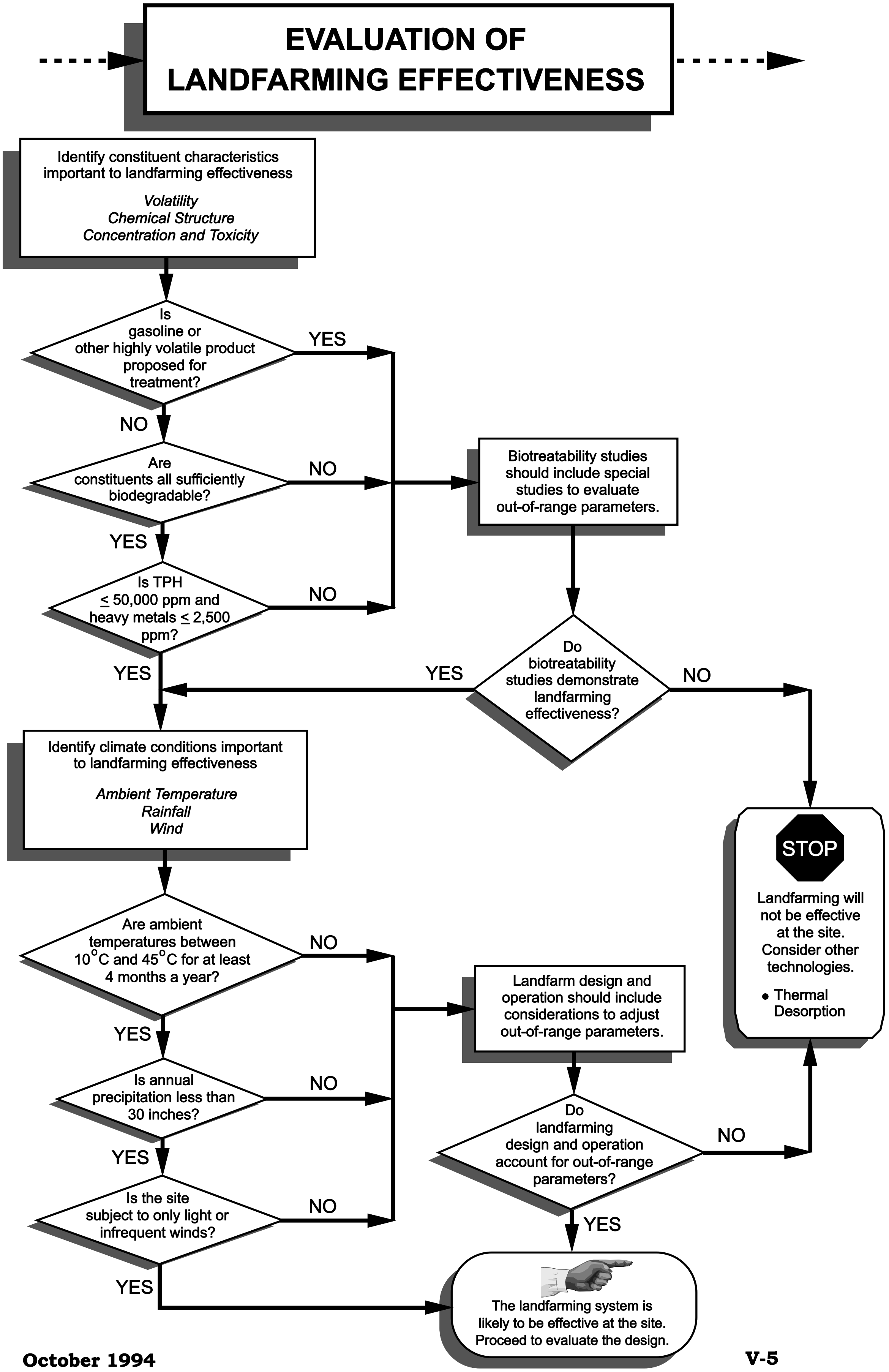
This chapter will assist you in evaluating a corrective action plan (CAP) that proposes landfarming as a remedy for petroleum contaminated soil. The evaluation guidance is presented in the three steps described below. The evaluation process, which is summarized in a flow diagram shown in Exhibit V-3, 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.

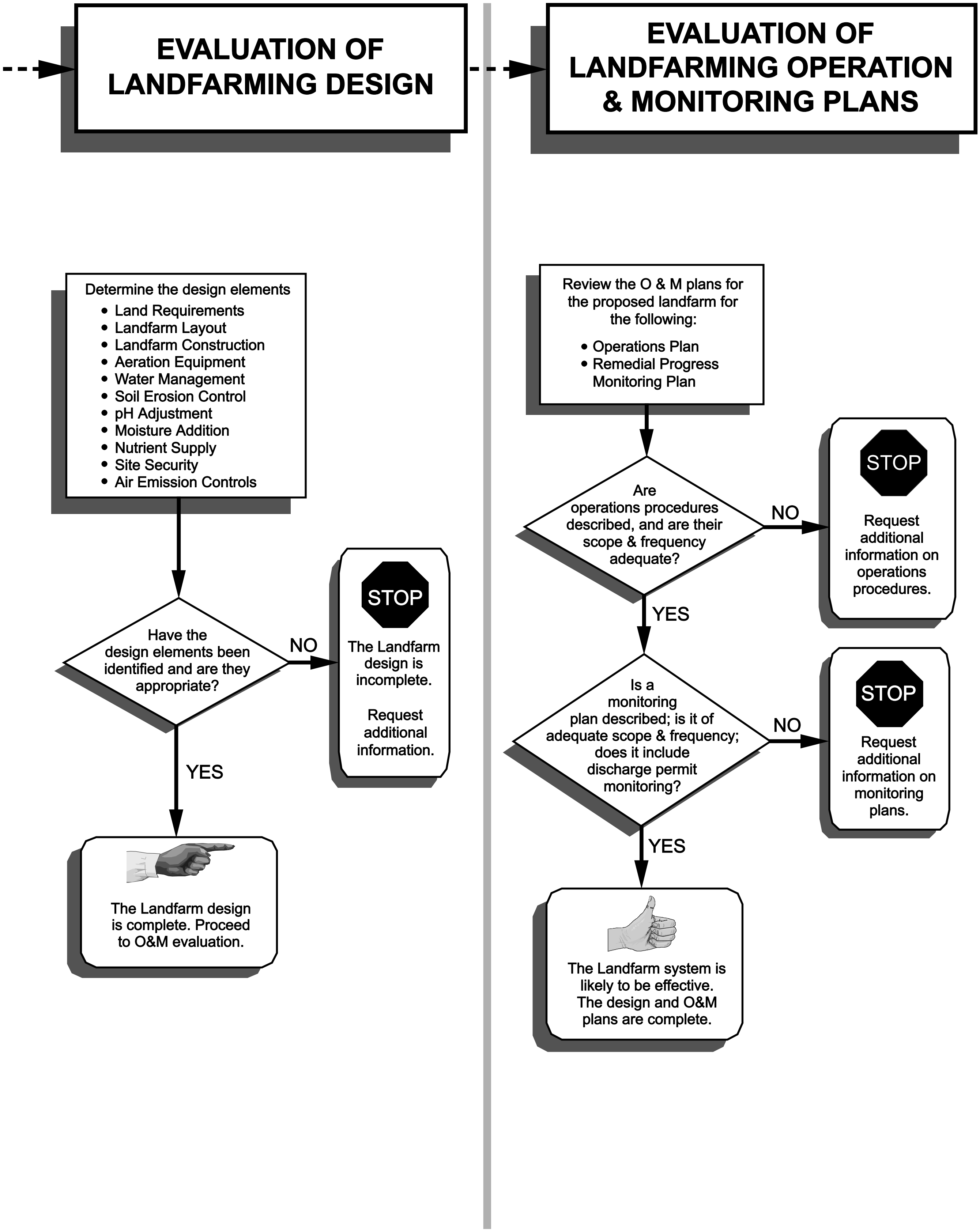
**Exhibit V-3**
**Landfarming Evaluation Process Flow Chart**



## 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% ≤ field capacity ≤ 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:

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

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:

$$\text{contaminant mass} =$$

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

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<br>and<br>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<br>or<br>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<br>and<br>TPH reduction < 95% | Effective. |
| Constituent concentration ≤ 0.1 ppm<br>or<br>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.

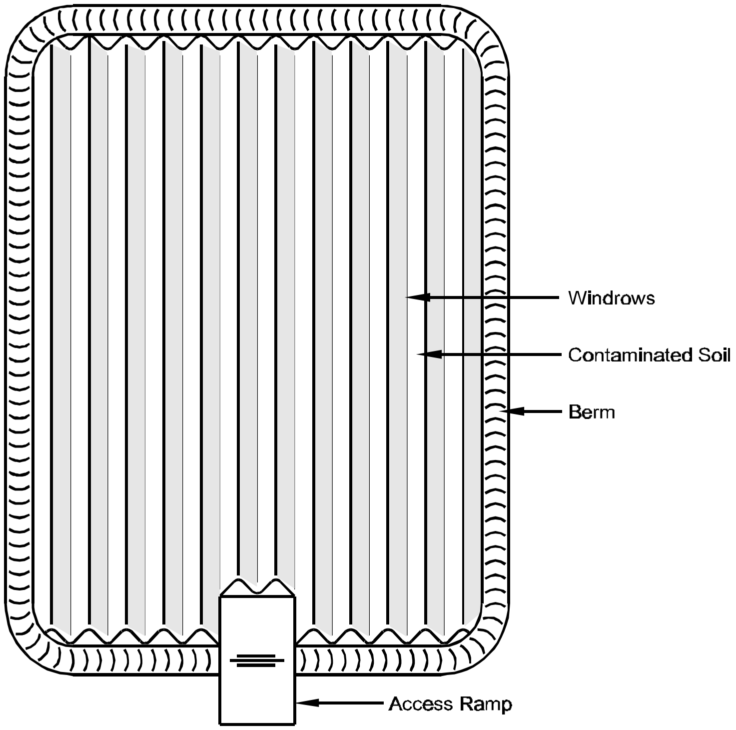
- *Landfarm Construction* includes: site preparation (grubbing, clearing and grading); berms; liners (if necessary); leachate collection and treatment systems; soil pretreatment methods (e.g., shredding, blending and amendments for fluffing, pH control); and enclosures and appropriate vapor treatment 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.

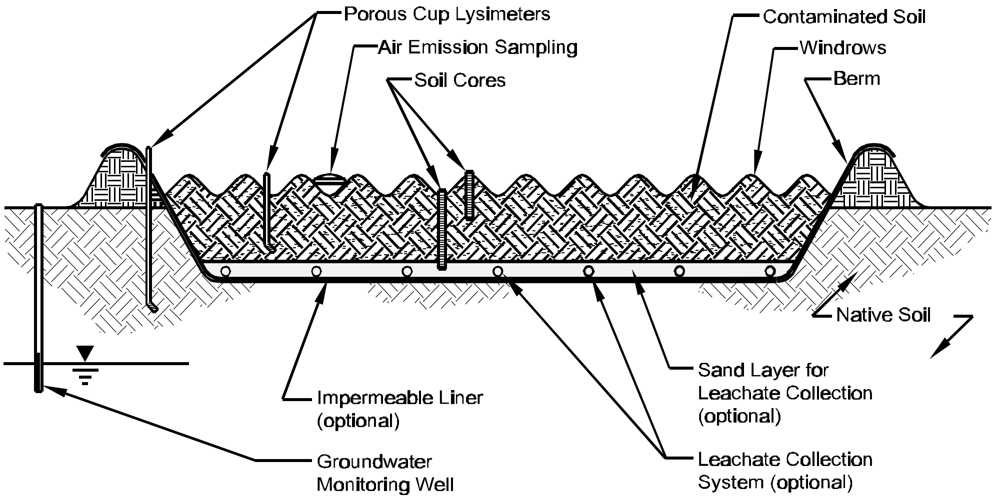
- *Soil Erosion Control* from wind or water generally includes terracing the soils into windrows, constructing water management systems, and spraying to minimize dust.

## 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. |

# References

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Freeman, H.M. *Standard Handbook of Hazardous Waste Treatment and Disposal*. New York, NY: McGraw-Hill Book Company, 1989.

Grasso, D. *Hazardous Waste Site Remediation, Source Control*. Boca Raton, FL: CRC Press, 1993.

Norris, R.D., Hinchee, R.E., Brown, R.A., McCarty, P.L., Semprini, L., Wilson, J.T., Kampbell, D.H., Reinhard, M., Bower, E.J., Borden, R.C., Vogel, T.M., Thomas, J.M., and C.H. Ward. *Handbook of Bioremediation*. Boca Raton, FL:CRC Press, 1994.

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Pope, Daniel F., and J.E. Matthews. *Environmental Regulations and Technology: Bioremediation Using the Land Treatment Concept*. Ada, OK: U.S. Environmental Protection Agency, Environmental Research Laboratory. EPA/600/R-93/164, 1993.

# 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

# Contents

# List Of Exhibits

# 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.

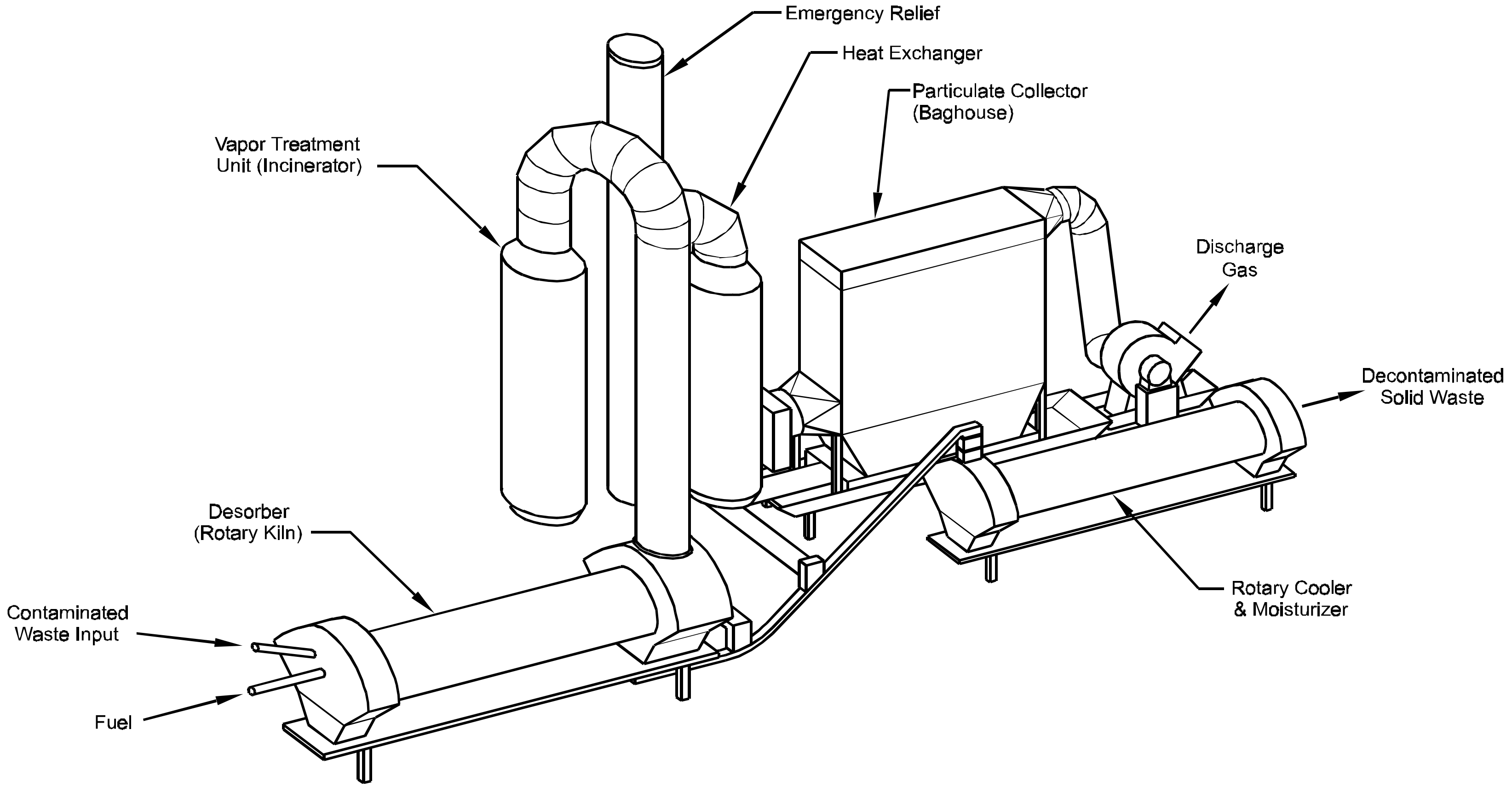
Some pre- and postprocessing of soil is necessary when using LTTD. Excavated soils are first screened to remove large (> 2 inches in diameter) objects. These may be sized (e.g., crushed or shredded) and then introduced back into the feed material. After leaving the desorber, soils are cooled, re-moistened 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

- Readily available equipment for onsite or offsite treatment.
- Very rapid treatment time; most commercial systems capable of over 25 tons per hour throughput.
- Cost competitive for large volumes (> 1,000 $yd^3$) of soils: $30-70/ton of contaminated soil, exclusive of excavation and transportation costs.
- Can be used to mitigate “hot spot” source areas with very high concentrations of petroleum hydrocarbons.
- 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).

### Disadvantages

- Requires excavation of soils; generally limited to 25 feet below land surface.
- Onsite treatment will require significant area (> ½ acre) to locate LTTD unit and store process soils.
- Offsite treatment will require costly transportation of soils and possibly manifesting.
- Soils excavated from below the groundwater table require dewatering prior to treatment because of high moisture content.

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

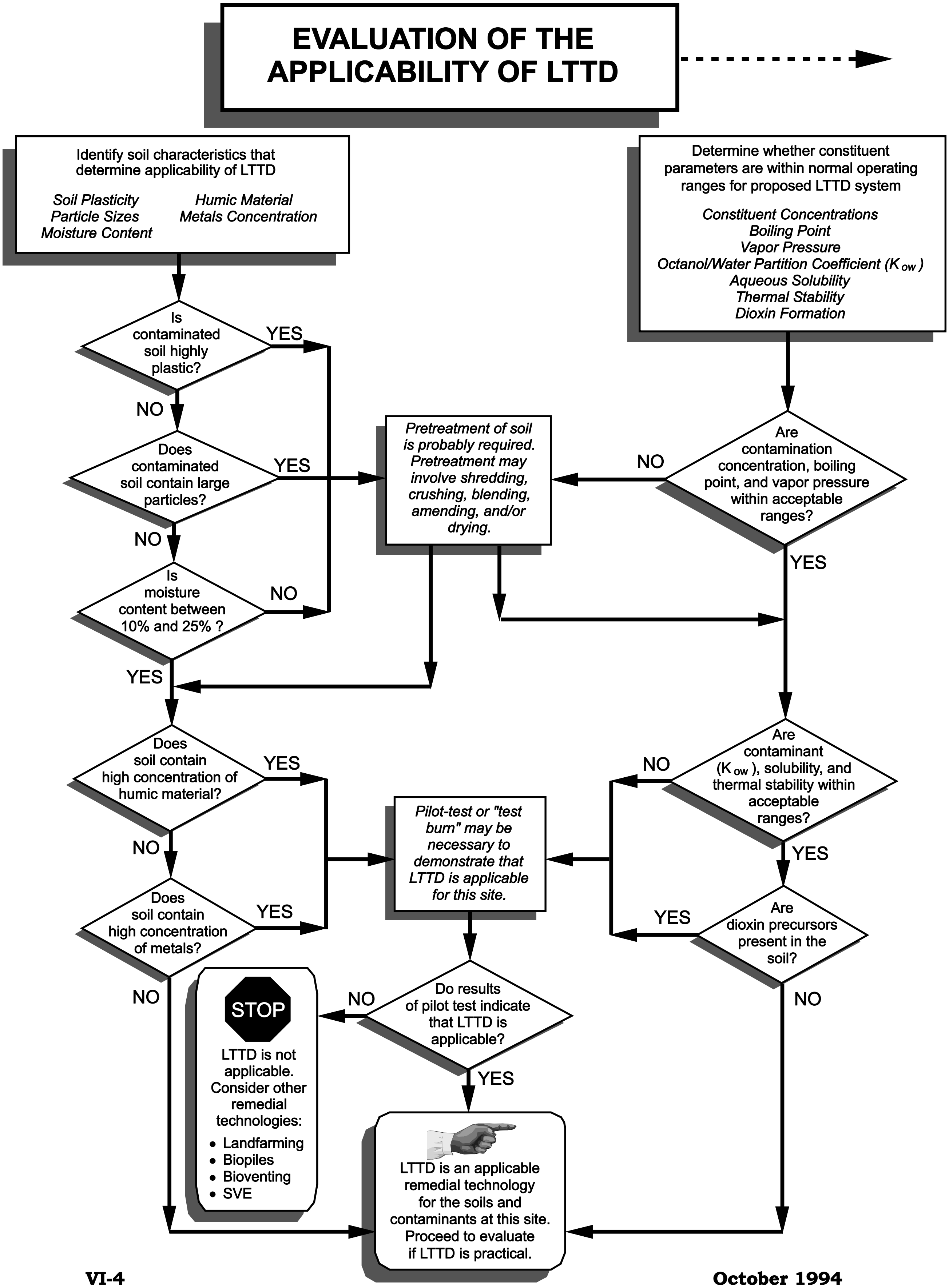
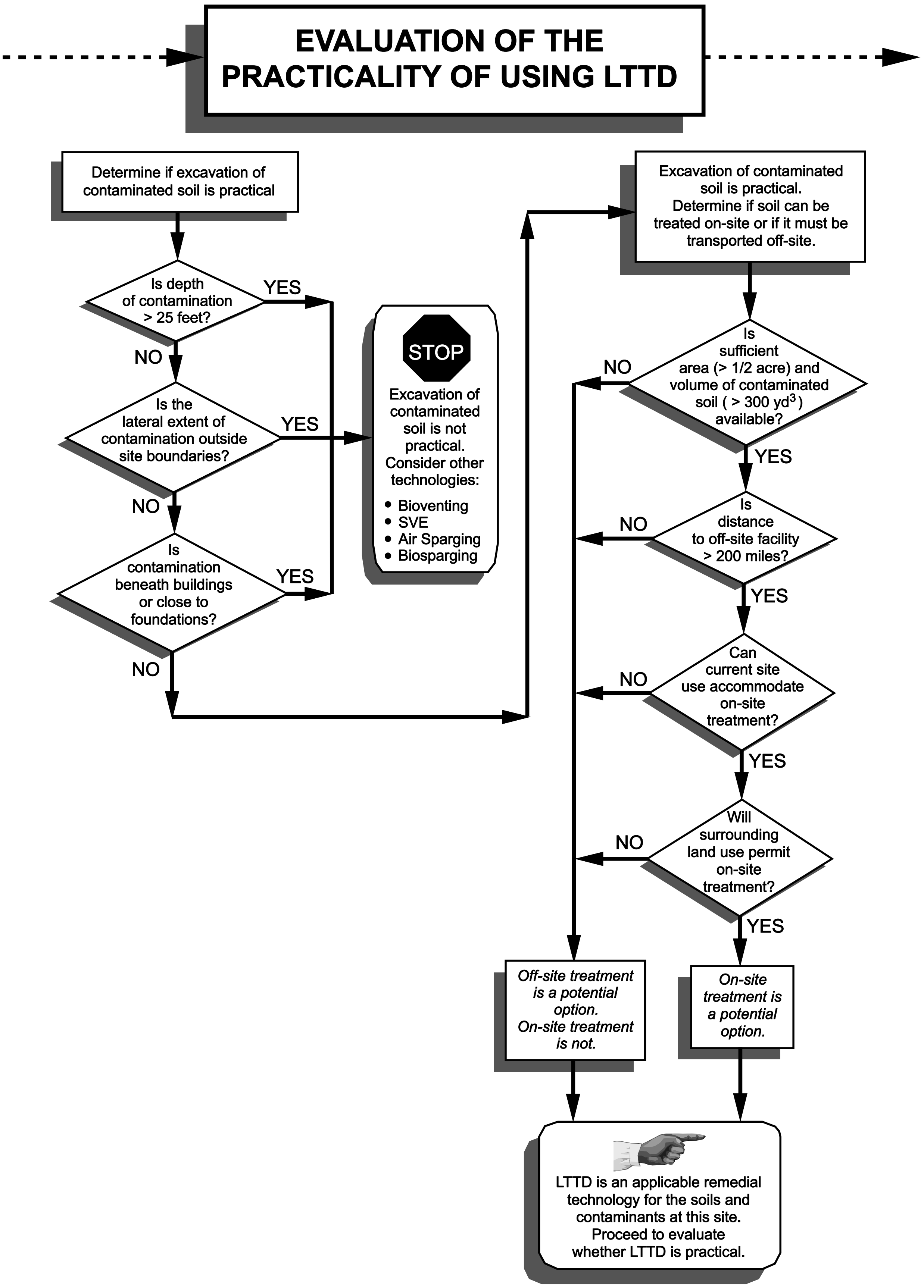
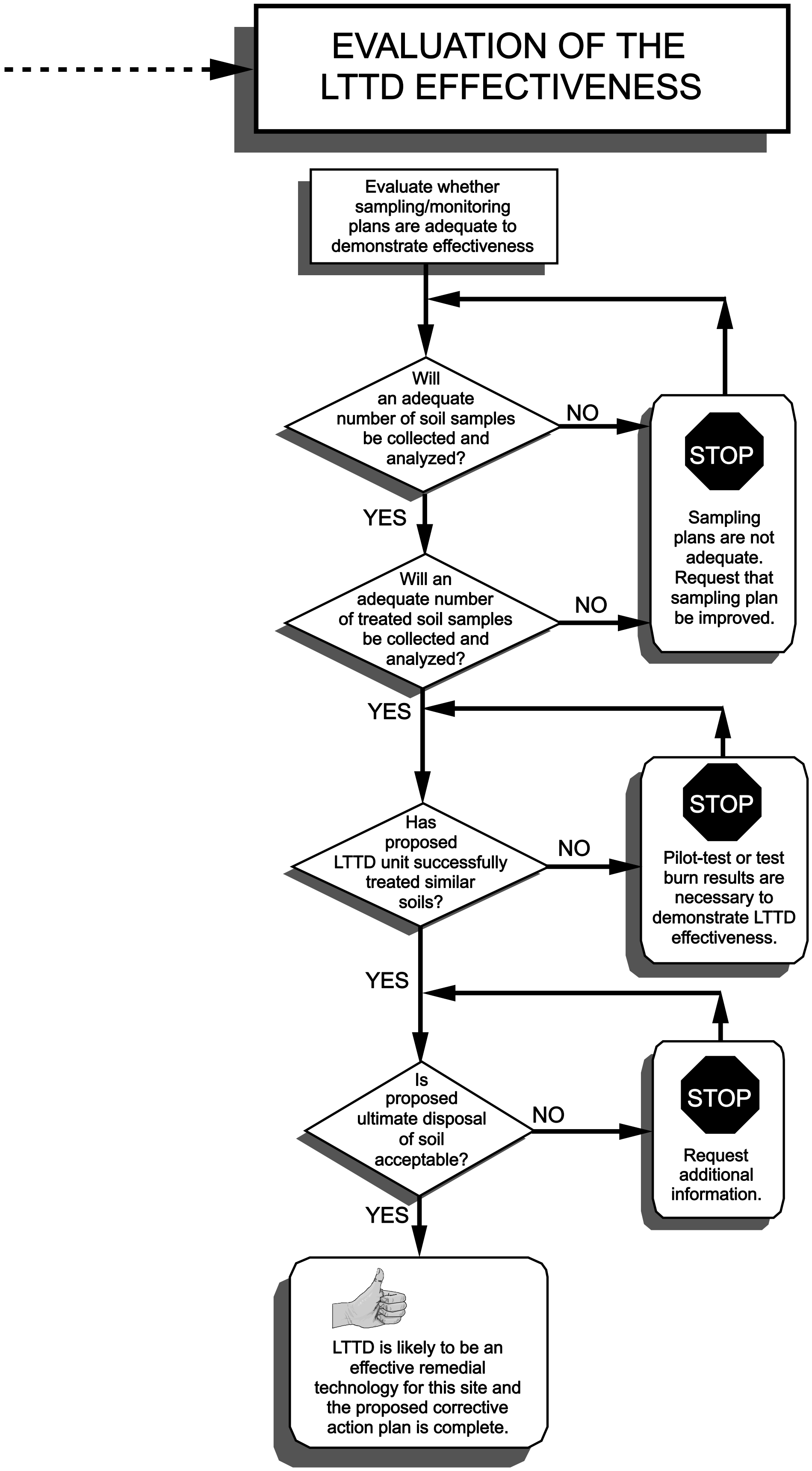


**Exhibit VI-3**
**Low-Temperature Thermal Desorption Process Flow Chart**



## 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

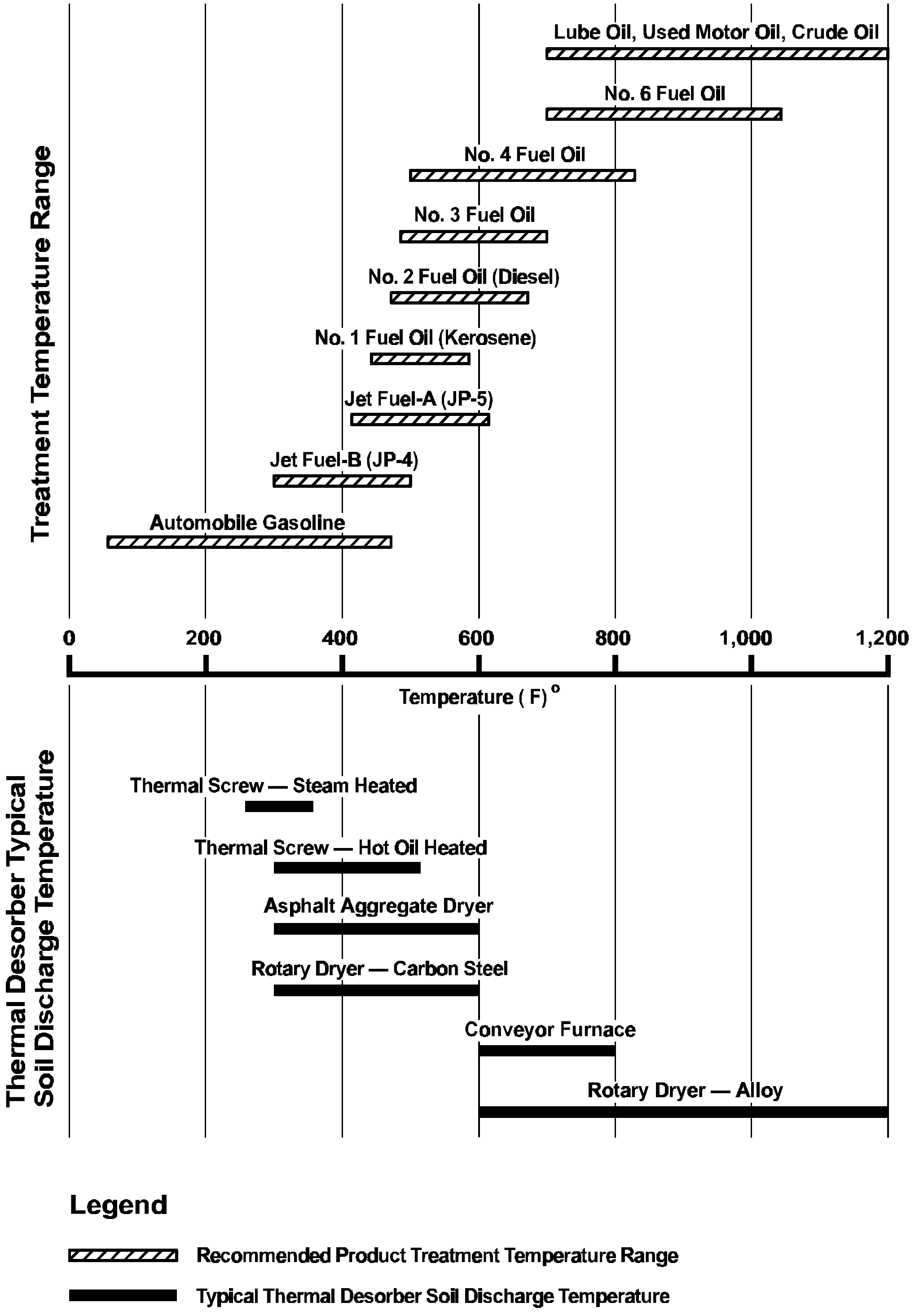


**Exhibit VI-5**
**Key Soil And Constituent Characteristics That Influence Applicability Of LTTD**

| 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.

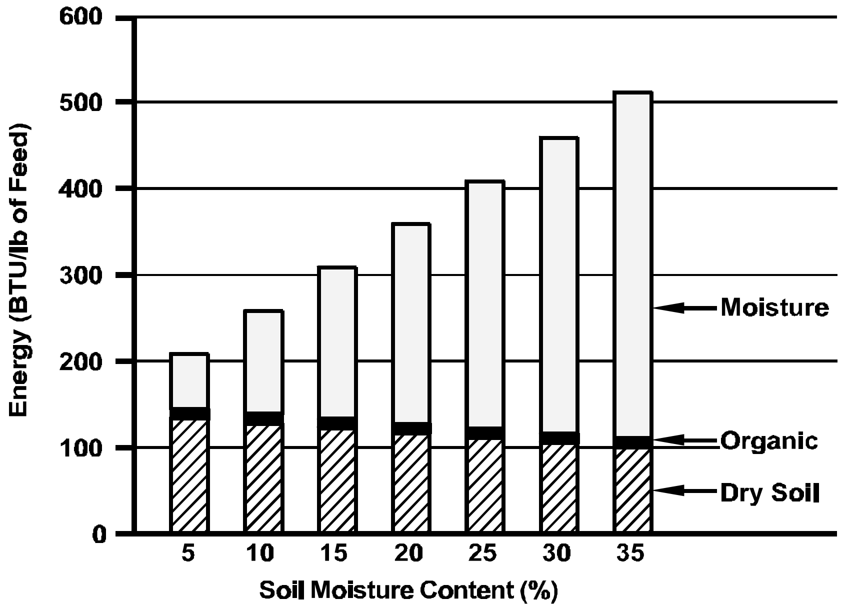
### *Particle Size Distribution*

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.

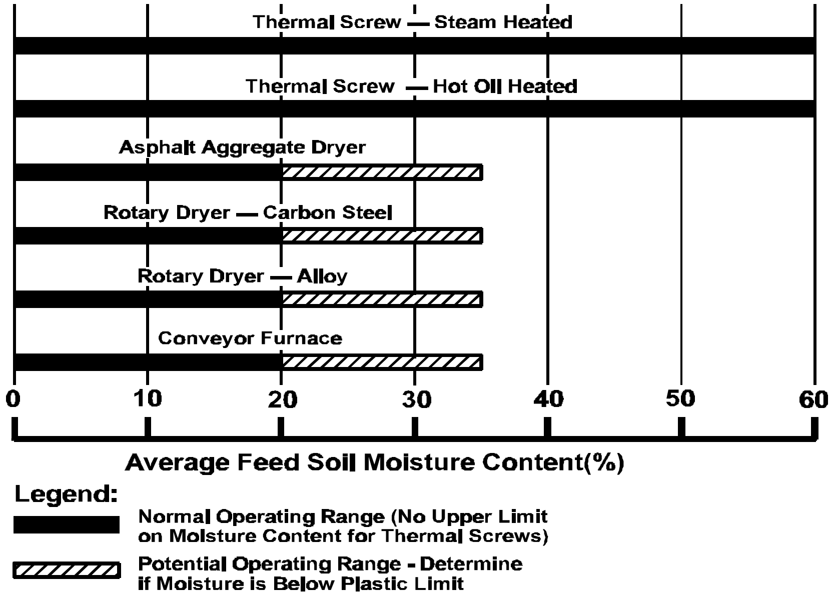
### *Moisture Content*

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:

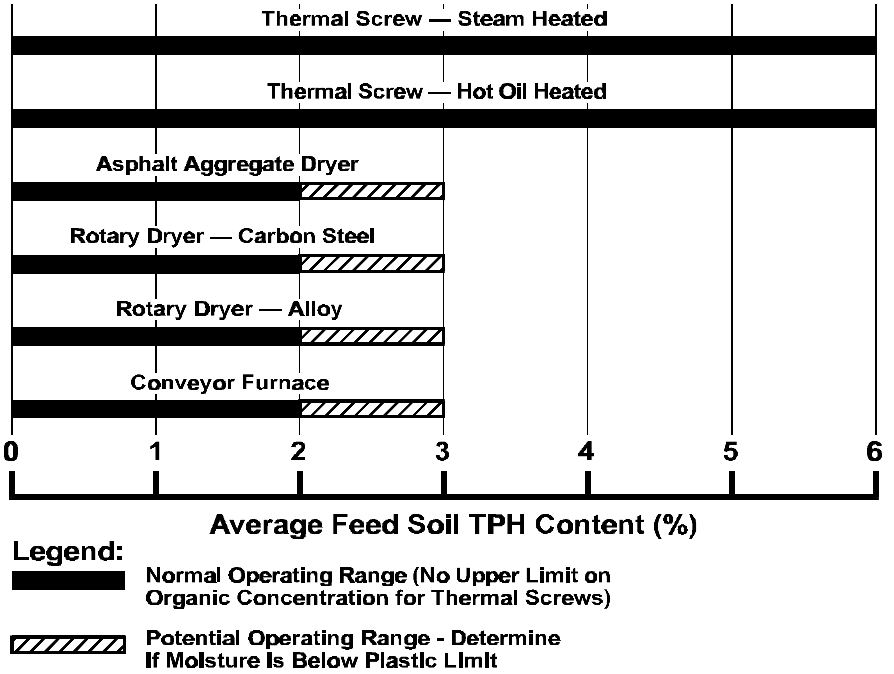
- Benzene, toluene, ethylbenzene, xylenes (BTEX)
- Total organic halides (TOX)
- Toxicity Characteristic Leaching Procedure (TCLP) for volatiles, semivolatiles, and metals
- Total metals
- Polychlorinated biphenyls (PCBs)
- Ignitability
- Corrosivity
- Reactivity

### *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*

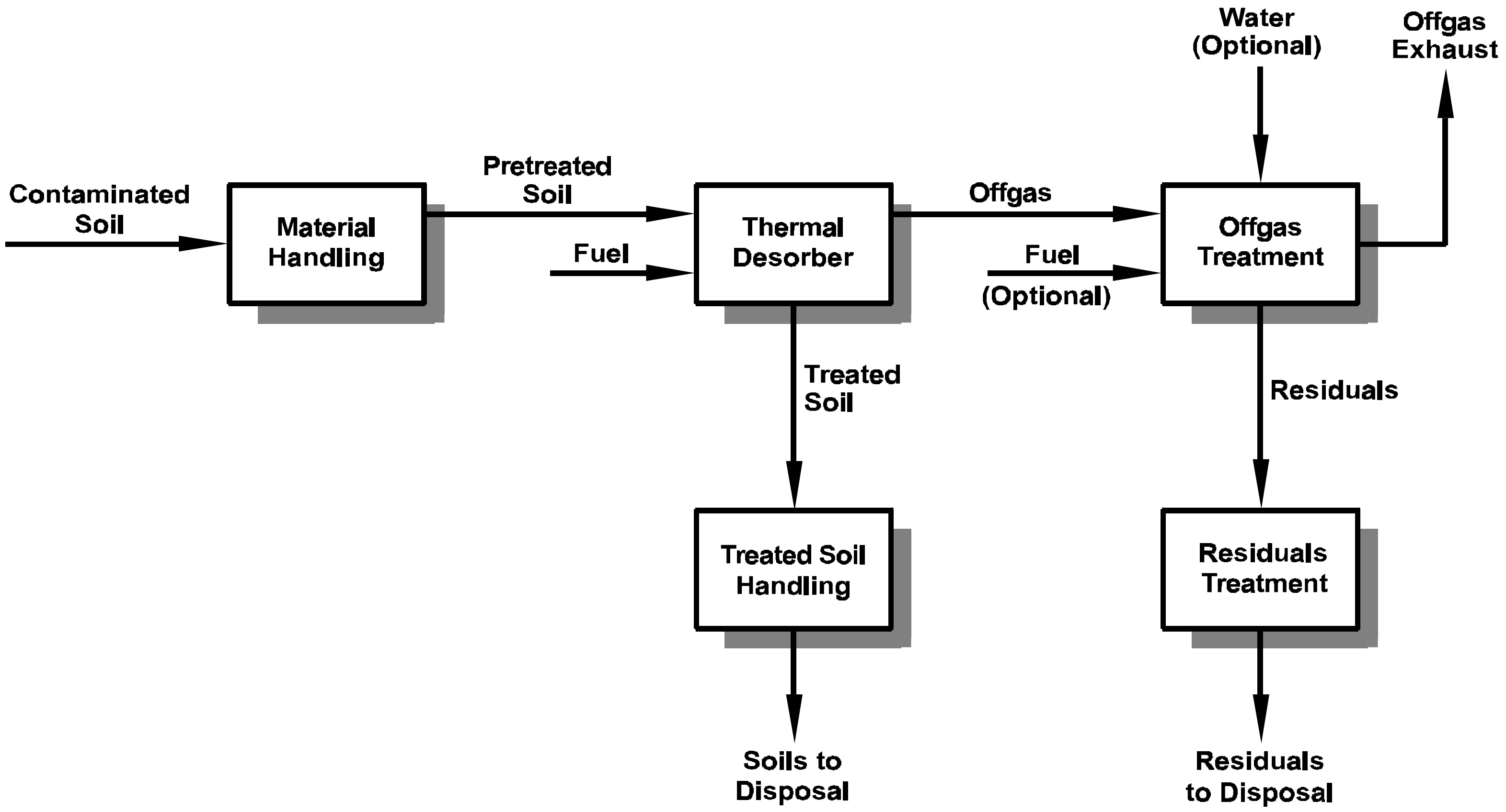
The term thermal desorber describes the primary treatment operation that heats petroleum-contaminated materials and desorbs organic materials into a purge gas. Mechanical design features and process operating conditions vary considerably among the various types of LTTD systems. Desorption units are available 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.

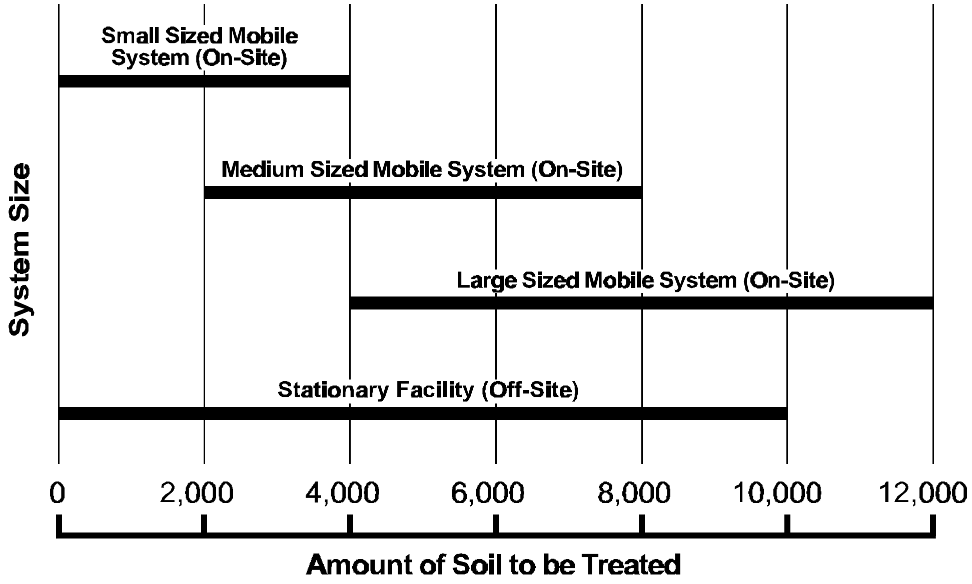
### Vertical And Horizontal Extent Of Contamination

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 Type | | | |
|---|---|---|---|
| Small Mobile | Medium Mobile | Large Mobile | Stationary Facility |
| 1 – 2 | 3 – 6 | 7 – 10 | NA |
| 5 – 15 | 15 – 30 | 30 – 50 | 30 – 120 |
| 5 – 15 [a] | 15 – 30 [a] | 30 – 50 | 30 – 100 [b] |
| 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 | ❍ Excavation walls<br>❍ Excavation floor | ❍ TPH, constituents of concern |
| LTTD treatment | Every 100 cu.yd. of feed soil and treated soil | ❍ Feed soil<br>❍ Treated soil | ❍ 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

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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

# Contents

# List Of Exhibits

# Chapter VII
# Air Sparging

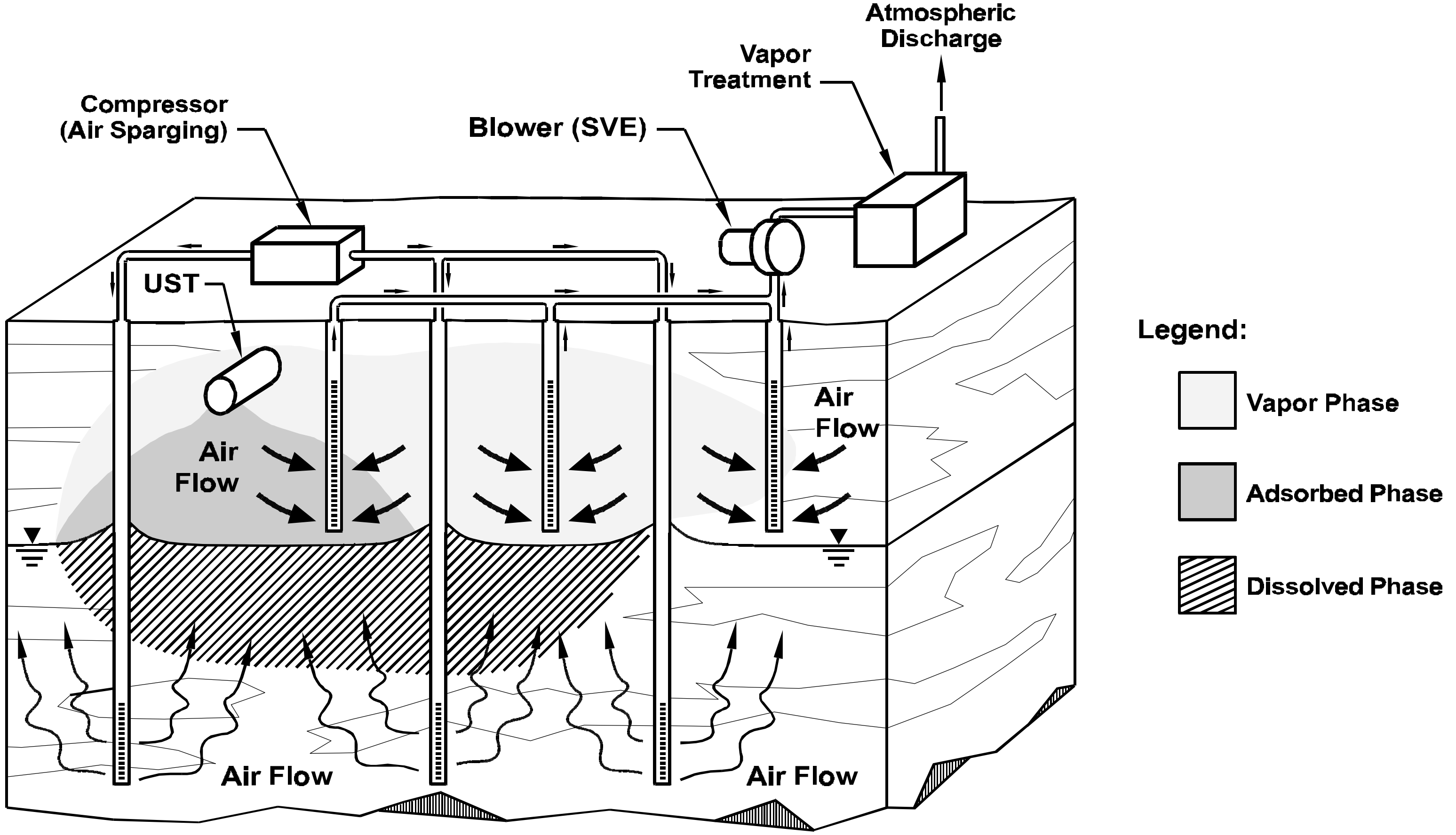
## Overview

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**

- Readily available equipment; easy installation.
- Implemented with minimal disturbance to site operations.
- Short treatment times: usually less than 1 to 3 years under optimal conditions.
- At about $20-50/ton of saturated soil, air sparging is less costly than aboveground treatment systems.
- Requires no removal, treatment, storage, or discharge considerations for groundwater.
- Can enhance removal by SVE.

**Disadvantages**

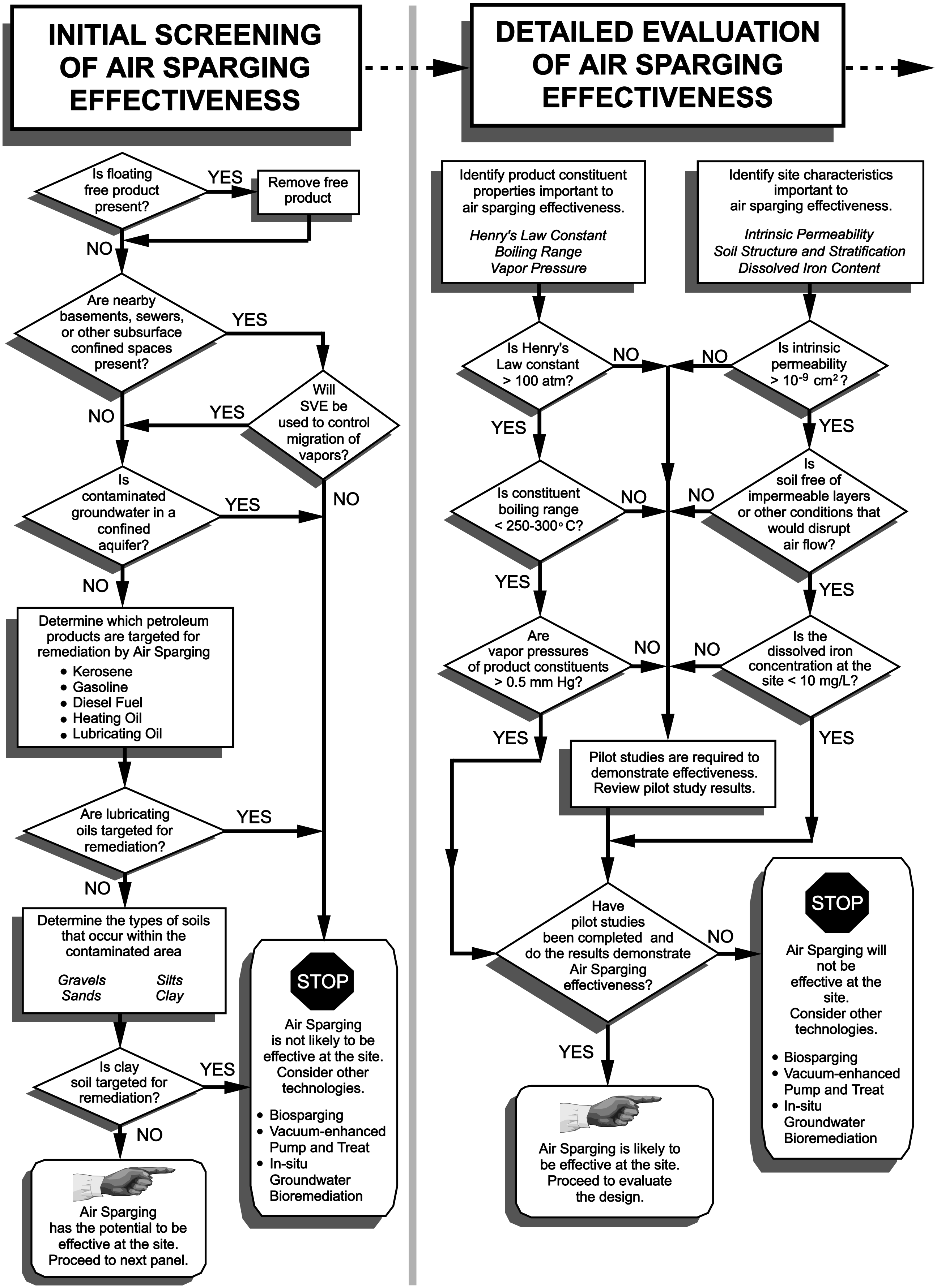
- Cannot be used if free product exists (i.e., any free product must be removed prior to air sparging).
- Cannot be used for treatment of confined aquifers.
- Stratified soils may cause air sparging to be ineffective.
- Some interactions among complex chemical, physical, and biological processes are not well understood.
- Lack of field and laboratory data to support design considerations.
- 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.

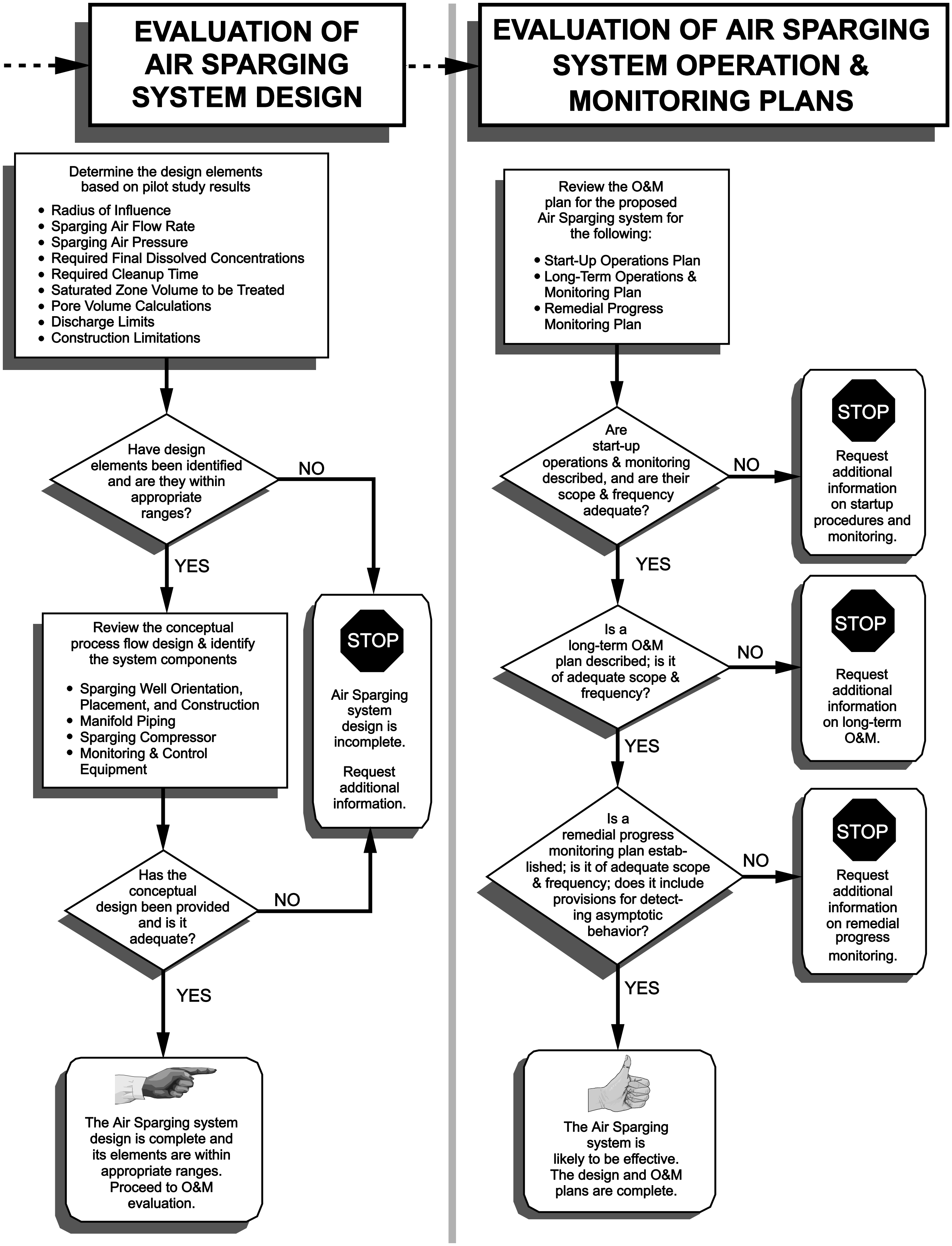
- **Step 2:** ***A detailed evaluation of air sparging effectiveness*** provides further screening criteria to confirm whether air sparging is likely to be effective. You will need to find specific soil and product constituent characteristics and properties, compare them to ranges where air sparging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

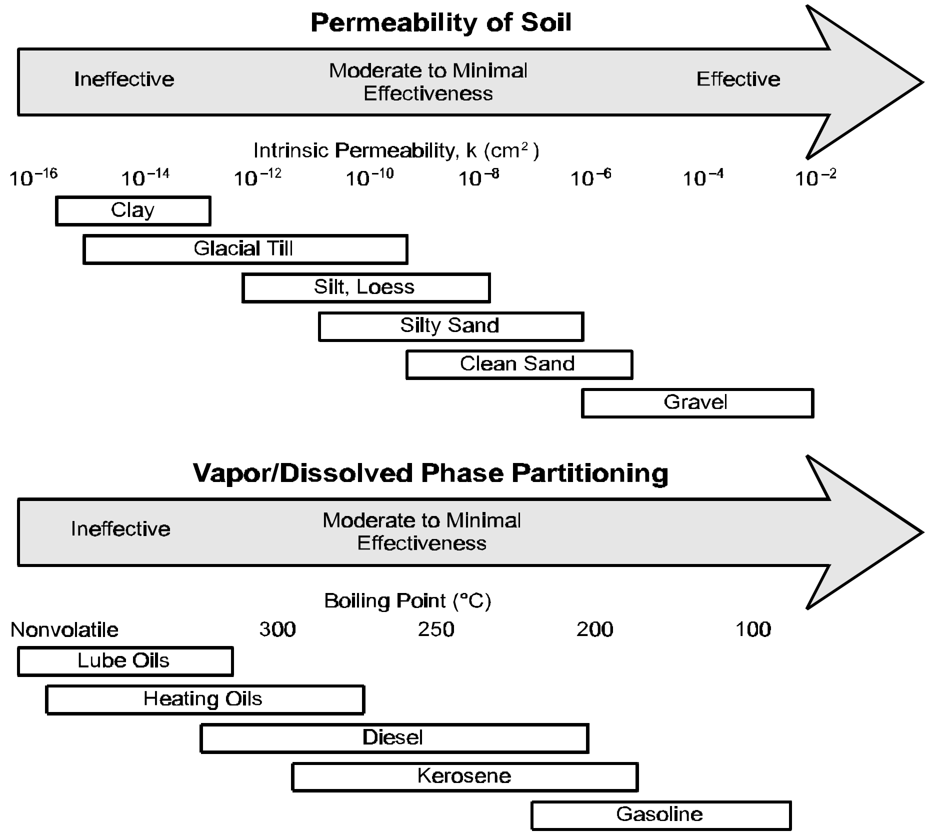
- *Vapor/dissolved phase partitioning* of the constituents determines the equilibrium distribution of a constituent between the dissolved phase and the vapor phase. Vapor/dissolved phase partitioning is, therefore, a significant factor in determining the rate at which dissolved constituents can be transferred 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
## Iniital 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)
$\mu$ = water viscosity ($g/cm \cdot sec$)
$\rho$ = 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:

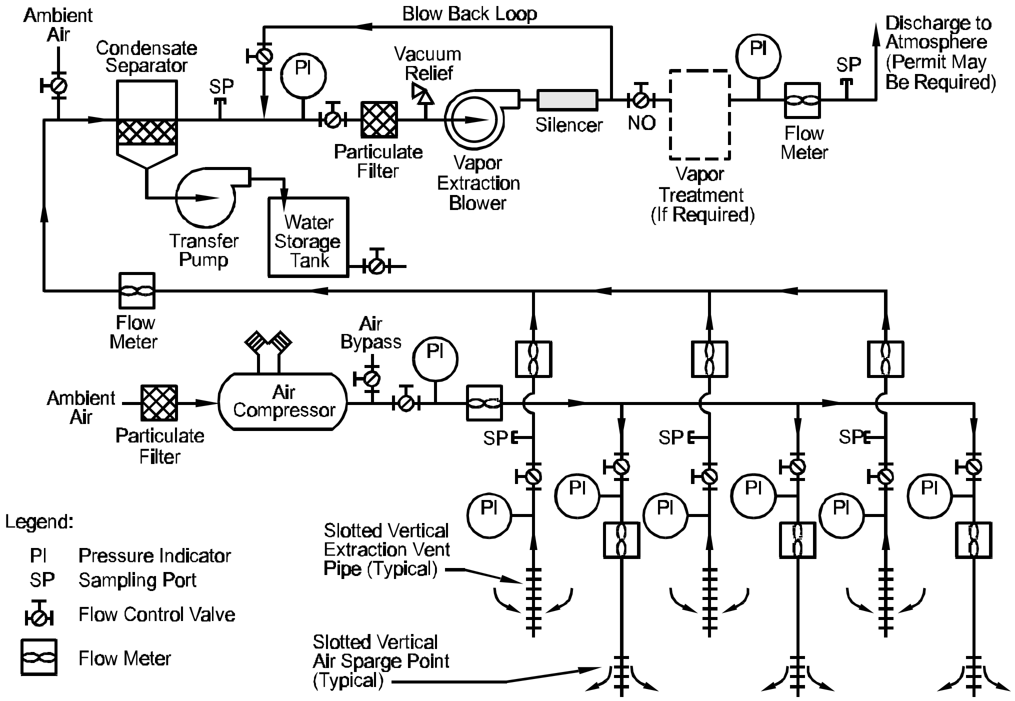
- ❍ Well orientation, placement, and construction details.
- ❍ Manifold piping.
- ❍ Compressed air equipment.
- ❍ Monitoring and controls.

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*

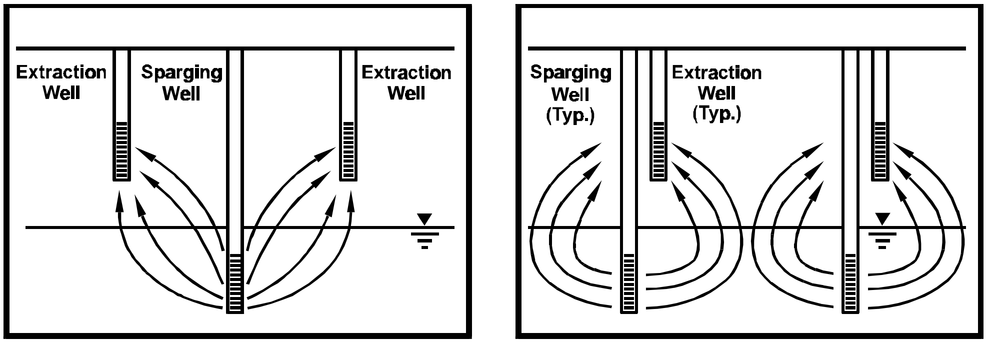
**Well Orientation.** An air sparging system can use either vertical or horizontal sparge wells. Well orientation should be based on site-specific needs and conditions. For example, horizontal systems should be considered when evaluating sites that will require 10 or more sparge or extraction points 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 | ❍ Deep contamination (> 25 feet)<br>❍ Depth to groundwater (> 10 feet)<br>❍ Fewer than 10 wells |
| Horizontal wells | ❍ Shallow groundwater table (< 25 feet)<br>❍ Zone of contamination within a specific stratigraphic unit<br>❍ System under an operational facility |

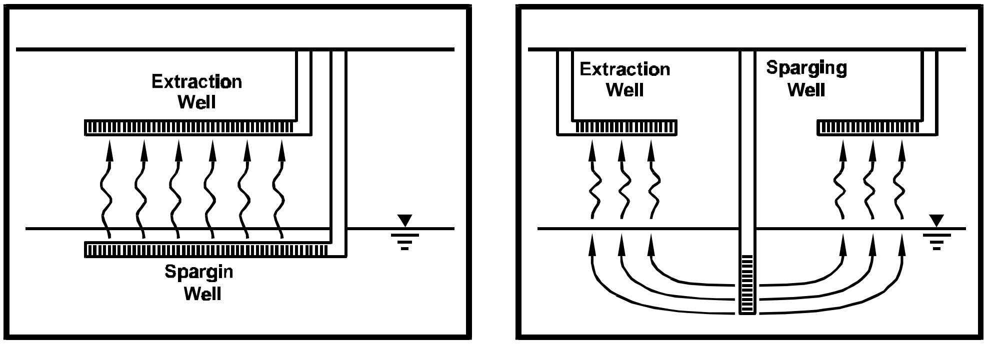
**Well Placement And Number of Wells.** Exhibit VII-16, Air Sparging/Vapor Extraction Well Configurations, shows various configurations that can be used in laying out air sparging systems used in conjunction with SVE. The essential goals in configuring the wells and monitoring points are (1) to optimize 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**



a) Spaced Configuration

b) Nested Wells



c) Horizontal Wells

d) Combined Horizontal/Vertical Wells

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

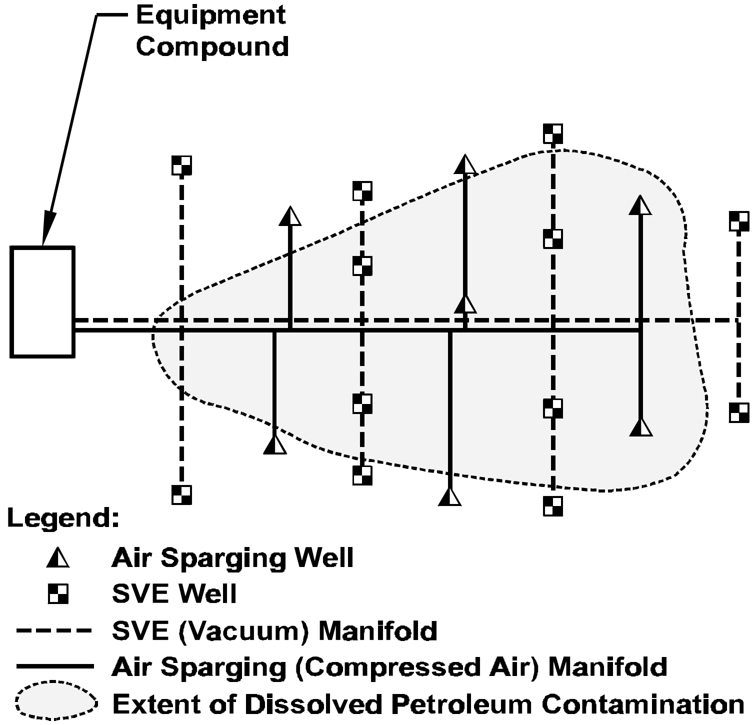
The number and location of extraction wells can be determined by using several methods as discussed in Chapter II: Soil Vapor Extraction. However, the following general points should be considered:

- 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.

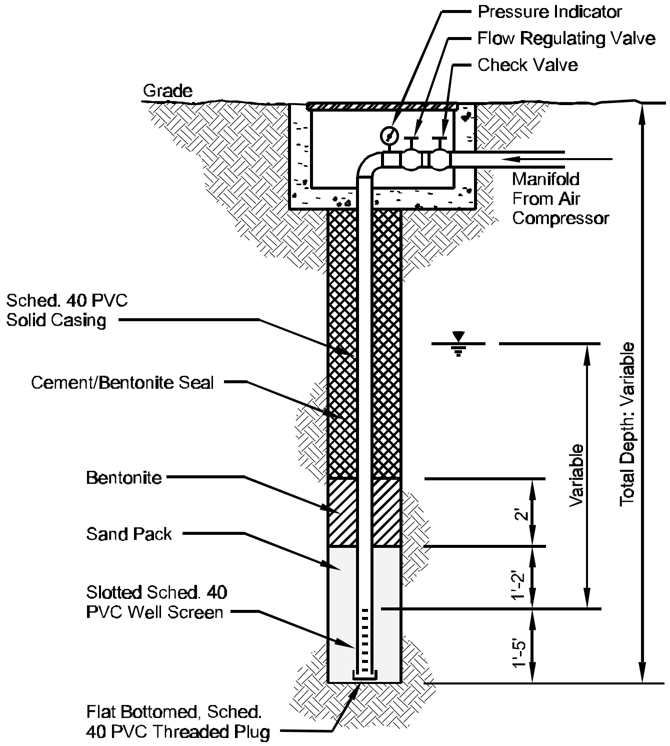
**Exhibit VII-17**
**Combined Air Sparging/SVE System Layout**



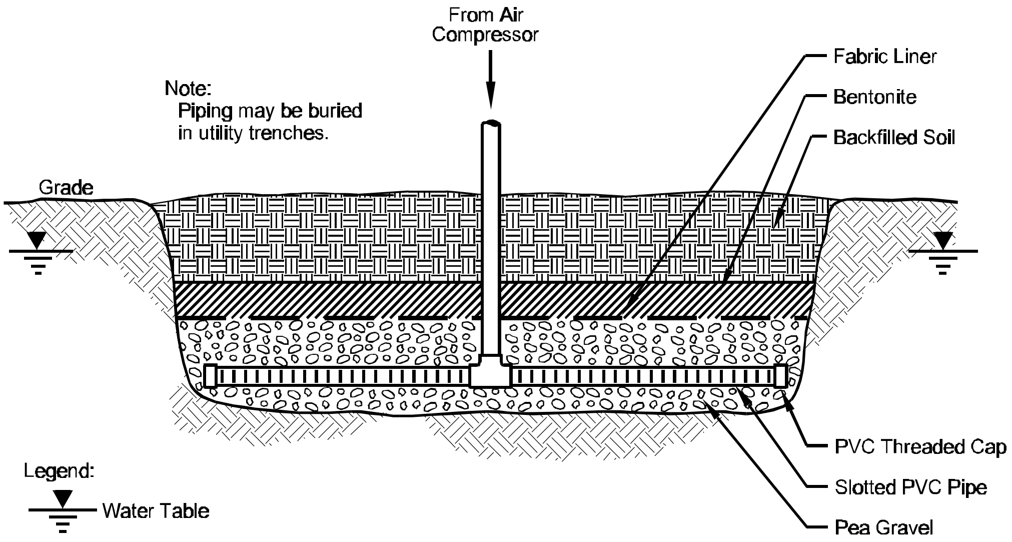
**Well Construction.** The air sparging (injection) wells are generally constructed of 1 to 5 inch PVC or stainless steel pipe. The screened interval is normally from 1 to 3 feet and is generally set from 5 to 15 feet below the deepest extent of adsorbed contaminants. Setting the screen at a deeper interval 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<br>❍ Manifold to blower<br>❍ Stack discharge | ❍ Pitot tube<br>❍ In-line rotameter<br>❍ Orifice plate<br>❍ Venturi or flow tube |
| Pressure gauge | ❍ At each injection and vapor extraction well head or manifold branch<br>❍ Before blower (before and after filters)<br>❍ Before and after vapor treatment | ❍ Manometer<br>❍ Magnehelic gauge<br>❍ Vacuum gauge |
| Vapor or air sparge temperature sensor | ❍ Manifold to blower<br>❍ Blower or compressor discharge (prior to vapor treatment) | ❍ Bi-metal dial-type thermometer<br>❍ Thermocouple |
| Sampling port | ❍ At each vapor extraction well head or manifold branch<br>❍ Manifold to blower<br>❍ Blower discharge | ❍ Hose barb<br>❍ Septa fitting |
| **Control Equipment** | | |
| Flow control valves/ regulators | ❍ At each vapor extraction well head or manifold branch<br>❍ Dilution or bleed valve at manifold to blower<br>❍ At header to each sparge point | ❍ Ball valve<br>❍ Gate valve<br>❍ Dilution/ambient air bleed valve<br>❍ Gate valve<br>❍ 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

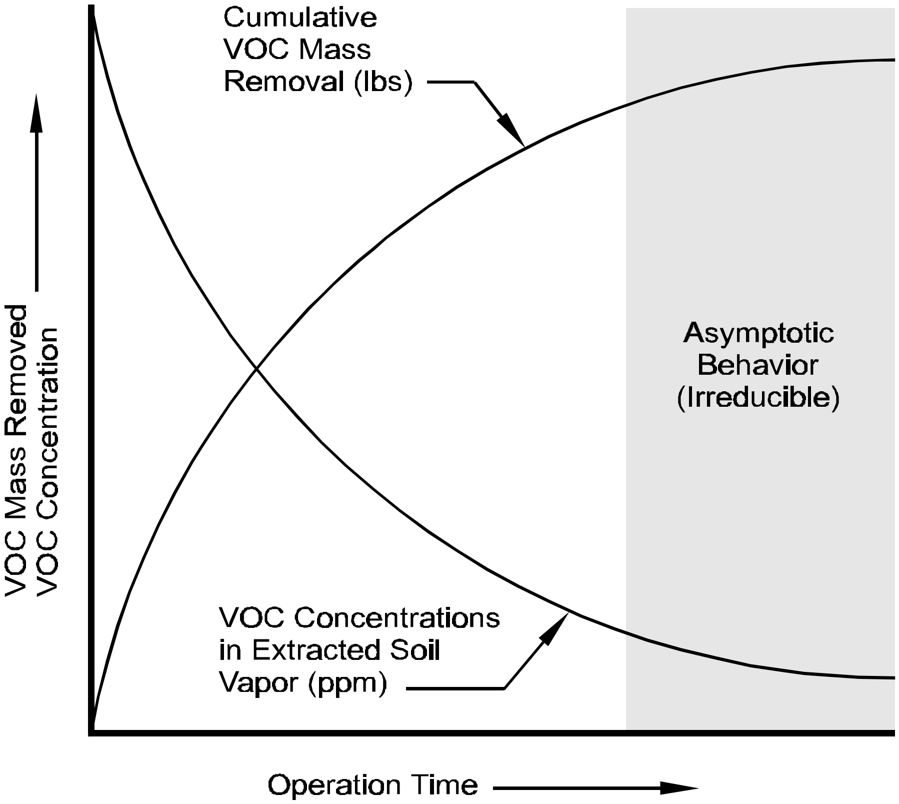
| Phase | Monitoring Frequency | What To Monitor | Where To Monitor |
|---|---|---|---|
| Startup (7-10 days) | At least daily | ❍ Sparge pressure<br>❍ Flow<br>❍ Vacuum readings (SVE)<br>❍ Vapor concentrations (SVE) | ❍ Air sparging wellhead<br>❍ Sparge and extraction wells<br>❍ Manifold<br>❍ Effluent stack |
| Long-term (ongoing) | Biweekly to monthly | ❍ Flow (SVE)<br>❍ Vacuum readings (SVE)<br>❍ Sparge pressure<br>❍ Vapor concentrations (SVE) | ❍ Extraction vents<br>❍ Manifold<br>❍ Air sparging wellhead<br>❍ 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

# Contents

# List Of Exhibits

# List Of Exhibits (cont'd)

# Chapter VIII
# Biosparging

## Overview

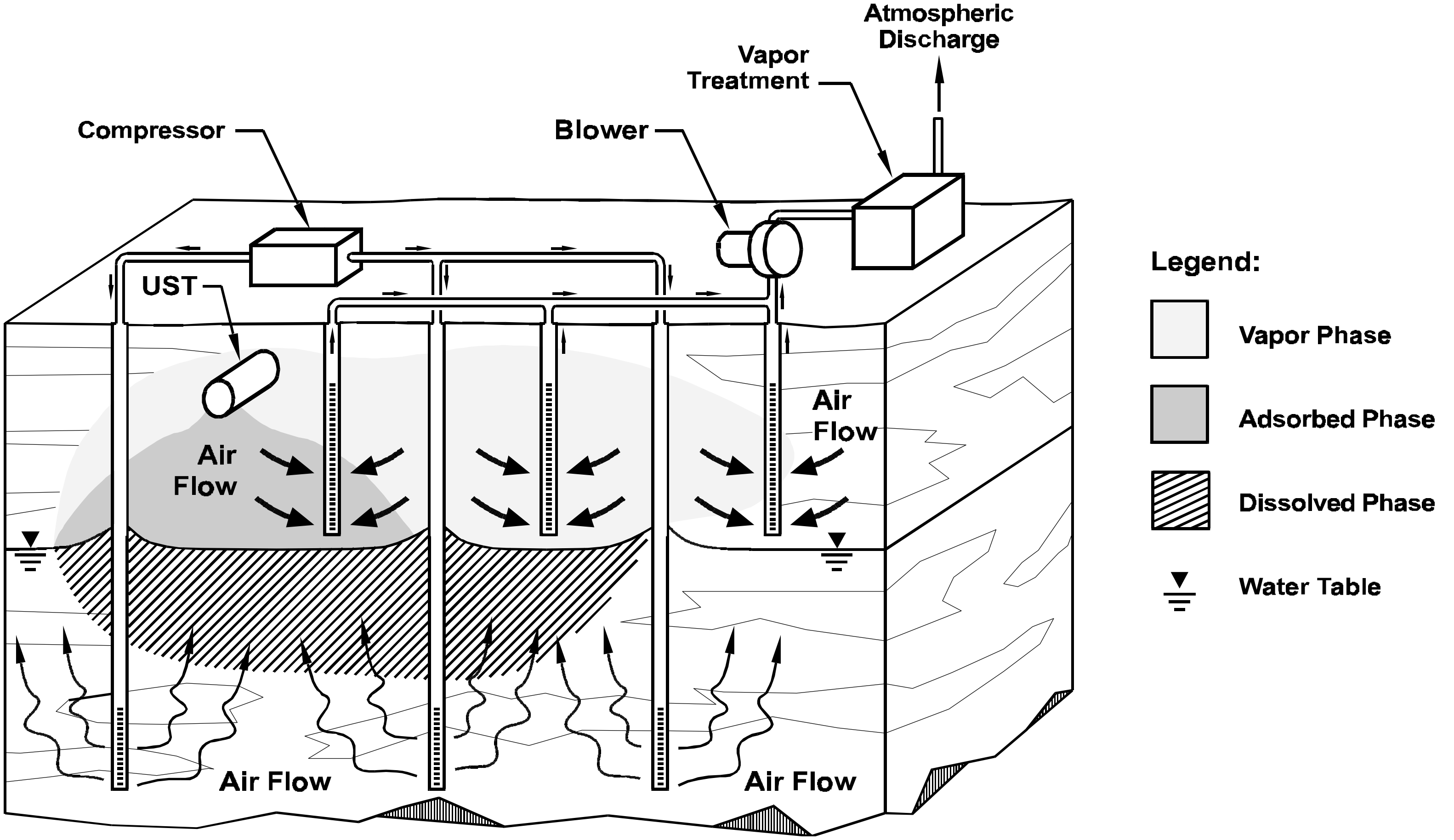
Biosparging is an in-situ remediation technology that uses indigenous microorganisms to biodegrade organic constituents in the saturated zone. In biosparging, air (or oxygen) and nutrients (if needed) are injected into the saturated zone to increase the biological activity of the indigenous microorganisms. 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

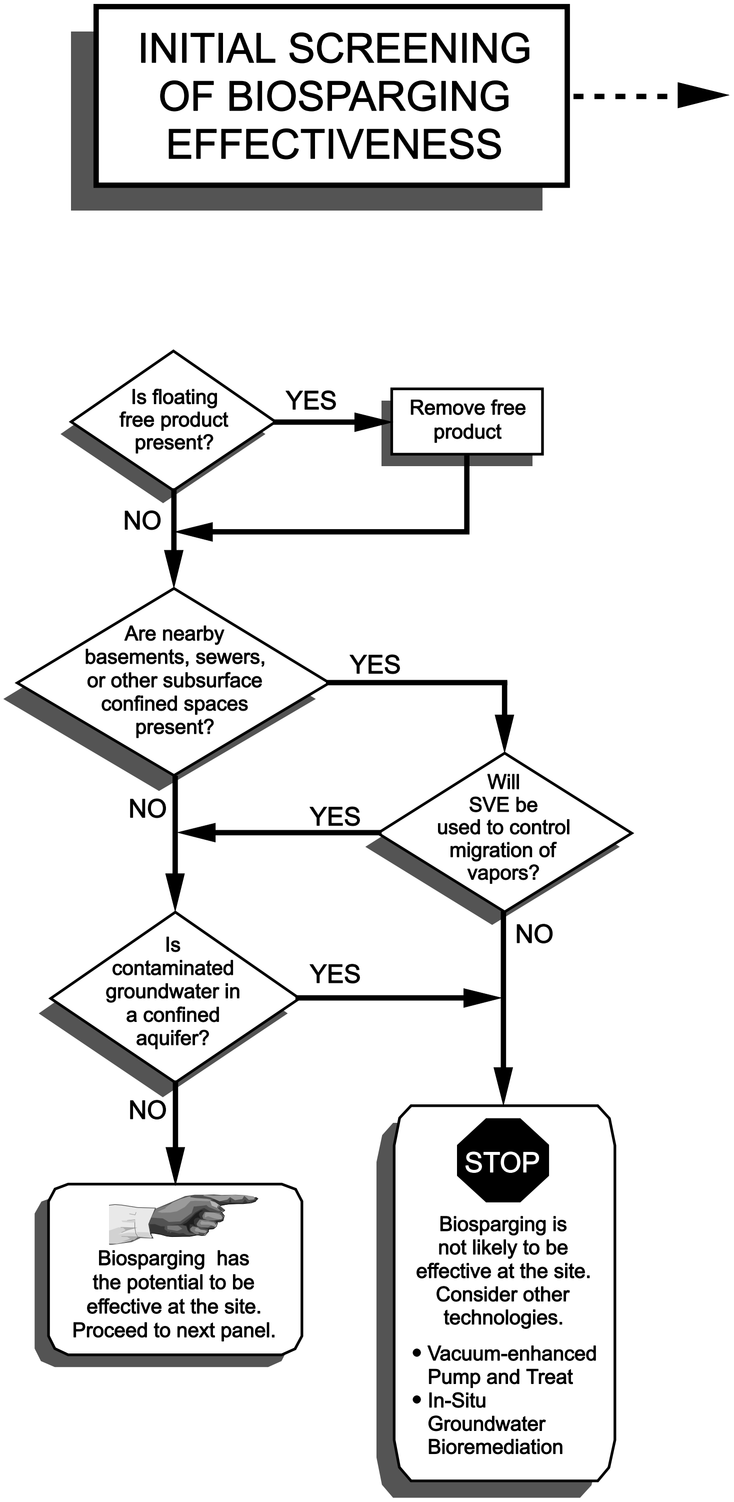
| Advantages | Disadvantages |
|---|---|
| ❍ Readily available equipment; easy to install. | ❍ Can only be used in environments where air sparging is suitable (e.g., uniform and permeable soils, unconfined aquifer, no free-phase hydrocarbons, no nearby subsurface confined spaces). |
| ❍ Creates minimal 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.

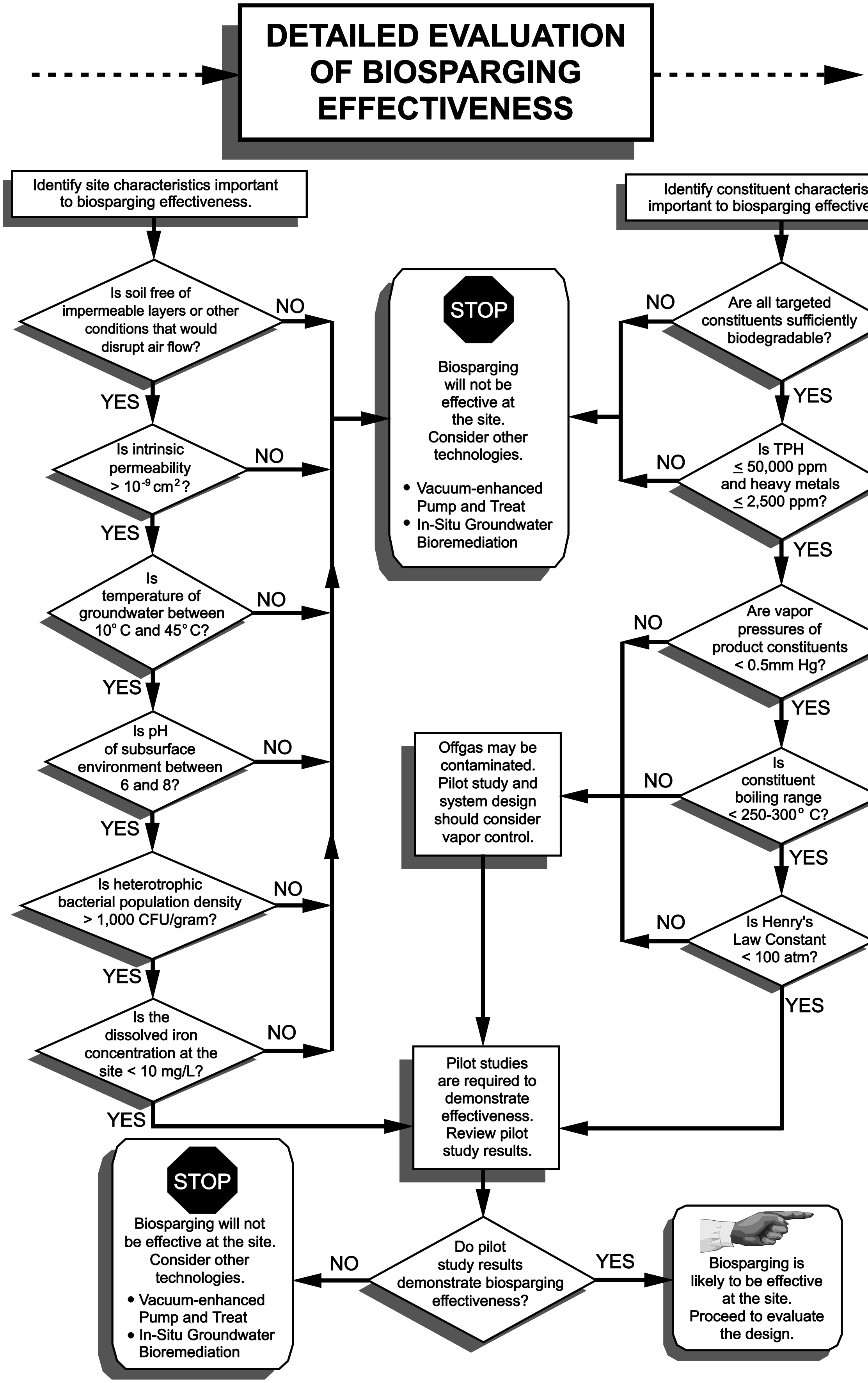
❍ **Step 1:** ***An initial screening of biosparging effectiveness*** allows you to quickly gauge whether biosparging is likely to be effective, moderately effective, or ineffective.

❍ **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.

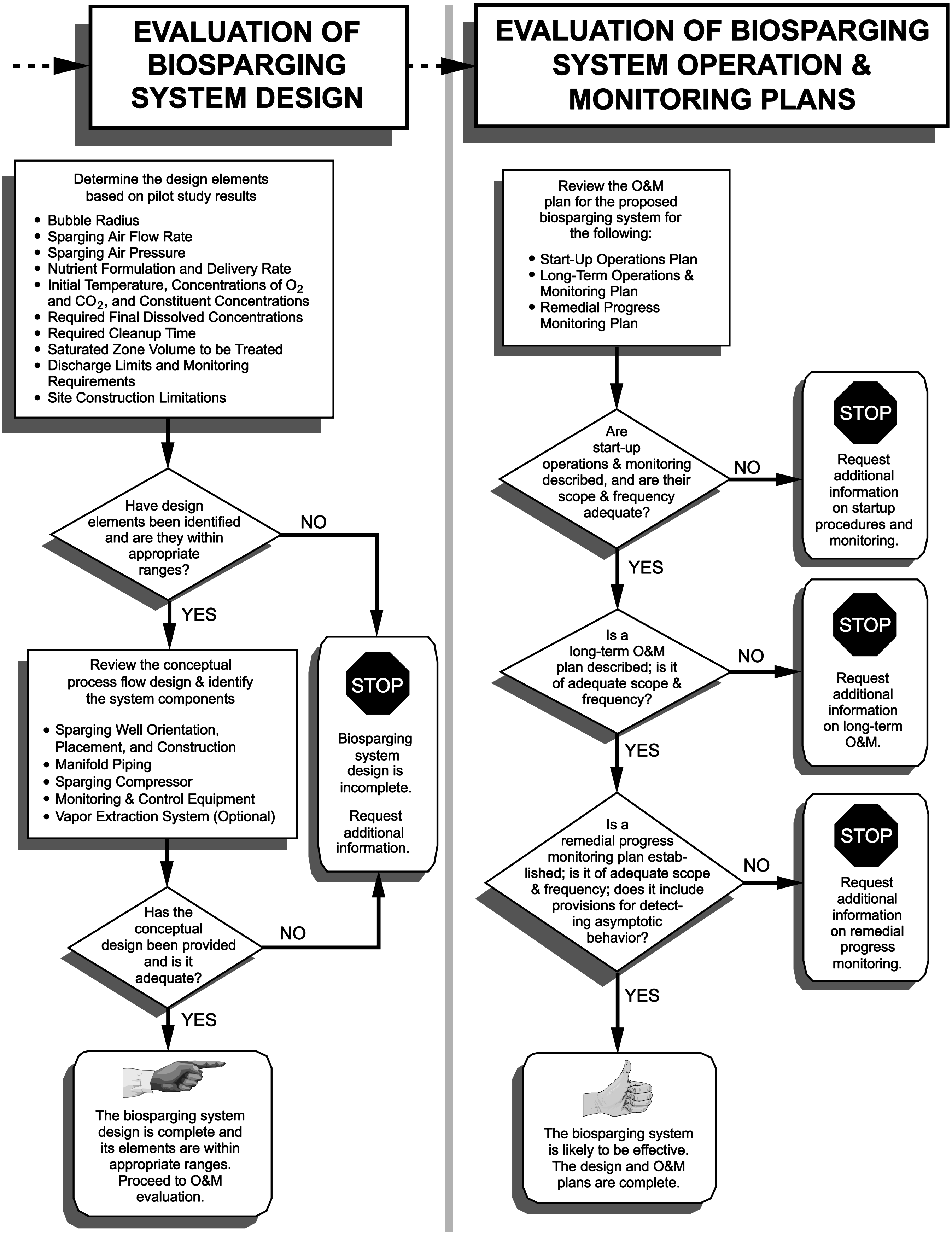
## Exhibit VIII-3
## Biosparging Evaluation Process Flow Chart



## 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:

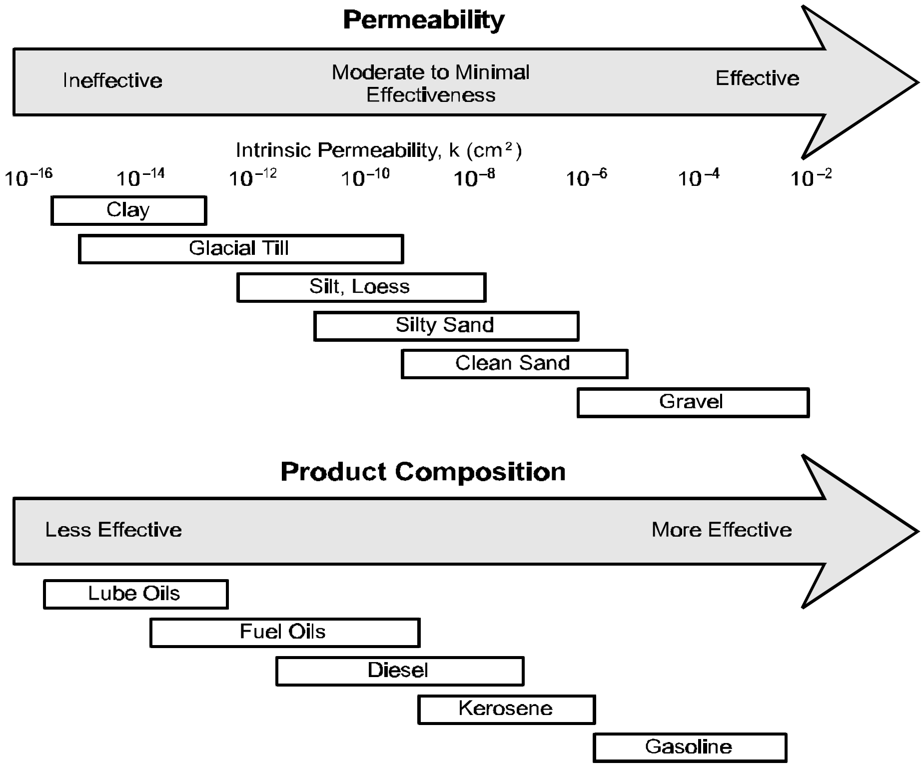
- The *permeability* of the soil which determines the rate at which oxygen can be supplied to the hydrocarbon-degrading microorganisms in the subsurface.

- 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 bioventing 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)
$\mu$ = water viscosity ($g/cm \cdot sec$)
$\rho$ = 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:

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

Different empirical formulas of bacterial cell mass have been proposed; the most widely accepted are $C_5H_7O_2N$ 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:l 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, I-pentane, n-octane | ❍ Gasoline |
| ↓ | Nonane | ❍ Diesel fuel |
| ↓ | Methyl butane, dimethylpentenes, methyloctanes | ❍ Gasoline |
| ↓ | Benzene, toluene, ethylbenzene, xylenes | ❍ Gasoline |
| ↓ | Propylbenzenes | ❍ Diesel, kerosene |
| ↓ | Decanes<br>Dodecanes<br>Tridecanes<br>Tetradecanes | ❍ Diesel<br>❍ Kerosene<br>❍ Heating fuels<br>❍ Lubricating oils |
| Less degradable | Naphthalenes<br>Fluoranthenes<br>Pyrenes<br>Acenaphthenes | ❍ Diesel<br>❍ Kerosene<br>❍ Heating oil<br>❍ 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<br>and<br>Heavy metals ≤ 2,500 ppm | Effective. |
| Petroleum constituents > 50,000 ppm<br>or<br>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<br>and<br>TPH reduction < 95% | Effective. |
| Constituent concentration ≤ 0.1 ppm<br>or<br>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.

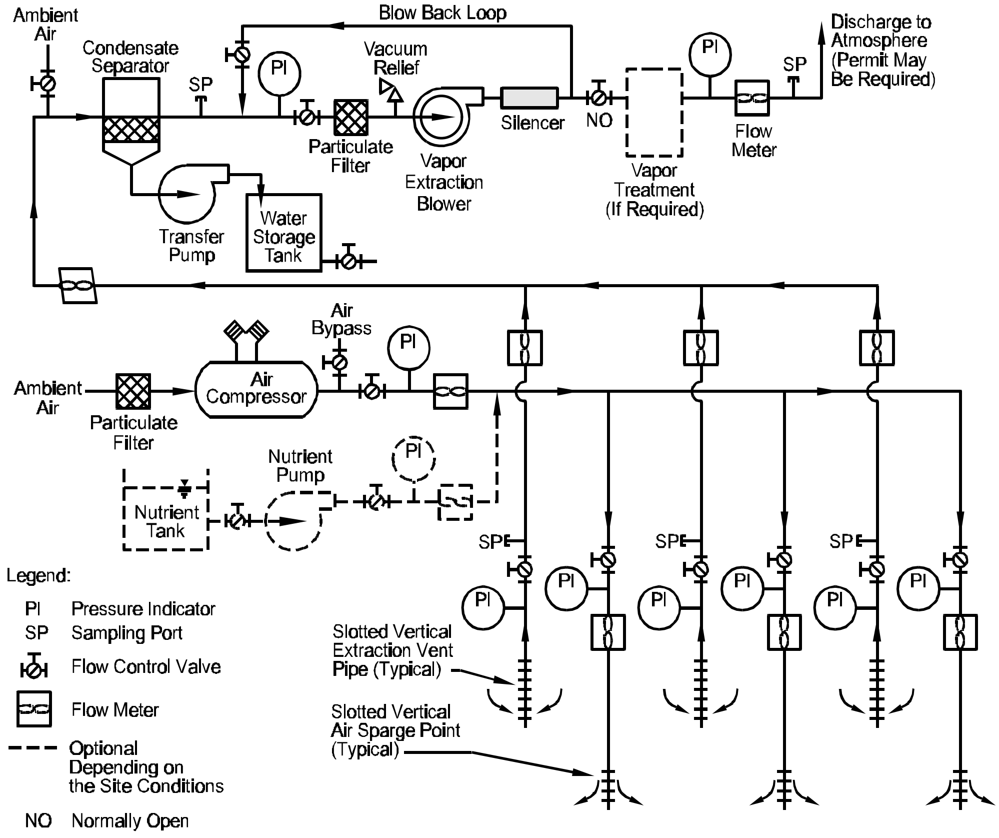
If an SVE system is used for vapor control, the following components and information will also be needed:

- 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)<br>❍ Depth to groundwater (> 10 feet)<br>❍ Fewer than 10 wells<br>❍ Thickness of saturated zone (> 10 feet) |
| Horizontal wells | ❍ Shallow groundwater table (< 25 feet)<br>❍ Zone of contamination within a specific stratigraphic unit<br>❍ System under an operational facility<br>❍ 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.

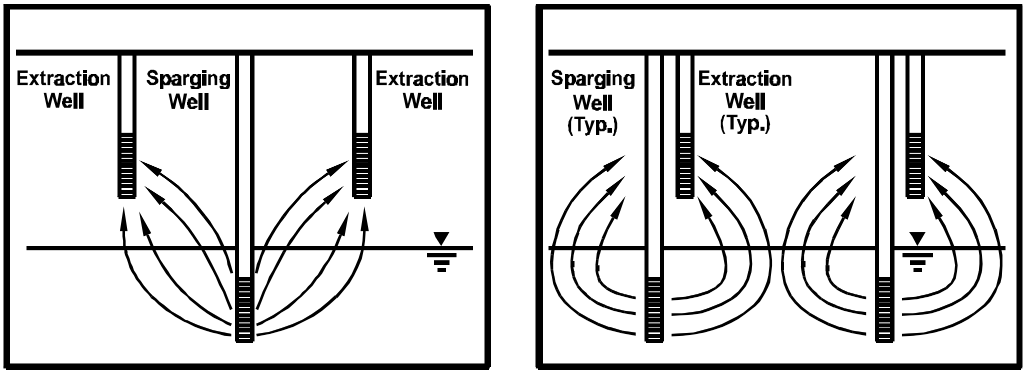
The number and location of extraction wells (if needed) can be determined by using several methods as discussed in Chapter II: Soil Vapor Extraction. However, the following general points should be considered:

- 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.

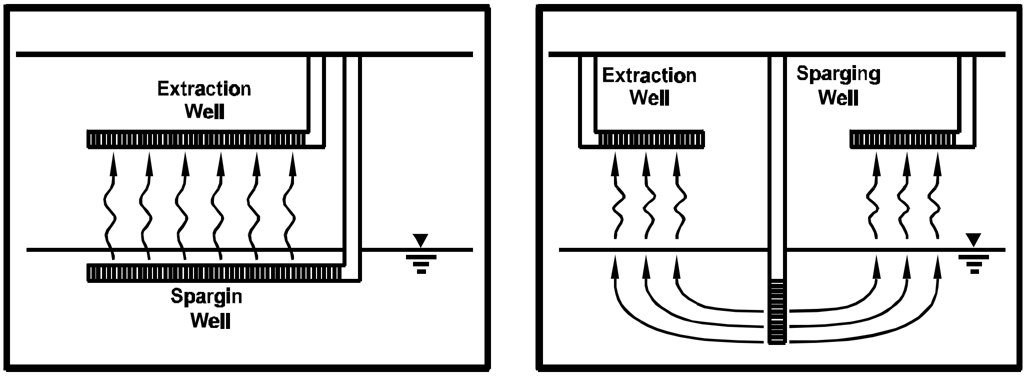
- At sites with stratified soils, wells screened in strata with low permeabilities might require closer well spacing than wells screened in strata with higher permeabilities.

## Exhibit VIII-18
## Biosparging/Vapor Extraction Well Configurations



a) Spaced Configuration

b) Nested Wells



c) Horizontal Wells

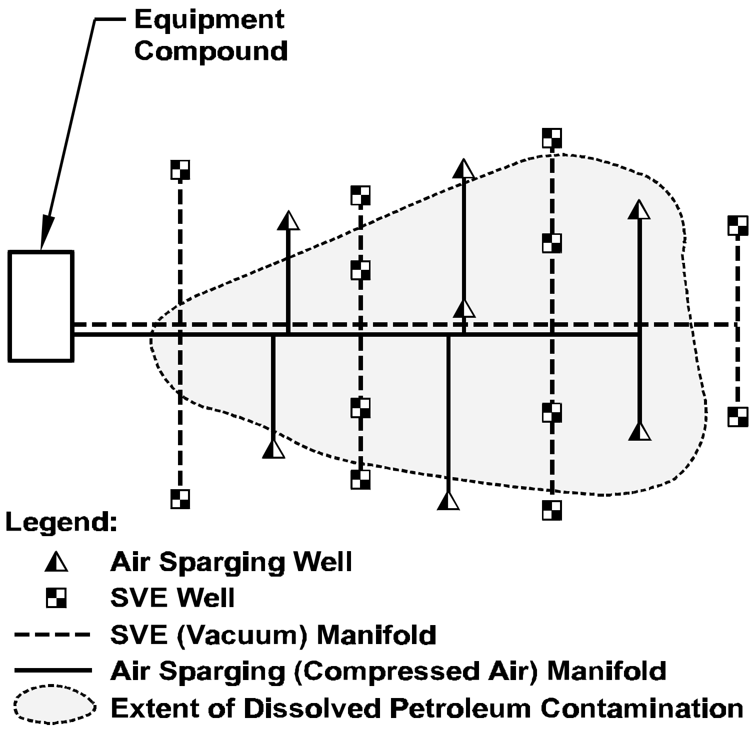
d) Combined Horizontal/Vertical Wells

*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**

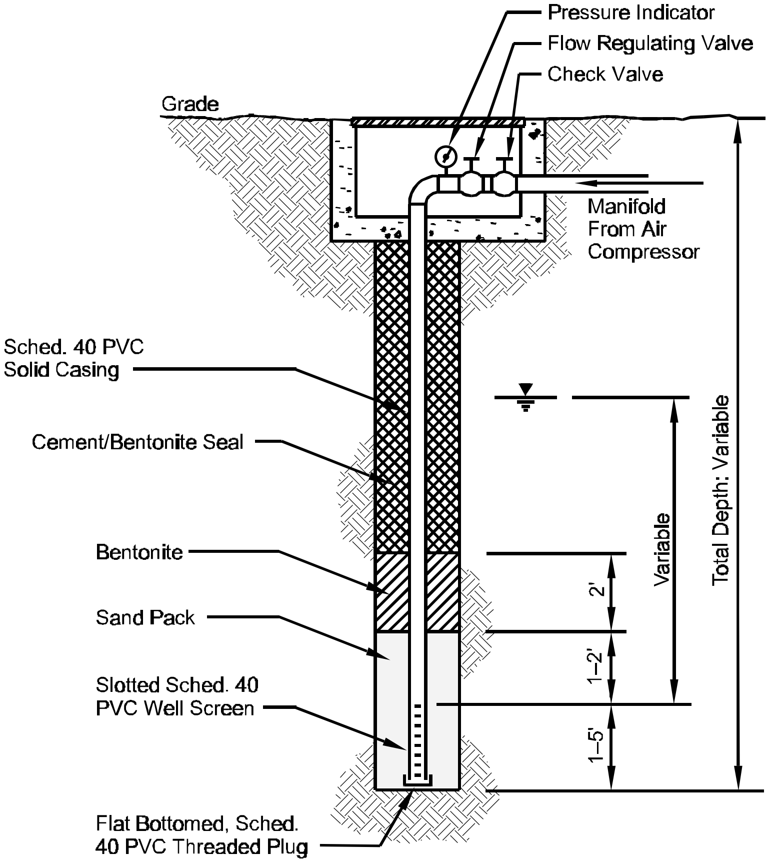


Injection wells should be fitted with check valves to prevent potential line fouling. Fouling occurs when pressure in the saturated zone forces water up the sparge point while the system is shut down. Each sparging well should also be equipped with a pressure gauge and flow regulator to enable adjustments 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

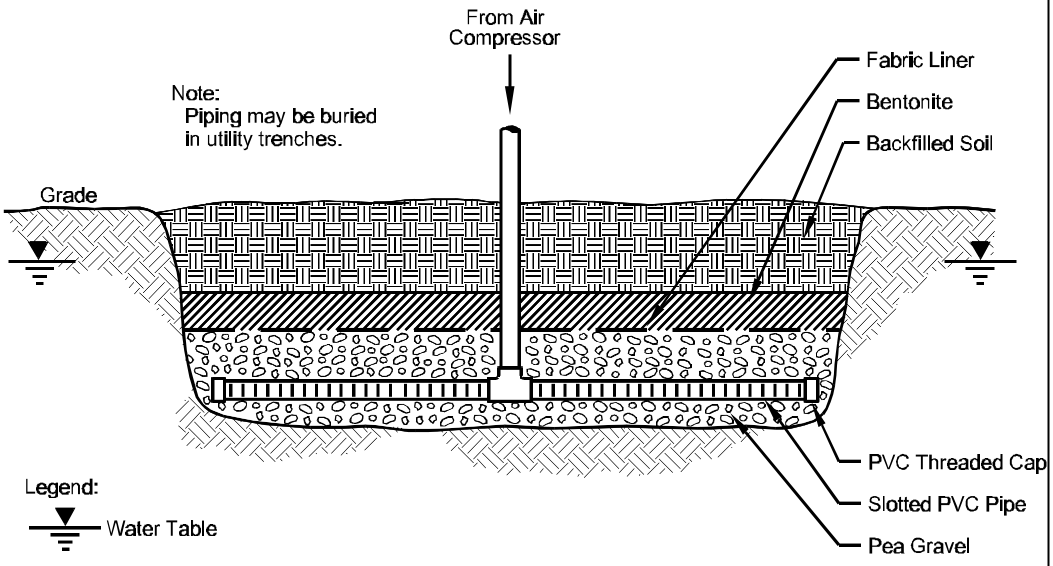


The pressurized air distribution system can be made of metal pipe or rubber-reinforced air hose. PVC pipe should not be connected directly to the compressor because of the high temperatures of air leaving the compressor which can diminish the integrity of the PVC. If pipe trenches are used for the distribution 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<br>❍ Manifold to blower<br>❍ Stack discharge<br>❍ Nutrient manifold | ❍ Pitot tube<br>❍ In-line rotameter<br>❍ Orifice plate<br>❍ Venturi or flow tube<br>❍ Turbine wheel |
| Pressure gauge | ❍ At each sparge and vapor extraction well head or manifold branch<br>❍ Before blower (before and after filters)<br>❍ Before and after vapor treatment | ❍ Manometer<br>❍ Magnehelic gauge<br>❍ Vacuum gauge |
| Sampling port | ❍ At each vapor extraction well head or manifold branch<br>❍ Manifold to blower<br>❍ Blower discharge | ❍ Hose barb<br>❍ Septa fitting |
| **Control Equipment** | | |
| Flow control valves/ regulators | ❍ At each vapor extraction well head or manifold branch<br>❍ Dilution or bleed valve at manifold to blower<br>❍ At header to each sparge point | ❍ Ball valve<br>❍ Gate valve<br>❍ Dilution/ambient air bleed valve<br>❍ Gate valve<br>❍ 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

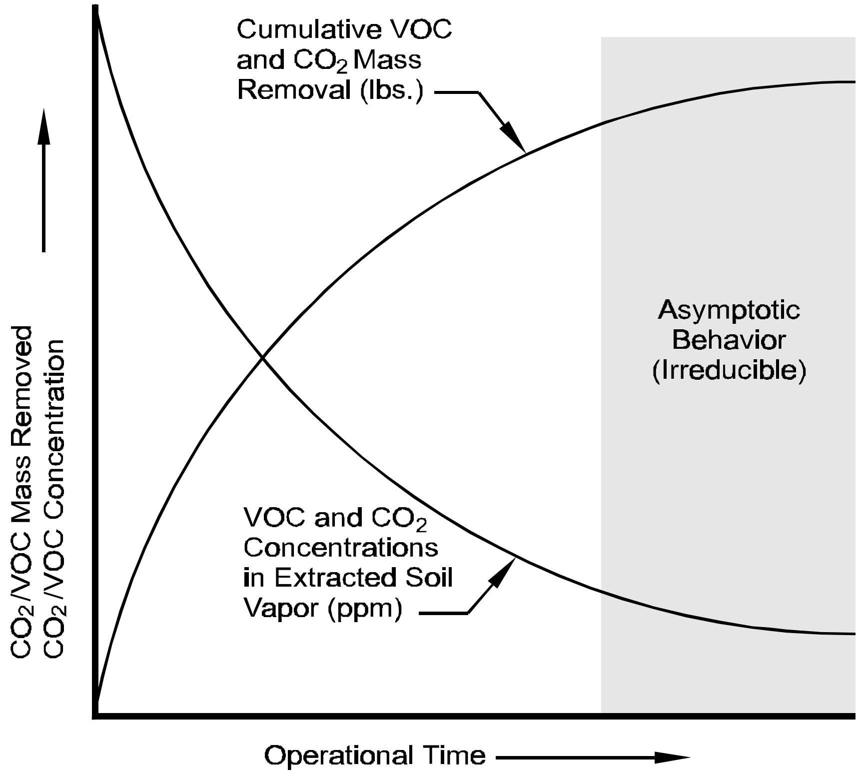
| Phase | Monitoring Frequency | What To Monitor | Where To Monitor |
|---|---|---|---|
| Startup (7-10 days) | At least daily | ❍ Sparge pressure<br>❍ Flow | ❍ Air sparging wellheads<br>❍ Sparge and extraction wells (if used)<br>❍ Manifold<br>❍ Extraction wells (if SVE is used) |
| | | ❍ Vacuum readings (if SVE is used)<br>❍ D.O., $CO_2$, pH | ❍ Groundwater and soil vapor monitoring points |
| | | ❍ Depth to groundwater | ❍ Groundwater monitoring wells |
| Remedial (ongoing) | Weekly to bi-weekly | ❍ Vacuum readings | ❍ Extraction wells (if SVE is used) |
| | | ❍ Vapor concentrations | ❍ Effluent stack (if SVE is used)<br>❍ Manifold (if SVE is used) |
| | | ❍ Sparge pressure and flow | ❍ Air sparging wellheads |
| | | ❍ D.O., $CO_2$, pH | ❍ Groundwater and soil vapor monitoring points |
| | Quarterly to annually | ❍ Dissolved constituent concentrations | ❍ 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.

# References

Norris, R.D., Hinchee, R.E., Brown, R.A., McCarty, P.L., Semprini, L., Wilson, J.T., Kampbell, D.H., Reinhard, M., Bower, E.J., Borden, R.C., Vogel, T.M., Thomas, J.M., and C.H. Ward. *Handbook of Bioremediation*. Boca Raton, FL:CRC Press, 1994.

Norris, R.D., Hinchee, R.E., Brown, R.A., McCarty, P.L., Semprini, L., Wilson, J.T., Kampbell, D.H., Reinhard, M., Bower, E.J., Borden, R.C., Vogel, T.M., Thomas, J.M., and C.H. Ward. *In-Situ Bioremediation of Ground Water and Geological Material: A Review of Technologies*. Ada, OK: U.S. Environmental Protection Agency, Office of Research and Development. EPA/5R-93/124, 1993.

Riser-Roberts, E. *Bioremediation of Petroleum Contaminated Sites*. NCEL, Port Hueneme, CA: C. K. Smoley Publishers, CRC Press, 1992.

Flathman, P.E. and D.E. Jerger. *Bioremediation Field Experience*. Environmental Research Laboratory, Ada, OK: Lewis Publishers, CRC Press, Inc., 1994.

Weston, Inc., Roy F. *Remedial Technologies for Leaking Underground Storage Tanks*. University of Massachusetts, Amherst, MA: Lewis Publishers, 1988.

U.S. Environmental Protection Agency (EPA). *A Technology Assessment of Soil Vapor Extraction and Air Sparging*. Cincinnati, OH: Office of Research and Development. EPA/600/R-92/173, 1992.

## 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 $\leq$ 50,000 ppm and heavy metals $\leq$ 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

# Monitored Natural Attenuation

# Contents

# List Of Exhibits

# List Of Exhibits (cont'd)

# Chapter IX
# Monitored Natural Attenuation

## Overview

The term "monitored natural attenuation" (MNA) refers to the reliance on natural attenuation processes (within the context of a carefully controlled and *monitored* site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods (EPA, 1999). Long-term performance monitoring is a fundamental component of a MNA remedy, hence the emphasis on "monitoring" in the term "monitored natural attenuation". Other terms associated with natural attenuation in the literature include "intrinsic remediation", "intrinsic bioremediation", "passive bioremediation", "natural recovery", and "natural assimilation". Note, however, that none of these are necessarily equivalent to MNA.

MNA is often dubbed "passive" remediation because natural attenuation processes occur without human intervention to a varying degree at all sites. It should be understood, however, that this does not imply that these processes necessarily will be effective at all sites in meeting remediation objectives within a reasonable time frame. This chapter describes the various chemical and environmental factors that influence the rate of natural attenuation processes. Because of complex interrelationships and the variability of cleanup standards from state-to-state and site-to-site, this chapter does not provide specific numerical thresholds to determine whether MNA will be effective.

The fact that some natural attenuation processes are occurring does not preclude the use of "active" remediation or the application of enhancers of biological activity (*e.g.,* electron acceptors, nutrients, and electron donors)[1]. In fact, MNA will typically be used in conjunction with, or as a follow-up to, active remediation measures, and typically only after source control measures have been implemented. For example, following source control measures[2], natural attenuation may be sufficiently effective to achieve remediation objectives without the aid of other (active) remedial measures, although this must be conclusively demonstrated by long-term performance monitoring. More typically, active remedial measures (*e.g.*, SVE, air-sparging) will be applied in areas with high concentrations of contaminants (*i.e.*, source areas) while MNA is employed

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[1] However, by definition, a remedy that includes the introduction of an enhancer of any type is no longer considered to be "natural" attenuation.

[2] Note that MNA may be an appropriate remediation option only after separate phase product has been removed to the maximum extent practicable from the subsurface as required under 40 CFR 280.64.

for the dilute contaminant plume.   In any case, MNA should be used very cautiously as the sole remedy at any given site since there is no immediate backup (although there should be contingency plans in place) should MNA fail to meet remediation objectives.

EPA does not consider MNA to be a “presumptive” or “default” remedy - it is merely one option that should be evaluated with other applicable remedies (EPA, 1999).  EPA does not view MNA to be a “no action” or “walk away” approach, but rather considers it to be an alternative means of achieving remediation objectives that may be appropriate for specific, well-documented site circumstances where its use meets the applicable statutory and regulatory requirements (EPA, 1999).  As there is often a variety of methods available for achieving remediation objectives at any given site, MNA may be evaluated and compared to other viable remediation methods (including innovative technologies) during the study phases leading to the selection of a remedy.  As with any other remedial alternative, MNA should be selected only where it meets all relevant remedy selection criteria, and where it will meet site remediation objectives within a time frame that is reasonable compared to that offered by other methods (EPA, 1999).  Exhibit IX-1 provides a summary of the advantages and disadvantages of using monitored natural attenuation as a remedial option for petroleum-contaminated soils and groundwater.

## Natural Attenuation Processes

Natural attenuation processes include a variety of physical, chemical, and biological processes that, under favorable conditions, reduce the mass, toxicity, mobility, volume, and/or concentration of contaminants in soil and/or groundwater.  Processes that result only in reducing the concentration of a contaminant are termed “nondestructive” and include hydrodynamic dispersion, sorption and volatilization.  Other processes, such as biodegradation and abiotic degradation (*e.g.*, hydrolysis), result in an actual reduction in the mass of contaminants and are termed “destructive” (Weidemeier, *et. al.*, 1999).  For petroleum hydrocarbons, biodegradation is the most important (and preferred) attenuation mechanism since it is the only natural process that results in actual reduction in the mass of petroleum hydrocarbon contamination.  Aerobic biodegradation consumes available oxygen resulting in anaerobic conditions in the core of the plume and a zone of oxygen depletion along the outer margins.  As illustrated by Exhibit IX-2, the anaerobic zone is typically more extensive than the aerobic zone due to the rapid depletion of oxygen, the low rate of oxygen replacement, and the abundance of anaerobic electron acceptors[3]  relative to dissolved oxygen (Weidemeier, *et. al.*, 1999).  For this reason, anaerobic biodegradation is typically the dominant process .  For both aerobic and anaerobic

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[3] Anaerobic electron acceptors include nitrate, sulfate, ferric iron, manganese, and carbon dioxide.  For aerobic respiration the electron acceptor is oxygen.

processes, the rate of contaminant degradation is limited by the rate of supply of the electron acceptor not the rate of utilization of the electron acceptor by the microorganisms. As long as there is a sufficient supply of the electron acceptor, the rate of metabolism does not make any practical difference in the length of time required to achieve remediation objectives.

## Corrective Action Plan (CAP)

The key components of a corrective action plan (CAP) that proposes MNA as a remediation alternative are:

- documentation of adequate source control,
- comprehensive site characterization (as reflected in a detailed conceptual site model),
- evaluation of time frame for meeting remediation objectives,
- long-term performance monitoring, and
- a contingency plan(s).

This chapter is intended to be an aide in evaluating a CAP that proposes MNA as a remedial option for petroleum-contaminated soil and groundwater. Note that a state may have specific requirements that are not addressed in this chapter. The evaluation process is presented in the four steps described below. A series of checklists have also been provided at the end of this chapter. They can be used as tools to evaluate the completeness of the CAP and to help focus attention on areas where additional information may be needed.

P **Step 1:** ***An initial screening of monitored natural attenuation applicability.*** This initial step is comprised of several relatively easily answered questions which should allow for a quick decision on whether or not MNA is even potentially applicable.

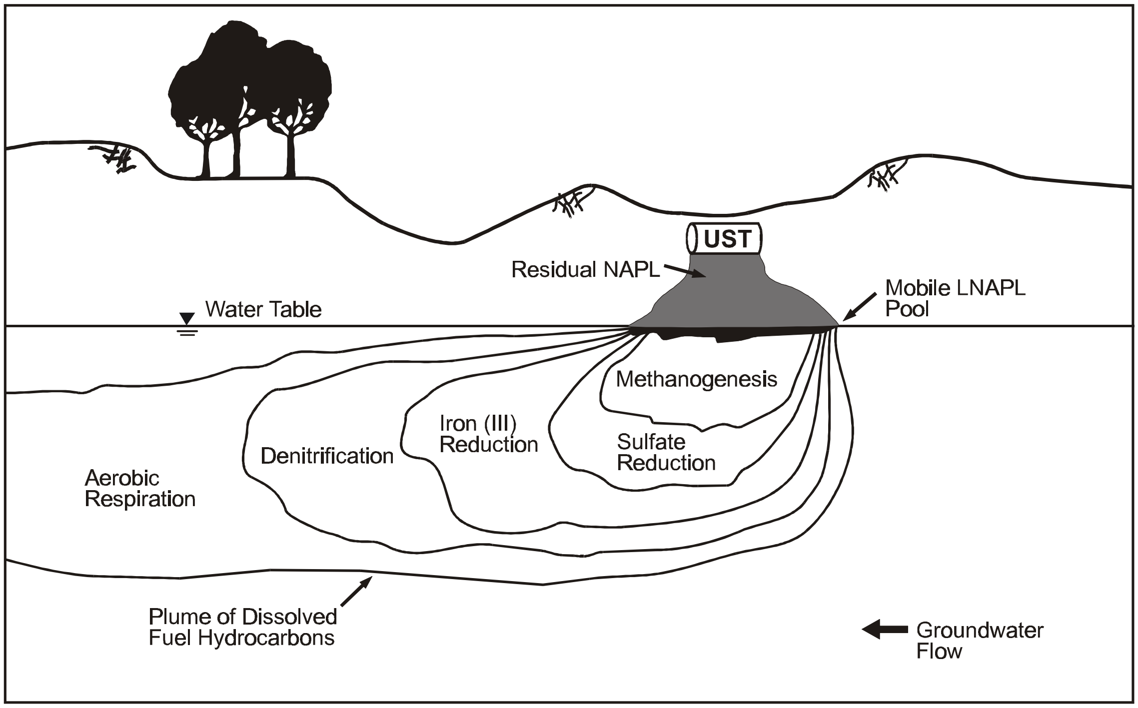
P **Step 2:** ***A detailed evaluation of monitored natural attenuation effectiveness***. This step provides further criteria to confirm whether monitored natural attenuation is likely to be effective. To complete this evaluation, you will need to review monitoring data, chemical and physical parameters of the petroleum constituents, and site conditions. You will then need to determine whether site and constituent characteristics are such that monitored natural attenuation will likely result in adequate reductions of contaminant concentrations.

P **Step 3:** ***An evaluation of monitoring plan***. Once it has been determined that MNA has the potential to be effective, the adequacy of the proposed long-term performance monitoring schedule must be evaluated.

## Exhibit IX-1
## Advantages And Disadvantages Of Monitored Natural Attenuation

| Advantages | Disadvantages |
|---|---|
| P Overall costs may be lower.<br>P Minimal disturbance to the site operations. | P Much less effective where TPH concentrations in soil are high (> 20,000 to 25,000 mg/kg). Not suitable in the presence of free product. |
| P Potential use below buildings and other areas that cannot be excavated. | P Not suitable when contamination has impacted a receptor (*e.g.*, impacted ground water supply well, vapors in a building). |
| P Does not generate remediation wastes. However, be aware of risks from methane produced during natural biodegradation of petroleum hydrocarbons. | P Despite predictions that the contaminants are stationary, some migration of contaminants may occur. Not suitable if receptors might be affected. |
| P Reduced potential for cross-media transfer of contaminants commonly associated with *ex-situ* treatment. | P Longer periods of time may be required to mitigate contamination (especially true for heavier petroleum products). |
| P Reduced risk of human exposure to contaminants near the source area. | P May fail to achieve the desired cleanup levels within a reasonable length of time (and an engineered remedy should instead be selected). |
| P Natural biodegradation may result in the complete destruction of contaminants *in-situ*. | P Site characterization will necessarily be more detailed, and may include additional parameters. Site characterization will be more costly. |
| P May be used in conjunction with, or as follow-up to, active remedial measures. | P Institutional controls may be necessary to ensure long term protectiveness. |
|  | P Performance monitoring will generally require more monitoring locations. Monitoring will extend over a longer period of time. |
|  | P It may be necessary to implement contingency measures. If so, this may increase overall cost of remediation. |
|  | P May be accompanied by changes in groundwater geochemistry that can mobilize other contaminants. |

## Exhibit IX-2
## Conceptualization of Electron Acceptor Zones In the Subsurface



(Adapted from Wiedemeier *et al.*, 1999. NOTE: Due to the presence of the mobile NAPL pool–"free product"–the site depicted in Exhibit IX-2 above would not be an appropriate candidate for MNA. After the free product has been removed from the subsurface to the maximum extent practicable, then the site may be evaluated as to whether or not it would be an appropriate candiate for MNA.)

- **Step 4:** ***An evaluation of the contingency plan.*** In the event that monitoring indicates that MNA does not appear to be effective in meeting remediation objectives in a reasonable time frame, a more aggressive remediation technology will need to be implemented. Several potential alternative technologies are presented in other chapters in this manual, and the applicable chapter should be consulted to evaluate the appropriateness of the contingency remedy.

# Initial Screening Of Monitored Natural Attenuation Applicability

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The policies and regulations of your state determine whether MNA will be allowed as a treatment option. As the first step in the screening process, determine if your state allows the use of MNA as a remedial option. For example, MNA may not be allowed if the contaminant mass is large enough that groundwater impacts are likely (or have already occurred), or if sampling indicates the presence of free product, or an existing contaminant plume isn't shrinking, or if there are potential receptors located nearby. Also be aware that it is possible that while allowing MNA as a remedial option, your state may have requirements that are more stringent than those described in this chapter.

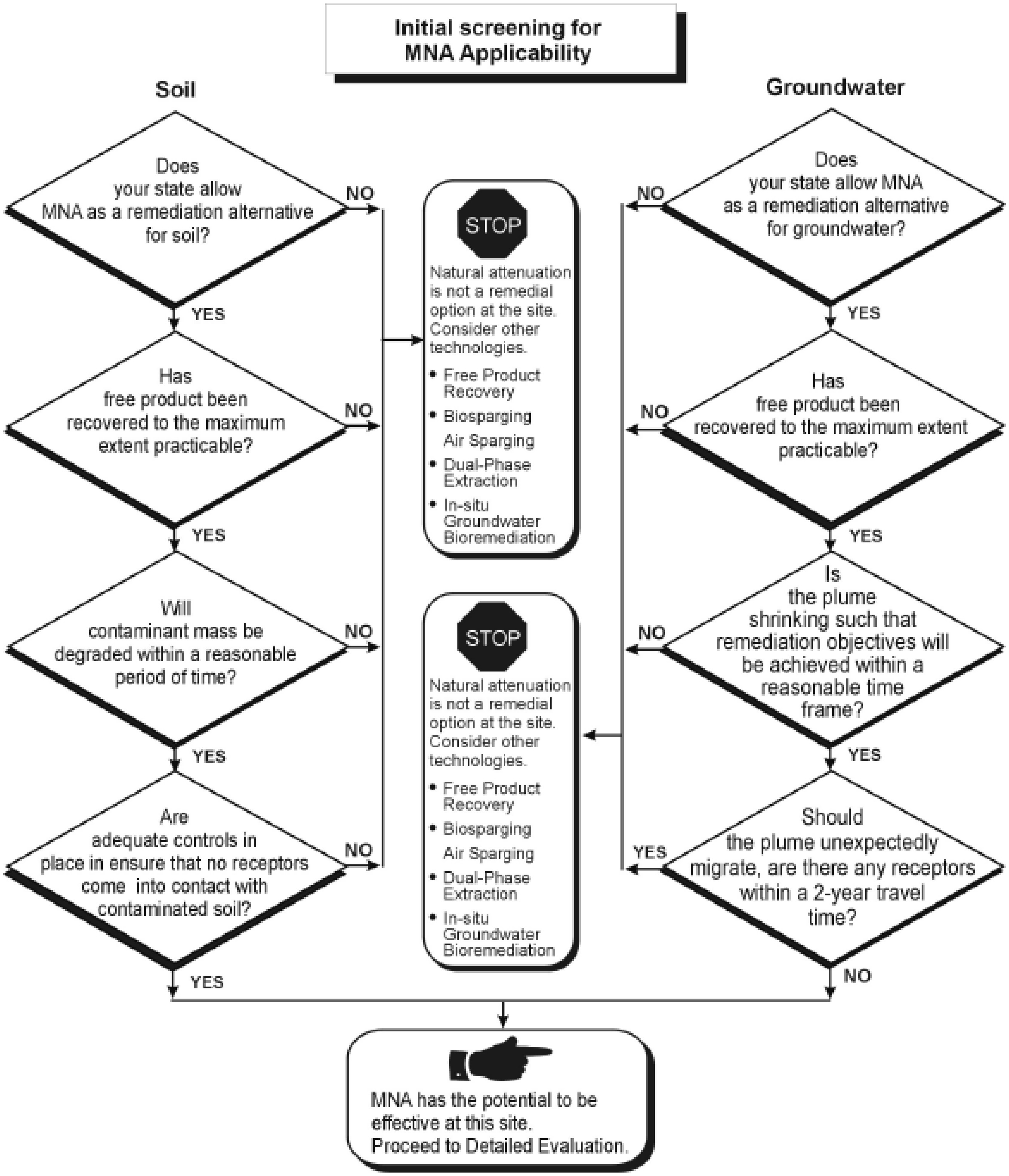
Although the specific screening criteria for both contaminated soil and groundwater might be expected to be very different due to the characteristics of the impacted media, they are actually quite similar. For both media the criteria focus on two elements: (1) source longevity and (2) potential receptor impacts. Source longevity influences not only the time to achieve remediation objectives but also the potential for groundwater contamination and plume migration. Receptors may be impacted through direct contact with source materials (such as residual soil contamination or free product), or through ingestion of dissolved-phase contaminants or inhalation of vapor-phase contaminants. The objective of the initial screening is to determine how long the source is likely to persist, and whether or not there are likely to be impacts to receptors during this time. The following section will provide guidance on how these criteria should be evaluated for either contaminated soil or contaminated groundwater. Exhibit IX-3 is a flow chart that can serve as a roadmap for the initial screening evaluation process. If results of the initial screening indicate that MNA is not likely to be effective, then other more aggressive measures (for example excavation of contaminated soil, or pump-and-treat for groundwater) should be employed.

## Contaminant Transport and Fate

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 hundreds of compounds. Transport and fate characteristics of individual contaminants are a function of their chemical and physical properties.

Each fuel constituent will migrate via multiple pathways depending on its chemical and physical characteristics. Consequently, different chemicals will have different migration pathways. For example, a portion of the benzene in the fuel will partition out of the pure ("free product") phase and into the vapor phase, the sorbed phase, and the dissolved phase. Although the majority of the benzene mass will stay in the free product phase, a significant portion will either volatilize or dissolve into either soil moisture in the vadose zone or groundwater in the saturated zone.

## Exhibit IX-3
## Initial Screening of Monitored Natural Attenuation Applicability



Only a relatively small percentage will sorb onto soil particles. If the soil contains a higher percentage of organic carbon, a higher percentage of benzene will potentially be sorbed. In contrast to benzene's behavior, ethylbenzene will more likely sorb onto soil particles and would not be as soluble in water. Exhibit IX-4 is a schematic illustration of the interrelationships among the attenuation processes that govern the partitioning of free product into the soil, water and air in the subsurface environment.

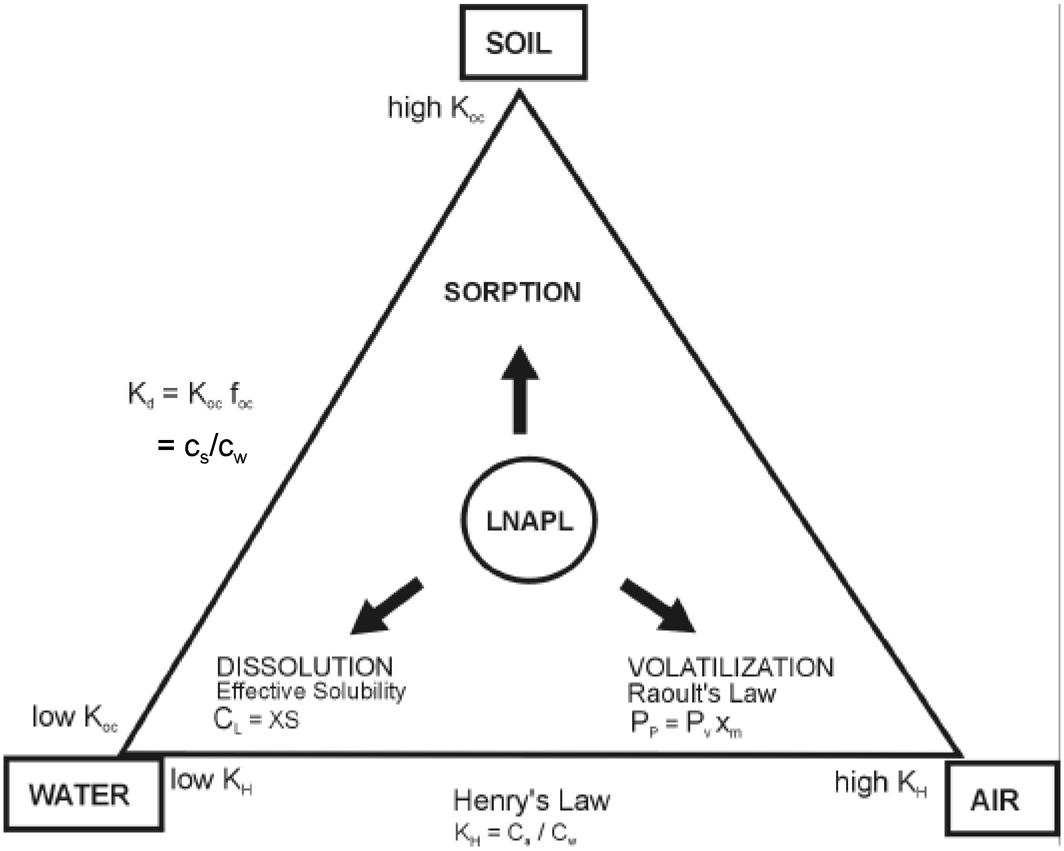
## Contaminated Soil

Often the primary concern associated with contaminated soil is that it can result in contamination of groundwater resources. Secondary concerns are direct exposure to the contaminated soil itself and vapors originating in the source area. However, given the particular conditions at a site, the relative order of these concerns may change. The potential for receptor impacts depends upon a number of site-specific conditions of which two of the most important are source mass and source longevity.

Despite the relatively low solubility of the hydrocarbons in petroleum fuels, they can be leached downward from the soil in the source area into the underlying groundwater. For the more soluble gasoline additives (for example MTBE and ethanol) this is especially true. Contaminated soil in the vadose zone can also be the source of vapors which migrate through the more permeable pathways in the soil and can accumulate in subsurface areas such as basements, parking garages, sewers and utility vaults. Where these vapors collect in sufficient quantity they can present an immediate safety threat from explosion, fire, or asphyxiation. Inhalation of lower concentrations of vapors over the long-term can lead to adverse health effects. All of these problems are magnified with increasing mass of contaminants and increasing amount of time that they are allowed to remain in the subsurface. The best way to reduce the likelihood of groundwater contamination and shorten the time required to achieve remediation objectives is to quickly and completely eliminate the mass of contamination in the subsurface. Contaminated soils may be remediated by a variety of *in situ* and *ex situ* technologies described in other chapters of this document. These include bioventing (Chapter III), soil vapor extraction (Chapter II), enhanced aerobic biodegradation (Chapter XII), chemical oxidation (Chapter XIII), low temperature thermal desorption (Chapter VI), biopiles (Chapter IV) and landfarming (Chapter V).

In several of the following sections on evaluation of MNA for soil-only sites (both in the initial and detailed evaluation sections) examples will be presented to illustrate the evaluation methodology. For consistency, three representative soils types are used with parameter values derived from the literature. Also, a hydrocarbon density of 730 kg/m$^3$ (typical of gasoline) was used and assumed to be representative of gasoline. Though it is possible that some of these examples may be representative of some actual sites, these exhibits are intended only to illustrate a methodology that could be used; in all cases site-specific data should be used to develop screening values.

## Exhibit IX-4
## Processes Governing the Partitioning of LNAPL Into the Soil, Water, and Air in the Subsurface Environment



where:
$K_d$ = the distribution coefficient
$K_{oc}$ = organic carbon normalized soil/water partition coefficient
$f_{oc}$ = fraction of organic carbon in soil
$C_L$ = effective solubility of a given solute
$X$ = mole fraction of a given solute in a mixture
$S$ = pure phase solubility of a given solute
$P_p$ = partial pressure of a given gas
$P_v$ = vapor pressure of a given gas
$X_m$ = mole fraction of a given gas in a mixture
$K_H$ = Henry’s law constant for a given solute
$C_a$ = concentration of a given solute in vapor phase
$C_w$ = concentration of a given solute in aqueous phase
$C_s$ = concentration of a given solute in soil phase

If there is a possibility that groundwater will be impacted, or if protection of a particular groundwater resource is of vital importance, then a more detailed analysis (including the collection and analysis of groundwater samples) should be conducted and the appropriateness of MNA as a remedial alternative should be based on groundwater criteria instead of soil criteria.

### *Source Mass*

Regardless of how biodegradable a contaminant may be, the larger the contaminant mass to be degraded, the longer it will take to do so. Obviously, the more biodegradable a contaminant is, the faster it will be degraded relative to a more recalcitrant (nondegradable) contaminant. The larger the source and the longer it resides in the subsurface, the greater the likelihood that groundwater contamination will occur. This is especially true when the depth to groundwater is relatively shallow, the amount of annual rainfall (and hence groundwater recharge) is high, and the soil is relatively permeable (and the soil surface is not covered with an impervious material such as asphalt or concrete).

Although an accurate estimate of the mass of the fuel release usually is not known, a legitimate attempt should be made to quantify the release volume. In the absence of reliable inventory data, the volume of fuel in the subsurface can be estimated by first determining the extent of contaminated soil and then integrating saturation data from soil samples over the volume of the contaminated soil mass. (For more information, see EPA, 1996b, Chapter IV.) The objective is to sufficiently characterize the extent and level of contamination with a minimum number of samples, although the accuracy of the volume estimate generally increases with an increasing number of samples. At a minimum, samples should be collected from locations where contamination is known to be greatest (*e.g.*, beneath the leaking UST or piping). Soil samples should be collected from the source area in the unsaturated zone and in the smear zone (if any) to define the three-dimensional extent of contamination.

These samples should be analyzed for the BTEX contaminants, TPH, and any other contaminants of concern at the site. If the primary contaminants of concern at the site are volatile organic chemicals (VOCs), monitoring of soil gas should supplement direct soil measurements at some locations. In addition, soil gas samples should be analyzed for oxygen, carbon dioxide, and methane (and sometimes hydrogen) to determine the microbial activity in the soils. As described above, reduced oxygen concentrations in the plume area (relative to background) and elevated carbon dioxide concentrations are a good indication that biodegradation is occurring.

Different soil types have different capacities for “holding” or “retaining” quantities of hydrocarbons released into the subsurface. The capacity for any particular soil type depends upon properties of both the soil and the type(s) of hydrocarbons released. In general, residual hydrocarbon saturation ($s_r$) increases with decreasing grain size. If it is assumed that a given volume of soil is initially hydrocarbon-free, the volume of hydrocarbon that the soil can retain is given by:

$$V_r = s_r \; n_e \; V_{soil}$$

where: $V_r$ = volume of hydrocarbon retained [$L^3$]

$s_r$ = residual hydrocarbon saturation [volume hydrocarbon/volume soil]
$n_e$ = effective porosity [volume pore space/volume soil]
$V_{soil}$ = volume of soil [$L^3$]

The above equation is simplistic and does not address factors such as spreading of the hydrocarbon, the rate at which the soil absorbs the liquid, or mass loss due to volatilization. However, it can be used as a screening criterion to determine whether a given UST release is likely to result in free product accumulation at the water table.

Exhibit IX-5 presents typical ranges for the concentration of hydrocarbons (*e.g.*, TPH) that each of three representative soil types could retain in the unsaturated zone. Values in the second column under "Concentration" are in terms of mass per square meter (kg/m$^2$). To obtain these values, first multiply the concentration in mg/kg by the bulk density of the soil (in kg/m$^3$) then divide by 1 million (to convert from mg to kg). Next, multiply the result by the thickness (in meters) of the contaminated soil. These concentrations can then be used to develop a rough "rule of thumb" to predict whether a spill will reach the water table. The volume of the material receiving the spill is estimated by multiplying the depth to ground water (in meters) by the "surface" area of the spill–this is the assumed thickness (in meters) of the contaminated soil. If no other information is available, assume the surface area is 1 m$^2$ (necessary to yield a volume). If the known (or suspected) volume of release (in gallons) divided by the volume (in cubic meters) to the water table exceeds the number of gallons per cubic meter (last column), then it is likely that free product will be present.

**Exhibit IX-5**
**Maximum Hydrocarbon Concentrations For Soil-Only Contamination**

| **Soil Type** | **Residual Hydrocarbon Saturation** | **Bulk Density[a] (kg/m$^3$)** | **Porosity[b]** | **Concentration** | | |
|---|---|---|---|---|---|---|
| | | | | mg/kg | kg/m$^2$ | gal/m$^3$ |
| silty clay | 0.05 to 0.25 | 1,350 | 0.36 | 10,000 to 49,000 | 13 to 66 | 5 to 24 |
| sandy silt | 0.03 to 0.20 | 1,650 | 0.41 | 5,000 to 36,000 | 9 to 60 | 3 to 22 |
| coarse sand | 0.01 to 0.10 | 1,850 | 0.43 | 2,000 to 17,000 | 3 to 31 | 1 to 11 |

Sources: [a] Boulding (1994), p.3-37. [b] Carsell and Parrish (1988)

Another use for the data in Exhibit IX-5 would be to compare measured hydrocarbon concentrations in soil samples with those in the table (second to last and next to last columns)—if measured concentrations are close to or exceed those in the table for a given soil type, then it could be expected that free product might accumulate at the water table. In situations where free product is present, monitored natural attenuation is not an appropriate remedial alternative because natural processes will not reduce concentrations to acceptable levels within a reasonable time period (*i.e.*, a few years). At all sites where investigations indicate that free product is present, Federal regulations (40 CFR 280.64) require that it be recovered to the maximum extent practicable. Free product recovery, and other engineered source control measures, are the most effective means of ensuring the timely attainment of remediation objectives. For more guidance on free product recovery, see U.S. EPA, 1996a.

From Exhibit IX-5 we see that one cubic meter of silty clay could potentially retain 5 to 24 gallons of gasoline assuming that it was spread evenly through the soil. For a LUST site where the depth to groundwater below the point of the release was, for example, 5 meters (15 feet), there is no information on the surface area of the spill, and the soil type is silty clay, then a release of up to 120 gallons (24 gallons per meter times five meters depth) might be retained within the unsaturated zone and free product would not be expected to accumulate on the water table. In contrast, a coarse sand might potentially retain a release of only 55 gallons. In either or both of these cases even if the release volume was small enough so that free product did not collect at the water table there could still be a groundwater impact through leaching of soluble hydrocarbons by infiltration of precipitation and groundwater recharge. In such an instance, release volumes much smaller than theoretically retained could result in significant and unacceptable groundwater impact.

### *Source Longevity*

Once it has been determined that the entire release volume will remain trapped within the vadose zone and there is no likelihood of groundwater contamination, the next step is to estimate the lifetime of the residual contamination. The two primary factors that control source longevity are: (1) mass of contaminants present in the source area, and (2) availability of electron acceptors, of which oxygen is the most important.

As previously discussed, the larger the contaminant mass, the longer the period of time required for it to be completely degraded. Across a wide range of concentrations, the rate of biodegradation of petroleum hydrocarbons follows a hyperbolic rate law:

$$V = V_{\max}\left[C / (K + C)\right]$$

where: $V$ = the achieved rate of biodegradation (mg/liter in groundwater or mg/kg in soil)

$V_{max}$ = the maximum possible rate of biodegradation at high concentrations of hydrocarbon

$C$ = the concentration of hydrocarbon (mg/liter or mg/kg)

$K$ = half-saturation constant (the concentration of hydrocarbon that produces one-half of the maximum possible rate of biodegradation; mg/liter in water or ppm [volume/volume in soil gas] or mg/kg in sediment)

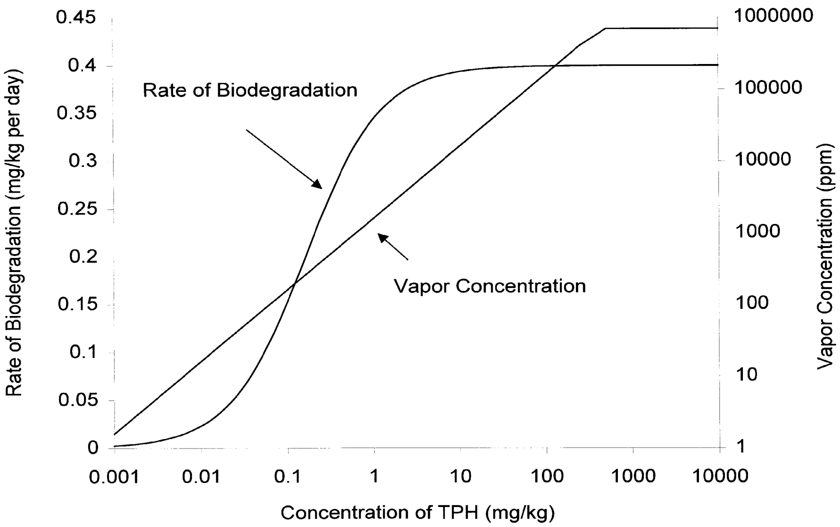
When hydrocarbon concentrations ($C$) are significantly lower than the half-saturation constant ($K$), the sum of ($K$+$C$) is approximately equivalent to $K$. Because $V_{\max}$ and $K$ are constants, the rate of biodegradation ($V$) is proportional to the concentration of hydrocarbon ($C$). As the concentration of hydrocarbon decreases through biodegradation, the rate of biodegradation declines as well (*i.e.*, biodegradation follows a first-order rate law). When hydrocarbon concentrations are significantly higher than the half saturation constant, the sum of ($K+C$) is approximately equivalent to $C$ and the value of $C/(K+C)$ approaches 1.0. Thus, the achieved rate of biodegradation ($V$) approaches the maximum rate ($V_{max}$). When $C$ is more than ten times the value of $K$, the rate of biodegradation will be more than 90% of the maximum rate ($V_{max}$). These relationships are illustrated in Exhibit IX-6.

In Exhibit IX-6, $V_{max}$ has been set at a value of 0.4 mg TPH per kg sediment per day. This corresponds to the $V_{max}$ published for aerobic degradation of aviation gasoline vapors by Ostendorf and Kampbell (1991). The concentration of hydrocarbon vapors was calculated from the concentration of TPH, assuming that the air-filled porosity was 10%, the water-filled porosity was 10%, the sediment bulk density was 1.8 kg/liter, and the partition coefficient of dissolved hydrocarbon between water and air was 0.24. The rate of biodegradation was calculated from the concentration of hydrocarbons vapors, using a half saturation constant for aerobic biodegradation of aviation gasoline vapors of 260 ppm (Ostendorf and Kampbell, 1991).

The point of the preceding discussion is that at the high hydrocarbon concentrations typical of source areas in the unsaturated zone, the amount of hydrocarbons degraded per unit time is approximately constant, regardless of the actual concentration of hydrocarbons (*i.e.*, biodegradation follows a zero-order rate law). And, because the rate of degradation is constant with time, the time required for complete biodegradation is directly proportional to the initial concentration of hydrocarbons to be degraded. The difference between such an approximate rate (zero-order) and the true rate (first-order) is less than the usual statistical variation in the measurements.

The applicability of the above equation has been demonstrated in the field by Moyer *et al.* (1996). Thier work demonstrates that a zero-order rate law is the appropriate law to describe the biodegradation of hydrocarbons in the unsaturated zone. They found that the half saturation constant for biodegradation of hydrocarbon vapors in a sandy soil varied from 0.2 mg/kg to 1.6 mg/kg. As explained in the preceding paragraphs, when hydrocarbon concentrations are more than ten times the half saturation constant (*i.e.*, 2 mg/kg to 16 mg/kg for this example), the rate of biodegradation will approach the maximum rate. Note that these concentrations are already near or below cleanup (or action) levels for hydrocarbons in soil at many sites. Consequently, it can be assumed that biodegradation of hydrocarbons, at least in the relatively shallow unsaturated zone, should follow a zero-order rate law all the way down to cleanup levels. Be aware that this approximation applies only to petroleum hydrocarbons in the unsaturated zone: a first-order rate law must be used to determine the rate of biodegradation of hydrocarbons dissolved in groundwater.

## Exhibit IX-6.
## Graph of hyperbolic rate law for aerobic biodegradation of gasoline



Generally, petroleum hydrocarbons will be degraded most rapidly by microorganisms that require oxygen to sustain their metabolism. In situations where there is an abundance of oxygen and an excess of hydrocarbons for them to metabolize, aerobic microorganisms should degrade hydrocarbons at or near the theoretical maximum rate. But, this rarely occurs in the field for a variety of reasons. Oxygen is rapidly depleted in source areas in particular. Oxygen diffusion from the atmosphere through the soil in the soil gas to the smear zone containing hydrocarbons is a slow process, and when subsurface oxygen is depleted, it takes a relatively long time to replenish. As a consequence, the rate of aerobic biodegradation is limited by the rate that oxygen is supplied to the microorganisms by diffusion through the vadose zone.

Aerobic biodegradation is most effective in soils that are relatively permeable (with a hydraulic conductivity of about 1 ft/day or greater) to allow transfer of oxygen to subsurface soils where the microorganisms are degrading the petroleum constituents. Not surprisingly, the length of time required for oxygen to diffuse into the soil increases as the depth increases. The diffusion rate is also proportional to the air-filled porosity of the soil and the steepness of the diffusion gradient. Finer textured materials have more water-filled porosity and less air-filled porosity at field capacity. Soils with a low oxygen diffusion capacity can hinder aerobic biodegradation. Exhibit IX-7 presents calculations of the rate that hydrocarbons that could be mineralized if oxygen diffusion was the limiting factor.

## Exhibit IX-7
## Rate of Aerobic Biodegradation of Hydrocarbons (mg/kg/d)that can be Sustained by Diffusion of Oxygen through the Vadose Zone (Calculated for a Smear Zone that is One Meter Thick)

| Depth to Top of Contaminated Soil (meters) | Silty Clay | Sandy Silt | Coarse Sand |
|---|---|---|---|
| 1 | 5 | 12 | 22 |
| 2 | 2 | 6 | 11 |
| 3 | 2 | 4 | 7 |
| 4 | 1 | 3 | 6 |

Comparing Exhibit IX-5 and Exhibit IX-7, it is readily apparent that aerobic degradation of hydrocarbons under natural conditions won't expeditiously cleanup contamination, especially in tight soils. Using the biodegradation-capacity data in Exhibit IX-7 and applying it to the range of contamination levels in Exhibit IX-5 for each of the three representative soil types, projections can be made on the length of time (in years) that would be required for aerobic biodegradation to completely mineralize residual gasoline in the unsaturated zone. As a rough approximation, the time required to degrade hydrocarbons in the vadose zone can be estimated by dividing the highest concentration of hydrocarbon (TPH in mg/kg) by the rate of biodegradation of hydrocarbon (mg/kg per day). For example, a silty clay is able to retain 10,000 mg/kg to 49,000 mg/kg of hydrocarbon at residual saturation, but will support aerobic degradation of only 5 mg/kg/day at a depth of only 1 meter below land surface. Even for this relatively shallow contamination, it is projected that complete degradation would require from 6 to 28 years. With each meter of increased depth, the length of time increases by a multiple of approximately this same amount. Thus, for a depth of 3 meters, the projected length of time ranges from 17 to 84 years (approximately 3 times the range of 6 to 28 years).

These calculations of the rate of biodegradation allowed by diffusion of oxygen put an upper boundary on the rate of biodegradation, and a lower boundary on the time required to clean up a spill of gasoline. For comparison, results are also presented (last column of Exhibit IX-8) of the calculated time required for clean up when the maximum rate of biodegradation ($V_{max}$ ) is relatively slow. The time required was calculated using the $V_{max}$ (0.41 mg/kg per day) reported by Ostendorf and Kampbell (1991) in the well-oxygenated unsaturated zone above the residually-saturated capillary fringe at an aviation gasoline release site in Michigan. The fertility of the sediment at this site is low, and as a consequence, the rate of biodegradation is slow compared to rates at other sites. When the rate of biodegradation is slow, the time required to clean up the gasoline may be longer than would be expected if the supply of oxygen supplied through diffusion was the limiting criteria.

### Exhibit IX-8
### Time Required (Years) To Consume Hydrocarbons Present At Residual Saturation

| | | Oxygen Diffusion-Limited Depth (meters) to top of contaminated soil in the vadose zone | | | | Bio-degradation -Limited |
|---|---|---|---|---|---|---|
| **Soil Type** | **TPH at Residual Saturation (mg/kg)** | **1** | **2** | **3** | **4** | **0.41 mg/kg per day** |
| silty clay | 10,000 to 49,000 | 6 to 28 | 11 to 56 | 17 to 84 | 23 to 113 | 67 to 326 |
| sandy silt | 5,000 to 36,000 | 1 to 9 | 2 to 17 | 4 to 26 | 5 to 34 | 33 to 240 |
| coarse sand | 2,000 to 17,000 | <1 to 2 | <1 to 4 | 1 to 6 | 1 to 8 | 13 to 113 |

These Exhibits (IX-5 through IX-8) demonstrate several important points. First, and most importantly, there is no substitute for field-measured rates of biodegradation. Estimates based on theory, microcosm studies, literature values, or modeling results should not be relied on as the sole basis for regulatory decision-making. Second, even for permeable material (*e.g.*, coarse sand) the concentration of hydrocarbon that can be biodegraded within a reasonable time frame (*e.g.*, 1 to 5 years) is relatively low. Third, although oxygen won't be the limiting criteria at many sites, the rate of aerobic biodegradation may still result in time frames measured in decades to achieve remediation objectives. And fourth, given the long projected times to achieve remediation objectives through reliance on natural processes alone, it will often be more effective and efficient to use an active remediation technology (e.g., bioventing, soil excavation, SVE) to mitigate the contaminant source even in the rare case where groundwater impacts are not anticipated.

### *Potential For Receptor Impacts*

For contamination which remains in the soil in the vadose zone, the primary potential impacts to receptors are from direct contact with (or ingestion of) contaminated soil, safety threats due to fire and explosion hazards from accumulations of vapors, and health effects cause by inhalation of vapors. Each of these potential impacts should be fully evaluated. It is important to determine whether there are receptors that could come into contact with contaminated soil. 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 them. However, if the contaminated soils might be excavated (*e.g.*, for construction) before contaminant concentrations have been adequately reduced, 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. The CAP should address these potential concerns and means of control.

Vapor generation and migration are generally of greater concern with the more volatile and flammable petroleum fuels (*e.g.*, gasoline). However, even with less volatile, combustible fuels (*e.g.*, heating oil) sufficient accumulations of vapors may occur. Like liquids, vapors move faster through the soil in zones of higher permeability than in zones of low permeability. Common vapor migration routes are in the coarse backfill around utility lines and conduits, in open conduits such as sewers, and through naturally permeable zones in the soil (*e.g.*, gravel stringers, fractures). Basements tend to draw in vapors in response to differential pressure gradients. In any of these situations, accumulations of vapors can present a safety threat from fire or explosion, as well as adverse long-term health effects. The potential for vapor generation and migration, and means to mitigate these hazards, should be addressed in the CAP.

## Contaminated Groundwater

The two most common sources of groundwater contamination are from contaminated soil and free product. If left unaddressed, contaminated soil and/or free product can be a source of groundwater contamination that may persist for decades to centuries. Under certain conditions vapors, which are released directly into the soil, can also result in groundwater contamination. While some states may have in place resource nondegradation policies that could drive cleanup decisions, more often than not these decisions are made based on health-related impacts to human receptors followed by consideration of potential impacts to third parties. The two primary questions to consider when evaluating the potential impacts of contaminated groundwater are: “How long will the contaminant plume persist?” and “Will the contaminant plume migrate from the source area and reach current or future receptors?”

### *Plume Persistence*

There are two key factors which control the persistence of a contaminant plume: (1) source mass, and (2) contaminant biodegradability. As one would expect, the larger the source mass the longer the persistence of the source and the greater the likelihood that a significant groundwater plume will form. If the volume of the release is sufficient such that free product is present on the water table, then MNA is not an appropriate remediation alternative. In fact, Federal regulations under 40 CFR 280.65 require that free product be recovered to the maximum extent practicable. For more information on free product recovery, see U.S. EPA, 1996a.

The longevity of the source is controlled by the rate of weathering of the residual fuel in the source area. If a portion the residual fuel is above the water table, volatilization also can remove contaminant mass. As groundwater flows past residual fuel, the water soluble constituents such as benzene, toluene, ethylbenzene, and three isomers of xylene (BTEX) plus oxygenates such as MTBE and ethanol will partition from the residual fuel mass into the groundwater and be transported downgradient. The concentration of any particular fuel constituent in groundwater is proportional to its mole fraction in the residual fuel. Over time, the mass of water soluble components remaining in the residual fuel is depleted and the groundwater concentrations of these components decrease. Conversely, as the mole fraction of less soluble components increases, their concentrations in the plume actually increase. Once the soluble components have dissolved into the groundwater, they can also be removed by biodegradation. The rate at which all these processes remove these components from residual fuel is roughly proportional to the fraction of the components that remain the residual fuel. As a consequence, the rate of overall weathering will typically follow a first order rate law with time.

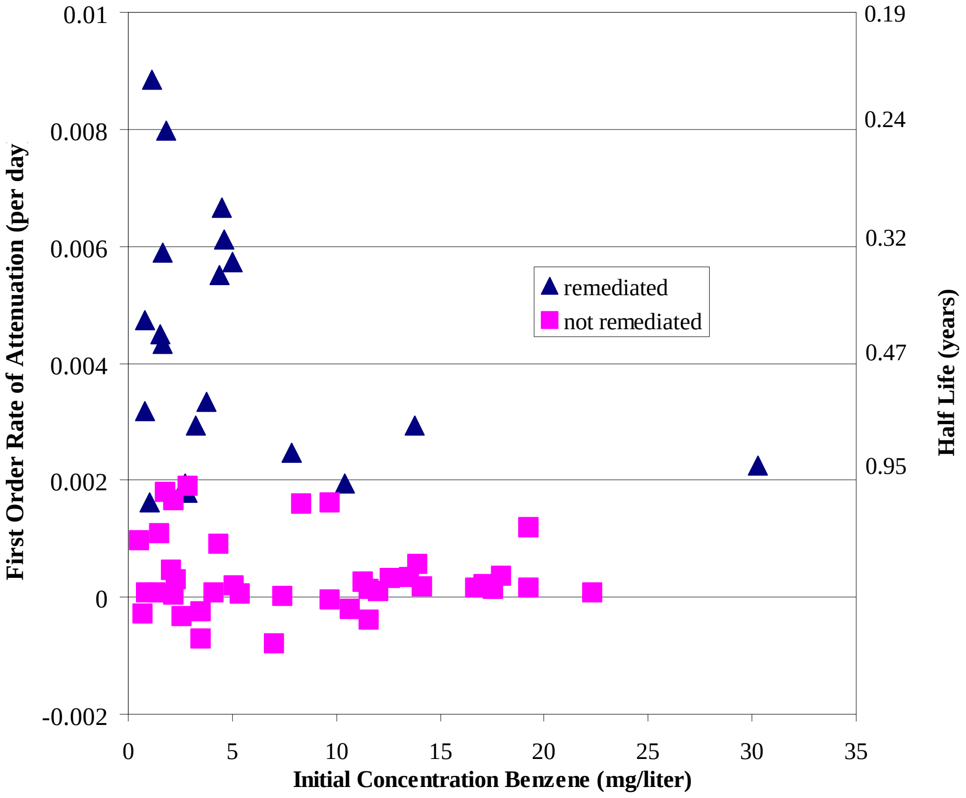
To estimate the achieved rate of attenuation of benzene and MTBE in groundwater in contact with residual gasoline, Peargin (2000) examined the long-term trends in the concentration of benzene and MTBE in monitoring wells that were screened in the LNAPL smear zone at 23 UST release sites. Source remediation had been completed at 8 of these sites; no remediation had been attempted at the remaining 15 sites. The first order rate of attenuation of benzene and MTBE was calculated from monitoring data from 79 wells for which statistically significant rates of attenuation could be derived. Exhibit IX-9 is a plot of the calculated attenuation rate versus initial benzene concentration for both remediated and non-remediated sites.

Although the rates of natural attenuation of benzene in the smear zone varied widely, there is a clear difference between rates at sites where active remediation had been completed, and sites with no active remediation. At sites with active remediation, the rate of attenuation of benzene in the source is near to or greater than 0.0022 per day, equivalent to a half-life of just under one year. At sites without remediation, the mean rate of attenuation of benzene is 0.00037 per day, equivalent to a half-life of more than five years. For benzene, the attenuation rate at remediated sites is about 6 times faster than that for the non-remediated sites. Peargin (2000) also presented data on the persistence of MTBE in wells in the smear zone. These data indicate the mean rate of attenuation at sites without remediation is 0.00011 per day, equivalent to a half life of seventeen years. For sites with active remediation the rate of attenuation of MTBE is 0.0035 per day, equivalent to a half-life of about 6 months. For MTBE, the attenuation rate at remediated sites is about 30 times faster than that for the non-remediated sites.

Note that for several of the non-remediated sites contaminant concentrations are increasing over time. It is also apparent that slower rates of attenuation of the source are associated with higher initial contaminant concentrations, thus, a longer period of time is required to achieve adequate reductions in concentration. For the case of both benzene and MTBE, significant reductions in the amount of time required to achieve cleanup goals can be realized if the source is adequately remediated. This is especially true with larger and more recent releases.

If the source contains sufficient mass of contaminants such that natural degradation will require longer than a decade (or other reasonable period of time), then MNA is generally not an appropriate remedial alternative. For a time frame of this duration, performance monitoring is going to be costly, and it is highly uncertain that the remedy will be protective. There is simply too much mass in the system and more aggressive measures should be implemented to reduce the mass in order for MNA to be able to achieve remediation objectives within a time frame that is reasonable.

## Exhibit IX-9
## Benzene Attenuation Rates Reported By Peargin (2000)



### *Plume Migration*

Because monitored natural attenuation relies on natural processes to prevent contaminants from migrating, it is important to determine the status of the contaminant plume (that is whether it is "stable"[4], shrinking, or expanding) and

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[4] By definition, a "stable" plume is one that forms where there is a continuous (infinite) source of contaminants such that concentrations within the plume never change (*i.e.*, neither increase nor decrease and, thus, "stable"). Only when the flux of contaminants into the plume is exactly equal to the mass of contaminants that are degraded is the plume truly "stable". If the mass into the plume exceeds the mass that is biodegraded, then the plume expands; if the mass into the plume is less than the mass degraded, then the plume contracts. In practice, it may be difficult (or impossible) to determine whether the plume is expanding, contracting or stable. And unless there is a continuous release, a source isn't truly infinite. But, the source mass may be so large and the flux of contaminants into the plume so great that for practical purposes it behaves as an infinite source and the plume expands (though maybe very slowly) for a very long period of time. The implications of an expanding or stable plume is that remediation objectives can never be achieved in a "reasonable" time frame because infinity is not a reasonable length of time. Only after the contaminant source has been eliminated and the plume has been demonstrated to be contracting should MNA be evaluated as a potential remedial alternative.

### Exhibit IX-10
### Initial Dissolved Concentrations (µg/L) Of Benzene And MTBE That Can Be Biodegraded To Target Levels Within Various Time Periods

| | **BENZENE - target 5 µg/L at end of interval** | | | |
|---|---|---|---|---|
| | 1 year | 2 years | 5 years | 10 years |
| Remediated Source (k= 0.0022/d) | 11 | 25 | 280 | 15,000 |
| Non-Remediated Source (k= 0.00037/d) | 6 | 7 | 10 | 20 |
| | **MTBE - target 20 µg/L at end of interval** | | | |
| | 1 year | 2 years | 5 years | 10 years |
| Remediated Source (k= 0.0035/d) | 72 | 260 | 12,000 | 7,000,000 |
| Non-Remediated Source (k= 0.00011/d) | 21 | 22 | 24 | 30 |

whether receptors might be impacted by the release. These impacts could include ingestion of groundwater, direct contact with contaminated groundwater at discharge points (*e.g.*, streams or marshes), or inhalation of contaminant vapors, especially in a basement or other confined space. As a safety measure, sentinel wells may be installed between the leading downgradient edge of the dissolved plume and a receptor (*e.g.*, a drinking water supply well). A contaminated sentinel well provides an early warning that the plume is migrating. As such, sentinel well(s) should be located far enough up gradient of any 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. For those responsible for site remediation, this is a signal that MNA is not occurring at an acceptable rate, or that site conditions have changed (*i.e.*, transience) and the contingency remedy should be implemented. Sentinel wells should be monitored on a regular basis to ensure that the plume has not unexpectedly migrated.

Exhibit IX-10 compares maximum dissolved concentrations of benzene and MTBE that can be degraded over various time periods at sites where sources have been remediated and where sources have not been remediated. Note that for sites where the sources have not been remediated, the maximum concentrations of benzene or MTBE that can be biodegraded within a decade are not too much higher than the target concentrations.

The CAP should contain information regarding the location of potential receptors, the quality of groundwater, depth to groundwater, rate and direction of groundwater flow and its variability, groundwater discharge points, and use of groundwater in the vicinity of the site. If potential receptors are located near the site, the CAP should also contain monitoring results that demonstrate that receptors are not likely to be exposed to contaminants. Determination of whether a receptor is in close proximity to a site may be considered in terms of either contaminant travel time from the toe of the plume to the receptor or the distance separating the toe of the plume 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 estimated only from site-specific data, which are the highest measured hydraulic conductivity, the hydraulic gradient, (effective) porosity, distance between the source and the nearest receptor, and the bulk density of the soil and its organic carbon content. The last two of these parameters, coupled with the contaminant's soil sorption constant ($K_{oc}$, which is discussed later), are necessary to determine if movement of the contaminant will be retarded by sorption to soil organic matter, or whether it will move at close to the velocity of the groundwater (i.e., not be retarded, hence "conservative"). It is important to realize that conservative contaminants (although initially at low concentrations) actually arrive at receptors *before* the time estimated based on average groundwater seepage velocity. The consequence is that estimated travel times based on average parameter values are longer than in actual fact, and receptors may be at risk sooner than anticipated. The subsurface migration of dissolved contaminants through porous media is as a dispersed plume rather than a concentrated, discrete slug. Whereas a slug that enters a well instantaneously raises the concentration of the extracted water to that of the slug, the leading edge of a contaminant plume is typically very dilute and concentrations in the well increase gradually with time. When contaminants first arrive at the well the concentration is very low, typically below even taste and odor thresholds. Continued exposure to such low, but gradually increasing, concentrations can cause receptors to become desensitized over time to the extent that they are unaware that their water is contaminated even though concentrations may be several hundreds of times greater than recognized taste and odor thresholds.

For biodegradable contaminants, a minimum travel time of 2 years or more should allow for an evaluation of the potential effectiveness of monitored natural attenuation and provide sufficient time to implement contingency measures should monitored natural attenuation prove to be ineffective in meeting remediation objectives. Therefore, if the maximum expected contaminant transport velocity (whether for a retard or conservative contaminant) at a site is 2 feet per day, it would require 2 years for such a contaminant to travel 1,500 feet (approximately ¼ mile). Therefore, at this site, all downgradient receptors within ¼ mile of the source should be identified and all wells be sampled and included in the regular monitoring program. It should be noted that the presence of layers of high permeability soil or rock, fractures or faults, karst, or utility conduits may accelerate the migration of contaminants. It is also possible that contaminants could be migrating along pathways that were undetected during characterization of the site. If less biodegradable and more mobile contaminants (such as MTBE) are of concern, then the travel time criteria should be reduced.

If the groundwater is potable and future land use is expected to be residential, potential future receptors should also be considered. If this information is not provided in the CAP, you will need to request the missing data. If contaminants are expected to reach receptors, an active remedial technology should be used instead of MNA.

Only under some rare circumstances might MNA be considered a remedial option even when there is potential for lingering groundwater contamination. For instance, active remediation to protect a groundwater resource may not be required if the affected groundwater is not potable (*e.g.*, because of high salinity or other chemical or biological contamination) nor will it be used as a potential source of drinking water within the time frame anticipated for natural attenuation processes to reduce contaminant concentrations to below established regulatory levels.

Exposure to petroleum contaminant vapors may also be a concern at some sites. Hazardous contaminants can volatilize from the dissolved-phase from a contaminated groundwater plume. 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 contaminants can also be significant if groundwater is used for bathing (even if it is not used for drinking), or even lawn irrigation and car washing. If vapor migration and associated health and safety risks are not addressed in the CAP, request additional information.

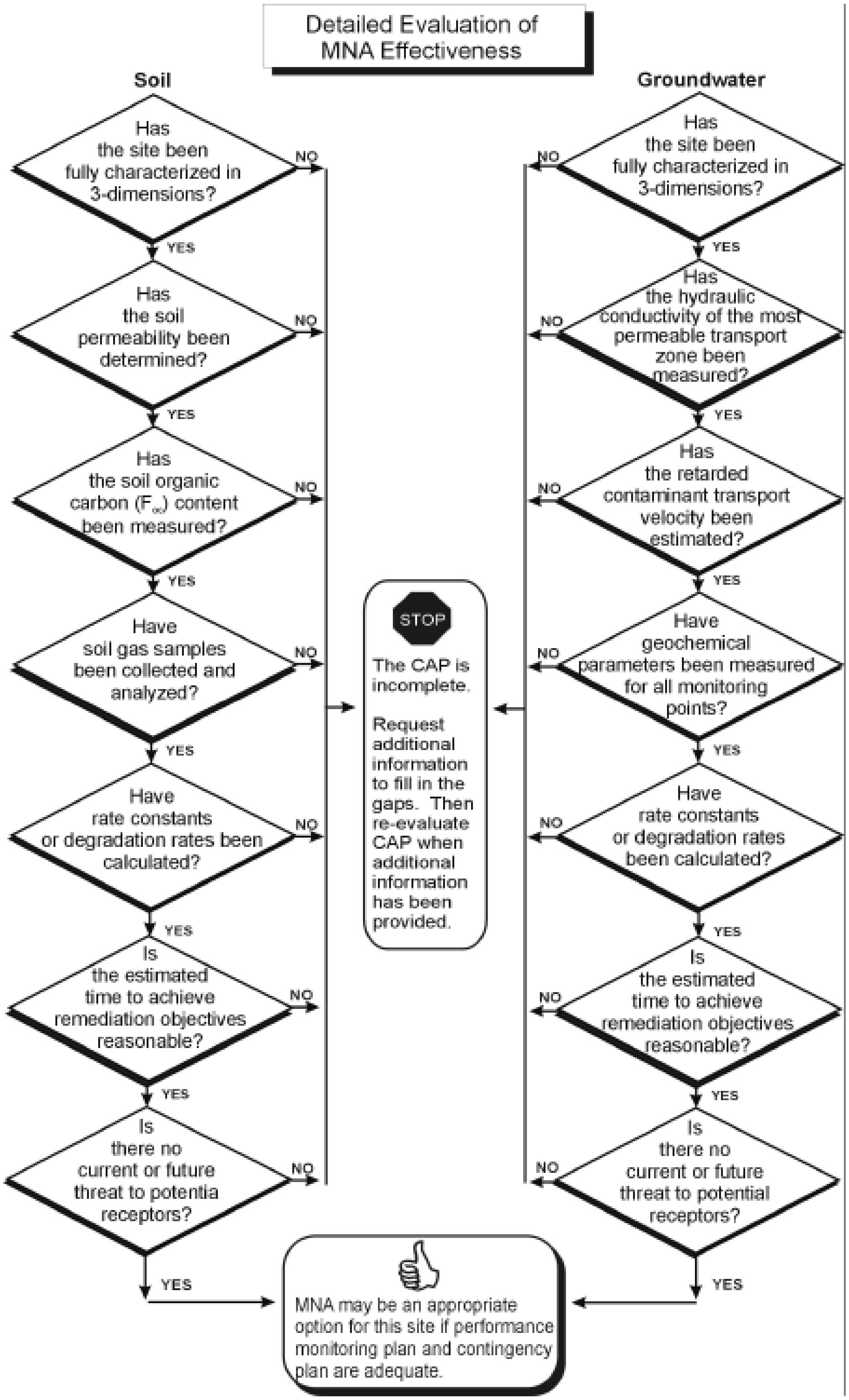
# Detailed Evaluation Of Monitored Natural Attenuation Effectiveness

Once the initial screen has been completed, and is has been determined that monitored natural attenuation could potentially be effective at a site, it is necessary to conduct a more detailed evaluation of the CAP to determine whether or not MNA is likely to be effective. Exhibit IX-11 is a flow chart that can serve as a guide through the detailed evaluation process. A thorough understanding of natural attenuation processes coupled with knowledge of the site conditions and the contaminants present will be necessary to make this determination. This section begins with a general overview of natural attenuation mechanisms and site characterization and before getting into the specific parameters that should be evaluated for an MNA remedy for contaminated soil and contaminated groundwater.

## Natural Attenuation Mechanisms

In order to assess site conditions to determine whether MNA is an acceptable alternative to active treatment, it is important to understand the mechanisms that degrade petroleum fuel components in soil and groundwater. Although it is not likely that all environmental conditions will be within optimal ranges under natural field conditions, natural attenuation processes will, to some degree, still be occurring. 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 concentrations but no net decrease in mass). Mechanisms that result in destruction of petroleum hydrocarbons (and other fuel components) are primarily biological. The primary non-destructive mechanisms are abiotic, physical phenomena, although some abiotic processes are destructive. However, because most of these processes are relatively insignificant for hydrocarbon fuel components they will not be presented in the following discussion. The primary biological mechanisms of

# Exhibit IX-11
# Detailed Evaluation of Monitored Natural Attenuation Effectiveness



MNA are aerobic and anaerobic metabolism. The primary physical mechanisms are volatilization, sorption, and dispersion. Characteristics of these mechanisms are summarized in Exhibit IX-12.

### *Biological Processes*

The driving force for the biodegradation of petroleum hydrocarbons is the transfer of electrons from an electron donor (petroleum hydrocarbon) to an electron acceptor. To derive energy for cell maintenance and production from petroleum hydrocarbons, the microorganisms must couple electron donor oxidation with the reduction of an electron acceptor. As each electron acceptor being utilized for biodegradation becomes depleted, the biodegradation process shifts to utilize the electron acceptor that provides the next greatest amount of energy. This is why aerobic respiration occurs first, followed by the characteristic sequence of anaerobic processes: nitrate reduction, manganese-reduction, iron-reduction, sulfate-reduction, and finally methanogenesis.

Aerobic biodegradation of petroleum fuel contaminants by naturally occurring microorganisms is more rapid than anaerobic biodegradation when there is an abundant supply of both electron acceptors and electron donors. Aerobic biodegradation occurs even at low concentrations of dissolved oxygen. Heterotrophic bacteria (i.e., those that derive carbon for production of cell mass from organic matter) are capable of carrying out aerobic metabolism at oxygen concentrations that are below the detection limit of most conventional methods for measuring oxygen content. The rate of oxygen depletion due to microbial metabolism typically exceeds the rate at which oxygen is naturally replenished to the subsurface. This results in the core region of the hydrocarbon plume being anaerobic (see Exhibit IX-2). Once the oxygen in the contaminated zone has been depleted (below about 0.5 mg/L), there is generally ample time for anaerobic reactions to proceed because the lifespan of contaminant sources and plumes is measured in years, even after most of the source material has been removed. In anaerobic biodegradation, an alternative electron acceptor (*e.g.*, $NO_3^-$, $SO_4^{2-}$, $Fe^{3+}$, $Mn^{4+}$, and $CO_2$) is used. Within only the past few years it has been realized that because there is a potentially much larger pool of anaerobic electron acceptors in groundwater systems, the vast majority of the contaminant mass removed from the subsurface is actually accomplished by anaerobes.

### *Physical Processes*

Physical processes such as volatilization, dispersion, and sorption also contribute to natural attenuation. Volatilization removes contaminants 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 contaminants, the expected mass loss due to volatilization is even lower. Dispersion ("spreading out" of contaminants through the soil profile or groundwater unit) results in lower concentrations of contaminants, 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

**Exhibit IX-12**
**Primary Monitored Natural Attenuation Mechanisms**

| Mechanism | Description | Potential For BTEX Attenuation |
|---|---|---|
| **Biological** | | |
| Aerobic Respiration | Microbes utilize oxygen as an electron acceptor to convert contaminants to $CO_2$, water, and biomass. | Most significant attenuation mechanism if sufficient oxygen is present. Soil air ($O_2$) $\geq$ 2 percent. Groundwater D.O. = measurable |
| Anaerobic Respiration<br>P Denitrification<br>P Sulfate reduction<br>P Iron reduction<br>P Manganese reduction<br>P Methanogenesis | Alternative electron acceptors (*e.g.*, $NO_3^-$, $SO_4^{2-}$, $Fe^{3+}$, $Mn^{4+}$, $CO_2$) are utilized by microbes to degrade contaminants. | Rates are typically much slower than for aerobic biodegradation but represent the major biodegradation mechanisms |
| **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. No net loss of mass. |
| 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. No net loss of mass. |

*Source: Adapted from McAllister and Chiang, 1994.*

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 contaminants reach a receptor).

## Site Characterization

Site characterization (and monitoring) data are typically used for estimating attenuation rates, which are in turn used to estimate the length of time that will be required to achieve remediation objectives. Exhibit IX-13 lists the data that should be collected during site characterization activities and summarizes the relevance of these data. In general, the level of site characterization necessary to support a comprehensive evaluation of MNA is more detailed than that needed to support active remediation. This is not to say, however, that a “conventional” site characterization (typically consisting of 1 up gradient well and 2-3 wells downgradient with long screened intervals that intersect the water table) is adequate even for active remediation technologies. The primary reason why active remediation technologies often fail to meet remediation objectives is not so much that the technologies don’t work, as it is that they are inappropriately designed and implemented based on information from inadequate site characterization. Many of these systems (especially pump-and-treat) are merely active containment measures, and while they often don't result in expeditious cleanup, they may at least serve to minimize the spread of contamination. Because an MNA remedy lacks an active backup system, it is even more important that site characterization be as accurate and comprehensive as possible.

Soil borings should be conducted such that continuous lithologic logs are generated that cover the interval from ground surface to significantly below the seasonal low water level. Care should be exercised to ensure that contaminants are not introduced into previously uncontaminated areas and that conduits for cross-contamination are not created—wells with long screened intervals that could interconnect different water-bearing strata should not be installed. Use of direct push technology is ideally suited for this purpose (see U.S. EPA, 1997, for more information). With increasing distance from the source area, delineation of preferential contaminant transport pathways is especially important because these pathways, which are often relatively small in scale, control contaminant migration. Monitoring wells should be "nested" and arrayed in transects that are perpendicular to the long axis of the plume. Several transects should be established to fully characterize both the subsurface stratigraphy and the contaminant plume in three-dimensions. In order to determine rates of biodegradation, several wells along the centerline of the plume are required. If an insufficient number of "cross-gradient" are installed, it will be impossible to determine where the centerline of the plume is located. Data from wells that are located off the centerline (in either the lateral or vertical direction) are erroneous, and lead to an overestimate of the rate of biodegradation. If the rate of biodegradation is overestimated, then the length of time required to reach remediation objectives will be underestimated. It is also especially important that all monitoring wells be sampled on a regular basis to ensure that seasonal variations in both water levels and contaminant concentrations are identified.

Data collected during site characterization should be incorporated into a conceptual site model. A conceptual site model is a three-dimensional representation that conveys what is known or suspected about contamination sources, release mechanisms, and the transport and fate of those contaminants. The conceptual site model should not be static–it should be continually refined as additional data are acquired. In some cases, new data may require a complete overhaul of the conceptual site model. The conceptual model serves as an aide in; directing investigative activities, evaluating the applicability of potential remedial technologies, understanding potential risks to receptors, and developing an appropriate computer model of the site.

"Conceptual site model" is not synonymous with "computer model," although a calibrated computer model may be helpful for understanding and visualizing current site conditions or for predicting likely future conditions. However, computer modelers should be cautious and collect sufficient field data to test conceptual hypotheses and not "force-fit" site data into a pre-conceived, and possible inaccurate, conceptual representation. After the site conceptual model has been developed, it is possible to evaluate the applicability of using a computer model for simulating the site.

Computer models will not be applicable at all sites for a variety of reasons. All models are based on a set of simplifying assumptions. These assumptions reduce the enormous complexity of a real-world site to a manageable scale, but at the price of increased uncertainty. Model developers identify significant processes that form the theoretical basis of the model. Mathematical relationships are then derived for these processes and solved for contaminant concentrations, mass balances, fluxes, velocities, etc. Many different approaches have been used. The simplest models typically have the most restrictive assumptions: one-dimensional steady-state flow of water and transport of contaminants, homogeneous soil properties, well-defined source terms, infinite aquifer extent, among others. These formulations lead to analytical solutions that are easy to use and require only a few input parameters. Although outwardly simple, these models may not be adequate to represent contaminant transport at a certain site. Proper use, however, requires that the site conceptual model match the assumptions of the theoretical model. However, evaluation of whether or not the assumptions of the model are met requires that sufficient data have been collected in order to develop a site conceptual model, because it cannot be assumed *a priori* that a simplified model is adequate to represent complex site conditions. When model assumptions are not met then other approaches must be pursued.

## Exhibit IX-13
## Site Characterization Data Used To Evaluate Effectiveness Of Monitored Natural Attenuation In Groundwater

| 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 | |
| Date of contaminant release | Compare expected extent without MNA to actual extent. |
| Historical concentrations along the primary flow path from the source to the leading edge | Estimate expected extent of plume migration. |
| Background electron acceptor levels up gradient of the source and plume | Evaluate status of plume (*i.e.*, steady state, decreasing, migrating). |
| Geochemical indicators of MNA: Alkalinity, hardness, pH, and soluble Fe and Mn, sulfate, nitrate, carbon dioxide, methane, (sometimes hydrogen) and redox potential both inside and outside the contaminant plume | Determine assimilative capacity of aquifer.<br>Evaluate the mechanisms and effectiveness of MNA processes. |
| 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.*

One type of model that might be used instead of an analytical solution is a numerical model. Numerical models allow for complex geology, variable boundary conditions, transient flow and transport conditions, among other features. The features of the site that commonly lead to selection of a numerical model are heterogeneous transport properties (*e.g.*, hydraulic conductivity, porosity, etc.), complex stratigraphy, and irregular flow boundaries. In general, as the complexity of the model increases, so does the amount and quality of data required as input. The complexity of some sites may preclude modeling because of the investment in data collection and analysis that would be required. Prime examples are karst and fractured rock sites where the cost of determining the location of preferential pathways that control contaminant migration is likely to be prohibitive. It cannot be assumed that site complexity and size are proportional—it may be just as prohibitively expensive to adequately model a small site as a large site.

Determining the values of input parameters to the model is a major concern (and usually a major expense). Subsurface properties may be difficult to measure and vary tremendously even over small distances. Some parameters required by the model may not be measured, but rather estimated from the scientific literature, rules-of-thumb, or “guesstimation”. Some required parameters may be theoretically ill-founded (*e.g.*, dispersivity) or based upon assumptions that may be only imperfectly met (*i.e.*, degradation by first order rate processes). Model results are only as good as the data that goes into them, assuming that the model being used is appropriate under the given conditions at the site. Where the input parameter sets are constructed from such a set of estimates and imperfect measurements, a large amount of uncertainty will exist in the model results. Without comparison to measured concentrations, fluxes and/or other model outputs, the ability of the model to reproduce observed field conditions will be unknown.

“Calibration” has been developed as the process for minimizing the differences between model results and field observations. Through model calibration a parameter set is selected that results in model output that best fits the observed data. But, because of the number of parameters that must be identified, calibration is known to produce non-unique results. This is particularly the case in heterogeneous environments where every parameter of the model can vary from point-to-point. Confidence in the model, however, is increased by using the calibrated model to predict the response to some additional concentration or flux data (*i.e.*, that were not previously used in calibration). At each step in this process additional site investigation data improves knowledge of the behavior of the system. Projecting future contaminant levels from observed current levels requires proper use of a simulation model. This process is uncertain for many reasons. Some of the simple reasons are related to inability to predict future land and water use, future weather patterns, uncharacterized subsurface variability, and others. Where confidence in the data is uncertain, the most conservative (*i.e.*, protective) assumptions and parameters should be used. As such, prediction can best be thought of as an extrapolation from existing conditions. Often, with each new set of field data, model input parameters are adjusted so that model output matches this most recent data, but earlier field conditions would not be accurately simulated using these newer input values. What this means is that model simulations of future behavior may be as inaccurate as are earlier simulations of present conditions. **Under no circumstances should predictive modeling be used as the sole justification for selecting an MNA remedy, nor for terminating long-term performance monitoring.**

## Contaminated Soil

A detailed analysis of whether MNA is likely to be effective in meeting remediation objectives is understandably more involved than the simple screening procedure outlined earlier. Exhibit IX-14 lists the factors which influence the effectiveness of MNA for contaminated soil. The CAP should be closely examined to ensure that each of these factors has been addressed. The significance of each of these factors is discussed in the following sections.

**Exhibit IX-14**
**Factors Affecting MNA Effectiveness: Contaminated Soil**

| Factor | Effect On Monitored Natural Attenuation |
|---|---|
| Permeability | Coarse-grained soils provide the greatest drainage and aeration, but may also promote contaminant leaching and migration. |
| Soil Structure and Layering | Layered soils inhibit vertical migration and dispersion of contaminants, but may promote lateral spreading. |
| Sorption Potential | Higher organic carbon content and smaller grain size in soil results in greater sorption of contaminants and retarded migration. |
| Soil Gas Composition | Presence of oxygen necessary for aerobic biodegradation. Measurement of other parameters provides information on biodegradation processes. |
| Soil Moisture | Required for microbial activity. Optimal moisture is between 12 and 30% by weight (75-90% of field capacity). |
| pH | Generally not a limiting factor within a wide range (4-9). Biodegradation activity is greatest between soil pH values of 6 to 8. |
| Temperature | Generally not a limiting factor within a wide range (0-45°C). |
| Microbial Community | Generally present in almost all subsurface environments. |

### *Permeability*

Soil “permeability” controls the rate at which fluids (gases and liquids) move through the unsaturated zone. This directly influences the rate at which contaminants are leached from the source area to the water table, as well as the rate of vapor movement through the soil. While there are a number of ways to measure the permeability of soil, arguably the most familiar measure is hydraulic conductivity, which is a function of the properties of both the porous medium and the fluid. Another common measure of permeability is intrinsic permeability, which is a function of the properties of only the porous medium. Intrinsic permeability and hydraulic conductivity are related through this equation:

$$K = k\frac{r\ g}{m}$$

where: $K$ = hydraulic conductivity
$k$ = intrinsic permeability
$r$ = density of the fluid (in this case, water)
$g$ = acceleration due to gravity
$m$ = viscosity (dynamic) of the fluid

Fine-grained soils (*e.g.*, clays and silts), have lower hydraulic conductivity than coarse-grained soils (*e.g.*, sand and gravel). Thus, sandy soils (which have a hydraulic conductivity of about 2 ft/day or greater) promote drainage and aeration, which is favorable to both the dispersion and biodegradation of contaminants. However, high permeability also promotes faster migration of contaminants, which could result in more rapid and severe groundwater impacts. Clays and silts on the other hand, which due to their high sorptive capacities (owing to both small particle size and higher organic matter content), typically result in slower migration (*i.e.*, retardation) of contaminants and less degradation than that observed in more permeable soils. Thus, even though biodegradation may take longer, there may be little or no impact to underlying groundwater resources.

### *Soil Structure and Layering*

Soil structure refers to the arrangement of soil particles into groups. Soil structure can enhance or inhibit contaminant migration. Layered soils tend to hinder the vertical migration of contaminants while enhancing lateral spreading. Soil macropores (naturally occurring fissures, cracks, root holes, or animal burrows), however, can facilitate the vertical interchange of contaminants from the ground surface through the soil to groundwater, as well as in the reverse direction. 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. Impervious soil covers (*e.g.*, concrete, asphalt) restrict the infiltration of water and air downward through the unsaturated zone, which can reduce the leaching rate of contaminants, in addition to the rate of oxygen replenishment. While both of these effects can lead to reduced rate of biodegradation, in some situations the benefit afforded by reduction in leaching of contaminants to the groundwater may offset the decrease in rate of biodegradation of contaminants.

### *Sorption Potential*

Sorption is the general term for the interaction between contaminants and particulate surfaces. There are two types of sorptive processes: adsorption, where an excess of contaminant molecules accumulate on the surface of the particle, and absorption, where there is relatively uniform penetration by contaminant molecules into the surface of the particle. Because the nature of the contaminant-solid interaction is difficult to measure even under laboratory conditions, and thus it is essentially wholly unknown in the field, the generic term “sorption” is used to describe the phenomena without regard to the exact mechanism. The solid, or sorbing material, is referred to as the sorbent; a contaminant, which sorbs to the solid sorbent, is referred to as a sorbate. Partitioning is the term used to describe the process by which the contaminant (usually from the liquid, gas, or dissolved phase) is sorbed onto the particle surface.

Sorption 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 sorb organic compounds. The range of organic carbon typically found in soil is from 1 to 3%. The organic matter content in subsurface soils is typically an order of magnitude or more lower than in surface soils because most organic residues are incorporated or deposited on the surface. 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.

Sorption is important because it slows down (or retards) the rate of advance of the contamination front in the subsurface. Contaminants that sorb tightly to soil particles may be less subject to transport in the gaseous phase or in solution, whereas contaminants that are not tightly sorbed can be transported through soils, aquatic systems, and the atmosphere. Sorption is usually reversible for petroleum fuel constituents, but the rates of sorption and desorption may not be the same. With respect to the impact on MNA, the higher the sorption potential, the greater the retardation of contaminant migration. Increased sorption will increase the time required for contaminants to reach receptors, allowing greater time for biodegradation to occur. Conversely, sorbed contaminants may not be available to microorganisms as a food source. In this case, the contamination may linger undegraded for exceedingly long periods of time during which they can act as a slow, steady source of contamination. This can be particularly troublesome where groundwater resources are impacted. If this is (or is likely to be) the situation, then more aggressive source mitigation efforts should be undertaken prior to selecting MNA as a remediation alternative.

Partitioning between the contaminant phase and the solid (soil) phase is described by the distribution (or sorption) coefficient ($K_d$), which is a function of the organic matter in the soil ($f_{oc}$) and the organic carbon partition coefficient ($K_{oc}$):

$$K_d = K_{oc} \cdot f_{oc}$$

where: $K_d$ = distribution coefficient
$K_{oc}$ = organic carbon partition coefficient
$f_{oc}$ = fraction of organic carbon in the soil

$K_{oc}$ values can range from $10^0$ to $10^7$. 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. The $K_{oc}$ values of BTEX contaminants are all low, indicating relatively weak sorption potential, as shown in Exhibit IX-15. None of the BTEX contaminants 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 contaminants will dissipate. Heavier petroleum constituents tend to have greater $K_{oc}$ values and will thus sorb more strongly to soils, retarding contaminant migration. MTBE and ethanol have even lower $K_{oc}$ values than the BTEX components; therefore MTBE and ethanol will sorb poorly onto organic matter in the soil.

### Soil Saturation Limit

Two of the primary concerns associated with contaminated soil are the potential for (1) generation of volatile emissions and (2) leaching of contaminants into groundwater. Each of these potentials is compound-specific and must be determined for each contaminant of concern.

**Exhibit IX-15**
**$K_{oc}$ Values For Common Petroleum Fuel Constituents**

| Contaminant | Soil Sorption Constant $K_{oc}$ (L/kg) |
|---|---|
| Benzene | 49 |
| Toluene | 95 |
| Ethylbenzene | 250 |
| m-Xylene | 190 |
| o-Xylene | 129 |
| p-Xylene | 260 |
| MTBE | 11 |
| Ethanol | 16 |
| Naphthalene | 1,300 |

Source: Suggested values from *CHEMFATE Database*, Syracuse Research Corp., http://esc.syrres.com/efdb/chemfate.htm

The soil saturation concentration ($C_{sat}$) corresponds to the contaminant concentration in soil at which the sorptive limits of soil particles, the solubility limits of soil pore water, and saturation of soil pore gas have been reached. Above this concentration, the soil contaminant may be present in free phase (*i.e.*, nonaqueous phase liquids for common petroleum hydrocarbons and other fuel additives). $C_{sat}$ is a function of the amount of contaminant in the vapor phase in the pore spaces of the soil in addition to the amount dissolved in the soil's pore water and the amount sorbed to soil particles. The equation for $C_{sat}$ is:

$$C_{sat} = \frac{S}{r_b}\left(K_d r_b + q_w + K_H q_a\right)$$

where: $C_{sat}$ = soil saturation concentration (mg/kg)
$S$ = solubility in water (mg/L)
$r_b$ = dry soil bulk density (kg/L)
$K_d$ = distribution coefficient
$q_w$ = water-filled soil porosity (vol/vol)
$K_H$ = Henry's Law constant (dimensionless)
$q_a$ = air-filled soil porosity (vol/vol)

At $C_{sat}$ for a given contaminant, the emission flux from soil to air reaches a plateau and emissions will not increase above this level no matter how much more chemical is added to the soil. Therefore, the inhalation route of exposure is not likely to be of concern for those contaminants with regulatory threshold concentrations (*e.g.*, site-specific screening levels, or SSLs) above $C_{sat}$. However, if the concentration of a contaminant is above $C_{sat}$, there is a potential for free phase liquid to be present and accumulations of NAPL may occur at the water table. In such cases further investigation of potential groundwater impacts is necessary.

The equation above may be modified so that it may be used to determine whether contaminant concentrations in soil are likely to result in groundwater impacts. The modified equation is:

$$C_t = C_w \left\{ (K_{oc} f_{oc}) + \frac{q_w + q_a K_H}{r_b} \right\}$$

where: $C_t$ = screening level in soil (mg/kg)
$C_w$ = target leachate concentration (mg/L)
$K_{oc}$ = organic carbon partition coefficient
$f_{oc}$ = fraction of organic carbon in the soil
$q_w$ = water-filled soil porosity (vol/vol)
$q_a$ = air-filled soil porosity (vol/vol)
$K_H$ = Henry's Law constant (dimensionless)
$r_b$ = dry soil bulk density (kg/L)

In the above equation, $C_w$ is set at the regulatory concentration limit for a specific contaminant. After plugging in site-specific values for the remainder of the parameters, $C_t$ yields the maximum allowable soil concentration for that contaminant. If this value is less than measured concentrations in the soil, then groundwater contamination is likely and MNA is not an acceptable remediation alternative on the basis of soil contamination. To determine if MNA may be appropriate for the site, a detailed evaluation of the potential groundwater impacts must be conducted. For more information on the Soil Saturation Limit, see U.S. EPA, 1996b.

### *Soil Gas Composition*

It is important to measure the concentration of oxygen, carbon dioxide, methane, and volatile organics in soil gas in the source area. This will yield information on the progress of biodegradation of petroleum contaminants. The oxygen concentration will yield information on the effectiveness of oxygen replenishment, which is essential for aerobic biodegradation. Carbon dioxide is an indicator of aerobic respiration as well. Methane production is the result of anaerobic metabolism. The concentration of volatile organics will indicate whether or not vapor migration could be a potential problem at the site. The presence of volatile organics is also an indicator of the distribution of contamination in the subsurface.

The vapor pressure of a contaminant is a measure of its tendency to evaporate, or to move from the product phase to air. Contaminants with higher vapor pressures (*i.e.*, those contaminants 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, contaminants with relatively low vapor pressures are less likely to vaporize and become airborne.

Volatilization from soil or groundwater is highest for contaminants with higher vapor pressures.

### *Soil Moisture*

Soil moisture is largely a function of precipitation in the region and the retention capacity of the soil. Infiltrating precipitation transports oxygen and nutrients as it percolates downward through the subsurface soils. In addition, water facilitates the movement of bacteria to other parts of the soil, where they can continue to degrade petroleum contaminants. However, especially in areas covered by pavement, replenishment of soil moisture is limited, and the amount of average annual rainfall may overestimate the amount of moisture replenishment that actually occurs. This is important because a moderate level of soil moisture is necessary to support the growth of microbial populations. Also, microbes can only utilize petroleum hydrocarbons when the hydrocarbons are in the dissolved phase. In the unsaturated zone, soil moisture content of 75 to 90 percent of field capacity, is considered optimal for aerobic microbial activity. High precipitation and highly permeable soils lead to increased leaching rates to groundwater.

### *pH*

Soils that have a pH of 6 to 8 generally promote optimal bacterial growth. However, the range under which significant biodegradation has been observed to occur is from 4 to 9 (Wilson, 2001). The significance of this is that biodegradation is not all that sensitive to pH, and minor variances from the optimal range usually will have no significant detrimental effect.

### *Temperature*

As with pH, the temperature range under which biodegradation occurs is quite broad; significant biological activity has been observed under near freezing conditions to almost boiling. This is not to say that the rate of biodegradation will be the same all year long. Especially in colder climates, biodegradation rates measured during the summer season should not be assumed to continue all year 'round. Temperature measurements are also important because certain parameters (*e.g.*, pH, concentration of dissolved gases) are temperature dependent.

### *Microbial Community*

Microbes capable of degrading petroleum products are present in almost all subsurface environments. Therefore, the exercise of collecting soil samples and conducting laboratory microcosm studies is generally not necessary. However, in some situations, it may be important to analyze soil samples with the intent of confirming the presence of hydrocarbon degrading microorganisms, and the absence of toxic levels of contaminants (*e.g.,* heavy metals, corrosive materials, and pesticides) that could inhibit the effectiveness of the microbial community. 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, such as those described in Section C.3.4, "Design, Implementation, and Interpretation of Microcosms Studies", in EPA's Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water (U.S. EPA, 1998) and/or Section 2, "Laboratory Studies", in EPA's report on Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions (U.S. EPA, 2000b).

### *Rate Constants and Degradation Rates*

The selection of MNA as an appropriate remedy for a given site should be based on a comparison of the rate of remediation that is expected using natural processes to the rate that is expected from active remediation. For most LUST sites, natural biodegradation will be the most important component of natural attenuation. Biodegradation reactions involving organic chemicals occur at rates which are a function of various site-specific environmental conditions. Projections of natural biodegradation should be extracted from site-specific data, and not from rates published in the literature for other sites. Degradation rate constants determined in the laboratory are generally higher than rates that occur under field conditions. This is particularly true when the rate in laboratory is limited by the activity of the microorganisms and the rate in the field is limited by the supply of oxygen. Wherever possible, field-determined rates should be used to estimate the time required to achieve remediation objectives. A site-specific rate may not be constant over time, in both the short-term (*i.e.*, seasonally) and the long-term. Under no circumstances should such estimates be used as justification to close a site. Site closure decisions should be based on monitoring data, not predictions.

### *Time To Achieve Remediation Objectives*

As with any remediation method, one of the fundamental questions that arises is "How much time will be required before remediation objectives are achieved?" Suitable methodology has been presented in the earlier "Screening" section. This same methodology should be employed here, but with site-specific parameters instead of the generic parameters we used to illustrate the methodology.

After estimating a time to achieve remediation objectives, it is necessary to evaluate whether or not this time is "reasonable" for a given site. As this is a site-specific decision, no single generic number can be presented in this chapter. In general, a "reasonable" time frame is one that is comparable to that which could be achieved through active remediation (U.S. EPA, 1999). Since there are typically a variety of potential remediation options for a given site, there is likely to be more than one estimate of time necessary to achieve remediation options. Evaluation of the most appropriate time frame must be determined through an analysis of the various remedy alternatives. Some of the factors that should be considered in making a determination as to which time frame (and remediation alternative) is most appropriate include:

- Subsurface conditions which can change over an extended time frame required to achieve remediation objectives;

- Whether the contamination, either by itself or as an accumulation with other nearby sources (on-site or off-site), will exert a long-term detrimental impact on available water supplies or other environmental resources;

- Uncertainties regarding the mass of contaminants in the subsurface and predictive analyses (*e.g.*, remediation time frame, timing of future demand, and likelihood of receptors coming in contact with contaminants);

- Reliability of monitoring (and, if implemented, institutional controls) over the entire length of the time period required to achieve remediation objectives;

- Public acceptance of the time frame required to reach remediation objectives; and

- Provisions by the responsible party for adequate funding of monitoring, performance evaluation, and regulatory oversight over the time period required to achieve remediation objectives.

In general the time frame required for MNA remedies is often longer than that required for more active remedies. As a consequence, the uncertainty associated with the above factors increases significantly. Adequate performance monitoring and contingency remedies should be utilized because of this higher level of uncertainty. When determining reasonable time frames, the uncertainty in estimated time frames should be considered, as well as the ability to establish performance monitoring programs capable of verifying the performance expected from natural attenuation in a timely manner. Statistical confidence intervals should be estimated for calculated attenuation rate constants (including those based on methods such as historical trend data and microcosm studies). When predicting remedial time frames, sensitivity analyses should also be performed to indicate the dependence of the calculated remedial time frames on uncertainties in rate constants and other factors. A statistical evaluation of the rate constants estimated from site characterization studies of natural attenuation of groundwater contamination often reveals that the estimated rate constants contain considerable uncertainty. As an example, analysis of natural attenuation rates from many sites indicates that a measured decrease in contaminant concentrations of at least one order of magnitude is necessary to determine the appropriate rate law to describe the rate of attenuation, and to demonstrate that the estimated rate is statistically different from zero at a 95% level of confidence (Wilson, 2001). Due to variability resulting from sampling and analysis, as well as plume variability over time, smaller apparent reductions are often insufficient to demonstrate (with 95% level of confidence) that attenuation has in fact occurred at all (U.S. EPA, 1999). When these conditions cannot be met using MNA, a remedial alternative that more likely would meet these expectations should be selected.

## Contaminated Groundwater

A detailed analysis of whether MNA is likely to be effective in meeting remediation objectives is understandably more involved than the simple screening procedure outlined earlier. Exhibit IX-16 lists the factors which influence the effectiveness of MNA for contaminated groundwater. The CAP should be closely examined to ensure that these factors have been addressed. The significance of each of these factors is discussed in the following sections.

### *Effective Solubility*

Solubility is the amount of a substance that will dissolve in a given amount of another substance (*e.g.*, water). Therefore, a contaminant's solubility provides insight to its fate and transport in the aqueous phase. Contaminants that are highly soluble (*e.g.* MTBE, ethanol) have a tendency to dissolve into the groundwater and are not likely to remain in the sorbed phase. They are also less likely to volatilize from groundwater into soil vapor. Conversely, chemicals that have low water solubilities tend to remain either in the sorbed phase or are likely to volatilize into soil vapor. In general, lower molecular weight contaminants tend to be more soluble and, therefore, migrate and disperse much more readily in groundwater or soil moisture than do heavier contaminants.

## Exhibit IX-16
## Factors Affecting MNA Effectiveness: Contaminated Groundwater

| Factor | Effect On Monitored Natural Attenuation |
|---|---|
| Effective Solubility | The greater the contaminant's solubility, the greater the dispersion in groundwater. However, in a mixture, the solubility of each component is reduced–effective solubility is less than pure phase solubility. |
| Henry’s Law Constant | A measure of a contaminant's tendency to partition between the aqueous phase and gaseous phase. The higher the Henry's law constant, the greater the tendency to volatilize from the dissolved phase |
| Groundwater Seepage Velocity | Higher velocity increases migration of dissolved contaminants, also promotes reoxygenation and replenishment of electron acceptors. |
| Sorption and Retardation | Higher organic carbon content and smaller grain size in soil results in greater sorption of contaminants and retarded migration. |
| Retarded Contaminant Transport Velocity | Due to effects of sorption, contaminant transport velocity is lower than groundwater seepage velocity. |
| Precipitation/Recharge | Primary benefit is in transport of dissolved oxygen into subsurface. Recharge can also cause plumes to dive and evade monitoring system. |
| Geochemical Parameters | Provide information on assimilative capacity of aquifer and the nature and effectiveness of biodegradation processes. |

When contaminants are released into the environment from a mixture such as a petroleum hydrocarbon fuel, the water solubility of each individual compounds is typically lower than its pure phase solubility. This reduced solubility is referred to as effective solubility and is a function of the mole fraction (or proportion) of a given component in the whole mixture. The effective solubility equation can be written as:

$$C_L = X \cdot S$$

where:
$C_L$ = effective solubility
$X$ = mole fraction of component in mixture (*e.g.*, NAPL)
$S$ = pure phase solubility in water

For complex mixtures it is necessary to estimate the weight percent and an average molecular weight of the unidentified fraction of the NAPL before the calculation can be completed. The effective solubility relationship indicates that for groundwater in contact with NAPL, the total concentration of the contaminant in the plume remains constant, even if the total concentration of the NAPL in the soil increases. Stated another way, aqueous-phase concentrations in leachate will increase together with soil concentrations only while the soil contaminants are sorbed (there is no NAPL present on the groundwater). Once the soil concentration reaches a point where NAPL is present, the concentration in the plume reaches a maximum concentration determined by the mole fraction of the contaminant in the NAPL and it's aqueous solubility. Exhibit IX-17 lists the solubility of the BTEX contaminants, MTBE, and ethanol. The higher the solubility, the more likely it is that the contaminant 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, other ethers) are transported farther and faster than hydrocarbons. Often these additives can be detected in distant wells long before hydrocarbons would arrive (if they weren't first biodegraded to below detection limits).

### Henry's Law Constant

Partitioning of a contaminant between the dissolved phase and the vapor phase is governed by Henry's law, and the Henry's law constant is a measure of a contaminant's tendency to volatilize from groundwater into soil gas. Henry's law states that the concentration of a contaminant in the gas phase is directly proportional to the compound's concentration in the dissolved phase.

The equation for Henry's law is:

$$C_g = K_H C_w$$

where: $C_g$ = contaminant concentration in gas phase (atm)
$K_H$ = Henry's law constant ($\text{atm} \cdot \text{m}^3/\text{mol}$)
$C_w$ = contaminant concentration in dissolved phase ($\text{mol/m}^3$)

As shown in Exhibit IX-18, the Henry's law constants for the BTEX compounds are relatively low, and those for MTBE and ethanol are even lower. This means that there will be relatively little volatilization from the dissolved phase to the gas phase, and there is even less tendency for this to occur as the plume dives below the top of the water table. The consequence of this is that volatilization can be neglected entirely when using models to simulate biodegradation. However, volatilization may be of concern with regard to the accumulation of vapors at unsafe or unhealthy levels in basements, parking garages, utility conduits, sewers, etc.

### Permeability

Aquifer "permeability" controls the rate at which liquids move through the saturated zone. This directly influences the rate at which contaminants are transported from source areas to receptors. While there are a number of ways to measure the permeability of aquifer media, arguably the most familiar measure is hydraulic conductivity, which is a function of the properties of both the porous medium and the fluid. Another common measure of permeability is intrinsic permeability, which is a function of the properties of only the porous medium. Intrinsic permeability (*k*) and hydraulic conductivity (*K*) are related through this equation:

$$K = k\frac{rg}{m}$$

## Exhibit IX-17
## Solubilities of Common Petroleum Fuel Constituents

| Constituent | Typical Percentage in Gasoline[a] | Pure Compound Solubility in Water[b] (mg/L) (25°C) | Effective Solubility in Water[c] (mg/L) (25°C) |
|---|---|---|---|
| Benzene | 1 to 4 | 1,780 | 24 to 95 |
| Toluene | 2 to10 | 515 | 12 to 60 |
| Ethylbenzene | 5 to 20 | 152 | 8 to 33 |
| m-Xylene | ↑<br>2 to 8<br>(all 3 isomers)<br>↓ | 160 | 3 to 13 |
| o-Xylene |  | 220 | 3 to 14 |
| p-Xylene |  | 215 | 4 to 16 |
| MTBE | 0 to 15 | 51,000[c] | 5,600 to 8,760 |
| Ethanol | 0 to 10 | infinite[c] | 57,000[d] |

Sources:

[a] *A Guide to the Assessment and Remediation of Underground Petroleum Releases*, API Publication 162, 3rd Edition, 1996.

[b] *Selection of Representative TPH Fractions Based on Fate and Transport Considerations, Volume 3*, Total Petroleum Hydrocarbon Criteria Working Group Series, 1997. *http://www.aehs.com/publications/catalog/contents/Volume3.pdf*

[c] Recommended values from *CHEMFATE Database*, Syracuse Research Corp., *http://esc.syrres.com/efdb/chemfate.htm*

[d] "Achieving Clean Air and Clean Water: the Report of the Blue Ribbon Panel on Oxygenates in Gasoline", September, 1999, *http://www.epa.gov/otaq/consumer/fuels/oxypanel/r99021.pdf*

## Exhibit IX-18
## Henry's Law Constants For Petroleum Fuel Constituents

| **Contaminant** | Henry's Law Constant (@20-25° C) |  |  |
|---|---|---|---|
|  | (atm • $m^3$/mol) | (conc/conc) | (atm) |
| Benzene | 5.55E-03 | 0.227 | 308 |
| Toluene | 6.64E-03 | 0.272 | 369 |
| Ethylbenzene | 7.88E-03 | 0.322 | 438 |
| m-Xylene | 7.43E-03 | 0.304 | 413 |
| o-Xylene | 5.19E-03 | 0.212 | 288 |
| p-Xylene | 7.66E-03 | 0.313 | 426 |
| MTBE | 5.87E-04 | 0.024 | 32.6 |
| Ethanol | 5.20E-06 | 0.0002 | 0.29 |

Source: Recommended values from *CHEMFATE Database*, Syracuse Research Corp., http://esc.syrres.com/efdb/chemfate.htm

where: $K$ = hydraulic conductivity
$k$ = intrinsic permeability
$r$ = density of the fluid (in this case, water)
$g$ = acceleration due to gravity
$m$ = viscosity (dynamic) of the fluid

Fine-grained media (*e.g.*, clays and silts), have lower hydraulic conductivity than coarse-grained soils (*e.g.*, sand and gravel). Thus, sandy media (which have a hydraulic conductivity of about 2 ft/day or greater) promotes groundwater reaeration, which is favorable to both the dispersion and biodegradation of contaminants. However, high permeability also promotes faster migration of contaminants, which could result in more rapid and severe groundwater impacts. Clays and silts on the other hand, which due to their high sorptive capacities (owing to both small particle size and higher organic matter content), typically result in slower migration (*i.e.*, retardation) of contaminants and less degradation than that observed in more permeable soils.

### *Groundwater Seepage Velocity*

Dispersion and migration of contaminants increases with increasing groundwater flow rate. True groundwater velocity is referred to as the seepage velocity. Seepage velocity can be calculated from:

$$q_s = -\frac{K\ I}{n_e}$$

where: $q_s$ = seepage velocity [L/T]
$K$ = hydraulic conductivity [L/T]
$I$ = hydraulic gradient [unitless]
$n_e$ = effective porosity [unitless]

For a given hydraulic gradient, the higher the hydraulic conductivity the higher the seepage velocity. Transport of dilute dissolved contaminants is a function of advection, dispersion, and chemical and physical reactions. Advection refers to the movement imparted by flowing groundwater, and the rate of transport is usually taken to be equal to the *average* linear groundwater velocity. Hydrodynamic dispersion occurs as a result of molecular diffusion and mechanical mixing and causes the dissolved contaminant plume to spread out with distance from the source. Molecular diffusion is generally only significant when groundwater movement is very slow. Mechanical mixing occurs as groundwater flows through the aquifer matrix twisting around individual grains and through interconnected pore spaces at differing velocities. The movement of some dissolved contaminants may also be affected by chemical and physical reactions, such as sorption and biodegradation, which act to reduce the transport velocity and decrease concentrations in the plume.

Classical tracer studies devised to study advection-dispersion phenomena typically employ a cylindrical column filled with a porous media. A continuous supply of tracer at a specified concentration is introduced at one end of the column under steady flow conditions and outflow concentrations are measured at various times after the tracer is injected. A graph of the outflow concentration with time is known as a breakthrough curve. Such a graph shows concentrations gradually increasing with time. The inflection point of this curve represents the arrival time of an undiluted slug of contaminant moving at the *average* linear groundwater velocity. There are two problems with the comparison of true contaminant transport and an undiluted slug. First, due to the presence of the porous media, slug (or plug) flow is impossible. Even at a relatively small scale (such as these cylindrical columns) the "plume" of tracer would be dispersed with distance in the column due to molecular diffusion and mechanical. Second, some of the tracer molecules are moving faster than the average linear groundwater velocity, and some are moving slower. This is also true for the water molecules although the velocity of individual water molecules is never measured. A common misconception is, thus, that due to dispersion, contaminants may move faster than groundwater. A correct statement is that some contaminants may move faster than the *average* linear velocity of the groundwater. This distinction is very important. It also leads to another important realization, which is that if some contaminant molecules are traveling faster than the average linear groundwater velocity, then the *maximum* linear groundwater velocity rather than the *average* linear groundwater velocity should be used to calculate how long (or short) a time it will take contaminants to first reach a receptor.

### Sorption and Retardation

As previously discussed in the soil contamination section, the organic carbon partition coefficient ($K_{oc}$) is an approximation of the propensity of a compound to sorb to organic matter found in the soil. The sorption coefficient ($K_d$) value is an expression of the tendency of a contaminant to remain sorbed on soil and is the product of $K_{oc}$ and the fraction organic carbon ($f_{oc}$) in the soil. Sorption tends to slow the transport velocity of contaminants dissolved in groundwater. When the average velocity of a dissolved contaminant is less than the average seepage velocity of the groundwater, the contaminant is said to be retarded. The coefficient of retardation, $R$, is used to "correct" the contaminant transport velocity. Under conditions where sorption is adequately described by $K_d$, (which is when the fraction of organic carbon is greater than 0.001), the retardation coefficient can be determined from:

$$R = 1 + \frac{r_b K_d}{n}$$

where: $R$ = coefficient of retardation [dimensionless]
$r_b$ = bulk density of soil in the aquifer [$M/L^3$]
$K_d$ = distribution coefficient [$L^3/M$]
$n$ = porosity [dimensionless]

Typical retardation coefficients for various organic compounds and different organic carbon content are given in Exhibit IX-19.

### Exhibit IX-19
### Retardation Coefficients For Different Organic Compounds And Different Organic Carbon Content

|  |  | Fraction of Total Organic Carbon ($f_{oc}$) in Soil |  |  |  |
|---|---|---|---|---|---|
| **Contaminant** | **log ($K_{oc}$)** | **0.0001 (low for aquifers)** | **0.001 (median for aquifers)** | **0.01 (high for aquifers)** | **0.1 (typical of soils)** |
| MTBE | 1.08 | 1.0 | 1.1 | 1.6 | 7 |
| Benzene | 1.58 | 1.0 | 1.2 | 2.9 | 20 |
| Ethylbenzene | 1.98 | 1.0 | 1.5 | 5.7 | 48 |
| Toluene | 2.13 | 1.1 | 1.7 | 7.6 | 68 |
| Xylene (mixed) | 2.38 | 1.1 | 2.2 | 13 | 120 |

Source: Wiedeimeier, *et al.*, 1999, Table 3-4, p. 145.

### *Retarded Contaminant Transport Velocity*

As mentioned in the preceding section, sorption tends to slow the velocity of contaminants in a plume, but not the seepage velocity of the groundwater itself. To “correct” for the effect of sorption, the coefficient of retardation is used to adjust the groundwater seepage velocity:

$$q_c = \frac{q_s}{R}$$

where: $q_c$ = contaminant velocity [L/T]
$q_s$ = groundwater seepage velocity [L/T]
$R$ = coefficient of retardation

From the retardation equation in the preceding section, when the distribution coefficient ($K_d$) is equal to zero (which means there is no sorption effect), then the coefficient of retardation is equal to unity and the contaminant velocity ($q_c$) is equal to the seepage velocity ($q_s$). As the value of $K_d$ increases, $R$ also increases, and the contaminant velocity becomes more retarded (*i.e.*, decreases).

Another method that is commonly used to determine retarded contaminant transport velocity is to divide the measured length of the contaminant plume by it’s known age. The advantage to this method is that the transport velocity is based on actual field data, and is therefore, site-specific. The danger inherent in this method is underestimation of the true transport velocity which leads to overestimation of the rate of biodegradation. This can occur if the measured length of the plume is shorter than the actual length of the plume. Such an underestimation of plume length is a common consequence of relying on “conventional” monitoring wells (rather than nested wells arrayed in transects) for delineation of the leading edge (or "toe") of the plume.

### *Precipitation/Recharge*

Recharge from precipitation can also cause contaminant plumes (even those comprised of contaminants that are less dense than water) to "dive" below the level of the water table. The plume migrates deeper and deeper with increasing distance from the source. As a consequence, the plume may migrate undetected below the screened intervals of shallow monitoring wells. Note that this phenomenon does not require a downward vertical gradient. It is a consequence of a layer of fresh water accumulating on top of the contaminant plume so gently that significant mixing does not occur (there will be some diffusion from the plume into the overlying clean water, but this is a very slow process). This is one of the primary reasons why nested, or multi-level, wells are absolutely required for an adequate site characterization. Even for typical less-dense than water contaminants such as BTEX, plume diving is a common phenomenon. In areas where much of the ground surface is covered with an impervious layer such as concrete or asphalt, actual recharge (especially in the source area) may be only a fraction of the total amount of annual rainfall. This may slow down the process of leaching contaminants from the source mass causing it to linger as slow, but relatively steady, source of groundwater contaminants for an extended period of time.

### *Geochemical Parameters*

Biodegradation of organic compounds results in measurable changes in the chemistry of the groundwater in the affected area. By measuring the temporal and spatial distribution of these chemical changes, it is possible to document and evaluate the extent to which natural attenuation processes are occurring. Isopleth (or isoconcentration) maps should be prepared for all contaminants of concern as well as each of the geochemical parameters discussed in this section. These maps will aide in the qualitative interpretation of data on the distribution and relative transport and degradation rates of the contaminants of concern. There are three general groups of chemical changes: electron acceptors, metabolic byproducts, and daughter products.

Electron acceptors are elements or compounds that occur in relatively oxidized states and include dissolved oxygen, nitrate, ferric iron, manganic manganese, hydroxide, sulfate, and carbon dioxide. These compounds are reduced through coupled oxidation and reduction reactions during microbial respiration to yield energy to the microorganisms for growth and activity.

Dissolved oxygen is typically the first electron acceptor to be utilized during the biodegradation of many organic compounds, including constituents of petroleum hydrocarbon fuels. As a consequence, the concentration decreases and dissolved oxygen concentrations below background levels indicate aerobic biodegradation is occurring. After dissolved oxygen concentrations in the aquifer fall below about 0.5 mg/L, anaerobic processes (initially denitrification) will begin if sufficient anaerobic electron acceptors are present. It is extremely difficult to get an accurate measurement of dissolved oxygen concentration. Several factors influence the aqueous solubility of dissolved oxygen including temperature. Other factors that can influence a reading include the instrument itself (the design, calibration, maintenance, and operation) and the sample collection technique (it is very easy to oxygenate a sample, yielding a falsely high level of dissolved oxygen). In spite of these difficulties, it is extremely important to collect groundwater samples for dissolved oxygen measurements as the difference between background concentrations and concentrations within the contaminant plume can be used to estimate the mass of contaminants that are aerobically biodegraded.

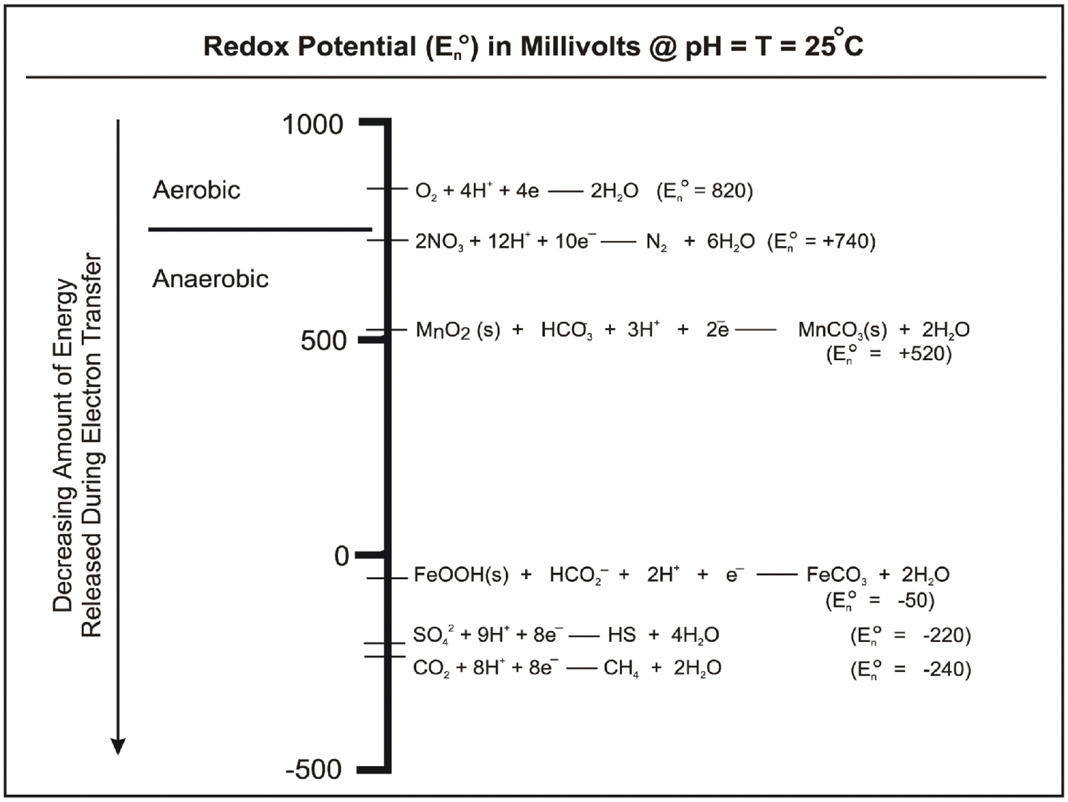
After dissolved oxygen has been depleted, biodegradation shifts from aerobic to anaerobic. The first anaerobic electron acceptor that may be utilized is nitrate by the process of denitrification. In the zone where denitrification is occurring, nitrate levels are lower than background. As with dissolved oxygen, the difference between levels within and outside the plume can be used to estimate the mass of contaminants being degraded by denitrification. The next electron acceptors to be oxidized under anaerobic conditions are manganic manganese, ferric iron, and sulfate. The final step in the anaerobic biodegradation series is methanogenesis, which utilizes carbon dioxide as the electron acceptor. As with nitrate (and dissolved oxygen before it), the difference between concentrations of these electron acceptors within and outside the plume can be used to estimate the mass of contaminants that are being degraded by each of these processes.

The sum of the estimated mass of degraded contaminants from all processes (both aerobic and anaerobic) can be used to provide an estimate of the biodegradative capacity of the subsurface system. Note that it is important to go through the exercise each time that samples are collected because natural processes are dynamic and even subtle changes can affect the rate and completeness of biodegradation. Such changes, if caught in time, will allow for contingency measures to be implemented should MNA prove not to be protective over the long period of time required to meet remediation objectives.

The second group of indicators of biodegradation are the metabolic byproducts. Each of the biodegradation processes mentioned above reduces an oxidized electron acceptor resulting in generation of measurable reduced species. 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. The oxidation-reduction (redox) potential of the groundwater changes, with conditions becoming more reducing, through the sequence oxygen, nitrate, iron, manganese, sulfate, and carbonate. The redox potential of groundwater generally ranges from 800 millivolts to about -400 millivolts (Exhibit IX-20). The lower the redox potential, the more reducing and anaerobic the environment. Although the redox potential cannot be used for quantitative interpretation, the approximate location of the fuel hydrocarbon plume can be identified in the field through measurement of redox potential if background organic carbon concentrations are low. NOTE: field measurements will likely not be in the same units as indicated in Exhibit IX-20.

Each biodegradation process is also associated with a characteristic hydrogen concentration. By carefully measuring dissolved hydrogen concentrations, it is possible to distinguish among the various anaerobic zones. This level of detail is especially important at sites with chlorinated solvents, and less important for petroleum fuel hydrocarbon sites. Aerobic respiration, denitrification, iron and manganese reduction, and sulfate reduction result in generation of carbon dioxide. Though it is difficult to obtain an accurate measure of dissolved carbon dioxide because of carbonate in the groundwater, elevated levels of carbon dioxide relative

## Exhibit IX-20
## Redox Potentials For Various Electron Acceptors



*Source: Modified from Norris et al., (1994)*

to background may be observed and it is possible to estimate the degree of microbiological activity. Another consequence of carbon dioxide production is an increase in alkalinity. Alkalinity is important in the maintenance of groundwater pH because it buffers the groundwater system against acids produced during aerobic and anaerobic biodegradation. Measurement of dissolved inorganic carbon provides sufficient information to calculate alkalinity and $CO_2$. The reduction of oxidized forms of iron and manganese ($Fe^{3+}$ and $Mn^{4+}$, respectively) results in the production of reduced species which are water soluble. Elevated levels of these reduced metals ($Fe^{2+}$ and $Mn^{2+}$, respectively) in the plume relative to background is indicative of anaerobic biodegradation. Hydrogen sulfide is produced during sulfate reduction. Methane is produced by methanogenesis, which occurs only under strongly reducing conditions.

The third group of chemical indicators is daughter products. For most petroleum hydrocarbons daughter products are not significant. For MTBE, however, one of the intermediate degradation products is *tertiary*-butyl alcohol (TBA) which is more difficult to remediate than MTBE itself, and more toxic. However, TBA is also used as a fuel oxygenate in its own right, as well as an impurity in MTBE. Some conventional analytical techniques actually degrade MTBE and form TBA during sample analysis. When this occurs, obviously the analytical results are not representative of what’s occurring in the subsurface. So, while the presence of TBA is of concern (and should be appropriately remediated) it does not necessarily indicate the biodegradation of MTBE and concentration data should not be used to establish biodegradation rates for MTBE–the estimated rate will likely be higher than what is actually occurring. Some of the daughter products of chlorinated solvents (particularly vinyl chloride) are of significant concern because of their toxicity.

### *Rate Constants and Degradation Rates*

Rate constants for biodegradation or for the rate of bulk attenuation of contaminants in groundwater can be used to estimate how far a plume may extend. In some cases these rates can be incorporated into computer models, and the models can be compared to the existing distribution of contamination to determine if a plume is expanding or receding. However, they can not be used to estimate how long a plume will persist in the absence of source control. For most plumes, the rate of attenuation in ground water is faster than the rate of attenuation of the source. As a consequence, the persistence of the plume is controlled by the rate of attenuation of the source, and the rate of attenuation of the source must be understood to be able predict the time required to achieve remediation objectives.

A decision on whether or not MNA is an appropriate remedy for a given site is usually based on estimates of the rates of natural attenuation processes, and biodegradation rates in particular, for most LUST sites. Biodegradation reactions involving organic chemicals occur at rates which are a function of various site-specific environmental conditions. Quantifying the rate of biodegradation is important for biologically-mediated remediation alternatives, and especially MNA, since this rate is used to estimate the time required to achieve remediation objectives. It is important to note, however, that there are different types of rate calculations and it is imperative to use the constant that is appropriate for the given situation or the resultant “answer” will be incorrect. Biodegradation rate constants generally fall into three categories:

- *concentration vs. time attenuation rate constant:* the rate constant, in units of inverse time (*e.g.*, per day, time$^{-1}$), is equal to the slope of the line plotted as natural log of concentration vs. time measured at a selected monitoring location. This constant represents the change in source strength over time and can be used to estimate the time required to reach a remediation goal. Concentration vs. time constants provide information regarding potential source persistence at a single location only–they cannot be used to evaluate distribution of contaminant mass within the source area.

- *concentration vs. distance attenuation rate constant:* the rate constant, in units of inverse time (*e.g.*, per day, time$^{-1}$), is derived by plotting the natural log of concentration vs. distance, and (only if the data follow a first-order decay pattern) calculating the rate as the product of the slope of the line and the groundwater seepage velocity. Plots of concentration vs. distance serve to characterize the distribution of contaminant mass within space at a given point in time, but a single plot yields no information about the variation in concentration over time. These constants cannot be used to estimate the time required to meet a remediation goal. They indicate how quickly contaminants are *attenuated* (*e.g.*, accounting for sorption, dispersion, and biodegradation) once they leave the source area, but provide no information on how quickly a residual source zone is being attenuated. Because most LUST sites will, to some degree, have a lingering residual source (despite best efforts to completely recover free product), these constants are inappropriate for estimating plume longevity for most sites.

- *biodegradation rate constant:* the rate constant is denoted by the Greek lambda ($\lambda$) and is in units of inverse time (*e.g.*, per day, $\text{time}^{-1}$). It can be derived in a variety of ways, including field tests and computer model simulations. The biodegradation rate constant is *NOT* the same as the concentration *vs.* distance attenuation rate constant since the latter reflects the combined effects of sorption, dispersion, and biodegradation. The biodegradation rate constant can be used to provide information on plume stability using models, but it *cannot* be used for estimating remediation time frames.

There are three commonly used models which describe the biodegradation of organic compounds in groundwater: (1) first-order decay, (2) Monod kinetics, and (3) "instantaneous reaction". Perhaps the most commonly used approach is to make the assumption that the biodegradation rate can be approximated using a first-order decay equation of the form:

$$C = C_0 \cdot e^{-kt}$$

where:

$C$ = biodegraded contaminant concentration
$C_0$ = initial contaminant concentration
$k$ = rate of decrease of contaminant ($\text{time}^{-1}$)
$t$ = time of interest

To estimate the time required to achieve a specific clean up goal, the above equation is rearranged to solve for $t$ as follows:

$$t = \frac{\ln(C / C_0)}{-k}$$

In this configuration, $C$ is the clean up goal concentration (or regulatory maximum allowable concentration), and $C_0$ is the most recent measured concentration. Note that if $k$ is in units of "per day" ($d^{-1}$), then $t$ will also be in days.

The first order decay model assumes that the solute degradation rate is proportional to the solute concentration. The higher the concentration, the higher the degradation rate. The primary advantage of this approach is that for many organic chemicals, $k$ has been determined from laboratory experiments. The weaknesses of the model are that it does not account for site-specific information such as the availability of electron acceptors, and there is often considerable uncertainty in extrapolating laboratory constants to the field environment. In fact, there is substantial evidence that the first-order model may overestimate the amount of aerobic biodegradation of petroleum hydrocarbons. Under no circumstances laboratory-derived attenuation rates be used as the sole justification for selecting an MNA remedy, evaluating the length of time required to meet remedial objectives, or in deciding to terminate long-term performance monitoring.

One final advantage of using the first-order model is that first-order rate constants may easily be converted to half-lives ($t_{½}$) since they are inversely related to one another:

$$t_{1/2} = \frac{0.693}{k}$$

A more complex, and more accurate, model is the Monod kinetic model which is also referred to as the Michaelis-Menten kinetic model. This model is the hyperbolic saturation function and, for calculating the reduction in contaminant concentration, has the form:

$$\Delta C = M_t m_{\max} \frac{C}{K_c + C} \Delta t$$

where:
$C$ = contaminant concentration
$M_t$ = total microbial concentration
$m_{\max}$ = maximum contaminant utilization rate per unit mass microorganisms
$K_c$ = half-saturation constant
$\Delta t$ = time interval of interest

This model is actually quite complex; the graph of this rate equation has regions that are zero-order, first-order, and mixed-order. The rate constant accounts for both the activity of the degrading population and the dependence of the reaction on the substrate concentration. Although this model may be the most accurate of the three models, the difficulty in estimating $m_{\max}$ and $K_c$ generally preclude its use under field conditions.

The “instantaneous reaction model” is also known as the electron-acceptor-limited model, and is used for simulating the aerobic biodegradation of petroleum hydrocarbons. The basis for this model is the observation that microbial biodegradation kinetics are fast in comparison with the transport of oxygen. The model assumes that the rate of utilization of the contaminant and oxygen by the microorganisms is very high, and that the time required to biodegrade the contaminant is very short (almost instantaneous) relative to the seepage velocity of the groundwater. The equation for the instantaneous reaction model using oxygen as the electron acceptor is:

$$\Delta C_R = -\frac{O}{F}$$

where:
$\Delta C_R$ = change in contaminant concentration due to biodegradation
$O$ = concentration of oxygen in groundwater
$F$ = utilization factor, the ratio of oxygen to contaminant consumed

The primary advantages of the instantaneous reaction model is that kinetic data are not required, because reactions are not limited by microbial kinetics. The model is, however, not applicable in all circumstances. Its applicability is limited to situations in which microbial biodegradation kinetics are fast relative to the rate of the groundwater flow that mixes electron acceptors with dissolved contaminants. There is increasing evidence that anaerobic biodegradation of petroleum hydrocarbons can be simulated using the assumption of instantaneous reactions (Wiedemeier, *et al.*, 1999).

### Plume Migration

In determining whether a plume is shrinking, “stable” or migrating, the uncertainty associated with defining the limits of contaminant plumes should be considered. For example, a plume is typically delineated for each contaminant of concern as a 2- or 3-dimensional feature. Plumes are commonly drawn either by hand or computer contouring programs which estimate concentrations between actual data points. In reality, a plume boundary is defined by a zone rather than a line. Fluctuations within this zone are likely to occur due to a number of factors (*e.g.*, analytical, seasonal, spatial, etc.) which may or may not be indicative of a trend in plume migration. Therefore, site characterization activities and performance monitoring should focus on collection of data of sufficient quality and quantity to enable decisions to be made with a high degree of confidence. The only appropriate sites for a MNA remedy, therefore, are those where the plume can be statistically demonstrated to be shrinking. (See footnote #4, p.IX-19.)

### Time Frame to Achieve Remediation Objectives

As with any remediation method, one of the fundamental questions that arises is “How much time will be required before remediation objectives are achieved?” At the current state of practice, the only practical approach available uses a statistical analysis of long term monitoring data from wells in the source area of the contaminant plume.

As an example of this approach, we’ll use data presented by Kolhatkar *et al.* (2000). They collected long-term groundwater monitoring data from three wells at a gasoline release site in New Jersey. Their original data displayed extreme oscillations bouncing up and down from less than 1 µg/L to a high value and back over a single sampling interval. Although the scatter in the data set is typical of the variation seen at many other sites, the influence of these outliers on the statistical estimate of the rate of attenuation was removed by editing the data set to remove those points where the concentration of MTBE was less than 1 µg/L. These edited data are tabulated as Exhibit IX-21 and presented graphically as Exhibit IX-22.

The first order rate constant for attenuation was extracted from the data by taking the natural logarithm of the concentrations of MTBE in each well at each date and then, for each well, performing a linear regression of the natural logarithm of concentration on the time when the sample was collected. The slope of the regression for each well is the instantaneous rate of change of concentration of MTBE with time. The slope is the negative of the first order rate constant for attenuation. The rates calculated from the data in Exhibits IX-21 and XI-22 are presented in Exhibit IX-23. For purposes of illustration, the concentration at the last time of sampling and the rate constants were used to forecast the time required to reach a cleanup goal of 20 µg/liter.

Because there is natural scatter in the long-term monitoring data, there is uncertainty in the estimate of the rate of natural attenuation, in the projected time frame to achieve clean up. To account for this uncertainty, a confidence interval was calculated for each estimate of the rate of attenuation at a pre-determined level of confidence of 90% and 95% (Exhibit IX-23). The level of confidence is simply the probability that the true rate is contained within the calculated confidence

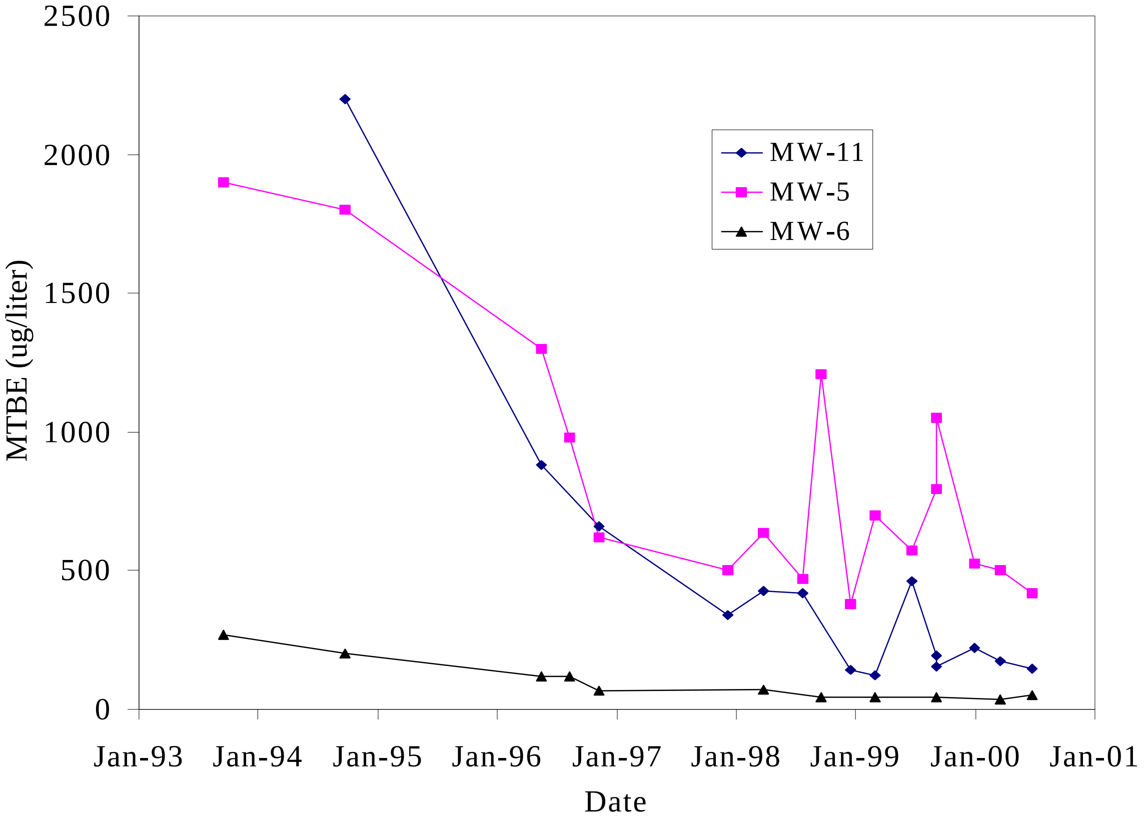
### Exhibit IX-21
### MTBE Concentration Measured In Monitoring Wells Over Time

| **MW-5** | | **MW-6** | | **MW-11** | |
|---|---|---|---|---|---|
| **Date** | **Concentration (ppb)** | **Date** | **Concentration (ppb)** | **Date** | **Concentration (ppb)** |
| 9/17/93 | 1,900 | 9/17/93 | 270 | 9/23/94 | 2200 |
| 9/23/94 | 1,800 | 9/23/94 | 200 | 5/17/96 | 880 |
| 5/17/96 | 1,300 | 5/17/96 | 120 | 11/7/96 | 660 |
| 8/10/96 | 980 | 8/10/96 | 120 | 12/8/97 | 339 |
| 11/7/96 | 620 | 11/7/96 | 66 | 3/27/98 | 426 |
| 12/8/97 | 500 | 3/27/98 | 71.2 | 7/23/98 | 419 |
| 3/27/98 | 635 | 9/18/98 | 44 | 12/16/98 | 144 |
| 7/23/98 | 470 | 3/1/99 | 42.2 | 3/1/99 | 123 |
| 9/18/98 | 1,210 | 9/7/99 | 43.2 | 6/21/99 | 464 |
| 12/16/98 | 379 | 3/20/00 | 36 | 9/7/99 | 195 |
| 3/1/99 | 700 | 6/22/00 | 51.2 | 9/7/99 | 155 |
| 6/21/99 | 574 | | | 12/30/99 | 220 |
| 9/7/99 | 792 | | | 3/20/00 | 173 |
| 9/7/99 | 1,050 | | | 6/22/00 | 146 |
| 12/30/99 | 525 | | | | |
| 3/20/00 | 501 | | | | |
| 6/22/00 | 420 | | | | |

interval. Given the need to protect human health and the environment, and the absence of an active remediation system to serve as a fail-safe, a 90% confidence level is a reasonable level of confidence for many sites. At other sites a more stringent confidence level (*e.g.* 95%) may be more appropriate, depending the level of risk that is acceptable.

In most applications of regression the user wishes to calculate both an upper boundary and lower boundary on the confidence interval that will contain the true rate at the pre-determined level of confidence. This is termed a "two tailed" confidence interval because the possibility of error (the tail of the probability frequency distribution) is distributed between rates above the upper boundary and

## Exhibit IX-22
## MTBE Concentration Measured In Monitoring Wells Over Time



## Exhibit IX-23
## Rates Of attenuation Of MTBE In Monitoring Wells And The Projected Time Required To Reach A Clean Up Goal Of 20 µg/L As Calculated From The Data Presented In Exhibits IX-21 And IX-22

| | **MTBE (µg/L)** | | **Estimated rate and time required** | | **Rate and time significant at 90% confidence** | | **Rate and time significant at 95% confidence** | |
|---|---|---|---|---|---|---|---|---|
| **Well** | **First Sample 1993** | **Last Sample 2000** | **Rate (per year)** | **Time (years)** | **Rate (per year)** | **Time (years)** | **Rate (per year)** | **Time (years)** |
| MW-5 | 1900 | 420 | 0.188 | 16 | 0.127 | 24 | 0.109 | 28 |
| MW-11 | 2200 | 146 | 0.453 | 4.4 | 0.365 | 5.4 | 0.337 | 5.9 |
| MW-6 | 270 | 51.2 | 0.290 | 3.2 | 0.246 | 3.8 | 0.231 | 3.8 |

below the lower boundary of the confidence interval. As a consequence, tables of critical values in statistical reference books and computer applications provide a "two-tailed" confidence interval. At a 80% level of confidence, the estimate will be in error 20% of the time. The true rate will be contained within the calculated confidence interval 80% of the time, 10% of the time the true rate will be faster than the upper boundary of the confidence interval, and 10% of the time the true rate will be slower than the lower boundary of the confidence interval. Using the data in Exhibit IX-21 for MW-5, the slope of a regression of the natural logarithm of concentration of MTBE on time is -0.188 per year. The first order rate of change of concentration of MTBE on time is -0.188 per year, corresponding to a rate of attenuation of +0.188 per year. The boundaries of the "two tailed" confidence interval on the rate at 80% confidence are 0.248 per year and 0.127 per year. This means that 80% of the time the true rate will be between 0.248 and 0.127 per year, that 10% of the time the true rate is greater than 0.248 per year, and 10% of the time the true rate is less than 0.127 per year. The true rate will be greater than 0.127 per year 90% of the time.

Long-term monitoring data at many sites typically exhibits a great deal of variation. These variations are not necessarily errors in sampling and analysis of groundwater samples. In many cases they reflect real changes in the plume caused by seasonal variations in precipitation and groundwater elevations. These variations are a natural property of the plume. Where long-term monitoring data define a statistically significant trend of increasing contaminant concentrations, such sites are not appropriate candidates for MNA. Where the long-term monitoring data exhibit a statistically significant trend of decreasing concentrations, such sites may be appropriate for MNA. If no trend is discernible, then additional data should be collected over time. If the variation is large enough, one boundary of the "two tailed" confidence interval will be a positive number and the other boundary will be a negative number. When zero is included in the confidence interval on the rate, there is no evidence in the data that the true rate is different from zero. If this is the case it is possible that attenuation is occurring in that particular well over time, but the monitoring data do not present evidence that attenuation is occurring at the predetermined level of confidence. The variation in the monitoring data is too great to determine the trend over time one way or the other. Again, there is no appropriate role for MNA at these sites, because it is impossible to predict how long it will take to reach the clean-up goals.

There is little value in estimating the shortest possible time that would be required to reach the goals for clean up; remedial options are compared and evaluated based on the greatest time required to reach goals. At the selected level of confidence, all the possibility of error should be assigned to rates that are slower that the lower boundary of the confidence interval. This is a "one-tailed" confidence level; it includes all true rates that are faster than the lower boundary of the confidence interval. A "one tailed" confidence interval can be calculated as the slower of the two confidence intervals from a "two-tailed" test that has twice the uncertainty. In the example above, where "two tailed" confidence intervals were calculated for a confidence level of 80%, the true rate will be greater than a rate of 0.127 per year 90% of the time. The "one tailed" confidence intervals reported in Exhibit IX-23 were calculated in this fashion.

Note that for a given number of observations, as the level of confidence is increased, the interval that is expected to contain the real value for the rate constant increases as well. As the level of confidence increases, the lower boundary on the rate constant decreases, and the projected time required to meet the clean up goal increases. In the examples presented in Exhibit IX-23, the estimated rate of natural attenuation of MTBE in MW-5 is 0.188 per year, which requires 16 years to attain a concentration of 20 µg/L. At a 90% confidence level, the lower boundary of the confidence interval is 0.127 per year, which requires 24 years to meet the goal. At a 95% confidence level, the lower boundary is 0.109 per year, which requires 28 years to reach the goal. At the 95% confidence level the upper bound of the time expected to reach the clean up goal has increased by a factor of almost two (from 16 years to 28 years). This does not necessarily mean that the actual time to achieve cleanup will be 28 years; it simply means that the length of time that will actually be required is estimated to be no more than 28 years at a 95% level of confidence.

The ability to extract a rate of attenuation from long term monitoring data is related to the number of measurements, and the time interval over which they are collected. As an example, the rate of attenuation extracted from the last three years of monitoring data for well MW-5 (3/27/98 to 6/22/2000 in Exhibit IX-21 and IX-22) is 0.106 per year, but the "one tailed" 90% confidence interval is all rates greater than -0.125 per year. The confidence interval includes zero. If only these three years of data were available, there would be no evidence of natural attenuation of MTBE in well MW-5 at 90% confidence. The rate extracted from the last four years of data (5/17/1996 to 6/22/2000) is 0.130 per year. The 90% confidence interval on the rate (0.0302 per year) would reach the clean-up goal in 100 years. As presented in Exhibit IX-23, the rate extracted using all the seven years of monitoring data is 0.188 per year. The 90% confidence interval on the rate would reach cleanup in 24 years. A few extra years of monitoring data have a strong influence on the ability to extract useful rate constants.

Rate constants for natural attenuation can be used to project the time required to reach a clean-up goal once the source has been adequately addressed. However, there are a number of key points to keep in mind. First, an appreciable record of long term monitoring data must be available to make a statistically valid projection of the rate of natural attenuation. As a practical matter it is difficult to extract rate constants that are statistically significant with fewer than six sampling dates, or with a sampling interval of less than three years. Second, it is unrealistic to expect just a few years of monitoring data to accurately predict plume behavior several decades into the future. Third, it is important to realize that these estimates are merely estimates and that the true rate is likely to change over time. Fourth, under no circumstances should such estimates be used as justification to close a site. Site closure decisions should be based on actual long term monitoring data, not predictions. Fifth, monitoring should continue at any given site for a specified period of time (typically 1 to 2 years or more) after cleanup goals have been achieved to ensure that contaminant levels do not rebound and exceed the required cleanup level due to long-term fluctuations in groundwater table elevation or changes in flux from lingering vadose zone contamination.

After estimating a time to achieve remediation objectives, it is necessary to evaluate whether or not this time is "reasonable" for a given site. As this is a site-specific decision, no single generic number can be presented in this chapter. In general, a "reasonable" time frame is one that is comparable to that which could be achieved through active remediation (U.S. EPA, 1999). Since there are typically a variety of potential remediation options for a given site, there is likely to be more than one estimate of time necessary to achieve remediation options. Evaluation of the most appropriate time frame must be determined through an analysis of the various remedy alternatives. Some of the factors that should be considered in making a determination as to which time frame (and remediation alternative) is most appropriate include:

- Classification of the affected resource (*e.g.*, drinking water source, agricultural water source) and value of the resource;
- Relative time frame in which the affected portions of the aquifer might be needed for future water supply (including the availability of alternate supplies);
- The stability of ground water flow in the aquifer. How might the plume change over the extended time frame necessary to achieve remediation objectives;
- Reliability of monitoring and of institutional controls over long time periods;
- Public acceptance of the time frame required to reach remediation objectives; and
- Provisions by the responsible party for adequate funding of monitoring and performance evaluation over the time period required to achieve remediation objectives.

## Long-Term Performance Monitoring

The two fundamental objectives of performance monitoring are to verify that: (1) contaminant levels are decreasing, and (2) contamination is not spreading (*i.e.*, the plume is not migrating, but rather is shrinking). Due to the potentially longer remediation time frames, potential for ongoing contaminant migration, and other uncertainties associated with using MNA, performance monitoring is of even greater importance for MNA than for other types of remedies. The monitoring program developed for each site should specify the location, number, frequency, and type of samples and measurements necessary to evaluate whether the remedy is performing as expected and is capable of attaining remediation objectives. The objectives for all monitoring programs should include the following:

- Demonstrate that natural attenuation is occurring according to expectations;
- Detect changes in environmental conditions (*e.g.*, hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of any of the natural attenuation processes;
- Identify any potentially toxic and/or mobile transformation products;
- Verify that the plume(s) is shrinking;
- Verify no unacceptable impact to downgradient receptors;
- Detect new releases of contaminants to the environment that could impact the effectiveness of the MNA remedy;
- Verify attainment of remediation objectives.

The frequency of monitoring should be adequate to detect, in a timely manner, the potential changes in site conditions listed above. At a minimum, the monitoring program should be sufficient to enable a determination of the rate(s) of attenuation and how that rate is changing with time. When determining attenuation rates, the uncertainty in these estimates and the associated implications should be evaluated (see McNab and Dooher, 1998). Flexibility for adjusting the monitoring frequency over the life of the remedy can be included in the monitoring plan. For example, it may be appropriate to decrease the monitoring frequency at some point in time, once it has been determined that natural attenuation is progressing as expected or very little change is observed from one sampling round to the next. In contrast, the monitoring frequency may need to be increased if unexpected conditions (*e.g.,* plume migration) are observed.  Exhibit IX-24 is a flowchart that can serve as a roadmap to guide you in evaluating the long-term performance monitoring plan. A table summarizing the contaminants to monitor and the suggested monitoring frequency is presented as Exhibit IX-25, while more specific details are discussed in the sections that follow.

Performance monitoring should continue until remediation objectives have been achieved, and generally for a period of 1 to 2 years longer to ensure that contaminant levels remain below target levels.  Under no circumstances should the results of predictive modeling (including statistical extrapolation) be used to justify a decision to terminate performance monitoring.  This decision should be based only on adequate field data that convincingly demonstrates that contaminant levels have met remediation objectives.  The institutional and financial mechanisms for maintaining the performance monitoring program should be clearly established in the remedy decision or other site documents, as appropriate.

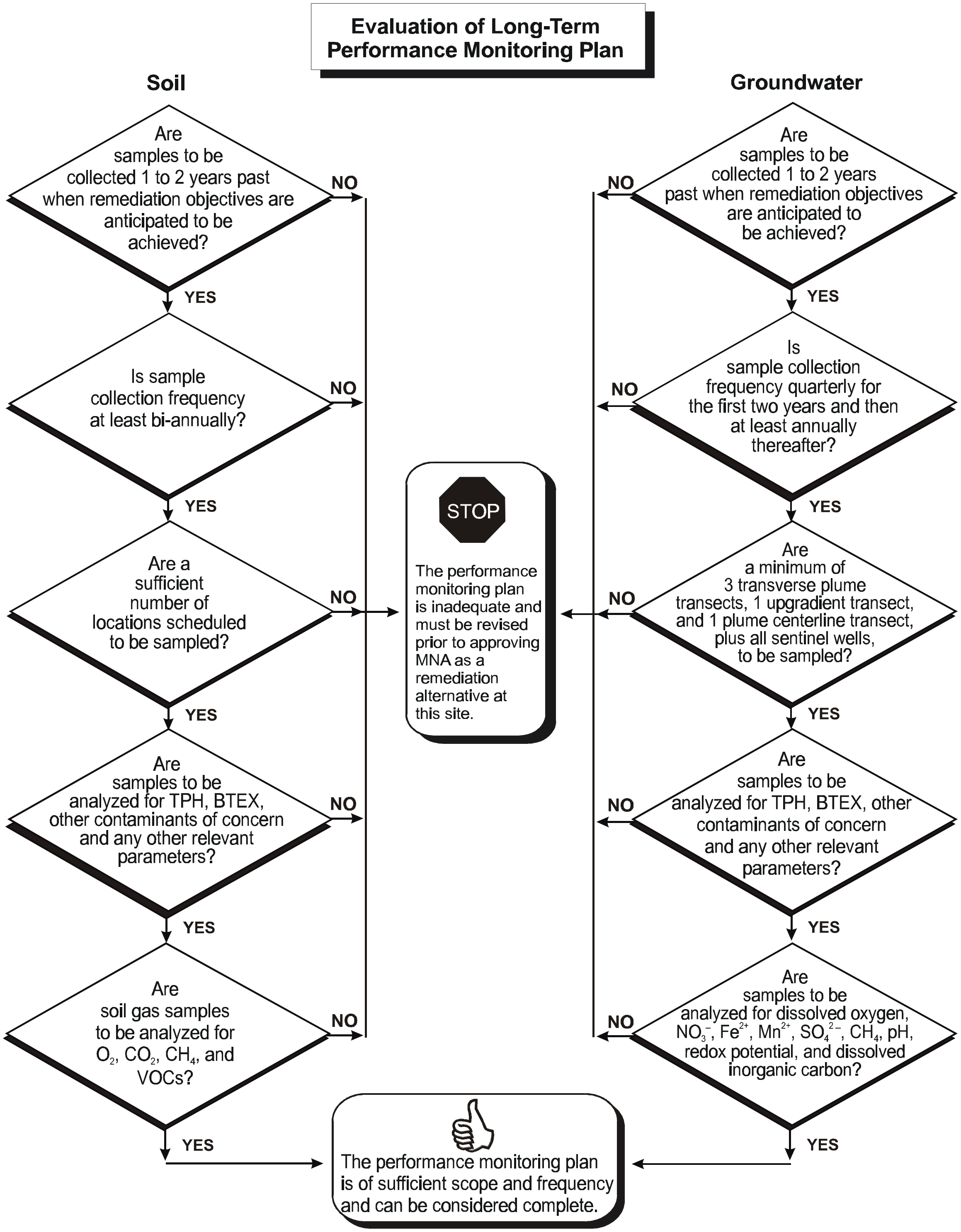
As with the active remediation technologies also described in this manual, if MNA does not appear to be effective in remediating the contamination at the site within a reasonable time frame, then an alternative active remedial technology (specified in the contingency plan section of the CAP) will be required.

## Contaminated Soil

For a given volume of contaminated soil, the objective of sampling is to collect a minimum number of samples such that, with a satisfactory degree of confidence, the spatial distribution of contamination is accurately defined.  Because this process will be repeated multiple times in the future, the methodology for selecting sampling locations and physically collecting the samples must be robust.

MNA is assumed to be effective if both the volume and the mass of contaminants are lower with each successive sampling event, and that after some reasonable period of time, contaminant levels fall below (and remain below) remediation objectives.  One of the challenges of routine soil sampling is collecting sequential samples that can be compared with earlier samples in the series.  Soil sampling is by its nature destructive, so once a discrete sample is collected, another one cannot be collected from exactly that same point in space.  There is an implicit assumption that a future sample, collected in close proximity to a past sample, will be close enough so that the analytical results can be compared to determine if concentrations are decreasing at that location.  At a minimum, samples should be collected from locations where contamination is known to be greatest (*i.e.,* source area) from previous sampling events.  Generally, eight samples per sampling event should be sufficient to demonstrate whether or not concentrations are decreasing.

Exhibit IX-24



Evaluation of Long-Term Performance Monitoring Plan

## Exhibit IX-25
## Performance Monitoring Frequency, Analytes, And Sampling Locations

| Medium | Monitoring Frequency | What To Monitor | Where/Number Of Samples To Monitor |
|---|---|---|---|
| Soil | at least bi-annually | BTEX; TPH; any other contaminants of concern; Soil gas $O_2$ ,$CO_2$, and $CH_4$. | a statistically significant number of continuous soil cores located throughout the area of contamination. |
| Groundwater | quarterly for the first two years, then at least annually thereafter. | BTEX; TPH; any other contaminants of concern; D.O., $Fe^{2+}$, $SO_4^{2-}$,$CH_4$, $NO_3^-$,$Mn^{2+}$ pH, and dissolved inorganic carbon. | a minimum of 3 perpendicular transects through the plume, 1 perpendicular transect up gradient of the plume, with multiple depth-discrete samples collected from each location, plus all sentinel wells (if any) |

Sampling events should occur at least bi-annually (*i.e.*, every two years) to demonstrate reductions in contaminant concentrations.

Soil samples should be analyzed for the BTEX contaminants, TPH, and any other contaminants of concern at the site. If the primary contaminants of concern at the site are volatile organic chemicals (VOCs), monitoring of soil gas should supplement direct soil measurements at some locations. In addition, soil gas samples should be analyzed for oxygen, carbon dioxide, and methane (and sometimes hydrogen) to determine the microbial activity in the soils. As described above, reduced oxygen concentrations and elevated carbon dioxide concentrations (relative to background) in both the source area, and soils overlying the dissolved plume, are a good indication that biodegradation is occurring.

## Contaminated Groundwater

Typically, groundwater monitoring wells are installed during site characterization activities (and often during active remediation), and, being permanent fixtures (relative to soil sampling locations) there is not as much uncertainty about the locations from which to collect groundwater samples (*i.e.*, wells) as there is about soil sample collection. The fundamental objectives, however, are the same: define the extent of contamination in three-dimensions, and identify trends in concentration levels.

Groundwater monitoring should be designed to ensure that the vertical and lateral extent of contaminants in groundwater is evaluated. Each distinct flow zone and geochemical regime should be monitored to assess remediation status. In general, for each distinct flow zone at the site, the following locations should be monitored: background, source area, main body of the plume, and the distal portions and boundaries.

Typical target zones for monitoring a contaminant plume include:

- *Source areas, and within and immediately downgradient of potential source areas*. The monitoring objective is to estimate a source mass which is critical for determining potential source longevity. These sampling points will also enable determination of future contaminant releases to the environment.

- *Flow zones with highest contaminant concentrations or hydraulic conductivity*. These are the zones where maintenance of a steady state or shrinking plume is a primary concern. A change in conditions in these zones may lead to a relatively rapid impact to a down-gradient receptor.

- *Distal or fringe portions of the plume.* These are areas where reductions of contaminants to levels required by remedial action objectives (*e.g.*, site-specific cleanup targets) may be attained most rapidly and where increases in concentrations that indicate impending plume expansion may be observed.

- *Plume boundaries.* Multi-level monitoring points should be placed at the side gradient, downgradient, and vertical plume boundaries, and between these boundaries and potential receptors. Results from these monitoring locations may directly demonstrate any unacceptable plume expansion.

- *Zones in which contaminant reduction appears to be recalcitrant.* These are the areas where attaining cleanup targets within reasonable time frames may be impeded due to site conditions (*e.g.*, presence of residual source materials, low flux of electron receptors). Such areas, if present, will be determined through data obtained throughout the performance monitoring period. These areas may require additional characterization and remedial actions to reduce contaminant concentrations to desired levels.

- *Background locations.* Background locations include monitoring points that are hydraulically up gradient and side gradient with respect to the plume. Multiple monitoring points should be used to determine the variability of background conditions. Data concerning the movement of electron receptors, donors, and any contaminants into the plume are required to interpret data from the plume. Background geochemical data is used to determine whether the observed differences in geochemical parameter concentrations within the plume are due to contaminant transformation processes rather than natural variations. Changes in geochemistry within the plume may not be directly related to attenuation of the contaminants, so geochemical changes outside the plume should be assessed and compared to geochemical changes taking place within the plume. If up gradient and lateral monitoring points show geochemical changes similar to changes in the plume, such changes may not be attributable solely to contaminant-related processes (*i.e.*, degradation), and therefore may not serve as supporting evidence for degradation processes.

Another type of well that should be monitored on a regular basis is a sentinel well. This is a well that is located between the leading downgradient edge of the dissolved plume and a receptor (*e.g.*, a drinking water supply well). A sentinel well(s) should be located far enough up gradient of any 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. A contaminated sentinel well provides an early warning that the plume is migrating. For those responsible for site remediation, this is a signal that MNA is not occurring at an acceptable rate and the contingency remedy should be implemented. For the downgradient well users, an alternate supply of water may be required.

In order to demonstrate that MNA is occurring, a sufficient number of monitoring wells that are appropriately located (both horizontally and vertically) are necessary. The density of sampling points will depend on site geology and hydrology, the overall size of the contaminant plume and the spatial scales at which contamination distribution varies horizontally, vertically, and temporally, and the desired level of confidence in the evaluation. Plumes vary significantly in concentration laterally and in vertical cross-section, making evaluation of contamination distribution and remedy performance difficult. Therefore, a dense network of multi-level monitoring points is required.

The recommended approach is to construct monitoring points that are positioned in transects both in the direction of groundwater flow as well as perpendicular to it (see Exhibit IX-26 for an optimal network design). The horizontal and vertical spacing of the monitoring clusters in each transect is determined by the scale of the hydrogeological heterogeneities that control contaminant transport and the dimension and spatial heterogeneity of the resulting contaminant distribution. The horizontal distance between transects is generally based on changes in contaminant concentration along the plume, and the location of the source and distal portions of the plume. The use of a transect-based approach to monitoring will greatly reduce the uncertainty in performance monitoring evaluations at sites by improving the definition of contaminant distribution and variability in three-dimensions. Transects also provide a better definition of contaminant distribution under conditions of changing hydraulic gradients. With reference to Exhibit IX-26, recommended transects would be as follows:

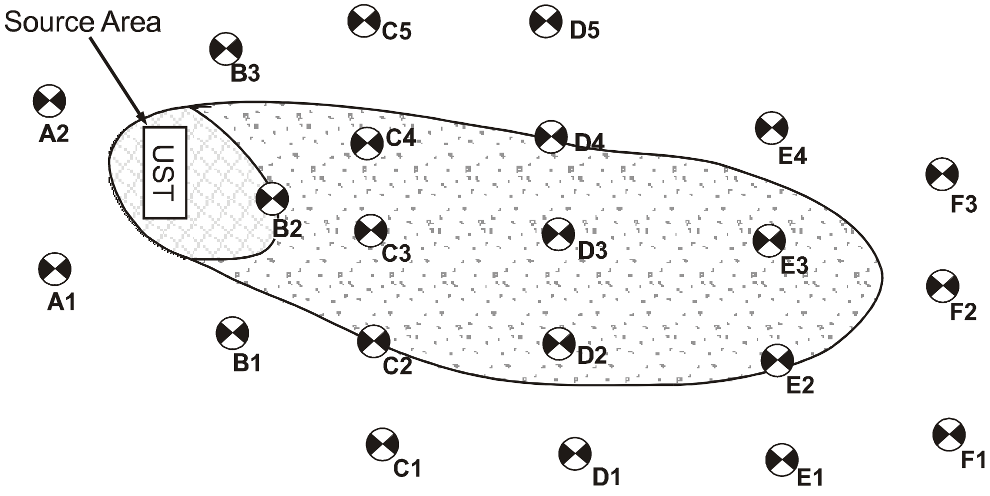
- source zone: B1 through B3
- mid-plume (transverse to flow): either C1 through C5, or D1 through D5
- plume toe: E1 through E4
- up gradient: A1 and A2
- plume centerline: B2-C3-D3-E3

Groundwater monitoring should be conducted no less than quarterly during the first two years to allow for determination of seasonal variation. Some sites may require quarterly (or more frequent) sampling for more than two years in order to establish a statistically significant trend. Thereafter, sampling frequency might then be reduced depending upon contaminant travel times and other site-specific factors (*e.g.*, travel time to nearest receptor). At a minimum, groundwater sampling should be conducted on an annual basis after the first two years.

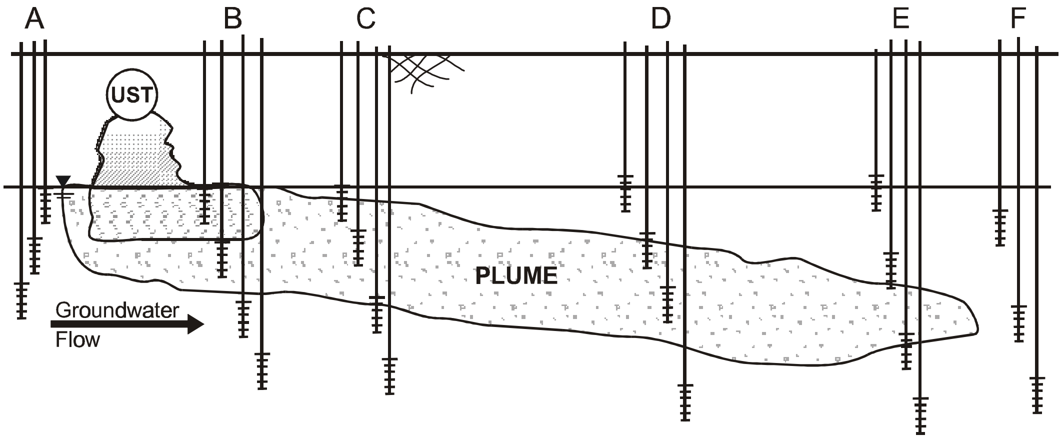
Groundwater samples should be analyzed for VOCs and other contaminants of concern, TPH (near the source area), dissolved oxygen, pH, temperature, redox potential, alkalinity, hardness, and other geochemical indicators as indicated in Exhibit IX-25. Isopleth (or isoconcentration) maps should be prepared for all contaminants of concern as well as each geochemical parameter. These maps will aide in the qualitative interpretation of data on the distribution and relative transport and degradation rates of the contaminants of concern.

## Exhibit IX-26
## Example of Optimal Groundwater Sampling Network Design for Performance Monitoring

Note: Figure not to scale.

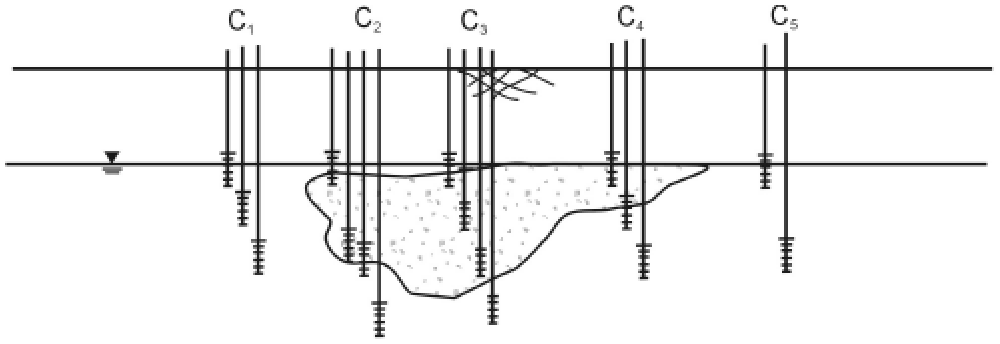


(A) Plan view of Optimal Groundwater Monitoring Network

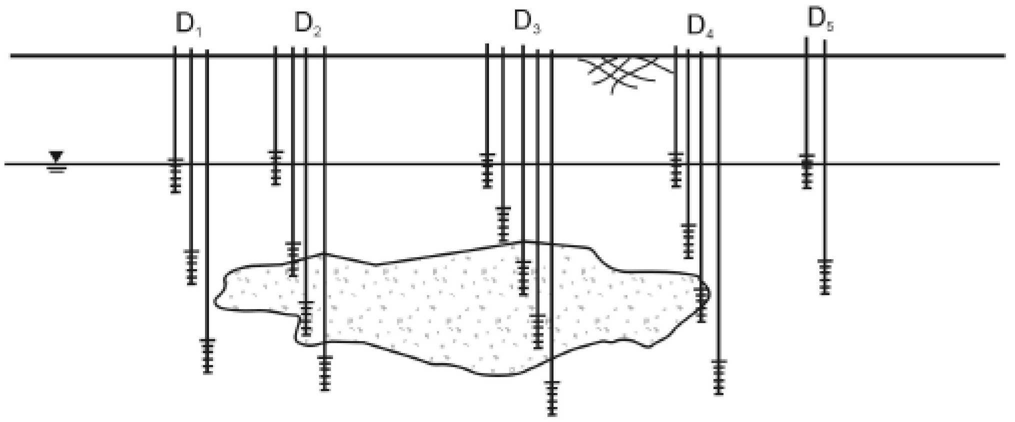


(B) Longitudinal Cross-Section of Optimal Groundwater Monitoring Network

**Exhibit IX-26**
**(continued)**



(C) Transverse Cross-section of Optimal Groundwater Monitoring Network at Transect "C"



(D) Transverse Cross-section of Optimal Groundwater Monitoring Network at Transect "D"

Note: Figure not to scale.

## Contingency Plan

A contingency remedy is a cleanup technology or approach specified in the site remedy decision document that functions as a "backup" remedy in the event that the selected remedy (in this case MNA) fails to perform as anticipated. A contingency remedy may specify a technology (or technologies) that is (are) different from the selected remedy, or it may simply call for modification of the selected technology, if needed. Contingency remedies should generally be flexible—allowing for the incorporation of new information about site risks and technologies. It is also recommended that one or more criteria ("triggers") be established, as appropriate, in the remedy decision document that will signal unacceptable performance of the selected remedy and indicate when to implement contingency remedies. In establishing triggers or contingency remedies, however, care is needed to ensure that sampling variability or seasonal fluctuations do not unnecessarily trigger a contingency.

### Contaminated Soil

Trigger criteria for contaminated soil should generally include, but not be limited to, the following:

- Contaminant concentrations in soil that are not decreasing as originally predicted during remedy selection;
- Migration of vapors into nearby structures (*e.g.*, sewers, basements);
- Near-source samples show large concentration increases indicative of a new or renewed release; and
- Changes in land use that might result in exposure.

Potential contingency remedies which are documented in other chapters of this guidance manual are: Thermal Desorption (Chapter VI), Land Farming (Chapter V), Biopiles (Chapter IV), SVE (Chapter II), Bioventing (Chapter III), Enhanced Aerobic Bioremediation (Chapter XII), and Chemical Oxidation (Chapter XIII).

### Contaminated Groundwater

Trigger criteria for contaminated groundwater should generally include, but not be limited to, the following:

- Increasing contaminant concentrations in groundwater or the appearance of free product in monitoring wells;
- Near-source wells exhibit large concentration increases indicative of a new or renewed release;
- Contaminants are identified in monitoring wells located outside of the original plume boundary;
- Impacts to nearby receptors (especially wells) indicating that MNA is not protective;
- Contaminant concentrations are not decreasing at a sufficiently rapid rate to meet the remediation objectives;
- Concentrations of geochemical parameters are changing such that they indicate a declining capacity to support biodegradation of contaminants; and
- Changes in land and/or groundwater use will adversely affect the protectiveness of the MNA remedy.

Potential contingency remedies which are documented in other chapters of this guidance manual are: Air Sparging (Chapter VII), Biosparging (Chapter VIII), In-Situ Groundwater Bioremediation (Chapter X), Dual-Phase Extraction (Chapter

XI), Enhanced Aerobic Bioremediation (Chapter XII), and Chemical Oxidation (Chapter XIII).

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## Checklists: Evaluating CAP Completeness andPotential Effectiveness of MNA

These checklists can help you to evaluate the completeness of the CAP and to identify areas that require closer scrutiny. As you go through the CAP, complete the appropriate checklists which follow. They can be attached to the CAP for quick future reference. If the answer to any of the questions below is no, then the CAP is incomplete and you will need to request additional information to determine if MNA will achieve remediation objectives at the site.

# Initial Screening–Soil Contamination ONLY

**Site Name:**_____________________________________ **Date** ______________

**Address1:**______________________________________ **Initials**_____________

**Address2:**___________________________________________

**Project/Case Number:**_______________________________

**Recommendation:**________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

| **Yes** | **No** | |
|---|---|---|
| o | o | Has source mass been estimated? ______________________________ |
| o | o | Is the source mass likely to remain trapped within the soil?___________ |
| | | _________________________________________________________ |
| o | o | Has source longevity been estimated? ___________________________ |
| o | o | Is the estimate of the length of time required to meet remediation objectives reasonable?_______________________________________ |
| | | ________________________________________________________ |
| o | o | Is there no threat of potential receptors coming in contact with contaminated soil?__________________________________________ |
| | | _________________________________________________________ |
| o | o | Is there no threat to potential receptors from vapor migration? |
| | | _________________________________________________________ |

# Initial Screening–Groundwater Contamination

**Site Name:**___________________________________ **Date** _____________

**Address1:**____________________________________ **Initials**___________

**Address2:**____________________________________

**Project/Case Number:**_______________________________

**Recommendation:**________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

| **Yes** | **No** | |
|---|---|---|
| o | o | Has free product (if present initially) been recovered to the maximum extent practicable?__________________________________________ |
| o | o | Has source mass been estimated? ______________________________ |
| o | o | Has the plume lifespan been estimated? _________________________ |
| o | o | Is the estimate of the length of time required to meet remediation objectives reasonable?_______________________________________<br>________________________________________________________ |
| o | o | Based on evaluation of field data, is the plume shrinking?________________<br>________________________________ |
| o | o | Are all potential receptors located at a distance represented by a minimum 2-year travel time?_________________________________ |

# Detailed Evaluation–Soil Contamination

**Site Name:**___________________________________ **Date** _____________

**Address1:**____________________________________ **Initials**___________

**Address2:**____________________________________

**Project/Case Number:**_______________________________

**Recommendation:**________________________________________________________

_________________________________________________________________________

_________________________________________________________________________

_________________________________________________________________________

| **Yes** | **No** | |
|---|---|---|
| o | o | Has comprehensive, 3-dimensional site characterization been completed?__________________________________________________ |
| o | o | Has soil permeability been measured?_____________________________ |
| o | o | Is soil structure and layering conducive to natural attenuation processes?___________________________________________________ |
| o | o | Has soil organic carbon content ($f_{oc}$) been measured?___________________________________________________ |
| o | o | Have soil saturation limits been calculated for all contaminants of concern?_____________________________________________________ |
| o | o | Are all soil saturation limits for all contaminants of concern below levels expected to cause unacceptable groundwater impacts? _______________<br>____________________________________________________________ |
| o | o | Have soil gas samples been collected and analyzed?_________________ |
| o | o | Have soil geochemical parameters been measured and are they likely to support long-term biodegradation?_______________________________<br>____________________________________________________________ |
| o | o | Have rate constants or biodegradation rates been calculated?_________________________________________________________<br>_______________________________________________________ |
| o | o | Is the estimated time to achieve remediation objectives reasonable?___________________________________________________ |
| o | o | Is there no current or future threat to potential receptors?_____________<br>_____________________________________________________________ |

# Detailed Evaluation–Groundwater Contamination

**Site Name:**____________________________________ **Date** _____________

**Address1:**_____________________________________ **Initials**___________

**Address2:**______________________________________

**Project/Case Number:**_______________________________

**Recommendation:**________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

| **Yes** | **No** | |
|---|---|---|
| ○ | ○ | Has comprehensive, 3-dimensional site characterization been completed?________________________________________________ |
| ○ | ○ | Has the hydraulic conductivity of the most permeable transport zone been measured?____________________________________________<br>________________________________________________________ |
| ○ | ○ | Has the retarded contaminant transport velocity been estimated?<br>_________________________________________________________ |
| ○ | ○ | Has the propensity for plume diving been determined?______________ |
| ○ | ○ | Have contaminants of concern been measured for all monitoring points?___________________________________________________ |
| ○ | ○ | Have geochemical parameters been measured for all monitoring points?___________________________________________________ |
| ○ | ○ | Have isopleth maps been prepared for each parameter?<br>________________________________________________________ |
| ○ | ○ | Have rate constants or biodegradation rates been calculated?__________<br>________________________________________________________ |
| ○ | ○ | Is the estimated time to achieve remediation objectives reasonable?_____<br>________________________________________________________ |
| ○ | ○ | Is there no current or future threat to potential receptors?____________<br>_________________________________________________________ |

# Long-Term Performance Monitoring–Soil Contamination

**Site Name:**___________________________________ **Date** _____________

**Address1:**____________________________________ **Initials**___________

**Address2:**______________________________________

**Project/Case Number:**_______________________________

**Recommendation:**________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

_______________________________________________________________________

| **Yes** | **No** | |
|---|---|---|
| ○ | ○ | Does the monitoring schedule extend for 1-2 years past when remediation objectives are expected to be achieved? ________________ |
| ○ | ○ | Is sample collection frequency at least bi-annually?__________________________________________________ |
| ○ | ○ | Are a sufficient number of locations to be sampled?_______________<br>________________________________________________________ |
| ○ | ○ | Are samples to be analyzed for BTEX, TPH, and other contaminants of concern (if any)?___________________________________________<br>_________________________________________________________ |
| ○ | ○ | Are supplemental soil gas samples to be collected and analyzed?_______<br>_________________________________________________________ |

# Long-Term Performance Monitoring–Groundwater Contamination

**Site Name:**________________________________ **Date** _____________

**Address1:**_________________________________ **Initials**___________

**Address2:**_____________________________________

**Project/Case Number:**_____________________________

**Recommendation:**_____________________________________________________

__________________________________________________________________

__________________________________________________________________

__________________________________________________________________

__________________________________________________________________

**Yes** **No**

o o Does the monitoring schedule extend for 1-2 years past when remediation objectives are expected to be achieved?_______________

_____________________________________________________

o o Is sample collection frequency at least quarterly for the first two years?_______________________________________________

o o Is sample collection frequency after the first two years at most annually?

_____________________________________________________

o o Are a minimum of 3 transverse plume transects, 1 up gradient transect, and 1 plume centerline transect scheduled to be sampled every sampling event?_______________________________________________

o o Are all sentinel wells (if any) scheduled to be sampled every sampling event?

_________________________________________________

o o Are samples to be analyzed for BTEX, TPH, and other contaminants of concern (if any)?_________________________________________

_____________________________________________________

o o Are samples to be analyzed for geochemical indicators and degradation products?___________________________________________________

________________________________________________

# Chapter X

# In-Situ Groundwater Bioremediation

# Contents

# List Of Exhibits

# 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.

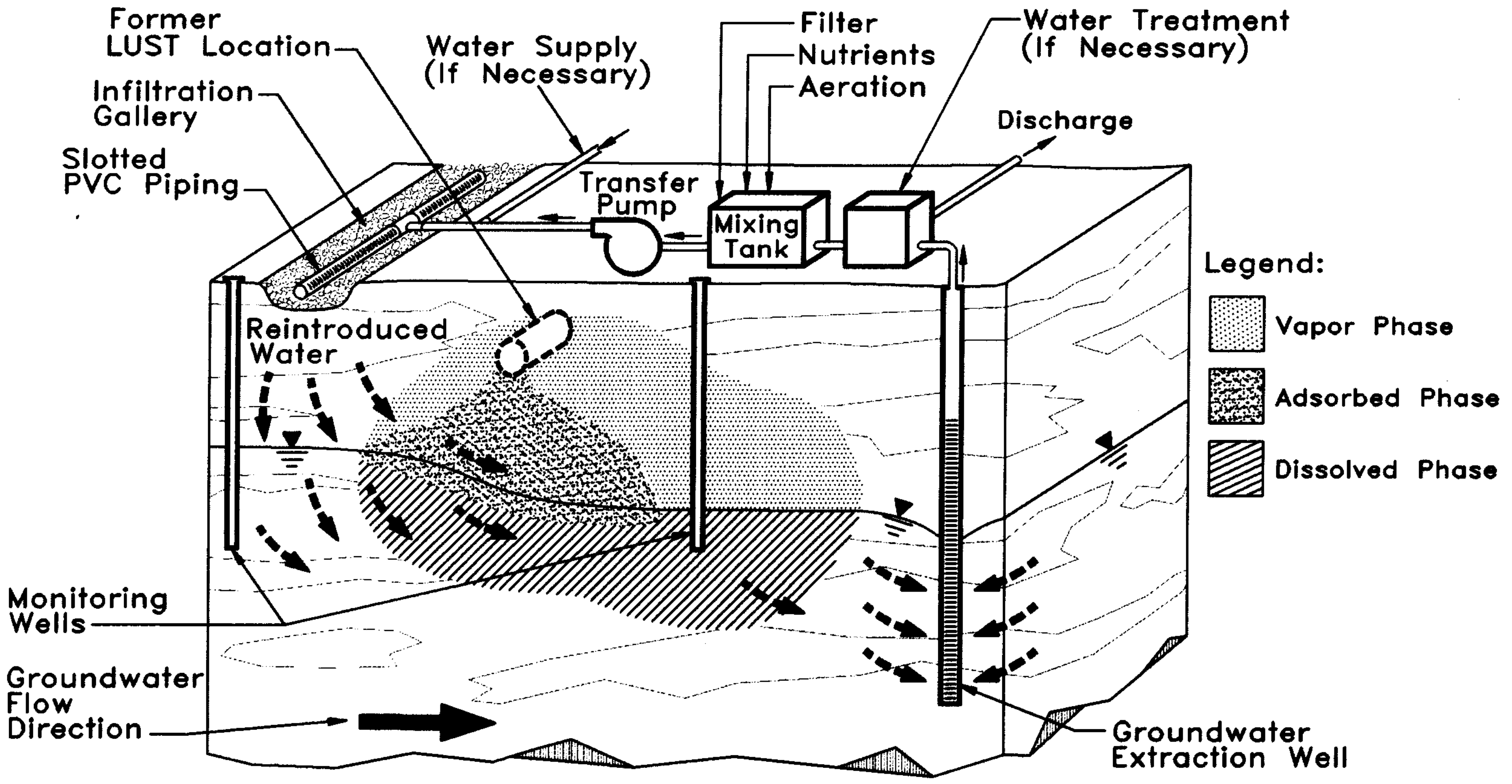
Bioremediation generally requires a mechanism for stimulating and maintaining the activity of these microorganisms. This mechanism is usually a delivery system for providing one or more of the following: An electron acceptor (oxygen, nitrate); nutrients (nitrogen, phosphorus); and an energy source (carbon). 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

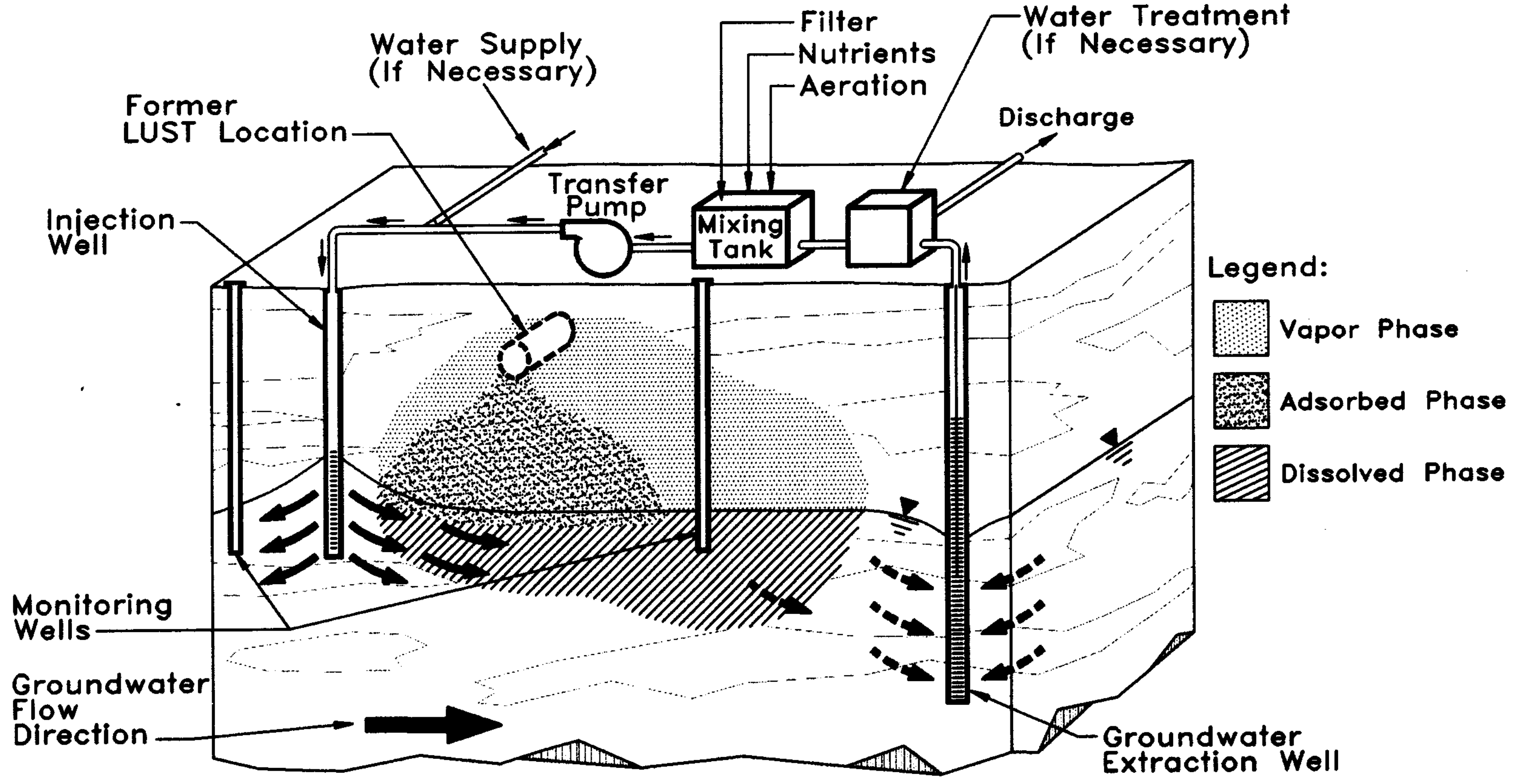
**Exhibit X-1**

**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 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

- 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.
- Application involves equipment that is widely available and easy to install.
- Creates minimal disruption and/or disturbance to on-going site activities.
- Time required for subsurface remediation may be shorter than other approaches (e.g., pump and treat).
- Is generally recognized as being less costly than other remedial options (e.g., pump and treat, excavation).
- Can be combined with other technologies (e.g., bioventing, soil vapor extraction) to enhance site remediation.
- In many cases, this technique does not produce waste products that must be disposed of.

### Disadvantages

- Injection wells and/or infiltration galleries may become plugged by microbial growth or mineral precipitation.
- High concentrations (TPH > 50,000 ppm) of low solubility constituents may be toxic and/or not bioavailable.
- Difficult to implement in low-permeability aquifers ($<10^{-4}$ cm/sec).
- Re-injection wells or infiltration galleries may require permits or may be prohibited. Some states require permit for air injection.
- May require continuous monitoring and maintenance.
- Remediation may only occur in more permeable layer or channels within the aquifer.

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

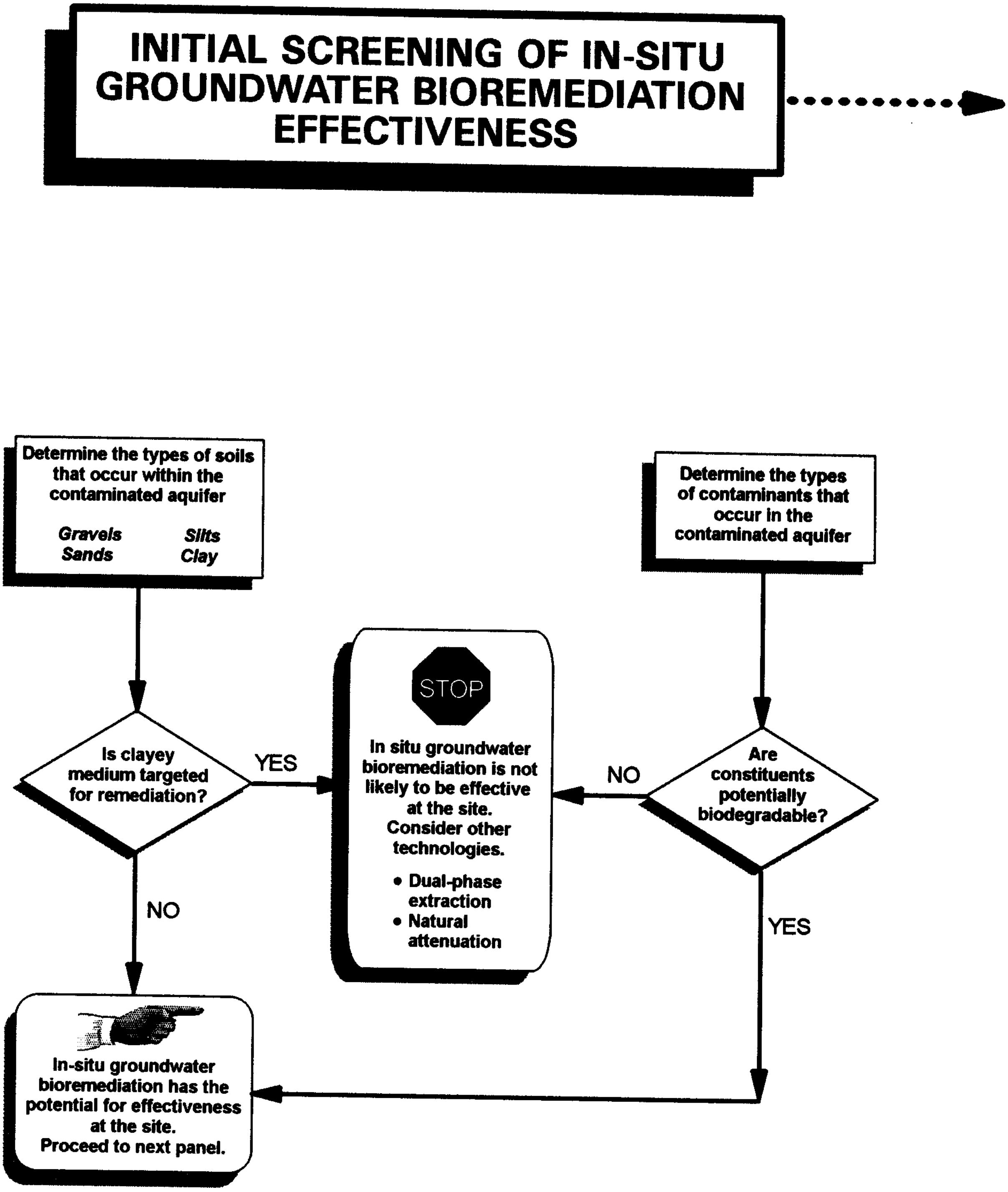


Exhibit X-4
In-situ Groundwater Bioremediation Evaluation Process Flow Chart

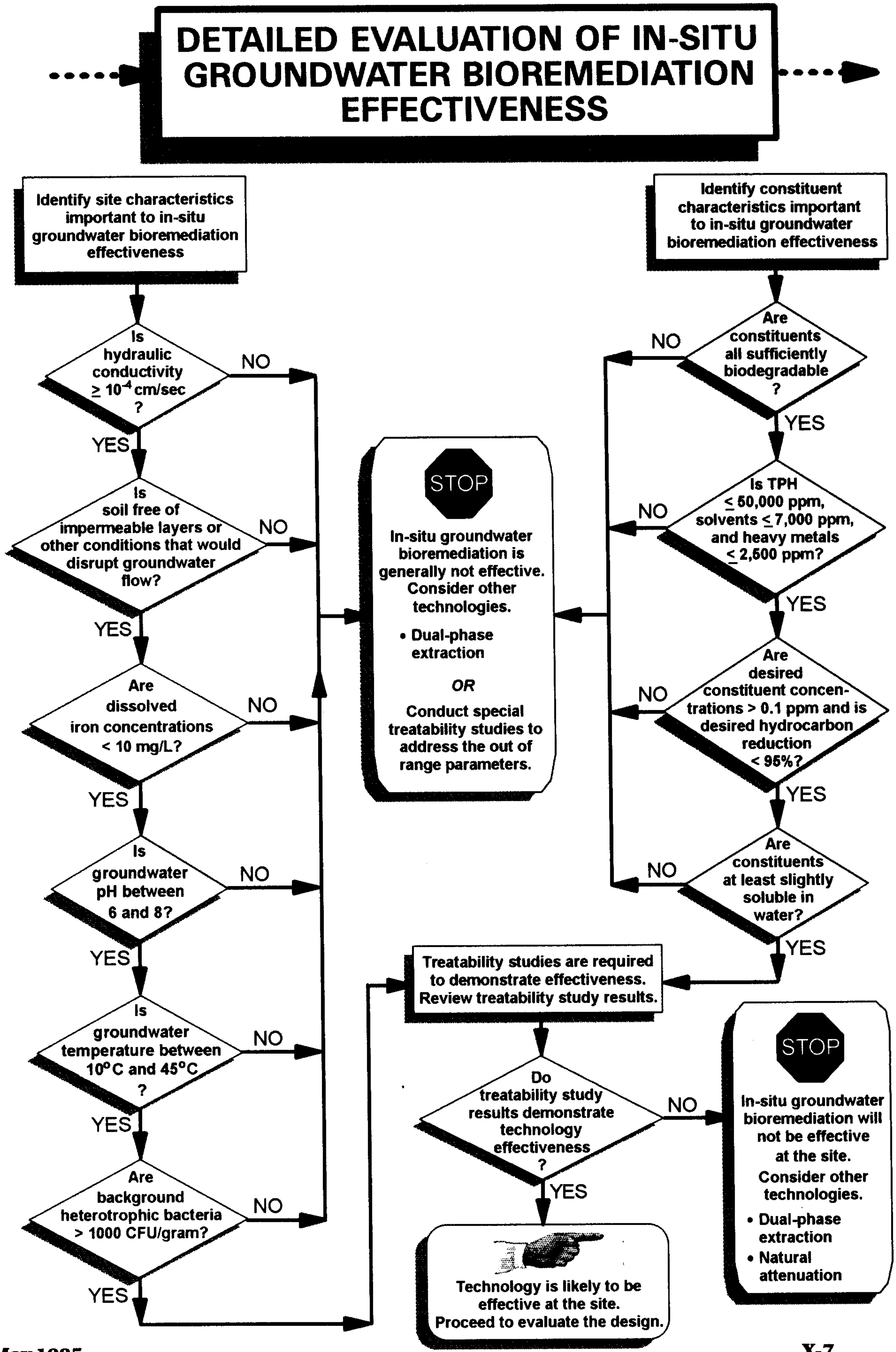
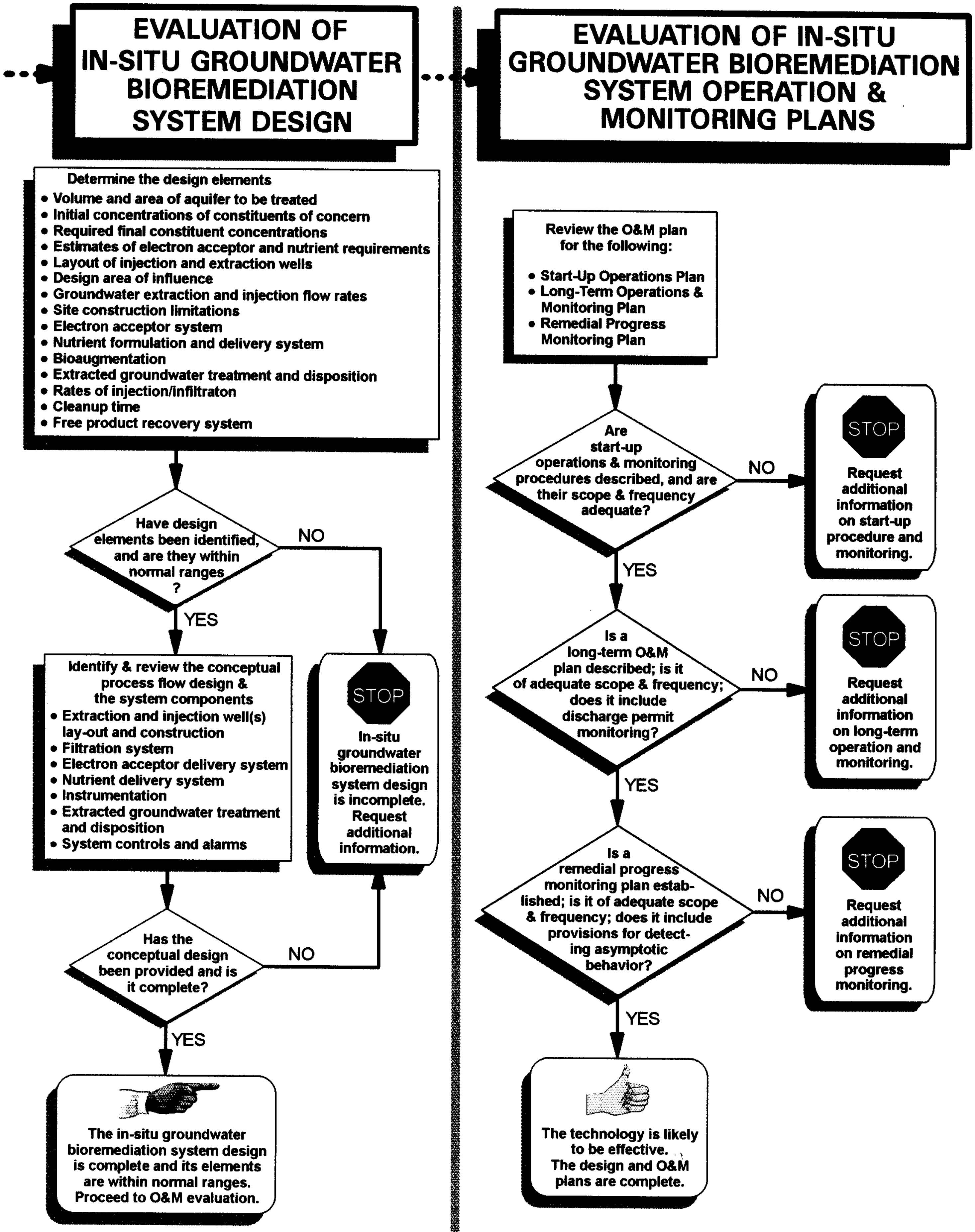


Exhibit X-4

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.

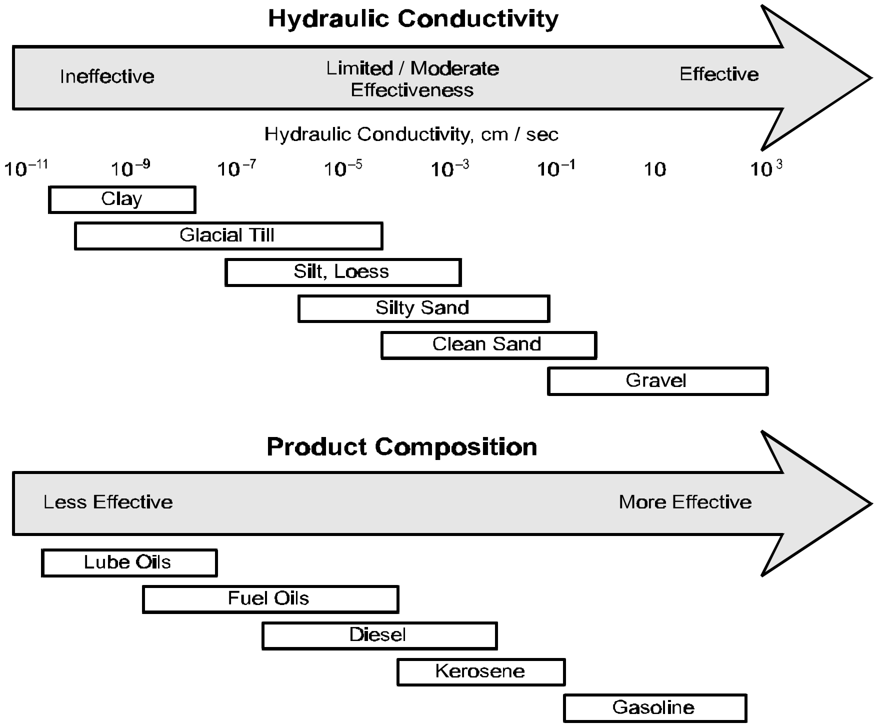
The chemical characteristics of the contaminants will dictate their biodegradability. For example, heavy metals are not degraded by bioremediation. The biodegradability of organic constituents depends on their chemical structures and physical/chemical properties (e.g., water solubility, water/octanol 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**

Hydraulic conductivity
Soil structure and stratification
Groundwater mineral content
Groundwater pH
Groundwater temperature
Microbial presence
Terminal electron acceptors
Nutrient concentrations

**Constituent Characteristics**

Chemical structure
Concentration and toxicity
Solubility

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 ($cm^2$),

$\mu$ = water viscosity (g/cm ·sec),

$\rho$ = water density ($g/cm^3$),

$g$ = acceleration of gravity ($cm/sec^2$).

At 20°C: $(\rho g/\mu) = 9.8 \times 10^4\ (\text{cm} \cdot \text{sec})^{-1}$. To convert k from $\text{cm}^2$ 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., > 400-500 mg/L carbonate hardness) tends to promote 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.

$$\text{Organic Matter} + O_2 + \text{Biomass} \rightarrow CO_2 + H_2O + \triangle H_f$$

where $\triangle H_f$ 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:l 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 | ❍ Diesel |
| | Dodecanes | ❍ Kerosene |
| | Tridecanes | ❍ Heating fuels |
| | Tetradecanes | ❍ Lubricating oils |
| Less degradable | Naphthalenes | ❍ Diesel |
| | Fluoranthenes | ❍ Kerosene |
| | Pyrenes | ❍ Heating oil |
| | Acenaphthenes | ❍ Lubricating oils |
| Resistant | Asphaltenes | ❍ Fuel oil no. 6 |
| | MTBE | ❍ 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,<br>Solvent constituents $\leq$ 7,000 ppm,<br>and<br>Heavy metals $\leq$ 2,500 ppm | Effective. |
| Petroleum constituents > 50,000 ppm,<br>Solvent constituents > 7,000 ppm,<br>or<br>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<br>and<br>Petroleum hydrocarbon reduction < 95% | Effective. |
| Constituent concentration ≤ 0.1 ppm<br>or<br>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 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;

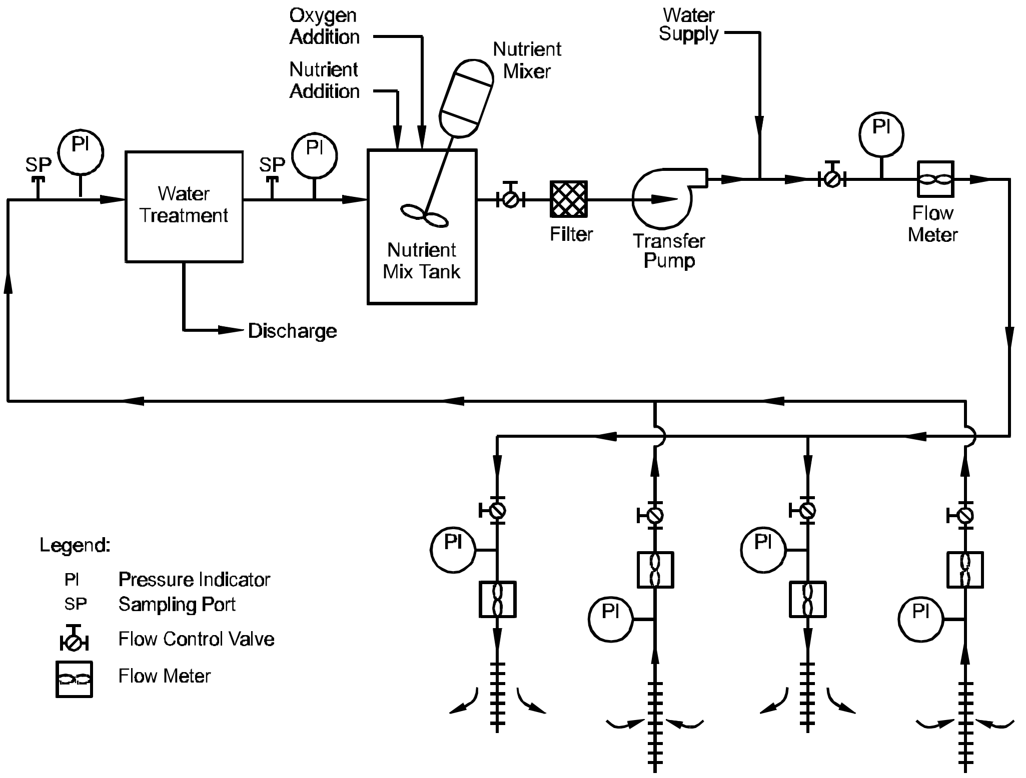
- Extracted groundwater treatment system (e.g., biological, chemical oxidation, granular carbon adsorption) and methods for disposal or re-use of treated groundwater (surface discharge, discharge to a sewer, re-injection);

- 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:

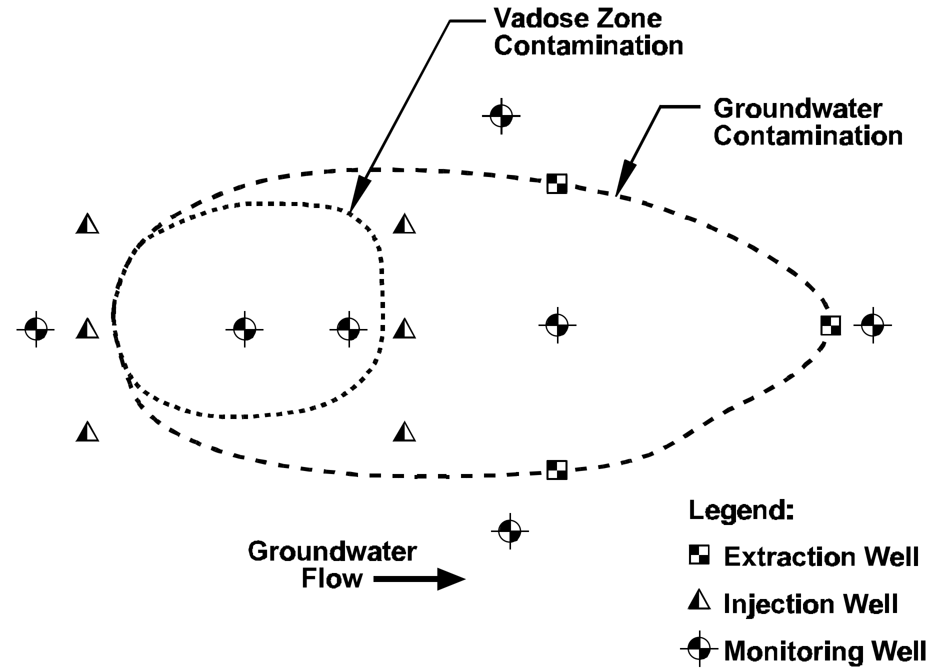
❍ Extraction wells should be located such that hydraulic control is achieved at the outer limits of the contaminant plume. In other words, the cones of depression created by the pumping wells should intersect so that hydraulic gradients throughout the plume are inward in the direction of the pumping 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.

### X-13
### Idealized Layout Of Extraction, Injection, And Monitoring Wells For In-Situ Groundwater Bi Exhibit oremediation



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<br>○ Injection volume | ○ Extraction and injection well heads or manifolds |
| | | ○ Electron acceptor concentration | ○ Monitoring wells |
| | Every 2-3 days | ○ Groundwater levels | ○ Monitoring wells |
| Remedial (ongoing) | Weekly | ○ Groundwater levels | ○ Monitoring wells |
| | | ○ Extraction and injection flow rates | ○ Extraction and injection wellheads or manifolds |
| | | ○ Concentration of electron acceptor, ammonia, phosphate, nitrate, pH, and conductivity | ○ Monitoring wells |
| | Monthly to quarterly | ○ Constituent concentrations in soil and groundwater | ○ Extraction, injection, and monitoring wells<br>○ 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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Sims, J.L., J.M. Suflita, and H.H. Russell. *In-situ Bioremediation of Contaminated Groundwater*. Washington, DC: U.S. Environmental Protection Agency, EPA/540/S-92/003, (NTIS: PB92-224336/XAB), February 1992.

Staps, S.J.J.M. *International Evaluation of In-Situ Biorestoration of Contaminated Soil and Groundwater*. Washington, DC: U.S. Environmental Protection Agency, Office of Emergency and Remedial Response. EPA 540/2–90/012, 1990.

Van der Heijde, P.K.M., and O.A. Elnawawy. *Compilation of Groundwater Models*. Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development, EPA/600/R–93/118, (NTIS: PB93-209401), May 1993.

# 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

# Contents

# List Of Exhibits

# 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

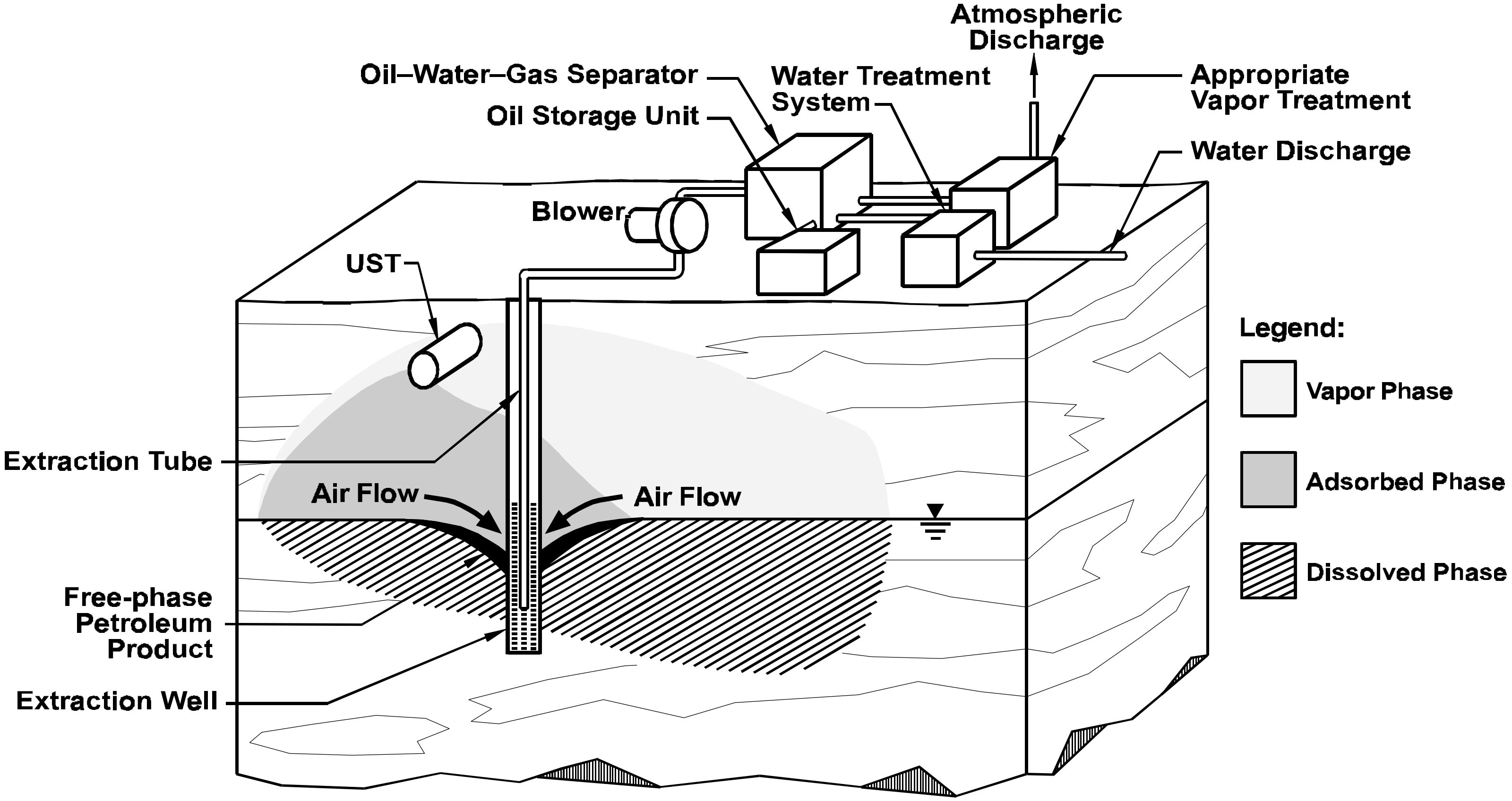
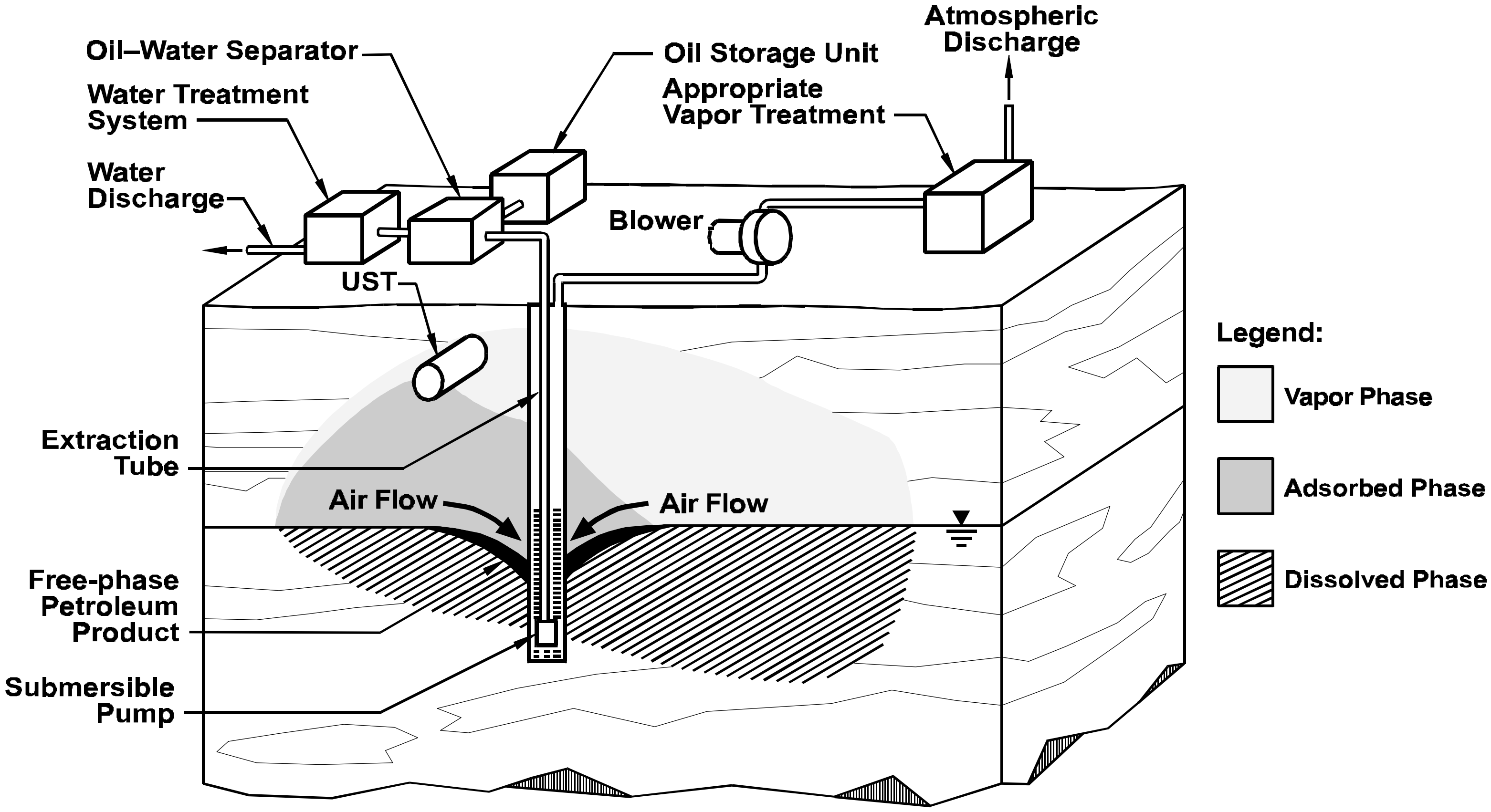


Exhibit XI-2

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.

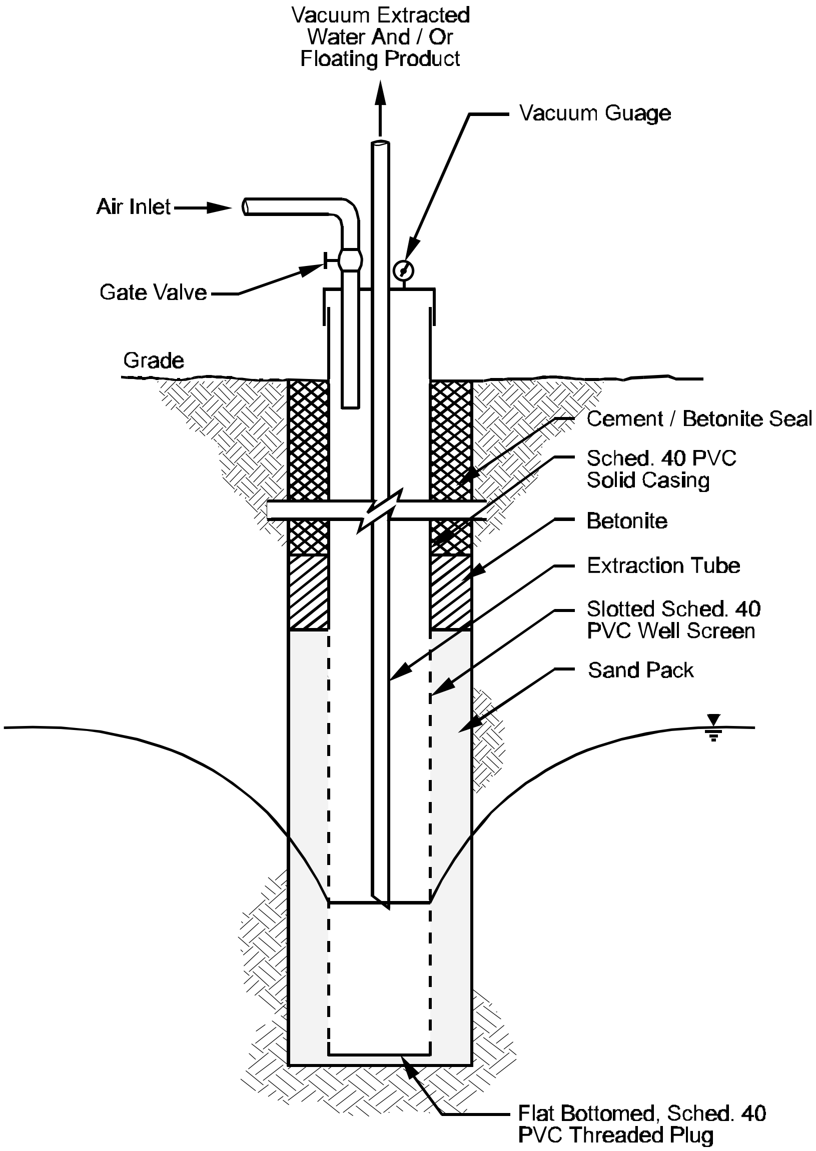
Vacuum groundwater extraction has been used for many decades as a standard method for extracting groundwater to control seepage or effect dewatering during construction and mining activities (Powers, 1981). Single-pump DPE systems represent a recent adaptation of this long-established technology to the 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.

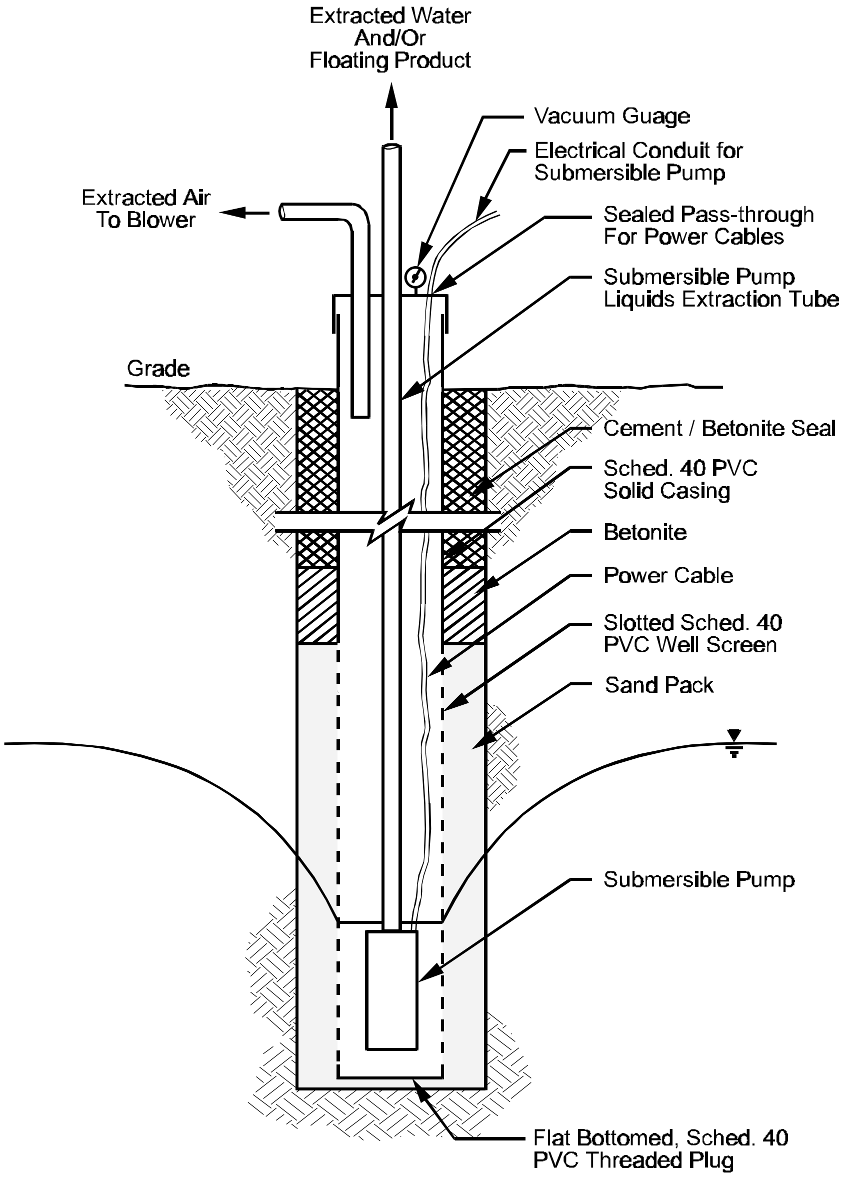
The vacuum applied to the subsurface with DPE systems creates vapor-phase pressure gradients toward the vacuum well. These vapor-phase pressure gradients are also transmitted directly to the subsurface liquids present, and those liquids existing in a continuous phase (e.g., water and "free" petroleum 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. | |

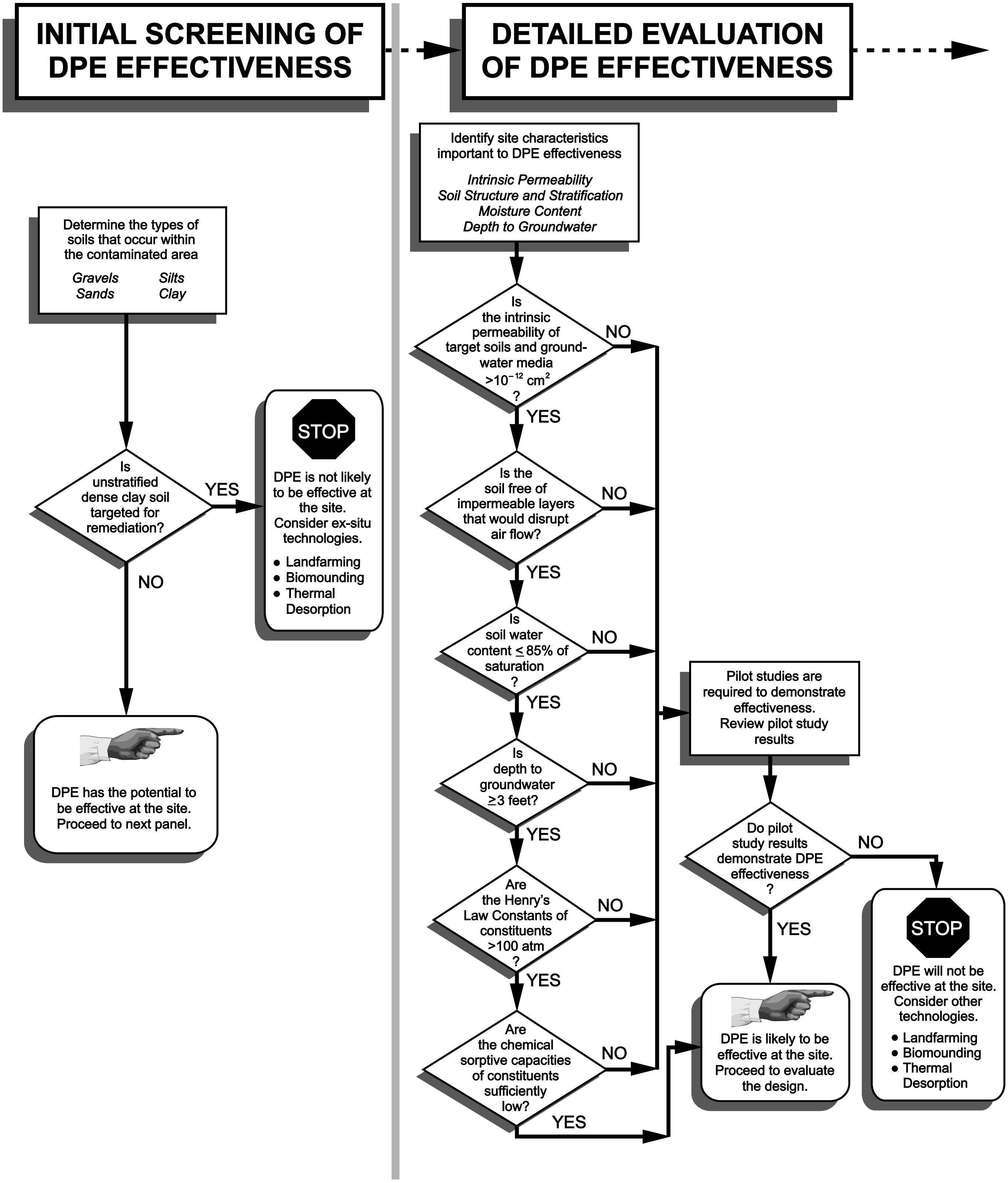
decisions you will make during your evaluation. The evaluation can be divided into the following steps.

- ***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.

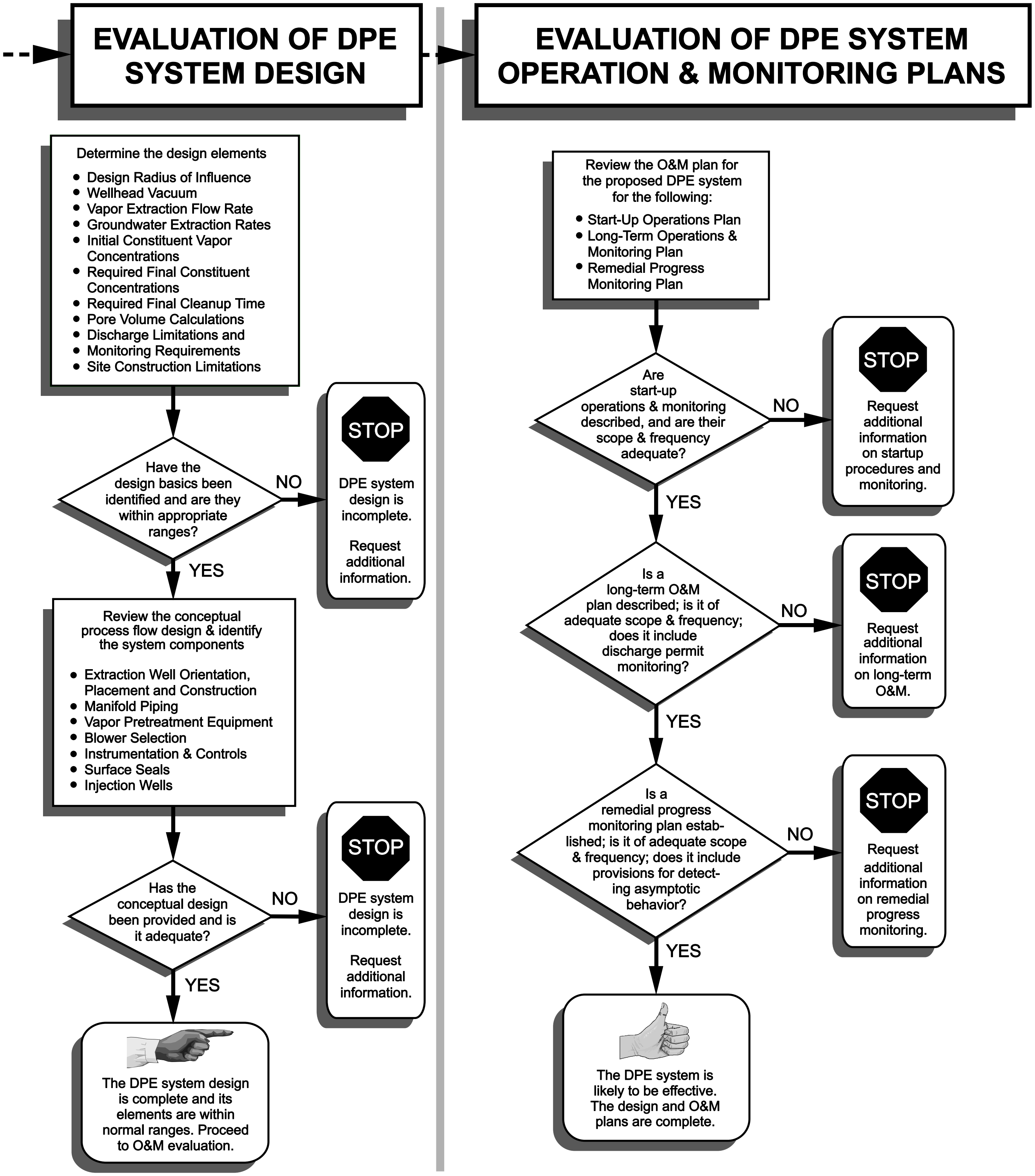
- ***Step 2: A detailed evaluation of DPE effectiveness***, which provides further screening criteria to confirm whether DPE is likely to be effective at a given site. To complete the detailed evaluation, you will need to identify key site characteristics and soil properties in the CAP, compare them 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.

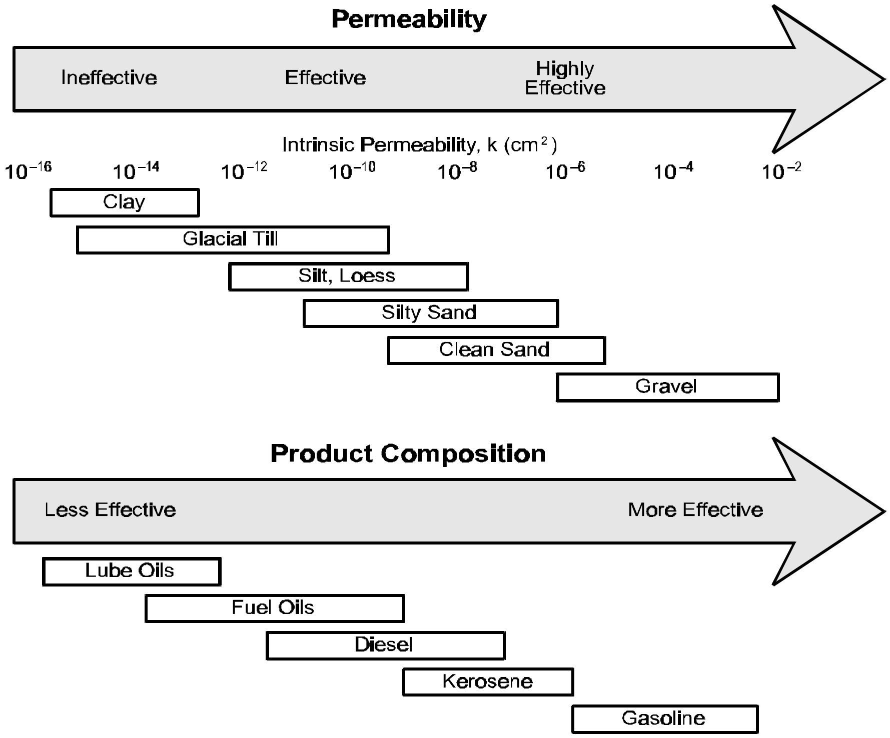
- ❍ *Volatilit*y of the petroleum constituents. Volatility determines the rate at and degree to which petroleum constituents will vaporize to the soil vapor state.

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 remediatioon 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 through 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 products composition present, you need to further evaluate the CPA 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 concentration 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<br>Soil structure and stratification<br>Moisture content in the unsaturated zone<br>Depth to groundwater | Effective volatility<br>Chemical sorptive capacity |

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., $< 10^{-11} \sim$ cm$^2$) can be dewatered if they are interbedded with coarser-grained sediments. The coarser-grained sediments are dewatered flrst, 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)
$\mu$ = water dynamic viscosity (g/cm $\cdot$ sec)
$\rho$ = 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 corbon-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 pteroleum 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 higher sorption decreases vandose and groundwater zones. Although higher sorptive 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 wil 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, DPEis 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 pilots-cale 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 reinfection (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 groundwaterseparately). 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)
$\varepsilon$ = 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.

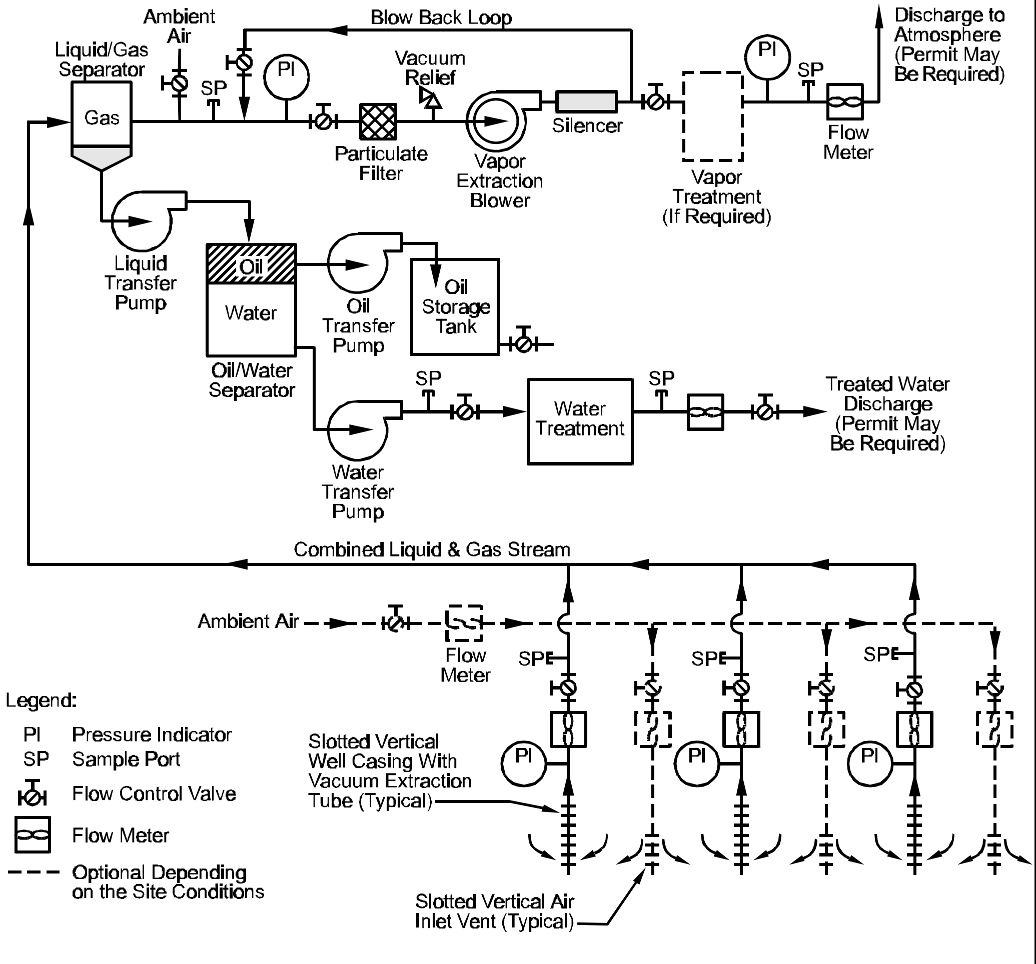
Then, space the wells evenly within the treatment area to provide areal coverage so that the areas of influence cover the entire area of contamination.

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

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

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,

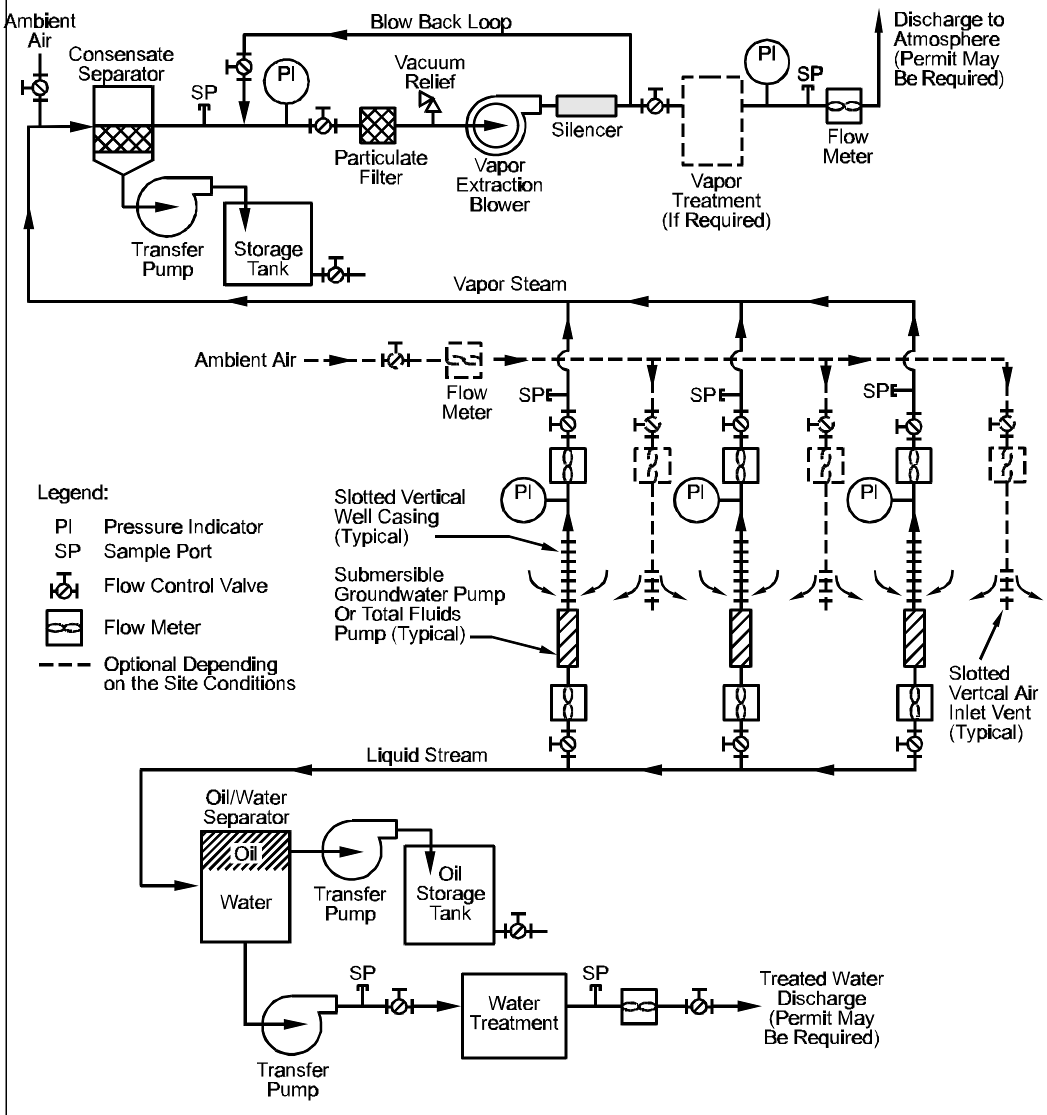
**Exhibit XI-13**
**Schematic of Single Pump DPE System**



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: $\varepsilon$ = 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 Ethology, 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.

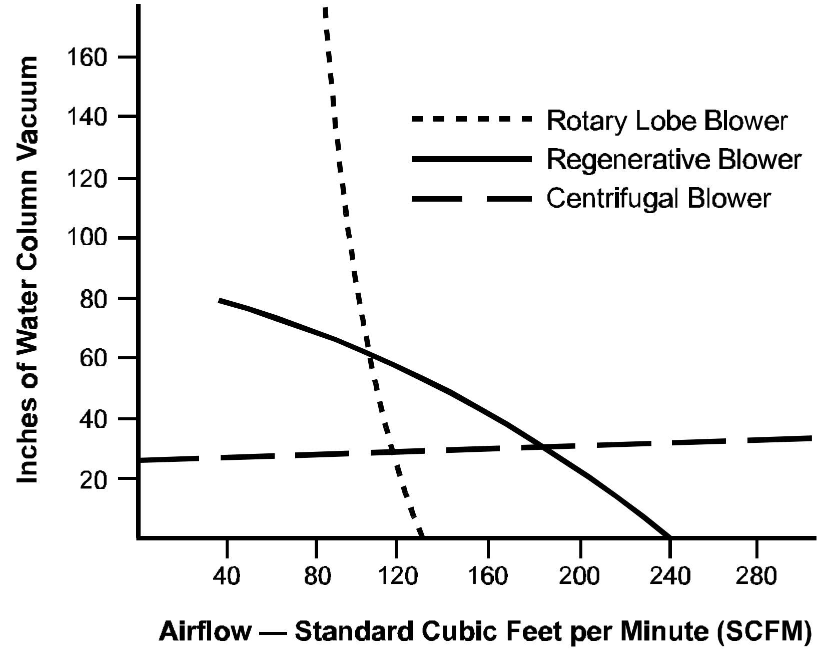
### *Blower Selection*

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**



Note: 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 Remedical Response Section, PUBL-SW 185-93, 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<br>❍ Manifold to blower<br>❍ Blower discharge | ❍ Pitot tube<br>❍ In-line rotameter<br>❍ Orifice plate<br>❍ Venturi or flow tube |
| Vacuum gauge | ❍ At each well head or manifold branch<br>❍ Before and after filters upstream of blower<br>❍ Before and after vapor treatment | ❍ Manometer<br>❍ Magnehelic gauge<br>❍ Vacuum gauge |
| Vapor temperature sensor | ❍ Manifold to blower<br>❍ Blower discharge (prior to vapor treatment) | ❍ Bi-metal dial-type thermometer |
| Sampling port | ❍ At each well head or manifold branch<br>❍ Manifold to blower<br>❍ Blower discharge | ❍ Hose barb<br>❍ Septa fitting |
| Vapor sample collection equipment (used through a sampling port) | ❍ At each well head or manifold branch<br>❍ Manifold to blower<br>❍ Blower discharge | ❍ Tedlar bags<br>❍ Sorbent tubes<br>❍ Sorbent canisters<br>❍ Polypropylene tubing for direct GC injection |
| **Control Equipment** | | |
| Flow control valves | ❍ At each well head or manifold branch<br>❍ Dilution or bleed valve at manifold to blower | ❍ Ball valve<br>❍ Gate/globe valve<br>❍ 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 DPEsystem 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**

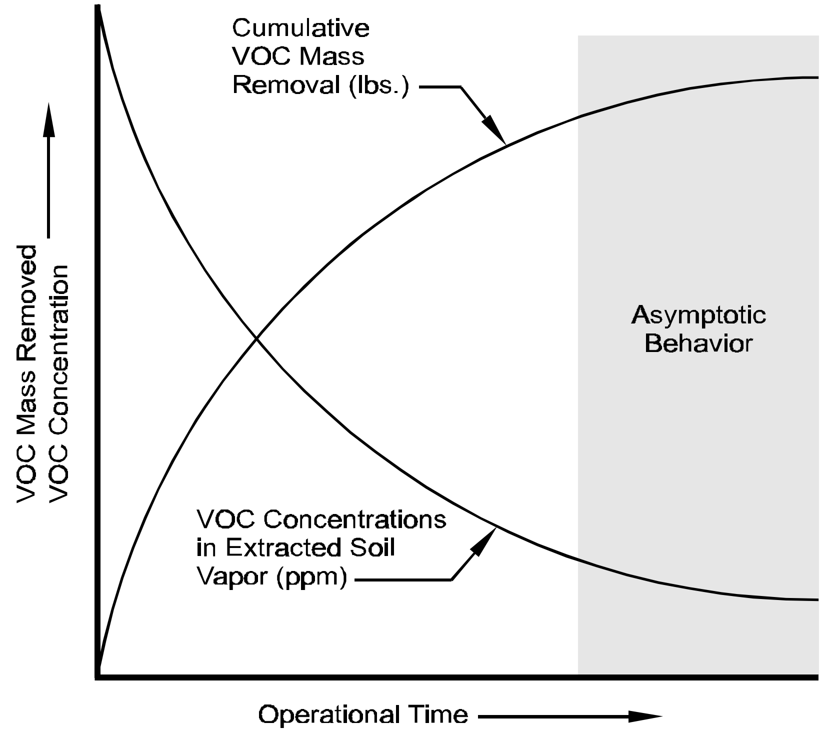
| Phase | Monitoring Frequency | What To Monitor | Where To Monitor |
|---|---|---|---|
| Start-up (7-10 days) | At least daily | ○ Flow<br>○ Vacuum readings<br>○ Vapor concentrations<br>○ Carbon dioxide<br>○ Oxygen | ○ Extraction vents<br>○ Manifold<br>○ Effluent stack |
| Remedial (ongoing) | Weekly to bi-weekly | ○ Flow-balancing<br>○ Flow<br>○ Vacuum<br>○ Vapor concentrations<br>○ Carbon dioxide<br>○ Oxygen | ○ Extraction vents<br>○ Manifold<br>○ 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 effective way to complete remediation.

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Johnson, R.L., Bagby, W., Matthew, P., and Chien, C.T. "Experimental Examination of Integrated Soil Vapor Extraction Techniques," in *Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*. National Ground Water Association, November, 1992.

Powers, J.P. Construction Dewatering, *A Guide to Theory and Practice*. Wiley Interscience, 1981.

U.S. Air Force. Technology Profile: *Vacuum-Mediated LNAPL Free Product Recovery/Bioremediation (Bioslurper)*. Air Force Center for Environmental Excellence, March 1994.

# Checklist: Can Dual-Phase Extraction Be Used At This Site?

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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

# Enhanced Aerobic Bioremediation

# Contents

# List of Exhibits

# List of Exhibits (continued)

# Chapter XII
# Enhanced Aerobic Bioremediation

## Overview

Enhanced aerobic bioremediation technologies are used to accelerate naturally occurring in-situ bioremediation of petroleum hydrocarbons, and some fuel oxygenates such as methyl tertiary-butyl ether (MTBE), by indigenous microorganisms in the subsurface. Enhanced aerobic bioremediation technologies include biosparging; bioventing[1]; use of oxygen releasing compounds; pure oxygen injection; hydrogen peroxide infiltration; and ozone injection[2]. These technologies work by providing a supplemental supply of oxygen to the subsurface, which becomes available to aerobic, hydrocarbon-degrading bacteria. The stoichiometric ratio of oxygen per hydrocarbon is 3 M $O_2$ per 1 mole of hydrocarbons. Oxygen is considered by many to be the primary growth-limiting factor for hydrocarbon-degrading bacteria, but it is normally depleted in zones that have been contaminated with hydrocarbons. By using these technologies, rates of biodegradation of petroleum hydrocarbons can be increased at least one, and sometimes several, orders of magnitude over naturally-occurring, non-stimulated rates.

Enhanced aerobic bioremediation technologies can be used to address contaminants in the unsaturated zone, the saturated zone, or both. Bioventing, for example, specifically targets petroleum hydrocarbon contaminants in the unsaturated zones and does not address contaminants in the capillary fringe or saturated zone. Most, but not all, enhanced aerobic bioremediation technologies primarily address petroleum hydrocarbons and some oxygenates that are dissolved in groundwater or are sorbed to soil particles in the saturated zone. The technologies are typically employed outside heavily contaminated source areas which will usually be addressed by more aggressive remedial approaches.

When used appropriately, enhanced aerobic bioremediation technologies are effective in reducing levels of petroleum contamination at leaking underground storage tank sites. Gasoline constituents dissolved in water are a likely target of enhanced aerobic bioremediations. Enhanced aerobic bioremediation technologies are most often used at sites with mid-weight petroleum products (e.g., diesel fuel,

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[1] For more information on Biosparging and Bioventing, see *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers* (US EPA 510-R-04-002), Chapter III (“Bioventing”) and Chapter VIII (“Biosparging”).

[2] Other enhanced aerobic bioremediation technologies, including surfactant enhanced microbubble injection and permeable polymeric tubing oxygen diffusion, are not discussed in this chapter because of their limited use and experimental status.

readily and can be removed more rapidly using other technologies (e.g., air sparging or soil vapor extraction). However, if these lighter products are present, enhanced aerobic bioremediation technologies can also effectively reduce contaminant concentrations. Heavier petroleum products such as lubricating oils generally take longer to biodegrade than the lighter products, but enhanced aerobic bioremediation technologies may still be effective at sites contaminated with these products.

It is generally not practical to use enhanced aerobic bioremediation technologies to address free mobile product or petroleum contamination in low permeability soil (e.g., clay). Because enhanced aerobic bioremediation is a relatively slow cleanup approach, it is not recommended to address current or imminent excessive human health or environmental risks.

Exhibit XII-1 summarizes the general advantages and disadvantages of enhanced aerobic bioremediation technologies. Discussions of bioventing and biosparging, two other enhanced aerobic bioremediation technologies, are provided in *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers* (US EPA 510-R-04-002, 2004), Chapter III ("Bioventing"), Chapter VIII ("Biosparging"), and Chapter X ("In-Situ Groundwater Bioremediation").

A brief description of several of the technologies is provided below.

## Oxygen Releasing Compounds

Various enhanced aerobic bioremediation approaches rely on oxygen releasing compounds to remediate petroleum contamination. More commonly used oxygen releasing compounds include calcium and magnesium peroxides that are introduced to the saturated zone in solid or slurry phases. These peroxides release oxygen to the aquifer when hydrated by groundwater as the peroxides are ultimately converted to their respective hydroxides. Magnesium peroxide has been more commonly applied in field applications than calcium peroxide because of magnesium peroxide's lower solubility and, consequently, prolonged release of oxygen. Magnesium peroxide formulations placed in the saturated zone during a short-term injection event can release oxygen to groundwater over a four- to eight- month period. Significant quantities of magnesium peroxide are required based on stoichiometry and the fact that 90% of the weight of the compound is not oxygen. Oxygen amounting to approximately 10% of the weight of magnesium peroxide placed in the saturated zone is released to the aquifer over the active period.

## Exhibit XII-1
## Enhanced Aerobic Bioremediation
## Primary Advantages and Disadvantages

### Advantages

- Works with and enhances natural in-situ processes already at play (typically uses natural groundwater gradient, naturally occurring biodegradation)
- Destroys the petroleum contamination in place
- Produces no significant wastes (off-gases or fluid discharges)
- Can be a low-energy approach
- Is relatively inexpensive
- Complements more aggressive technologies (e.g., groundwater extraction) and less aggressive approaches (e.g., intrinsic remediation) that can be integrated into site remediation
- Causes minimal disturbance to site operations
- Has simple operation and monitoring requirements
- Is potentially more reliable than other, more active remedial technologies (e.g., groundwater extraction and treatment)
- Can be used in tandem with other remedial technologies that address small amounts of residual soil and groundwater contamination

### Disadvantages

- May have longer remedial time frames than more aggressive approaches
- May not be able to reduce contaminants to background or very low concentrations
- Typically requires long-term monitoring of residual contamination in soil and groundwater
- May require permits for nutrient/oxygen injection
- May not be fully effective on all petroleum hydrocarbons and product additives (e.g., MTBE)
- Often must be accompanied by other technologies (e.g., product recovery) to address source areas
- May significantly alter aquifer geochemistry
- Can be misapplied to remediation at some sites if the conditions for use are not fully understood
- Oxygen supplied by enhanced aerobic bioremediation may be lost to chemical reactions in the subsurface which do not promote hydrocarbon contaminant oxidation and degradation.

Exhibit XII-2 compares the relative advantages and disadvantages of several different enhanced aerobic bioremediation technologies currently in use.

## Exhibit XII-2
## Enhanced Aerobic Bioremediation Technologies Comparative Matrix

| | Oxygen Releasing Compounds | Hydrogen Peroxide Infiltration | Pure Oxygen Injection | Ozone Injection | Biosparging | Bioventing |
|---|---|---|---|---|---|---|
| **Advantages** | | | | | | |
| No mechanical components required | X | | | | | |
| Minimal engineering design requirements | X | | | | | |
| Relatively low capital and operating costs | X | | | | | |
| Abiotic oxidation of contaminants contacting reagents | | X | | X | | |
| Remediates contamination in unsaturated soils | X | X | X | X | X | X |
| Locally saturates groundwater with oxygen to further enhance biodegradation and oxygen distribution | X | X | X | X | | |
| Can efficiently sustain widespread ambient (up to 8 mg/L) oxygen concentrations in groundwater | | | | | X | |
| Can efficiently sustain widespread ambient (up to ~21%) oxygen concentrations in unsaturated soils | | | | | | X |
| Generally considered safe | X | | | | | X |
| Electricity/power source generally not required | X | X | | | | |

## Exhibit XII-2
## Enhanced Aerobic Bioremediation Technologies Comparative Matrix (continued)

| | Oxygen Releasing Compounds | Hydrogen Peroxide Infiltration | Pure Oxygen Injection | Ozone Injection | Biosparging | Bioventing |
|---|---|---|---|---|---|---|
| **Disadvantages** | | | | | | |
| Heavy reliance on groundwater advection, dispersion, and diffusion to distribute oxygen can limit treatment coverage and prolong remediation | X | X | X | | | |
| Increased risk of fugitive vapors entering building structures and utility conduits, particularly in absence of vapor recovery technology (e.g., soil vapor extraction) | | | X | X | X | |
| Does not target or treat saturated zone | | | | | | X |
| On-site reactive chemical handling and storage required | | X | | | | |
| On-site gas production and delivery equipment (e.g., ozone generator) typically required | | | X | X | | |
| Relatively few petroleum remediation projects completed using this technology | | X | X | X | | |
| May require reinjection permits | X | X | | | X | X |
| Radius of influence limited if using “socks” | X | | | | | |
| Zone of influence may be limited with compounds that are suspended in a well. | X | | | | | |

Oxygen releasing compounds may be introduced into the saturated zone in several ways. The most common approaches include:

- Placing the compounds into drilled boreholes or other excavations (e.g., tank fields)
- Injecting a compound slurry into direct-push borings (e.g., Geoprobe)

- Mixing oxygen-releasing compounds directly with contaminated soil and then using the mixture as backfill or hauling it to a disposal site
- Suspending oxygen releasing compounds contained in "socks" in groundwater monitoring wells
- A combination of the above

Oxygen-releasing compounds may also be used to address source areas, entire plumes or plume tails (e.g., a treatment curtain aligned perpendicular to contaminant flow direction). Exhibit XII-3 provides a conceptual depiction of the deployment of oxygen releasing compounds to address a petroleum hydrocarbon plume. Many site-specific conditions must be considered before a remedial approach using this technology can be devised and implemented. One such site-specific concern is the proximity of drinking water supply wells to the treatment area and how the injected oxygen or other nutrients may affect these wells. Another concern is the limited zone of influence of oxygen releasing compounds when deployed in a well, which often provide increased oxygen levels only up to twice the diameter of the well. While the scope of this document does not allow a more in-depth discussion of this or other site-specific implementation, it is important to carefully consider site-specific issues (e.g., contaminant composition and behavior, site geology and hydrology) along with the conceptual information provided in this chapter.

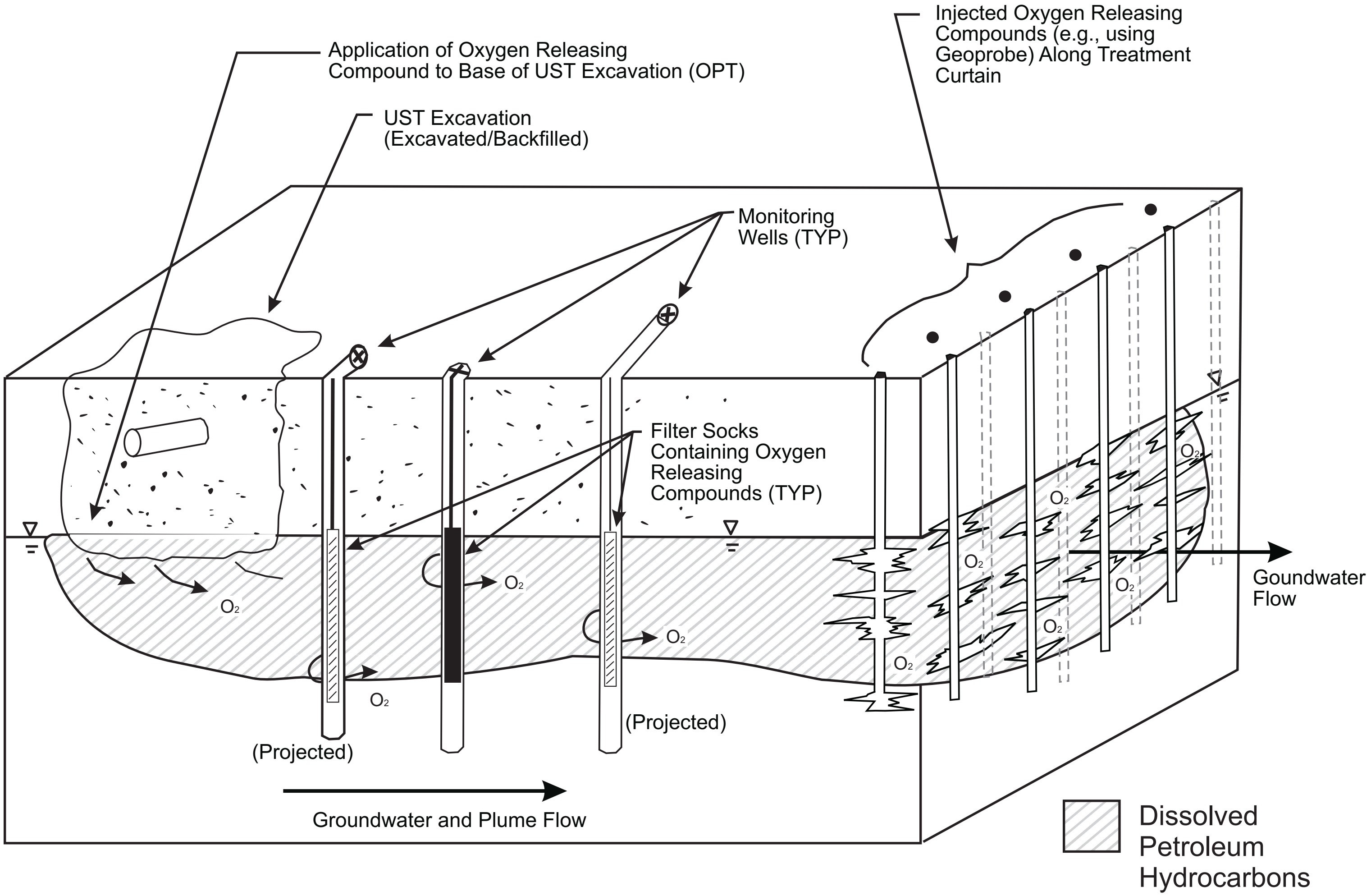
The following sections describe the use of pure oxygen injection, hydrogen peroxide infiltration, and ozone injection.

## Pure Oxygen Injection

Injecting pure oxygen into groundwater can be a relatively efficient means of increasing dissolved oxygen levels in groundwater to promote aerobic biodegradation of petroleum hydrocarbons. In contrast to other enhanced aerobic bioremediation technologies, there is no carrier (e.g., amended groundwater) or delivery media (e.g., oxygen releasing compounds slurry) associated with pure oxygen injection. Approximately one gram of oxygen is delivered to the subsurface for every gram of oxygen directed to the subsurface. Oxygen is several times more soluble in groundwater when it is introduced in pure form than if the dissolved oxygen is derived by forcing groundwater to come into contact with atmospheric air, such as occurs with biosparging. Dissolved oxygen concentrations of up to 40-50 parts per million(ppm) can be achieved through pure oxygen injection, which contrasts to dissolved oxygen concentration limits of approximately 8-10 ppm when the saturated zone is aerated using atmospheric air, which contains approximately 21% oxygen.

Pure oxygen is most commonly introduced into the subsurface via vapor-phase injection. Vapor-phase oxygen (approximately 95% oxygen) is injected into the saturated zone near the base of the dissolved petroleum hydrocarbon contamination using a network of sparge wells. Oxygen sparge rates lower than

## Exhibit XII-3
## Typical Enhanced Aerobic Remediation Using Oxygen Releasing Compounds



air sparge flow rates are used in order to maximize contact time between the oxygen and contaminated groundwater before the injected oxygen rises through the contaminated zone to the water table. Trapping of sparged oxygen in the soil matrix (e.g., in soil pore spaces or semi-confining laminates) beneficially prolongs contact between the pure oxygen and the oxygen-depleted groundwater. Series of vertical oxygen injection wells are often alternately sparged in order to increase dissolved oxygen levels more efficiently over larger areas.

The spacing of injection wells is typically site-specific and based on the thickness of contaminated material, geology, hydrogeology, and other factors affecting the delivery and distribution of dissolved oxygen. Volatile organic vapor production and migration concerns are reduced with oxygen sparging relative to air sparging because of the significantly lower oxygen sparge air flow rates. However, vapor production and migration can be a concern and should be evaluated on a site-specific basis. A conceptual schematic of a pure oxygen injection system is depicted in Exhibit XII-4.

### Hydrogen Peroxide Infiltration

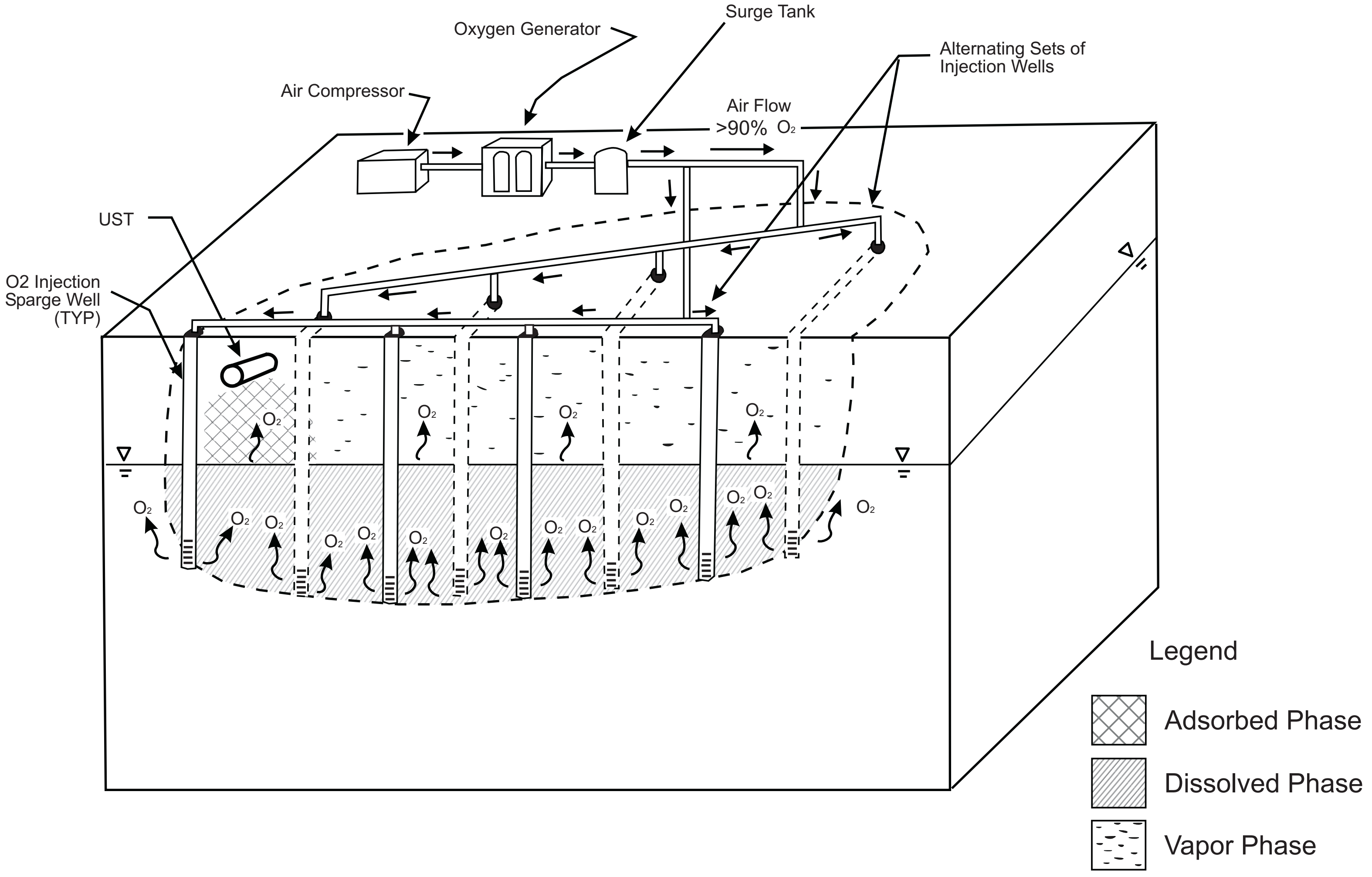
Extracted and treated groundwater is amended and mixed with hydrogen peroxide prior to re-infiltration or re-injection. The hydrogen peroxide-amended groundwater is pumped into infiltration galleries or injection wells located in or near suspected source areas. Generally, the infiltration/injection and groundwater extraction scheme is designed to promote the circulation and distribution of hydrogen peroxide and dissolved oxygen through the treatment area.

Exhibit XII-5 provides a conceptual illustration of a hydrogen peroxide enhanced aerobic bioremediation system. The precipitation of chemical oxidants (e.g., iron oxides) can present potentially significant equipment fouling problems in this type of system, depending on the concentrations of naturally occurring levels of inorganic compounds, such as iron, in the subsurface.

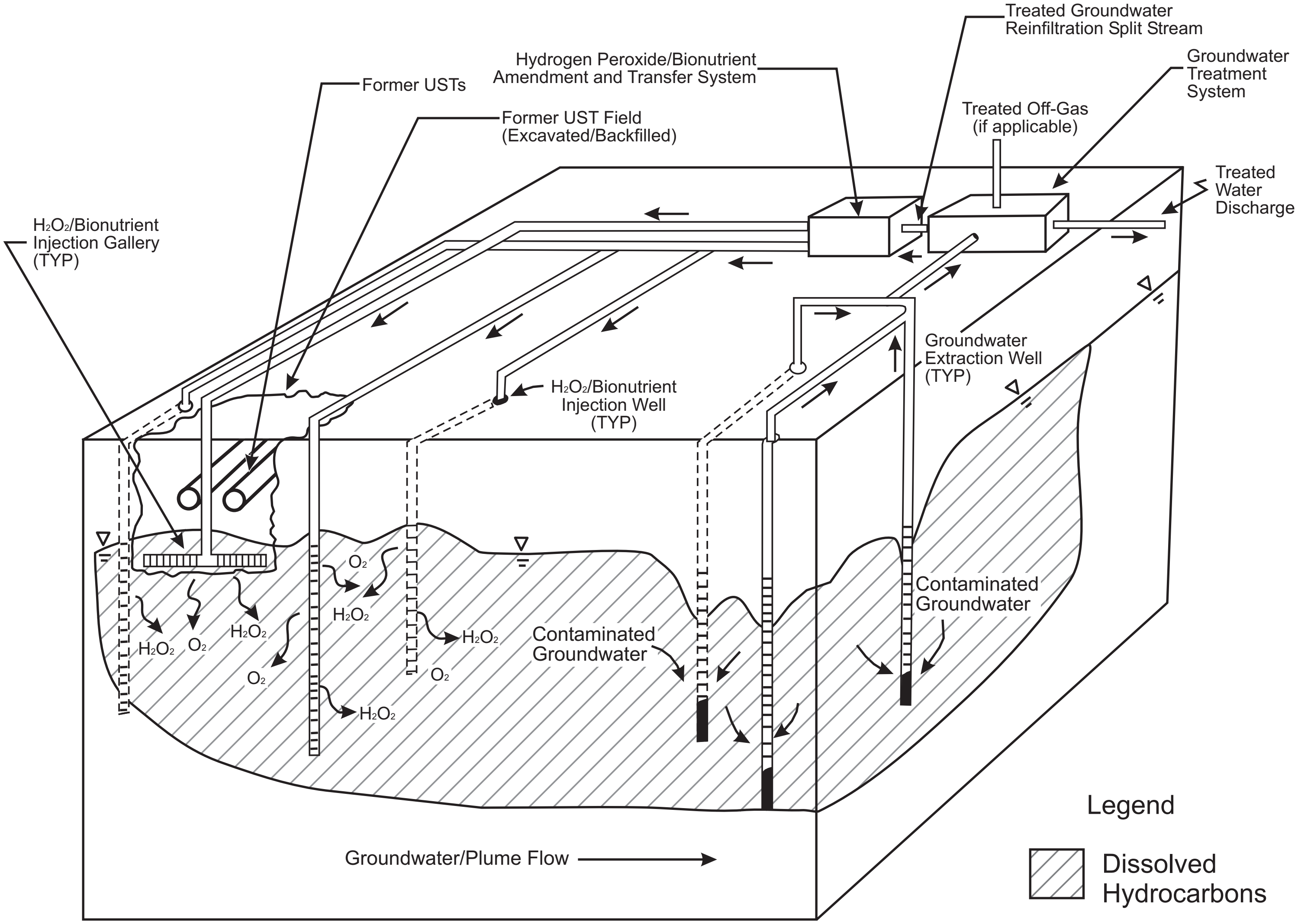
Introducing hydrogen peroxide, which is a chemical oxidant, to the saturated zone can significantly augment existing oxygen levels because it naturally decomposes rapidly, generating oxygen. For each part (e.g., mole) of hydrogen peroxide introduced to groundwater, one-half part of oxygen can be produced. Hydrogen peroxide has the potential of providing some of the highest levels of available oxygen to contaminated groundwater relative to other enhanced aerobic bioremediation technologies because it is infinitely soluble in water. In theory, 10% hydrogen peroxide could provide 50,000 ppm of available oxygen.

However, when introduced to groundwater, hydrogen peroxide is unstable and can decompose to oxygen and water within four hours. This limits the extent to which the hydrogen peroxide may be distributed in the subsurface before it is transformed. Introducing concentrations of hydrogen peroxide as low as 100 ppm can cause oxygen concentrations in groundwater to exceed the solubility limit of

# Exhibit XII-4
# Typical Enhanced Aerobic Remediation Using Pure Oxygen Injection



# Exhibit XII-5
# Typical Enhanced Aerobic Remediation Using Hydrogen Peroxide



oxygen in groundwater (40-50 ppm). When this occurs, oxygen gas is formed, which can be lost in the form of bubbles that rise through the saturated zone to the water table and into the unsaturated zone.

For enhanced aerobic bioremediation purposes, hydrogen peroxide is used at concentrations that maximize dissolved oxygen delivery to the petroleum-contaminated area while minimizing losses of oxygen through volatilization. Hydrogen peroxide is cytotoxic to microorganisms at concentrations greater than 100-200 ppm. This toxicity to aerobic petroleum degrading microbes can be amplified if carbon sources and nutrients are depleted in the contaminated media. Concentrations and application rates are typically determined on a site-specific basis, depending on site conditions, contaminant levels, and cleanup goals.

Hydrogen peroxide in a more concentrated form and in the presence of an iron catalyst can also be used to chemically oxidize site contaminants. This application of peroxide is not discussed in this chapter. When used in this manner, hydrogen peroxide's reaction with ferrous iron produces Fenton's reagent. Fenton's reagent chemical oxidation requires a comprehensive three-dimensional site characterization to locate preferential pathways for migration. It is important that any hydrogen peroxide remediation system contain an adequate number of soil vapor extraction wells to completely capture vapors. For more information on the use of hydrogen peroxide as an oxidant, see *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers* (US EPA 510-R-04-002), Chapter XIII, “Chemical Oxidation”.

The potential dangers of working with hydrogen peroxide should not be overlooked when considering the technology and determining how it should be applied. Hydrogen peroxide is an oxidant that can cause chemical burns. When introduced into a petroleum-contaminated area at high concentrations, hydrogen peroxide can produce heat and elevated oxygen levels that may lead to fire or explosions. Use of concentrated peroxide should be avoided to help reduce these hazards.

### Ozone Injection

Ozone injection is both a chemical oxidation technology and an enhanced aerobic bioremediation technology. Oxidation of organic matter and contaminants occurs in the immediate ozone application and decomposition area. Outside the decomposition area, increased levels of dissolved oxygen can enhance aerobic bioremediation. Ozone is a strong oxidant with an oxidation potential greater than that of hydrogen peroxide. It is also effective in delivering oxygen to enhance subsurface bioremediation of petroleum-impacted areas. Ozone is 10 times more soluble in water than is pure oxygen.

Consequently, groundwater becomes increasingly saturated with dissolved oxygen as unstable ozone molecules decompose into oxygen molecules. About one-half of dissolved ozone introduced into the subsurface degrades to oxygen within approximately 20 minutes. The dissolved oxygen can then be used as a source of energy by indigenous aerobic hydrocarbon-degrading bacteria.

Because of its oxidization potential, injected ozone can also be toxic to indigenous aerobic bacteria and can actually suppress subsurface biological activity. However, this suppression is temporary, and a sufficient number of bacteria survive in-situ ozonation to resume biodegradation after ozone has been applied.

Ozone may be injected into the subsurface in a dissolved phase or in gaseous phases. Groundwater is often extracted and treated, then used to transport (through re-injection or re-infiltration) the dissolved phase ozone and oxygen into the subsurface contaminated area. More commonly, however, gaseous ozone is injected or sparged directly into the contaminated groundwater. Because of its instability, ozone is generated on-site and in relatively close proximity to the target contaminated area. Typically, air containing up to 5% ozone is injected into strategically placed sparge wells. Ozone then dissolves in the groundwater, reacts with subsurface organics, and decomposes to oxygen. Vapor control equipment (e.g., an soil vapor extraction and treatment system) may be warranted when ozone injection rates are high enough to emit excess ozone to the unsaturated zone, which may slow deployment timetables in some states. In many states, vapor control equipment requires a permit for off-gas treatment.

**Special Considerations for MTBE**. The gasoline additive methyl tertiary butyl ether (MTBE) is often found in the subsurface when gasoline has been released. In addition, MTBE is sometimes discovered at spill sites of middle distillate petroleum products like diesel, jet fuel, kerosene, and fuel oil. As such, whenever a petroleum hydrocarbon spill is investigated and remediated, the presence/absence of MTBE in the soil and ground water should be verified.

Several crucial characteristics of MTBE affect the movement and remediation of MTBE, including:

- MTBE is more soluble in water than most C6-C10 gasoline-range hydrocarbons. For example, MTBE is 28 times more soluble in water than is benzene.

- MTBE is less volatile from water (i.e., has a lower Henry’s Constant) than most C6-C10 hydrocarbons. For example, MTBE is 11 times less volatile from water than is benzene.

- MTBE adheres less to soil organic matter than most C6-C10 hydrocarbons. This means that it has lower retardation and more rapid transport in groundwater than most gasoline-range compounds.

- At most sites, MTBE is less biodegradable in the subsurface than other gasoline compounds.

Because of these characteristics, some MTBE from a gasoline spill will be found with the BTEX compounds in the soil and groundwater near the site of petroleum release. But it is also quite common to find a dissolved-phase MTBE-only plume downgradient of the BTEX/TPH plume. Thus, when considering using enhanced aerobic bioremediation techniques for gasoline plumes that include MTBE, recognize that the MTBE may exist in two distinct regions:

- A near-source area where MTBE co-occurs with more readily biodegradable BTEX/TPH compounds
- A distal area where the only compound of concern is MTBE

Any petroleum impact remediation plan that addresses MTBE should account for the probable MTBE-only plume downgradient of the MTBE & hydrocarbon plume. The MTBE-only plume often has decreased levels of dissolved oxygen, due to its occurrence in the “oxygen shadow” region downgradient from the spilled petroleum source area where natural biodegradation is typically occurring (Davidson, 1995).

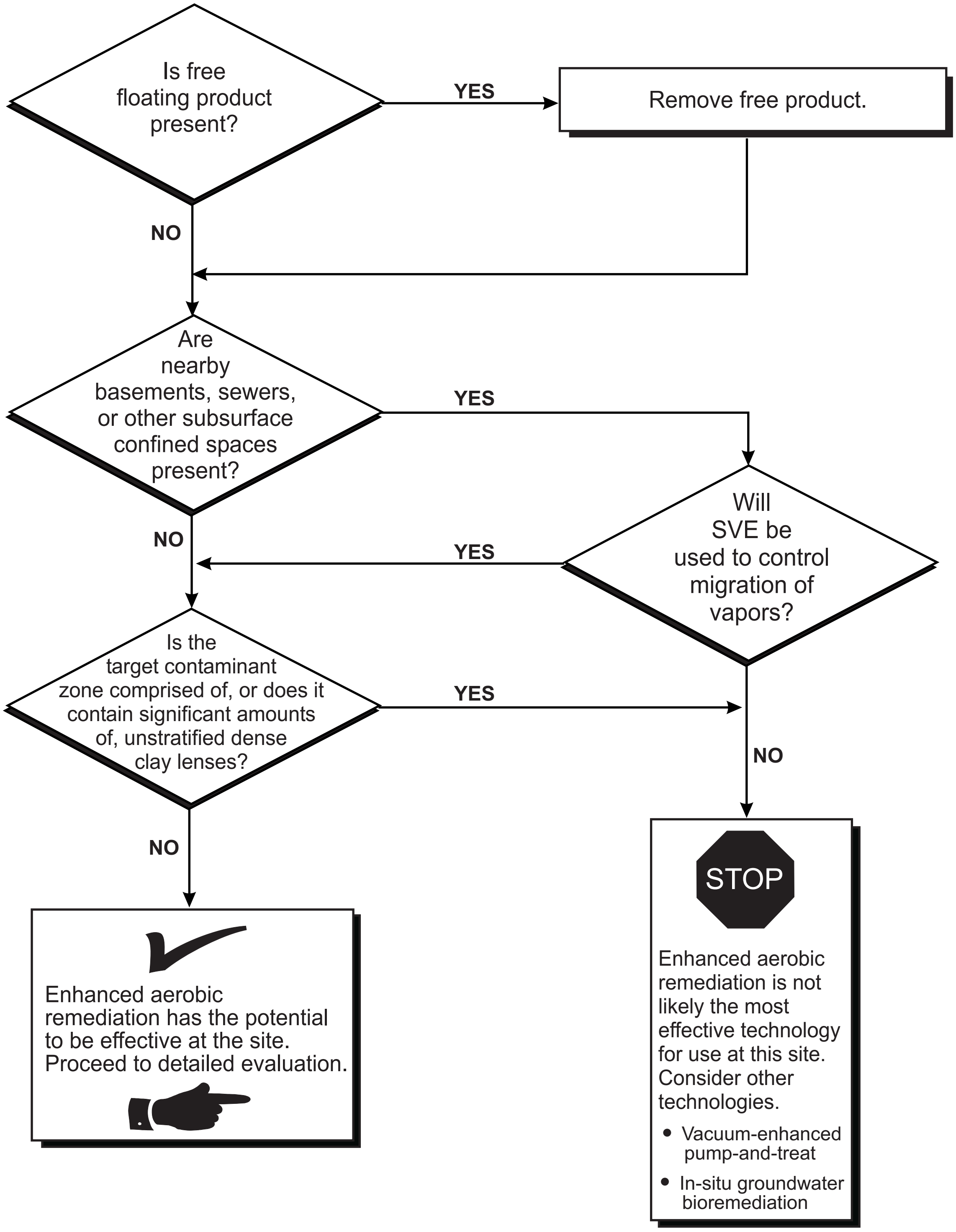
## Enhanced Aerobic Bioremediation Technology Effectiveness Screening Approach

The descriptions of the various enhanced aerobic bioremediation technologies in the overview provide the basic information needed to evaluate a corrective action plan that proposes enhanced aerobic bioremediation. To assist with evaluation of the enhanced aerobic bioremediation corrective action plan, a step-by-step technology effectiveness screening approach is provided in a flow diagram in Exhibit XII–6. This exhibit summarizes this evaluation process and serves as a roadmap for the decisions to make during evaluation of the corrective action plan. A checklist has also been provided at the end of this chapter, which can be used to evaluate the completeness of the enhanced aerobic bioremediation corrective action plan 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 enhanced aerobic bioremediation effectiveness*** allows quick determination of whether enhanced aerobic bioremediation should be considered as a remedial approach for the site.

- **Step 2:** ***A detailed evaluation of enhanced aerobic bioremediation effectiveness*** provides further screening criteria to confirm whether enhanced aerobic bioremediation is likely to be effective. First, certain site-specific data on the nature/extent of contamination, potential risk to human health/the environment, subsurface geology and hydrogeology, and other relevant site

## Exhibit XII-6
## Initial Screening for Potential Effectiveness of Enhanced Aerobic Bioremediation



characteristics need to be evaluated. Next, the site-specific data must be compared to the criteria provided in the Exhibit to assess whether enhanced aerobic bioremediation is likely to be effective.

# **Step 3:** ***An evaluation of the enhanced aerobic bioremediation system design*** in the corrective action plan allows a reviewer to determine whether basic design information has been defined, necessary design components have been specified, the construction process flow designs are consistent with standard practice, and adequate feasibility testing has been performed.

# **Step 4:** ***An evaluation of the operation and monitoring plans*** allows a reviewer to determine whether baseline, start-up and long-term system operation and monitoring are of sufficient scope and frequency and whether remedial progress monitoring and contingency plans are appropriate.

## Step 1 - Initial Screening of Enhanced Aerobic Bioremediation Effectiveness

This section reviews the initial screening tool to examine whether enhanced aerobic bioremediation is likely to be an effective approach to remediate the petroleum-impacted areas at a site. Before accepting enhanced aerobic bioremediation as the preferred remedial approach, determine whether the corrective action plan has taken into account key site-specific conditions. In addition, evaluate several "bright lines" that define the limits of enhanced aerobic bioremediation overall viability as a remedial technology. These bright lines will assist with evaluating the corrective action plan and determining whether enhanced aerobic bioremediation is appropriate as an appropriate solution. After establishing the overall viability of an enhanced aerobic bioremediation approach, look at basic site and petroleum contaminant information in order to further determine the expected effectiveness of enhanced aerobic bioremediation at the site.

### Overall Viability

The following site conditions are considered to be the “bright lines” that define the general limits of enhanced aerobic bioremediation viability at a site. If review of the corrective action plan indicates that any of the following conditions exist, enhanced aerobic bioremediation is not likely to be a feasible or appropriate remedial solution for the site.

- *Free mobile product is present and the corrective action plan does not include plans for its recovery*. Enhanced aerobic bioremediation will not effectively address free product that will serve as an on-going source of dissolved phase contamination. Biodegradation of the petroleum hydrocarbons occurs predominantly in the dissolved-phase because the compounds must be able to be transported across the microbial cell boundary along with water, nutrients, and metabolic waste products. Therefore, in the presence of free product, rates of hydrocarbon mass destruction using enhanced aerobic bioremediation will be limited by the rate at which the free product is dissolved into groundwater. The relatively low solubilities of petroleum hydrocarbon constituents will likely extend remediation for several years, and could allow further expansion of the contaminated area if free product is not removed. Additionally, some enhanced aerobic bioremediation technologies could actually spread the free product. For free product recovery approaches see *How to Effectively Recover Free Product At Leaking Underground Storage Tank Sites: A Guide for State Regulators,* US EPA 510-R-96-001, September 1996.

- *Potentially excessive risks to human health or the environment have been identified and the corrective action plan does not include a supplemental mitigation plan.* While enhanced aerobic bioremediation can reduce petroleum hydrocarbon concentrations in the subsurface, site conditions may limit the level of such reductions and can significantly extend remedial timeframes. Close proximity of the petroleum contamination to basements, utilities, water supply wells, surface water bodies, or other potential receptorsthat could pose excessive risks should be mitigated using technologies that complement enhanced aerobic bioremediation (e.g., soil vapor extraction (SVE), hydraulic controls to protect water supply wells). Without the use of other remedial approaches, enhanced aerobic bioremediation may not be able to reduce concentrations of petroleum contaminants to sufficiently low concentrations to protect receptors in the predicted timeframes.

- *The target contaminant zone includes unstratified dense clay.* For remedial success, enhanced aerobic bioremediation technologies must effectively introduce and distribute oxygen to indigenous microorganisms present in the treatment zone, allowing microbial populations to expand and metabolize the petroleum contaminants. With the relatively low permeabilities inherent to clay or clay-rich soils, oxygen and oxygen carrier media (e.g., air) cannot be easily introduced or distributed. Any distribution of oxygen that could be delivered to such soils (e.g., placement of oxygen releasing compounds in borings or excavations) would largely be controlled by molecular diffusion, a very slow and ineffective process. Treatment zone oxygen levels, therefore, would not be uniformly increased, and biodegradation of the petroleum hydrocarbons could not be effectively enhanced.

While these bright lines offer general guidance on the applicability of enhanced aerobic bioremediation technologies, there may be site-specific application-specific exceptions to the rule. It may be appropriate, for example, for enhanced aerobic bioremediation technologies to be used to address contamination on the periphery of contamination while a different technology is employed to treat the source zone.

## Step 2 - Detailed Evaluation of Enhanced Aerobic Bioremediation Effectiveness

### Potential Effectiveness of Enhanced Aerobic Bioremediation

Before performing a more detailed evaluation of enhanced aerobic bioremediation's potential saturated zone remedial effectiveness and future success at a site, it is useful to review several key indicators. Two factors influence the effectiveness of enhanced aerobic bioremediation at a site: saturated zone permeability, and biodegradability of the petroleum constituents.

# **Saturated soil permeability**. Soil permeability can strongly affect the rate at which oxygen is supplied and uniformly distributed to the hydrocarbon-degrading bacteria in the subsurface. Enhanced aerobic bioremediation of groundwater contaminants in fine-grained soils, or in clays and silts with low permeabilities, is likely to be less effective than in coarse-grained soils (e.g., sand and gravels) because it is more difficult to effectively deliver oxygen in low-permeability materials. In coarse-grained soils, oxygen can be more easily delivered to bacteria, and beneficial populations of hydrocarbon-degrading bacteria may come into contact with more of the petroleum, which enhances biodegradation.

# **Biodegradability**. Biodegradability is a measure of a contaminant's propensity to be metabolized by hydrocarbon-degrading microorganisms. Petroleum products are generally biodegradable, as long as indigenous microorganisms have an adequate supply of oxygen and nutrients. However, the rate and degree to which petroleum products can be degraded by the microorganisms present in the subsurface is largely determined by the relative biodegradability of the petroleum products. For example, heavy petroleum products (e.g., lubricating oils, fuel oils) generally contain a higher proportion of less soluble, higher molecular weight petroleum constituents that are biodegraded at a slower rate than more soluble, lighter fraction petroleum compounds (e.g., gasoline). As a general rule, these characteristics of petroleum compounds can limit biodegradation rates.

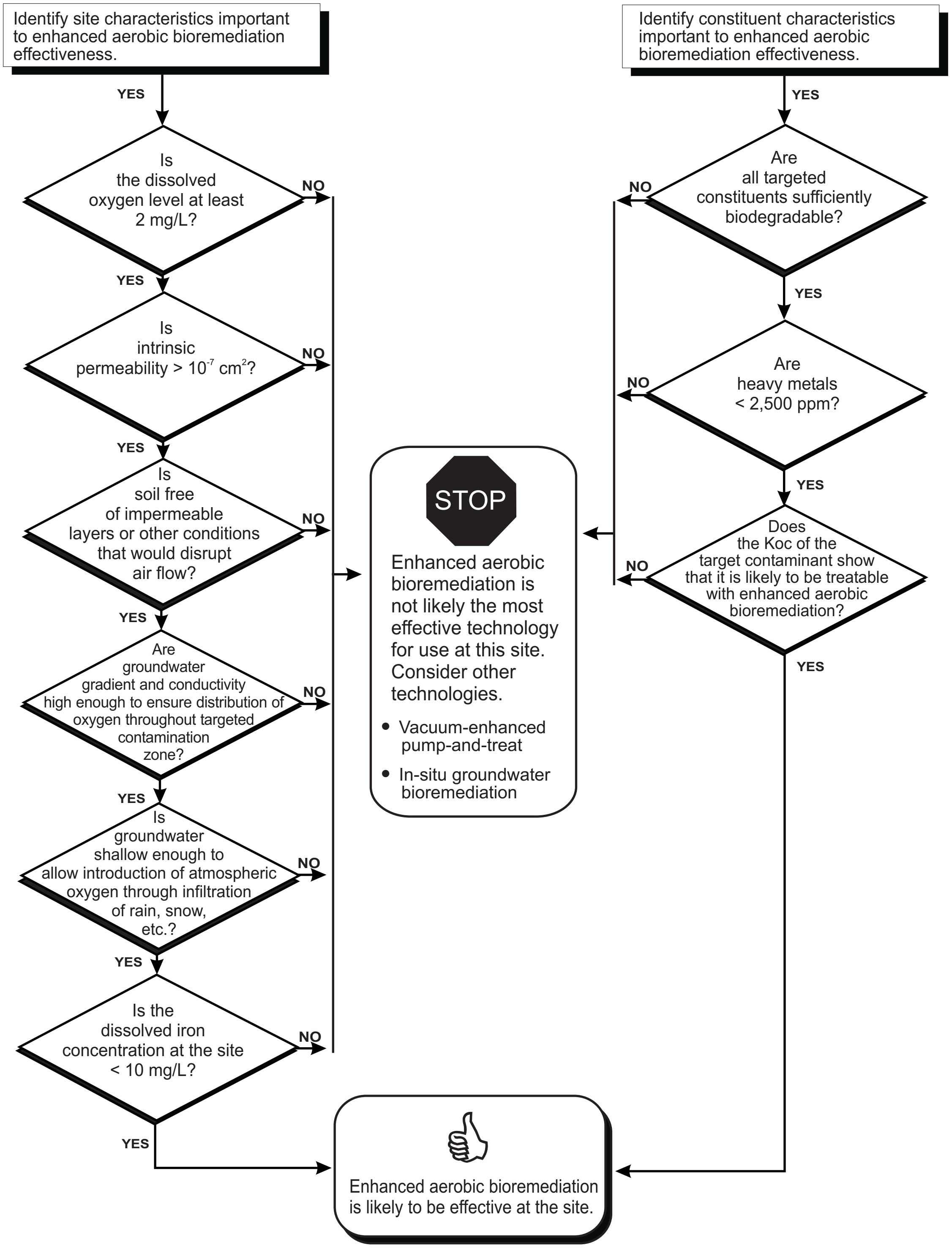
Less soluble compounds are generally less available in the aqueous phase for microorganisms to metabolize. Larger petroleum molecules can slow or preclude the transport of some of these molecules into microbial cells for degradation, and larger or longer chain length structural properties may hinder the ability of the micro-organisms' enzyme systems to effectively attack the compounds. Therefore, even under identical site conditions, bioremediation of a lubricating oil spill will generally proceed more slowly than at a gasoline release. However, cleanup goals are frequently tied to specific petroleum compounds rather than the range of organic constituents that may comprise a petroleum product. Therefore, when considering enhanced aerobic bioremediation, the biodegradability of specific petroleum compounds common to the petroleum product and cleanup goals are of greatest relevance. Even though bioremediation of lubricating oil contamination may occur relatively slowly, cleanup of a lubricating oil spill site via bioremediation may be achieved more quickly than bioremediation of a gasoline spill site because fewer compounds in lubricating oil dissolve in groundwater, reducing the number of target species to clean up.

Some chemical species present in gasoline, such as methyl tertiary-butyl ether (MTBE), are more recalcitrant to bioremediation than are some of the heaviest and most chemically complex petroleum compounds. The detailed enhanced aerobic bioremediation effectiveness evaluation section of this chapter consider the biodegradability of specific petroleum hydrocarbon constituents, such as the benzene, toluene, ethylbenzene, and xylene (BTEX) compounds, as well as that of fuel oxygenates, such as MTBE.

The following section provides information needed to make a more thorough evaluation of enhanced aerobic bioremediation effectiveness and help to identify areas that may require special design considerations. Exhibit XII-7 provides a stepwise process that reviewers should use to further evaluate whether enhanced aerobic bioremediation is an appropriate technology for a contaminated UST site. To use this tool, determine the type of soil present and the type of petroleum product released at the site.

To help with this more detailed evaluation, this section covers a number of important site-specific characteristics influencing the potential effectiveness of enhanced aerobic bioremediation that were not considered or fully explored in the initial screening of the remedial approach. Additionally, this section provides a more detailed discussion of key contaminant characteristics that influence the potential effectiveness of enhanced aerobic bioremediation. Key site and contaminant factors that should be explored in the detailed evaluation of enhanced aerobic bioremediation are listed in Exhibit XII-8. The remainder of this section details each of the parameters described in Exhibit XII-8. After reviewing and comparing the information provided in this section with the corresponding

# Exhibit XII-7
# Detailed Screening for Potential Effectiveness of Enhanced Aerobic Bioremediation



information in the corrective action plan, it should be possible to evaluate whether enhanced aerobic bioremediation is likely to be effective at the site.

### Exhibit XII-8
### Key Parameters Used to Evaluate Enhanced Aerobic Bioremediation Applicability

| Site Characteristics | Constituent Characteristics |
|---|---|
| *Oxygen Demand Factors*<br># Five-Day Biological Oxygen Demand ($BOD_5$)<br># Contaminant theoretical oxygen demand<br># Naturally occurring organic material (humic substances)<br>– Microbial population density/activity<br>– Nutrient concentrations<br>– Temperature<br>– pH | *Chemical Class and Susceptibility to Bioremediation*<br>*Contaminant Phase Distribution*<br>*Concentration and Toxicity* |
| *Advective and Dispersive Transport Factors*<br># Intrinsic permeability<br># Soil structure and stratification<br># Hydraulic gradient<br># Depth to groundwater<br># Dissolved iron content | *Bioavailability Characteristics*<br># Solubility<br># Organic carbon partition coefficient ($K_{oc}$)/sorption potential |

## Site Characteristics Affecting Enhanced Aerobic Bioremediation

The effectiveness of enhanced aerobic bioremediation depends largely on the ability to deliver oxygen to naturally occurring hydrocarbon-degrading microorganisms in the target treatment area. Oxygen can be introduced and removed from a contaminated groundwater zone in many different ways. Dissolved oxygen may enter the contaminated zone from any of the following sources:

# Flow of groundwater into the contaminated zone from background (upgradient) areas
# Precipitation infiltration
# Other enhanced aerobic bioremediation sources

Losses of oxygen from the contaminated zone may occur through:

- Biodegradation of organic contaminants
- Oxidation of naturally occurring organic and inorganic material in the soil
- Volatilization of dissolved oxygen
- Flow of groundwater containing depleted levels of dissolved oxygen leaving the contaminated zone

The success of enhanced aerobic bioremediation, therefore, hinges on the balance between oxygen sources, oxygen uptake, and the degree to which the transport of dissolved oxygen in groundwater is limited. To support aerobic biodegradation of petroleum contaminants, the most favorable dissolved oxygen (DO) level is 2 mg/L or higher. Anaerobic biodegradation processes in the anaerobic shadow become limited once dissolved oxygen levels approach or fall below 2 mg/L. Site characteristics affecting the delivery and distribution of oxygen in the subsurface and the effectiveness of enhanced aerobic bioremediation technology are discussed in the following sections.

**Oxygen Demand Factors.** Groundwater in petroleum spill source area and downgradient of the spill area is usually depleted of oxygen. This zone of oxygen-depleted groundwater, commonly referred to as the anaerobic shadow, results from the use of oxygen by naturally occurring microorganisms during aerobic metabolism of the spilled petroleum organic compounds. The oxygen is used in the microbiologically mediated oxidation of the petroleum contaminants. Aerobic biodegradation processes in the anaerobic shadow become limited once dissolved oxygen levels approach or fall below 2 mg/L. Enhanced aerobic bioremediation technologies can boost oxygen levels in the source area and in the anaerobic shadow to assist naturally occurring aerobic biodegradation processes but there are other oxygen demands that need to be considered before attempting to oxygenate the anaerobic shadow.

Each enhanced aerobic bioremediation technology has a particular way of delivering oxygen to the saturated zone. Once delivered to the saturated zone, dissolved oxygen can be further distributed in the treatment zone by groundwater advection and dispersion. However, from the point where it is introduced into the aquifer, dissolved oxygen concentration decreases along the groundwater flow path not only through mixing with the oxygen-depleted groundwater, but also because of biologically mediated and abiotic oxidation processes. The rate and degree to which oxygen concentrations decrease along the groundwater flow path and the degree to which the anaerobic shadow may be oxygenated depends, in part, on the degree to which oxygen is lost to microbiological and abiotic consumption in the saturated zone.

Demand for oxygen in the subsurface environment may stem from organic or inorganic sources. Microbial biodegradation of released petroleum hydrocarbons or naturally occurring organics (e.g., humic substances) as a carbon source by aerobic microorganisms will generate demand for oxygen.

**Oxygen Demand From Biodegradation of Organic Compounds.** Oxygen levels are generally depleted in the subsurface, but are particularly depleted at petroleum UST spill sites. This oxygen shortage results from the relative isolation of the subsurface from the oxygen-replenishing atmosphere, as well as the oxygen demands of naturally occurring organic and inorganic compounds and petroleum hydrocarbon releases. Because of these oxygen-depleted conditions, the most basic requirement for enhanced aerobic bioremediation is to deliver sufficient levels of oxygen to maintain an aerobic subsurface environment.

Exhibit XII-9 outlines the stoichiometric reactions for the complete oxidation or biodegradation of some common components of gasoline and other petroleum products. In theory, oxygen levels of at least 3 to 3.5 times the amount of subsurface petroleum mass that needs to be removed to meet cleanup goals must be delivered to the groundwater and distributed over the planned remedial period. Given typical oxygen solubility limits and the mass of contaminants that are often found at leaking underground storage tanks sites, delivering the required amount of oxygen can be a significant challenge. In practice, to convert one pound of hydrocarbon material into carbon dioxide and water requires between 3 and 5 pounds of available oxygen. This is valuable for evaluating the potential effectiveness of enhanced aerobic bioremediation.

**Exhibit XII-9**
**Organic Compound Oxidation Stoichiometry**

| Petroleum Hydrocarbon | Oxidation Reaction | Oxygen Requirement (gram $O_2$ per gram Contaminant) |
|---|---|---|
| Benzene | $C_6H_6 + 7.5\ O_2 \rightarrow 6CO_2 + 3H_2O$ | 3.1 |
| Toluene | $C_6H_5CH_3 + 9\ O_2 \rightarrow 7CO_2 + 4H_2O$ | 3.1 |
| Ethylbenzene | $C_2H_5C_6H_5 + 10.5\ O_2 \rightarrow 8CO_2 + 5H_2O$ | 3.2 |
| Xylenes | $C_6H_4(CH_3)_2 + 10.5\ O_2 \rightarrow 8CO_2 + 5H_2O$ | 3.2 |
| Cumene | $C_6H_5C_3H_7 + 12O_2 \rightarrow 9O_2 + 6H_2O$ | 3.2 |
| Naphthalene | $C_{10}H_8 + 12O_2 \rightarrow 10CO_2 + 4H_2O$ | 3.0 |
| Fluorene | $C_{13}H_{10} + 15.5O_2 \rightarrow 13CO_2 + 5H_2O$ | 3.0 |
| Phenanthrene | $C_{14}H_{10} + 16.5O_2 \rightarrow 14CO_2 + 5H_2O$ | 3.0 |
| Hexane | $C_6H_{14} + 9.5\ O_2 \rightarrow 6CO_2 + 7H_2O$ | 3.5 |

Because the solubility of $O_2$ by natural oxygen replenishment is limited and relatively low (9 mg/L at 25°C), only a small amount of organic or inorganic matter in the subsurface can consume all the naturally present dissolved $O_2$ in groundwater. For example, using the above stochiometric equation for the complete oxidation of benzene, oxidation of 2.9 mg/L of benzene would theoretically consume about 9 mg/L of $O_2$, leaving no residual oxygen in the water. It can be readily understood how external sources of oxygen enhanced aerobic bioremediation technologies can help aerobic bacteria by providing a source of energy so they may consume the petroleum as a source of carbon.

**Microbial Population**. Oxygen demand is also a function of the vitality of the microbial population. The larger and more active the population of aerobic microorganisms, the larger the biological oxygen demand. However, subsurface conditions may not be conducive to producing large numbers of microbial populations. Exhibit XII-10 shows the likely effectiveness of enhanced aerobic bioremediation as a function of the presence of heterotrophic bacteria in the subsurface.

**Exhibit XII-10**
**Relationship Between Heterotrophic Bacterial Counts And Likely Enhanced Aerobic Bioremediation Effectiveness**

| Background Heterotrophic Bacteria Levels | Enhanced Aerobic Bioremediation Effectiveness |
|---|---|
| >1,000 CFU/gram dry soil | Generally effective |
| <1,000 CFU/gram dry soil | May be effective; further evaluation needed to determine if toxic conditions are present |

**Nutrients**. The activity of the microbial population and the corresponding biological oxygen demand also depend on the availability of inorganic nutrients such as nitrogen and phosphate to support cell growth and sustain biodegradation processes. Nutrients may be initially available in sufficient quantities in the aquifer, but with time, they may need to be supplemented with additional nutrient loading to maintain adequate bacterial populations. Excessive amounts of certain nutrients (e.g., phosphate or sulfate) can repress bio-metabolism. 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.

However, to avoid over-application of nitrogen and phosphorus, which can unnecessarily incur added costs, plug wells, and even contaminate ground water with nitrate, it is important to understand how much carbon can be metabolized based on oxygen-limiting conditions. Nitrogen and phosphorus should be added to reach the proportions identified in the previous paragraph, based on the amount of carbon that can be metabolized at any given time compared to the total average concentration of carbon (i.e., petroleum contamination) in the subsurface. For example, if during full-scale operation a net 0.6 pound per hour of pure oxygen is introduced to the treatment area and is assumed to be completely consumed by aerobic microbial activity, approximately 0.17 pound per hour (4 pounds per day) of hydrocarbon is theoretically microbiologically oxidized (using a 3.5:1 oxygen:hydrocarbon stoichiometric ratio). Then, using the 100:10:1 to 100:1:0.5 C:N:P theoretically optimal ratio range for this example, between 0.4 and 0.04 pounds per day of nitrogen and 0.04 to 0.02 pounds per day of phosphorus may need to be added to the treatment area to keep up with the estimated carbon metabolism rate.

Alternatively, it would be reasonable for a practitioner to suggest monitoring oxygen demand during full-scale system operation before considering adding any nitrogen or phosphorus. If oxygen demand were to fall below about 10 mg/L in the petroleum contaminated area, the subsurface could be tested for nitrogen or phosphorus to determine whether insufficient concentrations of these micronutrients is limiting microbial activity. Only after this determination is made should nitrogen or phosphorus be added. Generally, nitrogen should not limit aerobic degradation processes unless concentrations fall significantly below 1 mg/L. This alternative may be particularly attractive at sites located near areas where aquifers already have nitrogen problems because it may be difficult to secure permits for the injection of these micronutrients. 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.

**pH.** Although the optimum pH for bacterial growth is approximately 7, enhanced aerobic bioremediation can be effective over a pH range of 5 to 9 pH units. Adjustment of pH conditions outside this range is generally not considered to be viable because it is difficult to overcome the natural soil buffering capacity, and because of the potential for rapid changes in pH to adversely affect bacterial populations. Oxygen releasing compounds may raise the pH even higher than the 5-9 range, which can be fatal to microbes.

**Temperature.** Oxygen uptake and bacterial growth rate are directly affected by temperature. From 10°C to 45°C, the rate of microbial activity typically doubles for every 10°C rise in temperature. Below 5°C, microbial activity becomes insignificant. In most areas of the United States, the average groundwater temperature is about 13°C. Groundwater temperatures may be somewhat lower or higher in the extreme northern and southern states. While individual microorganism growth rates decrease with temperature, a higher steady state biomass of active organisms (each one working more slowly, but more of them working) can result from lower temperatures. Because of this and the increased solubility of oxygen at lower temperatures, biodegradation can sometimes be as fast or faster at lower temperatures than at more moderate temperatures.

**Inorganic Oxygen Demand.** Oxygen demand arises from a depletion of subsurface oxygen from biological or inorganic processes coupled with poor oxygen replenishment. In contrast to surface water bodies, groundwater systems are typically isolated from the atmosphere, limiting the opportunity for natural oxygen to be replenished. This atmospheric isolation allows dissolved oxygen levels to become depleted and subsurface conditions to become geochemically reduced. Introducing and distributing oxygen under these reduced conditions are challenging for the application of enhanced aerobic bioremediation, because introduced oxygen may react with and become lost to organic or inorganic chemical constituents that would otherwise be relatively inconsequential to the environmental cleanup.

Exhibit XII-11 presents a sample of some common inorganic processes that consume oxygen in groundwater.[3] Corrective action plan data should be reviewed to identify what is already known about aquifer conditions in the area around the site to determine whether signficant reduced inorganic species exist in the subsurface that could remove oxygen from groundwater. If so, these species can limit the ability of biodegrading bacteria to effectively implement enhanced aerobic bioremediation. In such cases, soil core samples may need to be collected and analyzed for reduced iron, sulfide or other inorganic constituents. These samples can help to determine the potential loss of oxygen to the aquifer and to verify that enhanced aerobic bioremediation will be able to effectively deliver sufficient oxygen to overcome these limiting factors. This assessment cannot be made from analyses of groundwater samples, because the reduced inorganic complexes are primarily precipitated in the aquifer material.

**Exhibit XII-11**
**Inorganic Oxidation Processes That Consume Dissolved Oxygen In Groundwater**

| Process | Reaction |
|---|---|
| Sulfide Oxidation | $O_2 + ½HS^- \rightarrow ½SO^{2-} + ½H^+$ |
| Iron Oxidation | $¼O_2 + Fe^{+2} + H^+ \rightarrow Fe^{+3} + ½H_2O$ |
| Nitrification | $O_2 + ½NH^{4+} \rightarrow ½NO^{3-} + H^+ + ½H_2O$ |
| Manganese Oxidation | $O_2 + 2Mn^{2+} + 2H_2O \rightarrow 2MnO_2$ (s) $+4H^+$ |
| Iron Sulfide Oxidation | $15/4O_2 + FeS_2$ (s) $+ 7/2H_2O \rightarrow Fe(OH)_3$ (s) $+2SO_4^{2-} + 4H^+$ |

Many inorganic oxygen-consuming reactions produce solid precipitates that can accumulate in soil pore spaces. As discussed below, these precipitates can restrict soil permeabilities and thus further affect the ability of enhanced aerobic bioremediation technologies to deliver and distribute oxygen to hydrocarbon-degrading microorganisms.

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[3] From Freeze R.A. and John A. Cherry, 1979. Groundwater. Prentice Hall.

**Advective and Dispersive Transport Factors.** The site conditions affecting advection and dispersion of dissolved oxygen are outlined below. These conditions are:

- Intrinsic permeability
- Soil structure and stratification
- Hydraulic gradient
- Depth to groundwater
- Iron and other reduced inorganic compounds dissolved in groundwater

Each of these factors is described in more detail below.

**Intrinsic Permeability.** Intrinsic permeability is a measure of the ability of soil to transmit fluids. Intrinsic permeability is the single most important soil characteristic in determining the effectiveness of enhanced aerobic bioremediation, because intrinsic permeability controls how well oxygen can be delivered and dispersed to subsurface microorganisms. Hydraulic conductivity is a measure of the resistance of aquifer material to groundwater flow. This unit of measure is particularly relevant to understanding the ability to move oxygen dissolved in groundwater through the saturated treatment zone. Hydraulic conductivity is related to intrinsic permeability by the following equation.

$$K = \frac{k g}{m}$$

where: $K$ = hydraulic conductivity (L/T)
$k$ = intrinsic permeability ($L^2$)
$g$ = weight density of water ($F/L^3$)
$m$ = dynamic viscosity of water ($F \bullet T/L^2$)
L = mean grain diameter
T = transmissivity
F = fluid density

Intrinsic permeability often decreases near injection wells or infiltration galleries. This also commonly results from precipitation of carbonates, or precipitates of other minerals derived from fertilizer solutions. In general, oxygen is more easily distributed in soils with higher soil permeabilities (e.g., coarse-grained soils such as sands) than in soils with lower permeabilities (e.g., fine-grained clayey or silty soils).

Calculation of intrinsic permeability can be derived from hydraulic conductivity measurements taken from on-site pump testing. Pump test or slug test-derived permeability ranges are typically representative of average hydraulic permeability conditions for heterogeneous conditions. Alternatively, intrinsic permeability can be estimated from soil boring logs.

Permeabilities derived from pump or slug test analyses or estimated from boring logs are only approximations of actual subsurface conditions and should be regarded as such in the evaluation of enhanced aerobic bioremediation potential effectiveness.

Intrinsic permeability can vary over 13 orders of magnitude (from $10^{-16}$ to $10^{-3}$ $cm^2$) for the wide range of earth materials. Exhibit XII-12 provides general guidelines on the range of intrinsic permeability values over which enhanced aerobic bioremediation is likely to be effective.

The intrinsic permeability of a soil is likely to decrease as enhanced aerobic bioremediation progresses. If the soil intrinsic permeability indicates borderline potential effectiveness (e.g., $10^{-6} \leq k \leq 10^{-7}$), the geochemistry should be further evaluated.

**Exhibit XII-12**

**Intrinsic Permeability And Enhanced Aerobic Bioremediation Effectiveness**

| Hydraulic Conductivity (K) (in ft/s) | Intrinsic Permeability (k) (in $ft^2$) | Enhanced Aerobic Bioremediation Effectiveness |
|---|---|---|
| $K > 10^{-6}$ | $k > 10^{-12}$ | Effective to generally effective |
| $10^{-6} \leq K \leq 10^{-7}$ | $10^{-12} \leq k \leq 10^{-13}$ | Possibly effective; needs further evaluation |
| $K < 10^{-7}$ | $k < 10^{-13}$ | Marginally effective to ineffective |

**Soil Structure and Stratification.** Often, soils in a target treatment area are not uniformly permeable (heterogeneous), but rather have large-scale or small-scale variations in permeability. Soil heterogeneity plays a very important role in enhanced aerobic bioremediation technologies because oxygen introduced to the subsurface is distributed preferentially along higher permeability layers in the saturated soil. For example, in a heterogeneous soil comprised of sand, silt and clay layers, oxygen may be effectively distributed through the sand layer to successfully reduce petroleum hydrocarbons there, but will be ineffectively delivered and distributed to the silt and clay layers. The relatively slow diffusion transport mechanism will become as important or more important than advection and dispersion in the distribution of oxygen to microorganisms in the silt and clay layers. If the silt and clay layers are thick relative to the sand horizon and contain significant petroleum hydrocarbon mass, enhanced aerobic bioremediation technologies may not be efficient or effective. In this case, the dissolved petroleum hydrocarbon mass will appear to shrink as the most permeable zone (i.e., the sand) will have undergone significant enhanced aerobic bioremediation treatment.

However, the petroleum mass in the silt and clay horizons will likely not biodegrade, and will also likely diffuse into the sand zone, causing a rebound in dissolved hydrocarbon concentrations at the site.

Unless site soils are homogeneous, average soil intrinsic permeability may not adequately determine the viability of enhanced aerobic bioremediation approaches because discrete low permeability soil horizons may exist, and these horizons might contain a large fraction of the subsurface petroleum mass. In most cases, it is prudent to evaluate petroleum mass distribution across all soil types to determine whether enhanced aerobic bioremediation is likely to be effective and will achieve cleanup objectives. If select soil horizons containing hydrocarbon mass are not expected to be effectively treated using enhanced aerobic bioremediation , enhanced aerobic bioremediation may not be viable for the site. For example, if 50% of the contaminant mass is contained and isolated in low permeability soil horizons and the site cleanup goals is a 95% reduction in petroleum contaminant concentrations, then it is reasonable to conclude that the goal cannot be achieved using enhanced aerobic bioremediation. However, in such circumstances, combining enhanced aerobic bioremediation with other technologies that enhance the permeability of low permeability horizons in the contaminated zone (e.g., soil fracturing) could be considered. Soil fracturing could allow dissolved oxygen and other microbial nutrients to be effectively delivered through the engineered fractures in low permeability soil. However caution should be observed when considering this option because the same fractures produced to enhance permeability for nutrient delivery could also be a potential preferential flow path for contaminant plume migration.

**Hydraulic Gradient.** Enhanced aerobic bioremediation technologies ultimately rely on groundwater advection and dispersion (i.e., flow) to distribute dissolved oxygen to the subsurface. Distribution of introduced dissolved oxygen is most effective under hydrogeologic conditions conducive to higher groundwater flow rates. These conditions exist when the combined values of hydraulic gradient and hydraulic conductivity are relatively high.

Note that state regulations may either require permits for nutrient injection or prohibit them entirely. Depending on the specific enhanced aerobic bioremediation technology and the state in which the site is located, permits that may be required include underground injection, treated groundwater discharge (to sanitary or storm sewer, or air (soil vapor) discharge. Several federal, state and local programs exist that either directly manage or regulate Class V aquifer remediation wells, and many of these require permits for underground injection of oxygen or bionutrients.

As the hydraulic gradient increases, the groundwater velocity increases proportionately. This same relationship exists between groundwater velocity and soil permeability. Groundwater velocity is inversely proportional to soil porosity. As porosity increases, groundwater velocity decreases. For purposes of evaluating the feasibility of using an enhanced aerobic bioremediation technology, keep in mind that the principal direction of groundwater flow and oxygen transport is along the line of maximum hydraulic gradient.

To maximize the distribution of dissolved oxygen through and biodegradation rates in the contaminated zone, enhanced aerobic bioremediation technologies often introduce dissolved oxygen at levels that exceed the solubility limit of oxygen in groundwater under atmospheric conditions. However, when the oxygen is not rapidly dissipated or used (e.g., as an electron acceptor during microbial respiration), the oxygen can partition out of the dissolved-phase and be lost to the unsaturated zone as a gas.

**Depth to Groundwater.** The depth to groundwater at a site can also affect the availability and transport of dissolved oxygen to the subsurface. Infiltrating precipitation, such as rainfall or snow, is a source of dissolved oxygen to the saturated zone. When groundwater is relatively deep or confined, less precipitation infiltrates, minimizing the amount of atmospheric dissolved oxygen that reaches the groundwater. Also, pavement prevents infiltration of rainfall or snowmelt At sites where the water table is close to the surface, more mixing of groundwater with air-saturated precipitation occurs, resulting in more opportunity for groundwater to be oxygenated. When this occurs, dissolved oxygen levels in groundwater can even approach those found in streams and other surface water bodies.

**Iron and Other Reduced Inorganic Compounds Dissolved in Groundwater.** In addition to being a significant oxygen sink, the effective intrinsic permeability of the saturated zone can be significantly reduced if the enhanced aerobic bioremediation treatment zone contains naturally elevated levels of reduced iron (e.g., ferrous iron, or $Fe^{+2}$) or other mineral species. The net impact of elevated levels of reduced species can therefore be a loss of delivered oxygen and a decreased ability to distribute any excess oxygen to the aerobic microorganisms involved with the degradation of the petroleum hydrocarbons. Precipitation of oxidized inorganic complexes and biological mass can foul monitoring and injection well screens and potentially aquifer pore space where oxygen is delivered to the subsurface.

Exhibit XII-13 can be used as a guide to help determine whether the corrective action plan has considered site levels of dissolved iron and if dissolved iron levels at the site could have an adverse effect on the enhanced aerobic bioremediation approach.

In some situations, hydraulic gradients can be enhanced to help increase groundwater flow and oxygen delivery rates and flush dissolved oxygen through the contaminated zone. One common approach is to create an artificial gradient by removing groundwater downgradient of the source area, treating it, and re-introducing it in the upgradient source area. For example, hydrogen peroxide enhanced aerobic bioremediation applications often require extracting

**Exhibit XII-13**
**Relationship Between Dissolved Iron And Enhanced Aerobic Bioremediation Effectiveness**

| Dissolved Iron Concentration (mg/L) | Potential Effectiveness of Enhanced Aerobic Bioremediation |
|---|---|
| $Fe^{+2} < 10$ | Enhanced aerobic bioremediation will likely be effective. |
| $10 \geq Fe^{+2} \geq 20$ | Enhanced aerobic bioremediation injection wells and delivery systems will require periodic testing and may need periodic replacement. |
| $Fe^{+2} > 2$ | Enhanced aerobic bioremediation may not be cost effective due to loss of dissolved oxygen to the formation and equipment maintenance problems associated with inorganic precipitation. This would especially be the case where groundwater is extracted, treated, amended with oxygen (e.g., hydrogen peroxide) and reinjected. |

contaminated groundwater from the downgradient portion of the dissolved hydrocarbon plume, treating the extracted groundwater for hydrocarbons, and re-injecting the treated groundwater amended with hydrogen peroxide into one or more upgradient locations.

This lowers the groundwater level in the downgradient extraction locations and raises it in upgradient injection locations, which provides an artificially increased gradient. This, in turn, increases the rate of groundwater and oxygen flow across the contaminated zone.

Even with preferential hydrogeologic conditions, distributing dissolved oxygen throughout the subsurface is difficult because of the inherent limits of groundwater flow and the number of oxygen “sinks,” or uptakes, that can exist, particularly in areas contaminated with petroleum hydrocarbons. These limitations frequently require that the corrective action plan call for placement of a large number of oxygen delivery points in the treatment area to decrease enhanced aerobic bioremediation technology’s reliance on groundwater flow as the principal source of distributed oxygen.

In addition to being a parameter considered in evaluating the potential effectiveness of enhanced aerobic bioremediation, hydraulic gradient is an engineering design issue. If the gradient is not steep enough to provide adequate flow and oxygen transport through the contaminated zone, then certain engineering provisions (e.g., spacing application points more closely, creating artificial hydraulic gradients) can be added to the design to enhance oxygen distribution. However, economic considerations limit the extent to which design changes can be made in an enhanced aerobic bioremediation delivery system to ensure adequate oxygen distribution.

## Constituent Characteristic Affecting Enhanced Aerobic Bioremediation

It is important to evaluate the potential impacts of site contaminants on the performance of the proposed enhanced aerobic bioremediation approach. In particular, it is important to review how the chemical structure, chemical properties, concentrations and toxicities of the petroleum contaminants can influence remedial performance.

**Chemical Class and Susceptibility to Bioremediation.** Petroleum products are complex mixtures of hundreds or even thousands of hydrocarbon chemical constituents, other chemical constituents and additives. Each of these constituents has a different atomic structure that determines, in part, its relative biodegradability. Although nearly all constituents in petroleum products found at leaking underground storage tank sites are biodegradable to some extent, constituents with more complex molecular structures are generally less readily biodegraded than those with simpler structures. On the other hand, 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 XII-14 lists the relative biodegradability of various petroleum products and constituents. The exhibit shows that hydrocarbon molecules containing a higher number of carbon atoms (e.g., lubricants with 26- to 38-carbon chains) degrade more slowly, and perhaps less completely, than those with shorter carbon chains (e.g., gasoline). However, cleanup goals are frequently tied to a small subset of chemical compound components of the various petroleum products in Exhibit XII-9 rather than a total petroleum hydrocarbon concentration. Often chemical compounds in petroleum products identified in Exhibit XII-14 as being less readily biodegradable are not present at contaminated sites at levels significantly above cleanup standards because of the low solubility characteristic that these compounds can have. Consequently, cleanup standards for contaminants in less readily biodegradable petroleum formulations may be reached through enhanced aerobic bioremediation more quickly than those for more soluble compounds in more biodegradable formulations.

Certain petroleum constituents are more recalcitrant than most other constituents. For example, MTBE, a gasoline additive, is frequently found at leaking UST sites because of its environmental persistence and its apparent resistance to bioremediation. Some researchers have estimated that the half-life of MTBE in the environment is at least two years, whereas the typical half-life for BTEX compounds in the environment is approximately two to three months.

## Exhibit XII-14
## Composition And Relative Biodegradability Of Petroleum Products

| Product | Major Components | Relative Product Biodegradability |
|---|---|---|
| Natural Gas | Normal and branched-chain alkanes. One to five carbons in length. *Examples: ethane, propane.* | **Higher** |
| Gasoline | Normal and branched hydrocarbons between 6 and 10 carbons in length. *Examples: n-butane, n-pentane, n-octane, isopentane, methylpentanes, benzene, toluene, xylenes, ethylbenzene*. | |
| Kerosene, Diesel | Primarily 11 to 12 carbon hydrocarbons, although the range of carbons extends well above and below this range. Generally contains low to non-detectable levels of benzene and polyaromatic hydrocarbons. Jet fuel oils have a similar composition. *Examples: n-nonane, n-decane, n-dodecane, naphthalene, n-propylbenzene*. | |
| Light Gas Oils (e.g., No 2 Fuel Oil) | Twelve to 18 carbon hydrocarbons. Lower percentage of normal alkanes than kerosene. These products include diesel and furnace fuel oils (e.g., No. 2 fuel oil). *Examples: fluorene, naphthalene, phenanthrene, isopropylbenzene*. | |
| Heavy Gas Oils and Light Lubricating Oils | Hydrocarbons between 18 and 25 carbons long. | |
| Lubricants | Hydrocarbons between 26 and 38 carbons long. | |
| Asphalts | Heavy polycyclic compounds. | **Lower** |

Therefore, one should carefully consider the biodegradability of the target contaminants when forecasting the potential effectiveness and usefulness of an enhanced aerobic bioremediation technology. The enhanced aerobic bioremediation design and implementation should focus on the most recalcitrant compounds within the released petroleum product, unless another remedial technology is being proposed to address those compounds.

It is not necessarily the most recalcitrant or most difficult compound to bioremediate that determines the duration of a remediation project. For example, the baseline concentration of the most recalcitrant site compound may be much closer to its respective cleanup goal or an acceptable risk-based concentration than a more readily biodegradable petroleum constituent at a baseline level much greater than its cleanup goal. In this case, the more biodegradable constituent may initially be the focus of the enhanced aerobic bioremediation design and cleanup. As remediation progresses, the mix of petroleum products remaining should periodically be compared to the site's proposed cleanup level to determine whether the remedial approach needs to be enhanced to address the remaining target compounds.

Researchers have estimated and published biodegradation rate constants for various petroleum hydrocarbons. These rate constants can indicate the relative biodegradability of petroleum hydrocarbon constituents under field conditions. However, actual degradation rates for target contaminants may depend on constituent-, site-, and enhanced aerobic bioremediation implementation-specific conditions. For example, the mixture and concentrations of the different petroleum constituents in the site soil and groundwater may play an important role in determining relative degradation rates. The amount of natural organic matter in the soil and the degree to which the petroleum constituents attach themselves to it will affect the relative rates of biodegradation. These issues, especially as they relate to contaminant characteristics that affect aerobic bioremediation, are discussed below.

**Contaminant Phase Distribution.** Spilled petroleum products may be partitioned into one or more phases and zones in the subsurface including:

- Unsaturated soils (sorbed phase)
- Saturated soil (sorbed phase)
- Dissolved in groundwater (aqueous phase)
- Unsaturated soil pore space (vapor phase)
- Free mobile product (liquid phase)
- Free residual product smeared onto soil above and below the water table

Understanding how the petroleum contaminant mass is distributed in the subsurface can be important to both evaluating the applicability of enhanced aerobic bioremediation and identifying a particular enhanced aerobic bioremediation technology that will be effective. Depending on site-specific cleanup goals and contaminant levels, a disproportionate amount of contaminant mass in one medium or another could preclude the use of enhanced aerobic bioremediation technologies. For example, if a relatively large portion of the mass of a site target compound (e.g., benzene) is held in residual free product that is vertically smeared above and below the water table, enhanced aerobic bioremediation may not be able to achieve the site cleanup goals within a reasonable period of time. However, in such a case, enhanced aerobic bioremediation could still potentially be used at the fringes of the contaminated area while a more aggressive technology is employed in the residual-free product zone.

Information on the distribution of target compounds in the subsurface can also be used to help identify the most appropriate enhanced aerobic bioremediation technology for a site. Depending on where most of the target contaminant mass is located, one or more of the enhanced aerobic bioremediation technologies may be viable. For example, a disproportionate amount of target contaminant mass in the unsaturated soil would logically lead to the selection of an unsaturated zone enhanced aerobic bioremediation approach (e.g., bioventing). On the other hand, if a disproportionate amount of target contaminant mass is in the saturated zone, one of the enhanced aerobic bioremediation technologies that introduces high concentrations of dissolved oxygen to the subsurface may be a reasonable approach.

**Concentration and Toxicity.** High concentrations of petroleum organics or heavy metals in site soils and groundwater have traditionally been thought to be potentially toxic to, or inhibit growth and reproduction of, biodegrading bacteria. Soil containing petroleum hydrocarbons in amounts greater than 50,000 ppm, or heavy metals in excess of 2,500 ppm, was thought to be inhibitory and/or toxic to many aerobic bacteria. However, it is becoming increasingly evident that many microorganisms are able to tolerate and adapt to petroleum concentrations well above 50,000 ppm. Some researchers have even reported being able to isolate living bacteria directly from gasoline product.

While it appears that bacteria may be more adaptable than initially believed, to the extent that these higher levels of petroleum hydrocarbons represent a large mass of contamination in unsaturated or saturated soil in contact with groundwater, the adapted populations of bacteria may not be able to address the contaminant mass in a reasonable timeframe. When considering the feasibility of enhanced aerobic bioremediation, it is important to evaluate the mass of the target contaminants of concern relative to potential biodegradation rates and the cleanup timeframe objective.

It is possible that the effects of elevated contaminant levels can include partial biodegradation of only a fraction of the hydrocarbons at reduced rates, or reduced bacterial reproduction rates or metabolism, resulting in minimal or no appreciable soil treatment. The guidance threshold values summarized in Exhibit XII-15 can be compared to average site concentrations provided in the corrective action plan as another way of forecasting the potential effectiveness of enhanced aerobic bioremediation. Again, it is important to recognize that the values shown in Exhibit XII-15 are guidance values only.

As outlined in Exhibit XII-15, the threshold petroleum concentrations above which biodegradation is inhibited could also indicate the presence of free or residual product in the subsurface. In the initial effectiveness screening of enhanced aerobic bioremediation (Step 1), one of the feasibility bright lines discussed was the absence of free mobile product. If threshold soil petroleum levels exist, then free or residual petroleum product most likely exists in the soil, and enhanced aerobic bioremediation will not be effective without first removing the product through other remedial measures.

**Exhibit XII-15**
**Constituent Concentration and Enhanced Aerobic Bioremediation Effectiveness**

| Contaminant Levels (ppm) | Enhanced Aerobic Bioremediation Effectiveness |
|---|---|
| Petroleum constituents ≤ 50,000<br>Heavy metals ≤ 2,500 | Possibly effective |
| Petroleum constituents > 50,000<br>or<br>Heavy metals > 2,500 | Not likely to be effective either due to toxic or inhibitory conditions to bacteria, or difficulty in reaching cleanup goal within reasonable period of time |

**Bioavailability Characteristics.** The extent to which and the rate at which a particular petroleum hydrocarbon compound can be biodegraded by microorganisms depends not only on the compound's inherent biodegradability, but also on the availability of the compound to hydrocarbon-degrading bacteria (“bioavailability”). Several contaminant properties contribute to bioavailability in the subsurface. In particular, the compound-specific properties of solubility and the organic carbon partition coefficient ($K_{oc}$) help establish the relative bioavailability of contaminants. These properties can be used to help determine the susceptibility of the contaminant mass to enhanced microbial degradation and, ultimately, the potential effectiveness of enhanced aerobic bioremediation. Note that some compounds (e.g., MTBE) may be relatively bioavailable, but are difficult to biodegrade. Special considerations for MTBE are discussed beginning on page XII-39. This section continues with a discussion of the parameters of solubility and $K_{oc}$ and their influence on enhanced aerobic bioremediation effectiveness.

**Solubility.** Solubility is the maximum concentration of a chemical that can be dissolved in water at a given temperature without forming a separate chemical phase on the water (i.e., free product). Most petroleum compounds have relatively low solubility values, thus limiting the concentrations of contamination that can be dissolved in groundwater and limiting their bioavailability in the aqueous phase. This is because less contaminant mass is able to reside in groundwater for biodegradation relative to contaminants with higher solubility limits. However, the solubility values for petroleum hydrocarbons range significantly – over four orders of magnitude – as shown in Exhibit XII-16. The solubility values in Exhibit XII-16 represent those of pure phase chemicals. For example, benzene dissolved in water by itself (with no other compounds present) can reach a maximum concentration in water of about 1.79 g/L before a separate phase develops. When multiple compounds are present such as at a petroleum release site, effective solubility values can be expected to be lower. While not representing effective solubility concentrations that may exist at particular petroleum release sites, the values present in Exhibit XII-16 provide a sense for the relative solubility concentrations for a range of fuel components. It is beyond the scope of this document to describe the chemistry involved and how effective solubility might be estimated.

**Exhibit XII-16**
**Solubility Values And Organic Partition Coefficients For Select Petroleum Hydrocarbon Constituents**

| Compound | Molecular Weight (g/mol) | Solubility in Water (g/L) | Organic Carbon Coefficient ($K_{oc}$ in mL/g) |
|---|---|---|---|
| MTBE | 88.15 | 51 | 12 |
| Benzene | 78 | 1.79 | 58 |
| Toluene | 92.15 | 0.53 | 130 |
| Ethylbenzene | 106.17 | 0.21 | 220 |
| Xylenes (total) | 106 | 0.175 | 350 |
| Cumene | 120.19 | 50 | 2,800 |
| Naphthalene | 128 | 0.031 | 950 |
| Acenaphthene | 154 | .0035 | 4,900 |

Compounds with higher solubility values are generally smaller, lower molecular weight molecules (e.g., benzene). When spilled, these compounds exist in groundwater at higher relative concentrations and move more quickly through the aquifer than do compounds of higher molecular weights. These compounds are generally more biodegradable because of both their relatively smaller size and bioavailability in the aqueous phase, because proportionately more contaminant mass is in the groundwater where it may be mineralized by aerobic bacteria.

Larger and higher molecular weight hydrocarbon molecules are generally less soluble in water; therefore, their dissolved concentrations in groundwater tend to be limited (e.g., acenaphthene ). This property not only reduces the availability of these hydrocarbons to biodegradation, it also limits the mass of these contaminants that can migrate with groundwater over time. For bioremediation of higher molecular weight compounds at a particular site, these two factors may offset one another. In simpler terms, bioremediation of the larger hydrocarbons may take longer, but there is more time to complete the biodegradation because the contamination is not moving away from the treatment area as quickly. The most appropriate remediation for sites that are contaminated mostly with heavy petroleum constituents might be excavation and application of an off-site remedial technology, such as thermal desorption, or proper disposal of the contaminated soil.

Solubility is also an indicator of likely contaminant sorption onto soil. When contaminants are sorbed onto soil particles, they are less available for bioremediation. A compound with a relatively high solubility has a reduced tendency to sorb to soil contacting contaminated groundwater. Conversely, contaminants with relatively low solubility values will generally have an increased tendency to sorb to soil contacting contaminated groundwater. This concept is described in more detail below.

**$K_{oc}$ Factor.** When groundwater is contaminated by a release from a petroleum underground storage tank, the proportion of hydrocarbon mass in the soil is often far greater than that dissolved in groundwater. This is due in part to the relatively low solubility thresholds for petroleum contaminants. However, another factor is the relatively strong tendency for most petroleum hydrocarbons to sorb to naturally occurring organic carbon material in the soils. This tendency, along with the sheer mass of soil relative to groundwater in a contaminated area, can lead to hydrocarbon mass distributions that are so lopsided they can make the mass in the dissolved-phase appear insignificant. However, because bioremediation occurs in the dissolved phase, that portion of a petroleum mass is always significant in a bioremediation project. It is important to also know how the target organic petroleum compounds are partitioned between the dissolved and unsaturated and saturated sorbed phases.

$K_{oc}$ is a compound-specific property that helps define the equilibrium condition between organic carbon and the contaminant concentrations in an aqueous solution. Using site-specific soil organic carbon content data (i.e., fraction of organic content or foc), $K_{oc}$ can be used to determine the equilibrium contaminant concentrations between groundwater and soil below the water table. The typical organic carbon content in surface soils ranges from 1 to 3.5 percent. In subsurface soils, organic carbon content is an order of magnitude lower because most organic residues are either incorporated or deposited on the surface.

The equation below shows how $K_{oc}$ is defined and used with site-specific fraction of organic carbon ($f_{oc}$) data to determine the soil-to-groundwater concentration equilibrium ratio, $K_d$. Knowing the contaminant concentration in one media (e.g., groundwater), the contaminant concentration in the other media (e.g., soil) can be predicted using the site- and constituent-specific $K_d$ sorption constant.

$$K_d = f_{oc} \text{ x } K_{oc}$$

where:

$K_d$ = grams contaminant sorbed/grams organic carbon
= grams contaminant/mL solution
$K_{oc}$ = compound-specific sorption constant and
$f_{oc}$ = fraction of organic carbon in site soil

Higher $K_{oc}$ and $K_d$ values indicate more contaminant mass is likely to be retained in soil and therefore less readily bioavailable. Conversely, lower $K_{oc}$ and $K_d$ values indicate lower contaminant concentrations will exist in equilibrium in soil for given concentrations in groundwater. Exhibit XII-16 provides petroleum constituent $K_{oc}$ values for a list of common petroleum hydrocarbon. A comparison of the solubility and $K_{oc}$ values for the sample group of petroleum hydrocarbons reveals the inverse relationship between the two parameters. For example, compounds with higher solubility values have lower $K_{oc}$ constants.

The relative proportions of contaminants in the sorbed and dissolved phases is important to establish when evaluating the likely effectiveness of enhanced aerobic bioremediation. A disproportionate amount of target hydrocarbon contaminant mass sorbed to the soil, and therefore less bioavailable, may signal that enhanced aerobic bioremediation by itself may not be an effective method of reducing subsurface contaminant mass. In this case, it may be necessary to combine enhanced aerobic bioremediation with other technologies that can help bring more contaminant mass out of the sorbed phase and into the dissolved phase so it can be biodegraded. This highlights the importance of establishing a cleanup goal up front.

In the absence of site-specific data that reveal the distribution of contaminant mass, solubility and $K_{oc}$ data can be used to obtain a general understanding of the likelihood that enhanced aerobic bioremediation is applicable at the site. Petroleum contaminants with generally high solubility limits and low $K_{oc}$ values tend to be more bioavailable in groundwater, and the contaminant mass can often be destroyed by enhanced aerobic bioremediation technologies. When contaminant solubility constants are generally low and $K_{oc}$ values are high, enhanced aerobic bioremediation will be limited in its effectiveness.

**Special Considerations for MTBE.** Not all sites have indigenous microbial suites capable of degrading MTBE. The MTBE chemical bonds are strong and not easily cleaved through chemical or biological means. As such, when enhanced aerobic bioremediation is to be utilized for addressing MTBE, it may be prudent to verify that native MTBE-degraders exist at a site, before implementing a costly and complex enhanced aerobic bioremediation plan. This can be done with standard microcosm tests. Such laboratory test can be also used to optimize the Enhanced aerobic bioremediation procedures for the site so as to insure enhanced biodegradation of both petroleum compounds and MTBE. If the microcosm tests indicate that insufficient MTBE-degrading microbes exist at a site, then it may be necessary to bioaugment the site by increasing the numbers of microbes. Caution is necessary when bioaugmenting with a cultured microbial suite as the technical effectiveness, cost-effectiveness, and longevity of microbes need to be well understood. Due to the vagaries of geochemistry and microbiology in the subsurface, site-specific microcosms and/or pilot tests may be advisable before full-scale implementation of a bioaugmentation system.

When MTBE biodegrades, it often produces an intermediary product called tertiary butyl alcohol (TBA). The subsurface creation of TBA has been noted at some enhanced aerobic bioremediation field sites that contain MTBE. Therefore, any enhanced aerobic bioremediation application at a site containing MTBE has the potential to create TBA. This constituent of concern has been noted to rapidly disappear from the subsurface at some biodegradation sites, while at other sites, the TBA seems to be recalcitrant. Field workers need to be aware of the possible subsurface creation of TBA, and seek to avoid creating a undesirable, recalcitrant TBA plume.

The presence of TBA in the subsurface at an MTBE-impacted site is not definitive proof of MTBE biodegradation. TBA is a gasoline additive that can be present in concentrations of up to 9.5% by volume, and it is often found in commercial-grade MTBE at 1-2% by volume. Therefore, it is possible to detect subsurface TBA at an MTBE site, even if no MTBE biodegradation is occurring. Careful study of TBA/MTBE ratios, as well as their plume patterns relative to each other and relative to the enhanced aerobic bioremediation activitie,s can help to determine if the TBA was in the original gasoline spill or if it is present due to biodegradation of TBA. It is also important to note that as an alcohol, TBA can be difficult to detect at low levels in water samples; detection limits from laboratory analyses can vary widely, and many analyses will not find TBA when it is present in low concentrations.

When considering enhanced aerobic bioremediation for a site that also contains the gasoline additive methyl tertiary butyl ether, the presence of MTBE mandates that several issues be considered. Exhibit XII-17 provides a list of the questions that should be asked before enhanced aerobic bioremediation is considered for treating MTBE at a petroleum UST site.

## EXHIBIT XII-17
## MTBE Considerations For Applying Enhanced Aerobic Bioremediation

# Does the presence of MTBE require treating a larger region of the aquifer?

# Does the presence of MTBE require treating a deeper portion of the aquifer, especially in the downgradient area of the plume where MTBE plumes sometimes “dive” ?

# Does either of these mandates require installing more oxygen application points?

# Are native MTBE-degrading microbes known to exist at that specific site? Are they sufficient in number to be effective? Are they located where the MTBE presently is? Are they located where the MTBE will be in the future?

# Is the addition of an MTBE-degrading microbial suite needed?

# Has the greater mobility of the MTBE been accounted for in the plan?

# Does the presence of more readily biodegradable compounds (example: BTEX) indicate a delay before MTBE is consumed by microbial populations? If so, what are the implications of this?

# Is the same remediation method being used for the hydrocarbons also sufficient to address the MTBE? Does the site contain a sufficient oxygen load and appropriate microbial suite (native or bioaugmented)?

# Has the corrective action plan accounted for the possible biological formation of the intermediary product tertial butyl alcohol (TBA), including the possibility of creating an undesirable TBA plume?

# Has the corrective action plan accounted for the possible biological formation of the intermediary product tertial butyl alcohol (TBA), including the possibility of creating an undesirable TBA plume?

The various technical issues raised in Exhibit XII-17 demonstrate that while enhanced aerobic bioremediation for MTBE and other similar oxygenates can be promising, a number of special factors should be considered before moving forward with application of an enhanced aerobic bioremediation project for MTBE. Although the addition of supplemental microbial suites (bioaugmentation) is beyond the scope of this chapter, it can be considered for such sites. For more information on the use of bioaugmentation, see *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers* (US EPA 510-R-04-002), Chapter X (“In-Situ Groundwater Bioremediation”).

As discussed earlier, assessing the applicability of an enhanced aerobic bioremediation plan for MTBE is more complex than a similar assessment for other gasoline compounds.  While typical gasoline compounds like BTEX have been found to be nearly ubiquitously biodegradable under a wide variety of subsurface conditions, the same cannot be said for MTBE.  Studies of MTBE biodegradability have produced highly variable results..  Therefore, it is not yet possible to make universal statements about enhanced aerobic bioremediation effectiveness for MTBE.  Instead, the reviewer is advised to carefully consider site-specific conditions before committing to enhanced aerobic bioremediation for MTBE.  Exhibit XII-18 on the next page provides some guidance.

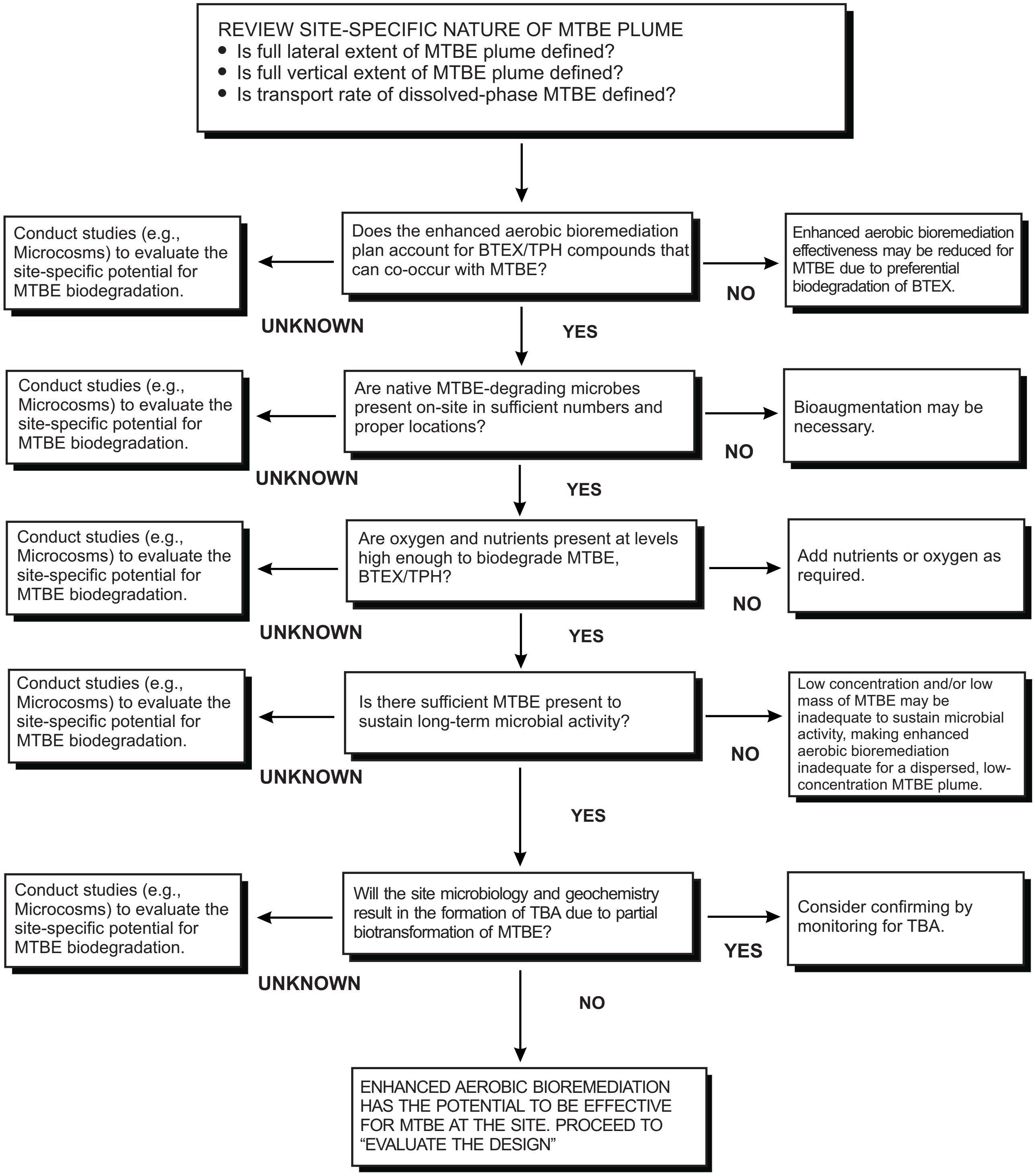
Because MTBE biodegradability still appears to be site-specific and because the state of knowledge is still developing, it may be advisable to conduct site-specific microcosm studies using the intended enhanced aerobic bioremediation method before committing to a full-scale remediation plan for MTBE.  Such microcosm studies may investigate: MTBE biodegradation under varying conditions, the need for bioaugmentation, the production of TBA, etc.

### Step 3 - Evaluation of Enhanced Aerobic Bioremediation Design

This section provides guidance on reviewing and evaluating the enhanced aerobic bioremediation design.  It focuses on prompting reviewers to identify and review key elements of corrective action plans to help ensure they demonstrate a coherent understanding of the basis for the enhanced aerobic bioremediation system design.  In addition, this section provides information on typical enhanced aerobic bioremediation technology components to help verify that the corrective action plan has included the basic equipment requirements for the remedial system.

It is assumed that the detailed technology screening process (described in Steps 1 and 2) has verified that enhanced aerobic bioremediation appears to be appropriate and is expected to be an effective cleanup approach, given site-specific conditions.  If the enhanced aerobic bioremediation effectiveness evaluation has not been completed, it is strongly recommended that this be done before the design is evaluated.

## Exhibit XII-18
## Detailed Evaluation of Enhanced Aerobic Bioremediation Effectiveness for MTBE



## Design Basis

Review of the corrective action plan should find consistency between site characterization work and information that is presented as the basis for the enhanced aerobic bioremediation design in the corrective action plan. To conduct the enhanced aerobic bioremediation effectiveness evaluation, the reviewer should have a solid understanding of the nature and extent of the site-specific petroleum constituents of concern, including an understanding of the contaminant phases present and the relevant site chemical, physical, and biological properties. When preparing and reviewing the corrective action plan design, the reviewer should also understand the site geology and hydrogeology, and the risks associated with the contamination. These data, which should have been developed and interpreted as part of the site characterization effort, serve as the foundation for the remedial system design.

While the site characterization data provide the core raw materials for the design, further refinement is often needed and useful. For example, while the site characterization work may identify potential human or ecological receptors that may be exposed to the contamination, specific cleanup goals may not have been established. In such cases, the specific remedial goals would need to be developed and identified in the corrective action plan through one or more established approaches, such as adopting state-published cleanup standards, developing site-specific risk-based standards acceptable to the state, or employing other state-specific and approved methods.

The corrective action plan may also include the results and interpretation of follow-up studies completed after the original site characterization. The need for such studies is often identified after a review of the site characterization shows that additional information is needed to complete the remedial system design. For example, the site characterization may suggest that one or more of the constituents of concern is believed to be marginally biodegradable, and the level of expected biodegradation is difficult to predict from the existing data.

Examples of typical information expected to be developed during the site characterization, or as a result of follow-up studies that are completed to support the basis for the technology selection and design of the corrective action plan, are summarized in Exhibit XII-19. Each of the items listed in Exhibit XII-19 is described in more detail below.

### Cleanup Goals

The evaluation of alternative remedial approaches and the subsequent design of the selected approach are strongly influenced by the cleanup goals that the remediation program must achieve. Often, preliminary goals identified during the site characterization work evolve as a better understanding of site conditions and potential receptors is attained. However, owing to their importance for remediation planning and design, the cleanup goals should be fully evolved and solidified in the corrective action plan.

**Exhibit XII-19**
**Enhanced Aerobic Bioremediation Design Basis Factors**

| Design Basis Factor | Source(s) of Design Information |
|---|---|
| **Cleanup Goals**<br># Target contaminant levels (soil and groundwater)<br># Remediation timeframe | Receptor survey, pre-design exposure or risk assessment analyses (potentially including numerical modeling), or state requirements |
| **Geology**<br># Uniformity<br># Stratigraphy<br># Geochemistry<br># Bedrock<br># Soil permeabilities | Site characterization soil borings, well installations, sampling/analysis, and site observations. Local geologic studies. |
| **Hydrogeology**<br># Depth to groundwater<br># Groundwater elevation and gradient<br># Aquifer/water bearing unit class (e.g, confined, unconfined, perched, bedrock)<br># Hydraulic parameters (e.g., conductivity, transmissivity, storativity, effective porosity)<br># Modeling results | Site characterization well gauging, aquifer pump testing, data analyses, and local hydrogeologic studies. |
| **Petroleum Contamination**<br># Target chemical constituents<br># Target contaminant and total hydrocarbon mass estimates (sorbed, dissolved, liquid and vapor phases)<br># Extent (vertical and lateral)<br># Bioavailability<br># Biodegradability<br># Fate and transport characteristics | Soil, groundwater and other media sampling/laboratory analysis, review of published data on contaminants and data interpolation and analysis. |

Cleanup goals usually provide the end-point concentrations for petroleum constituents in soil and groundwater that are acceptable to state or other regulatory agencies. These cleanup thresholds could be goals that represent any of the following:

- Health-based numeric values for petroleum chemical constituents published by the respective regulatory agency
- Cleanup goals developed and proposed by the contractor specifically

for the contaminated site that are acceptable to the Implementing Agency

- Goals derived from site-specific risk assessment involving contaminant fate and transport modeling coupled with ecological and human-health risk assessment
- Generic state cleanup goals

Additional project goals that may or may not be regulatory requirements include hydraulic control of the contamination, a cleanup timeframe, or other performance goals established in the corrective action plan. Regardless of what the cleanup goals are and how they are established, the state-sanctioned goals should noted in the corrective action plan and recognized as a *fundamental* basis for the technology selection and design.

The cleanup goals presented in the corrective action plan answer important questions relevant to the viability of the selected remedial approach and the adequacy of the remedial design. These two critical questions are:

- Can the cleanup concentration goals be met by the designed enhanced aerobic bioremediation system?
- Can sufficient oxygen be delivered to the contaminated area to enable contaminants to be biodegraded to meet cleanup goals within a reasonable period of time?

Each of these questions is discussed in more detail in the paragraphs that follow.

- *Can the cleanup concentration goals be met by the designed enhanced aerobic bioremediation system?*

Below a certain “threshold” petroleum constituent concentration, bacteria may not be able to derive sufficient carbon from petroleum biodegradation to sustain vigorous levels of biological activity. As concentrations of petroleum contaminants fall below the threshold, further biodegradation of the petroleum hydrocarbons can become relatively insignificant. The level of diminishing returns is site-specific and representative of petroleum contamination that has been reduced in concentration to the technological limit of the specific enhanced aerobic bioremediation.

Although the threshold limit of enhanced aerobic bioremediation approaches can vary greatly, depending on bacteria-, petroleum constituent- and site-specific factors, it is generally observed that petroleum constituent soil concentrations cannot be reduced below 0.1 ppm without using supplemental technologies. In addition, reductions in total petroleum hydrocarbons (TPH) of greater than 95 percent can be very difficult to achieve because of petroleum products often contain “recalcitrant” or non-degradable petroleum hydrocarbons.

While further bioremediation of petroleum contaminant levels in the subsurface may become limited at some point due to the limited availability of a useable carbon source, it is quite possible that the target chemical constituents that may exist in soil and groundwater at that time may meet the cleanup standards. Even though total hydrocarbon levels may remain elevated in subsurface soil, the chemical constituents comprising the hydrocarbon mass may be those that are less soluble and of reduced environmental concern.

**Exhibit XII-20**
**Cleanup Concentrations Potentially Achieved By Enhanced Aerobic Bioremediation**

| Cleanup Requirement | Feasibility of Meeting Cleanup Levels |
|---|---|
| Petroleum constituent concentration in soil >0.1 ppm (each contaminant with corresponding dissolved levels in groundwater) and TPH reduction < 95% | Feasible |
| Constituent concentration in soil $\leq$ 0.1 ppm (each contaminant with corresponding dissolved levels in groundwater) or TPH reduction $\geq$ 95% | Potentially infeasible to remediate in reasonable timeframe; laboratory or field trials may be needed to demonstrate petroleum concentration reduction potential |

If comparing existing levels of site petroleum contamination to the cleanup goals indicates that either of these guidance criteria summarized in Exhibit XII-20 is exceeded, the proposed enhanced aerobic bioremediation. The system design may not achieve the expected remedial objectives in a reasonable time frame.

\# *Can sufficient oxygen be delivered to the contaminated area to enable contaminants to be biodegraded to meet cleanup goals within a reasonable period of time?*

Cleanup goals establish the concentrations and allowable residual mass of petroleum constituents that can acceptably remain in the subsurface soil and groundwater subsequent to remediation. The difference between the current level of petroleum mass in the soil and groundwater and the allowable residual mass left in the subsurface is the mass that needs to be biodegraded using enhanced aerobic bioremediation. Using the theoretical 3 to 3.5 pounds of $O_2$ to degrade roughly 1 pound of petroleum hydrocarbon ratio discussed earlier, it is possible to estimate the minimum mass of $O_2$ needed to achieve the required petroleum mass biodegradation. This value assumes that there are no significant oxygen “sinks” in the subsurface (e.g., mineral species that oxidize such as iron) that would increase the total demand for oxygen.

For example, if the corrective action plan data indicate that approximately 5,000 pounds of petroleum hydrocarbons are in the site subsurface but the cleanup goals allow only 500 pounds to remain after remediation (based on allowable soil and groundwater constituent concentration limits), then 4,500 pounds of hydrocarbons require bioremediation. Assuming anaerobic biodegradation and abiotic degradation of site contamination are negligible, and that there are no other sources of oxygen or significant oxygen losses or sinks, and 3.5 pounds of $O_2$ are needed to aerobically biodegrade each pound of petroleum, then it can be estimated that a minimum of 15,750 pounds of oxygen would need to be provided by the enhanced aerobic bioremediation technology during remedial program implementation. During review of the corrective action plan, therefore, estimate the oxygen mass required to bioremediate the contamination and determine how the demand will be met by the proposed enhanced aerobic bioremediation system.

Furthermore, if pure oxygen injection is the proposed enhanced aerobic bioremediation technology, and the remediation timeframe is 3 years, the corrective action plan design should show how the pure oxygen injection system will be able to deliver and distribute a minimum of 15,750 pounds of oxygen over the 3-year period. In other words, the corrective action plan should demonstrate that an average of at least 0.6 pounds of pure oxygen per hour can be delivered over the 3-year period.

The example discussed above assumes that losses of oxygen to the aquifer are negligible. In reality, as discussed earlier in this chapter, significant losses of oxygen can occur from the application of the enhanced aerobic technology itself and from abiotic and microbiologically mediated reactions with the aquifer material. An attempt should be made to estimate what these potential oxygen losses could be in order to factor those losses into the oxygen delivery plan and cleanup schedule.

If the corrective action plan does not estimate the oxygen and bio-nutrient delivery requirements or does not demonstrate how the oxygen and bio-nutrient delivery requirements will be met by the enhanced aerobic bioremediation system, the corrective action plan may be incomplete. Under such circumstances, it may be prudent to request that this information be provided before approving the plan. Similarly, if site-specific cleanup goals have not been clearly established in the corrective action plan or previously, it may be appropriate to refrain from completing the review of the design until this critical information is provided.

### Enhanced Aerobic Bioremediation Technology Selection

With the design basis established in the corrective action plan, the corrective action plan can be reviewed to confirm that enhanced aerobic bioremediation is a reasonable site-specific choice of remediation technology. Depending on project-specific circumstances, there can be only one or a few enhanced aerobic bioremediation technologies equally viable and appropriate for a site.

Alternatively, site-specific or project-specific circumstances may suggest that one of the enhanced aerobic bioremediation would address the on-site contamination better than any other technology.

Exhibit XII-2 presents the key advantages and disadvantages of each of the enhanced aerobic bioremediation technologies. Use these factors to evaluate the feasibility of using an enhanced aerobic bioremediation approach. Other differences between and among alternative enhanced aerobic bioremediation technologies can help to distinguish their most appropriate application(s). A key characteristic useful for evaluating the feasibility and appropriateness of a proposed enhanced aerobic bioremediation technology is oxygen delivery efficiency. More information on how this characteristic can be used is provided in the next paragraphs.

**Oxygen Delivery Efficiency.** All enhanced aerobic bioremediation technologies need to deliver oxygen to the subsurface to encourage aerobic biodegradation of petroleum contamination to occur. The effectiveness of each enhanced aerobic bioremediation technology is directly related to the amount of oxygen it can deliver and uniformly distribute in the contaminated area. Because of this commonality, it makes sense to explore the relative efficiency with which each technology is able to deliver oxygen to the treatment area as a distinguishing feature.

Oxygen produced from the decomposition of compounds used in enhanced aerobic bioremediation approaches follows the stoichiometric relationships shown in Exhibit XII-21. For instance, for every two parts of hydrogen peroxide injected, only one part of oxygen is produced. In contrast, one part ozone yields 1.5 parts of oxygen, a seemingly more efficient means of generating oxygen.

**Exhibit XII-21**
**Basic Stoichiometry Oxygen Production From Chemical Decomposition**

| Enhanced Aerobic Bioremediation Technology | Basic Oxygen-Producing Stoichiometry |
|---|---|
| **Oxygen-Producing Compounds** | |
| Hydrogen Peroxide | $2H_2O_2 \rightarrow 2H_2O + O_2$ |
| Ozone | $O_3 \rightarrow 1.5\ O_2$ |
| **Oxygen Releasing Compounds** | |
| Magnesium Peroxide | $MgO_2 + H_2O \rightarrow Mg(OH)_2 + \frac{1}{2}O_2$ |
| Sodium Peroxide | $Na_2O_2 + H_2O \rightarrow NaOH + H_2O_2$ |

A more practical way of measuring oxygen delivery efficiency is to determine the total amount of mass of carrier material (e.g., groundwater containing hydrogen peroxide) that needs to be delivered to the subsurface in order to deliver 1 gram of oxygen. In essence, this is a measure of the amount of effort, energy, and perhaps, time required to deliver oxygen using the different enhanced aerobic bioremediation technologies. Exhibit XII-22 compares seven alternative methods of delivering oxygen to the subsurface using this measure of delivery efficiency. It compares:

- Three approaches that use groundwater as the oxygen carrier
  - Re-injection of groundwater fully aerated with ambient air
  - Re-injection of groundwater fully aerated with pure oxygen
  - Re-injection of groundwater containing 100 ppm of hydrogen peroxide

- One method that delivers oxygen in the solid phase (oxygen releasing compounds)

- Three approaches that deliver oxygen in the vapor phase
  - Ozone injection
  - Biosparging/bioventing
  - Pure oxygen injection

While the re-infiltration of hydrogen peroxide-amended groundwater may be the least efficient method of oxygen delivery to the contaminated area, the hydraulic gradients induced by this activity may enhance the distribution of oxygen in the subsurface. For more information on factors affecting the distribution of oxygen in the subsurface, refer to discussions presented earlier as part of the detailed enhanced aerobic bioremediation effectiveness evaluation.
Each of the major headings in the table above is discussed in more detail below.

## Design Components

Although the design elements of alternative enhanced aerobic bioremediation technologies can vary significantly, Exhibit XII-23 describes the most common design elements. Several of the more important elements are discussed below to assist with evaluation of the corrective action plan.

**Oxygen and Bio-nutrient Delivery Design** should be based primarily on petroleum mass reduction requirements, site characteristics and cleanup goals. Oxygen will generally need to be applied at a minimum 3:1 ratio relative to the petroleum hydrocarbon mass targeted for remediation. Bio-nutrient formulation and delivery rate (if needed) will be based on soil sampling. 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 and/or air injection or prohibit them entirely.

## Exhibit XII-22
## Relative Oxygen Delivery Efficiencies For Various Enhanced Aerobic Bioremediation Technologies

| Oxygen Delivery Approach | Description | Oxygen Concentration in Delivery Material (mg/L) | Mass of Oxygen Carrier per Unit Mass of Oxygen Delivered (g/g) | Relative Oxygen Delivery Efficiency |
|---|---|---|---|---|
| **Aqueous-Phase Oxygen Delivery** | | | | |
| Re-injection of Aerated/ treated Groundwater | Ambient Air Saturated | 9 | 110,000 | Lowest ↑ |
| Re-injection of Pure Oxygen-Amended Groundwater | Pure $O_2$ Saturated | 45 | 22,000 | |
| Re-injection of $H_2O_2$-Amended Groundwater | 100 mg/L of $H_2O_2$ | 50 | 20,000 | |
| **Solid-Phase Oxygen Delivery** | | | | |
| Injection of Oxygen-Releasing Compounds | Mg-peroxide | N/A | 10 | |
| **Vapor Phase Oxygen Delivery** | | | | |
| Injection of Ozone | 5% Ozone (Converted to $O_2$) | 98 | 12 | |
| Biosparging with Air or Oxygen, or Bioventing | 21% Oxygen (Ambient) | 275 | 4 | ↓ |
| Injection of Pure Oxygen | 95% Oxygen | 1,250 | 1 | Highest |

**Exhibit XII-23**
**Common Enhanced Aeration Remediation Design Elements**

# Oxygen and Bio-nutrient Delivery Design
– Theoretical oxygen mass requirement
– Bio-nutrient needs (e.g., N, P )
– Application delivery rate
– Number and depth of application points/position
– Equipment

# Permit Requirements and Thresholds
– Underground injection/well installation
– Air injection into subsurface
– Groundwater (wastewater) discharge
– Air (soil vapor) discharge

# Performance Monitoring Plan
– Ongoing distribution of oxygen and bio-nutrients
– Expansion of microbial population
– Reduction in contaminants (sorbed and dissolved phases)

# Contingency Plan
– Inadequate oxygen distribution
– Stagnation or die-off of microbial population
– Lower-than-expected petroleum mass reduction rates
– Excessive contaminant migration
– Build-up of excessive recalcitrant petroleum constituents
– Fugitive (soil vapor) emissions
– Difficult-to-treat/fouling of treated wastewater discharge
– Clogging of equipment or injection areas with iron oxide or biomass
– Other contingencies

**Permit Requirements and Thresholds** should be identified in the design so that the system can be constructed to comply with permit requirements and constraints. Depending on the specific enhanced aerobic bioremediation technology and the state in which the site is located, permits that may be required include underground injection, treated groundwater discharge (to sanitary or storm sewer, or air (soil vapor) discharge.

Several federal, state, and local programs regulate Class V aquifer remediation wells, and many require permits for underground injection of oxygen or bio-nutrients. On the federal level, management and regulation of these wells fall primarily under the underground injection control program authorized by the Safe Drinking Water Act (SDWA). Some states and localities have used these authorities, as well as their own authorities, to extend the controls in their areas to address concerns associated with aquifer remediation wells. Aquifer remediation injection wells are potentially subject to at least three categories of regulation.

First, a state's underground injection control (UIC) program, operating with approval from the federal program, may have jurisdiction over such wells. Second, in some states without UIC programs, the state's program for groundwater protection or pollution elimination program requirements may apply to remediation wells. Third, remediation wells may be regulated by federal and state authorities, through Superfund programs, corrective action programs under RCRA (including the UST program), or other environmental remediation programs. In the case of remediation programs, the regulatory requirements typically address the selection of aquifer remediation as a cleanup alternative and establish the degree of required cleanup in soil and groundwater, while deferring regulation of the injection wells used in the remediation to other programs. In the case of voluntary cleanup programs, some concern exists because they may not be approved or completed according to standards typical of cleanups overseen by a state or federal agency.[4]

**Performance Monitoring** should be accounted for in the design in the form of a written plan that can be used to objectively evaluate enhanced aerobic bioremediation system performance. The plan should clearly describe the approaches and methods that will be used to evaluate enhanced aerobic bioremediation system effectiveness in each of the following:

- Delivering oxygen (and bio-nutrients) to the subsurface
- Distributing oxygen and bio-nutrients through the contaminated area
- Increasing microbial population density
- Reducing sorbed and dissolved phase petroleum concentrations
- Achieving other performance requirements consistent with site-specific cleanup goals

**Contingency Plans** should also be accounted for and prepared as part of the design. The design should anticipate low-likelihood problems and potentially changing environmental conditions, as well as outline specific response actions that may be taken. Examples include response actions to take if any performance monitoring data indicate the following:

- Inadequate oxygen distribution
- Stagnation or die-off of microbial populations
- Low petroleum mass reduction rates
- Excessive contaminant migration

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[4] US EPA, Ofice of Solid Waste memo dated 12/27/00 on the Applicability of RCRA Seciton 3020 to In-Situ Treatment of Ground Water.

- Recalcitrance of constituents
- Fugitive emissions
- Any other reasonably plausible scenario that can arise under site-specific conditions and project-specific circumstances.

## Components of Enhanced Aerobic Bioremediation Systems

After review of factors that affect the selection and design of a particular enhanced aerobic bioremediation technology and the critical elements that should be included in the corrective action plan for enhanced aerobic bioremediation,, it is now appropriate to discuss major components of various enhanced aerobic bioremediation systems.

Exhibit XII-24 summarizes some of the major equipment components associated with each of the more common enhanced aerobic bioremediation technologies. Depending on which enhanced aerobic bioremediation technology has been selected in the corrective action plan, a subset of these major system components should be presented and discussed and schematically depicted (e.g., process flow diagram) in the corrective action plan. The design should relate capacities of these equipment components to design requirements (e.g., required oxygen production/delivery rates).

As shown in Exhibit XII-24, enhanced aerobic bioremediation systems employing oxygen-releasing compounds appear to require the least equipment in part because there is no need for any mechanical equipment once the oxygen-releasing compounds are deployed. By contrast, re-injection of hydrogen peroxide-amended groundwater requires the most equipment and a large number of mechanical components (e.g., pumps, blowers, etc.).

While the sets of major equipment components used by the enhanced aerobic bioremediation technologies differ significantly, the use of wells by each different approach warrants recognition and further discussion. In particular, the orientation, placement, number and construction of this common design element is worthy of a brief review.

**Injection, Extraction and Re-infiltration Wells**. Three important considerations for these wells are orientation, placement and number, and construction.

- **Well Orientation.** Both horizontal and vertical wells can be used to treat subsurface petroleum releases with any of the various enhanced aerobic bioremediation systems. Hydrogen peroxide-amended groundwater can be re-infiltrated using either vertical or horizontal wells. Although vertical wells are more common for ozone or pure oxygen injection, horizontal wells can be used.

## Exhibit XII–24
## Major Components of Enhanced Aerobic Bioremediation Systems

| Component | Function |
|---|---|
| **Oxygen Releasing Compound Systems** | |
| Borings and Excavations | Used to inject or place a slurry of oxygen releasing compounds so that oxygen may be slowly imparted to the water bearing zone. |
| Application Wells | Often used to suspend a solid form of oxygen releasing compounds to provide oxygen to groundwater. |
| Monitoring Wells | Used to evaluate effectiveness of remedial approach. Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination generally indicate how effectively oxygen is being delivered/dispersed and contaminants are being reduced. |
| **Hydrogen Peroxide Injection Systems** | |
| Extraction Wells | Often used to extract contaminated groundwater downgradient of the contaminated area for treatment and re-injection in the upgradient source area for plume containment and/or accelerated groundwater flow through the contaminated area. |
| Injection Wells or Infiltration Galleries | Injection wells, infiltration galleries or a combination of these are typically used to re-inject treated and hydrogen peroxide-amended groundwater so that dissolved oxygen may be flushed through the treatment zone. |
| Extraction, Injection, Transfer, and Metering Pumps and Tanks | Extraction, injection, transfer, and metering pumps are used for various purposes including: transferring groundwater from and back into the ground; transferring extracted groundwater between different components of the treatment system; and metering hydrogen peroxide and bio-nutrients into the infiltration system to maintain design concentrations. |
| Groundwater Treatment Equipment | Extracted groundwater may be treated to remove petroleum hydrocarbons by various means such as: oil/water separation; air stripping; or granular activated carbon sorption or others. |
| Instrumentation and Controls | Used to integrate and activate/deactivate system components. Help maintain the balance of flows consistent with the design and to safeguard against inadequate treatment or inappropriate discharges. |

## Exhibit XII–24
## Major Components of Enhanced Aerobic Bioremediation Systems (continued)

| Component | Function |
|---|---|
| **Hydrogen Peroxide Injection Systems (continued)** | |
| Monitoring Wells | Used to collect environmental samples analyzed in laboratories and field to evaluate on-going effectiveness of remediation.  Groundwater well samples tested for dissolved oxygen and contamination to evaluate overall effectiveness of oxygen delivery/dispersal and the contaminant reductions over time. |
| **Pure Oxygen Injection Systems** | |
| Sparging Wells | Used as conduits to bubble pure oxygen into contaminated groundwater.  The oxygen is delivered to the base of the soil and groundwater petroleum contamination so that it will  rise through the contaminated material providing oxygen to the hydrocarbon degrading bacteria. |
| Air Compressing Equipment | Used to pressurize ambient air to: prepare it for subsequent treatment to increase Oxygen levels/purity; and to provide pressure needed to inject oxygen and ambient air beneath the water table. |
| Oxygen Generating Equipment | Used to generate nearly-pure oxygen gas (~ 95%) from ambient air.  Synthetic zeolite sorbers are frequently employed to simply remove nitrogen from ambient air to produce high-purity oxygen. |
| Instrumentation and Controls | Used to integrate and activate/deactivate system components to maintain the balance of flows consistent with design and to safeguard against inadequate treatment or inappropriate discharges. |
| Monitoring Wells | Used to collect environmental samples tested in laboratories and the field to evaluate on-going effectiveness of remediation.  Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination generally indicate how effectively oxygen is being delivered or dispersed and contaminant reductions are occurring. |

## Exhibit XII–24
## Major Components of Enhanced Aerobic Bioremediation Systems (continued)

| Component | Function |
|---|---|
| **Ozone Injection Systems** | |
| Sparging Wells | Used as a conduit to inject ozone into contaminated groundwater. The ozone is sparged near the base of the soil and groundwater petroleum contamination so that it may contact the contaminants and provide oxygen to the hydrocarbon degrading bacteria. |
| Air Compressing Equipment | Used to pressurize ambient air needed to generate ozone and to provide the pressure needed to inject the ozone beneath the water table. Air compressor equipment must supply oil and contaminant free air to minimize in-line reactions with and premature decomposition of ozone. |
| Ozone Generating Equipment | Used to generate ozone gas on-site, typically at concentrations of about 5%. |
| Soil Vapor Extraction/<br>Treatment Equipment (Optional) | Used, if necessary, to control fugitive soil vapor ozone and volatilize organic compounds emissions in the unsaturated zone. May consist of low vacuum/flow blower to generate vacuum conditions in unsaturated zone and collect the vapors. Vapor treatment may consist of granular activated carbon or biofilters for low contaminant concentration air stream. |
| Instrumentation and Controls | Used to integrate and activate/deactivate system components to maintain the balance of flows consistent with the design and to safeguard against inadequate treatment or inappropriate discharges. |
| Monitoring Wells | Used to collect environmental samples tested in laboratories and the field to evaluate ongoing effectiveness of remediation. Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination generally indicate how effectively oxygen is being delivered or dispersed and contaminant reductions are occurring. |

Well orientation should be based on site-specific needs and conditions. For example, horizontal systems should be considered when evaluating sites that require re-infiltration of amended groundwater into shallow groundwater at relatively high flow rates. They are also readily applicable if the affected area is located under a surface structure (e.g., a building), or if the thickness of the saturated zone is less than 10 feet.

# **Well Placement and Number of Wells**. The number and location of wells are determined during the design to accomplish the basic goals of: (1) optimizing reliable oxygen and bio-nutrient delivery to the contaminated area; and (2) providing conduits to measure enhanced aerobic bioremediation system performance. For hydrogen peroxide re-infiltration systems this typically means placing re-injection wells in the source area(s) while extracting groundwater from downgradient locations aimed at simultaneously providing enhanced hydraulic gradient and accelerated oxygen distribution across the impacted area. The number, location, and design of the extraction wells will largely be determined from site-specific hydrogeology, the depth(s) and thickness(es) of the contaminated area(s), and the results of field-scale pilot testing and hydraulic modeling.

Determining the number and spacing of the wells for ozone or pure oxygen injection may also be determined through field-scale pilot testing. However, the following general points should be considered.

# Closer well spacing is often appropriate in areas of high contaminant concentrations to enhance contaminant contact and oxygen delivery/distribution where the oxygen demand is the greatest.

# Direct delivery of oxygen into the contaminated material using closer well spacings can deliver and disperse more quickly than oxygen delivery through groundwater advection/dispersion and could significantly decrease the treatment timeframe.

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

# **Well Construction.** Enhanced aerobic bioremediation system wells are generally constructed of one- to six-inch diameter PVC, galvanized steel, or stainless steel pipe. Oxygen or ozone injection sparge wells have screened intervals that are normally one to three feet in length and situated at or below the deepest extent of sorbed contaminants. Injection sparge points must be properly grouted to prevent the injected oxygen from moving directly up the well annulus to the unsaturated zone rather than being forced into the contaminated aquifer ("short circuiting" of the

injected oxygen). When horizontal injection wells are used, they should be designed and installed carefully to ensure that the injected oxygen exits along the entire screen length.

Re-infiltration wells typically have screen lengths that extend from the base of the wells into the unsaturated zone. Groundwater extraction wells should ideally be screened in the saturated interval containing the greatest mass of hydrocarbons. Field-scale pilot studies and subsequent data analysis and hydraulic modeling can help to determine the configuration and construction design of groundwater extraction and injection wells.

## Step 4 - An Evaluation of the Operation and Monitoring Plan

### Remedial Progress Monitoring

Significant uncertainties associated with site conditions can remain even as remedial designs are completed and implemented. In the post-remedial startup period, these unknowns frequently can result in operations that vary from the design. These variances can be small or large and often require adjustments to account for unforeseen conditions and optimize system performance. Unfortunately, in many cases, the need for these adjustments can go unrecognized for a long time.

In some cases, the delay in recognizing that remedial system adjustments are necessary may be attributed to relatively slow responses in subsurface conditions to the applied technology (e.g., increases in microbial population and biodegradation of contaminants). Because these subsurface responses to the applied remedial technology can be delayed, there is often the tendency to give the remedial program more time to work (sometimes up to years) before making system modifications or adjustments. In other cases, the delay may stem from misuse or misinterpretation of site data leading to a belief that the remedial system is performing well when it is not. An example of this misuse is the practice of using groundwater analytical data from oxygen delivery wells as an indicator of remedial progress. In this case, an assessment is biased by the localized effects of bioremediation in the immediate vicinity of the oxygen delivery wells, but does not provide an objective measure of the enhanced aerobic bioremediation system's ability to distribute oxygen and promote biodegradation throughout the treatment area.

Wells that are used to carry out remedial actions should not be used as monitoring wells. Monitoring wells should be separate wells used only for that purpose. If remediation involves injection of gases, the monitoring wells should be tightly capped until used. If they are not capped, the monitoring wells can provide a path of least resistance for the injected air to return to the surface. Air can channel to a monitoring well, then bubble up through the standing water in the well preferentially removing contaminants from the area in and immediately around the well while the rest of the aquifer is short circuited.

However, at many sites remedial system operational efficiencies are not optimized simply because an adequate performance monitoring plan has either not been developed or has not been fully implemented.  In such cases, the designed remedial system may be installed, started up, and allowed to run its course with insufficient numbers or types of samples collected to determine whether the remedial system is performing in accordance with design expectations.  The result of such monitoring approaches can be the discovery of a sub-standard or failed remediation program years after its implementation.

The previous section discussed the importance of developing a comprehensive remedial progress monitoring plan.  Because of its importance, this section covers the topics that should be addressed in such a plan to ensure objective gauging of remedial system performance and necessary optimization adjustments can be made early on and throughout the duration of enhanced aerobic bioremediation.  In particular, a focused discussion on performance sampling and enhanced aerobic bioremediation system evaluation criteria is provided to assist with the corrective action plan review.

## Evaluation Sampling

Evaluation sampling is performed to gauge the effectiveness of the enhanced aerobic bioremediation system relevant to design expectations.  Based on a comparison of the actual field sampling data to design and operational expectations, timely modifications to the system or operating procedures (if any) can be made to optimize system performance early in the remediation program. Projects with regular performance reviews guided by the results of such sampling/monitoring programs have a greater chance of achieving the design remedial goals within desired time frames, potentially at lower cost.

Various environmental media are sampled to evaluate system performance. Groundwater, soil, and soil vapors from the treatment area and vicinity are commonly sampled to determine the degree to which the enhanced aerobic bioremediation system is meeting the basic objectives of the approach, including:

- Delivering oxygen to the saturated zone at required design rates
- Distributing dissolved oxygen across the target contaminated area to restore and maintain aerobic conditions
- Reducing concentrations of petroleum hydrocarbons in soil and groundwater at design rates through biodegradation of the petroleum compounds

Exhibit XII-25 identifies those parameters that are commonly measured in groundwater, soil, and soil vapor samples to help evaluate enhanced aerobic

## Exhibit XII-25
## Common Performance Monitoring Parameters and Sampling Frequencies

| Analytical Parameter | Sampling Frequency | | | Purpose |
|---|---|---|---|---|
| | Startup Phase (7-10 days) | Remediation/Post-Application Long-Term Monitoring Phase (on-going) | | |
| | *Daily* | *Weekly to Monthly* | *Quarterly to Annually* | |
| **Groundwater** | | | | |
| Dissolved Oxygen | X | X | | Determines system's effectiveness in distributing oxygen and ability to maintain aerobic conditions (i.e., dissolved oxygen > 2 ppm) in treatment area. Provides data to optimize system performance. |
| Redox Potential | X | X | | Yields data on system's ability to increase the extent of aerobic subsurface environment. |
| pH | X | X | | Confirms pH conditions are stable and suitable for microbial bioremediation or identifies trends of concern. |
| $H_2O_2$ or Ozone | X | X | | Provides information on distances these oxygen-producing compounds can be transmitted by the remedial system before decomposing |
| Bio-nutrients | | | X | Determines if bio-nutrients injected into the groundwater are being consumed during bioremediation or accumulating and potentially degrading groundwater quality |
| Petroleum COCs | | | X | Indicates remedial progress |

## Exhibit XII-25
## Common Performance Monitoring Parameters and Sampling Frequencies (continued)

| **Analytical Parameter** | **Sampling Frequency** | | | **Purpose** |
|---|---|---|---|---|
| | **Startup Phase (7-10 days)** | **Remediation/Post-Application Long-Term Monitoring Phase (on-going)** | | |
| | ***Daily*** | ***Weekly to Monthly*** | ***Quarterly to Annually*** | |
| **Groundwater (continued)** | | | | |
| Degradation Daughter Constituents (e.g., TBA) | | | X | Offer direct evidence of contaminant bioremediation and enhanced aerobic bioremediation effectiveness |
| Water Table Elevations | X | X | | Determines if hydraulic conditions (groundwater flow) are consistent with design intent or if enhanced aerobic bioremediation technology application has had an unanticipated affect on these conditions |
| **Soil Vapor** | | | | |
| Carbon dioxide | X | X | | Provides evidence of biodegradation |
| Oxygen | X | X | | Indicates potential losses of introduced oxygen through the unsaturated zone |
| Volatile Petroleum COCs | X | X | | Suggests residual sources in soil or fugitive emissions associated with the remedial effort |
| Fugitive Ozone or Hydrogen Peroxide | X | X | | Determines losses of oxygen-yielding reagents delivered to the subsurface |
| **Soil** | | | | |
| Petroleum COCs | | | X | Provide a measure of remedial progress and the extent to which biodegradation of sorbed contaminants is limited by |

bioremediation progress and system performance. A brief description of the respective sampling frequencies and the relevance and significance of each parameter to the performance evaluation are also provided in the exhibit. A key element is the location(s) where performance evaluation sampling takes place relative to subsurface oxygen delivery points. As stated in the exhibit, performance evaluation samples should not normally be collected from oxygen delivery locations.

The performance of the enhanced aerobic bioremediation system should be determined by the chemistry and microbiology of soil and groundwater located between, around, and downgradient of oxygen delivery locations rather than inside or in the immediate vicinity of the oxygen delivery points. Conditions inside or in the immediate vicinity of oxygen injection locations have been preferentially altered by enhanced aerobic bioremediation to enhance biodegradation of the petroleum contaminants. Therefore, data from these locations are not representative of the subsurface conditions that exist beneath most of the site. To understand the effect the enhanced aerobic bioremediation system is having on the subsurface conditions as a measure of its performance, samples of soil, groundwater and soil gas should be collected from alternate locations.

In reviewing of the performance monitoring plan in the corrective action plan, a reviewer should verify that a sufficient number of sampling locations exist between oxygen application points to provide the necessary performance sampling data. A description of how these data may be used to evaluate the enhanced aerobic bioremediation system performance is provided below.

Particular attention should be taken with respect to sampling groundwater, soil vapor, and soil. In reviewing a sampling plan, pay attention to the proposed sampling frequencies and methods. Some factors to look for include:

**Groundwater sampling.** Samples should be collected from monitoring wells located in and around the treatment area and from extraction wells (if used). Samples should not be collected from oxygen delivery wells for evaluating system performance because they would only be representative of highly localized effects of the remediation program.

**Soil vapor sampling.** Samples should be collected from monitoring wells located in and around the treatment area that are screened in the unsaturated zone and from soil vapor extraction wells (if used). Samples should not be collected from oxygen delivery wells for evaluating system performance because they would only be representative of highly localized effects of the remediation program.

**Soil sampling.** Samples should be collected from borings or using Geoprobe sampling equipment in and around the treatment area. Soil samples should consistently be collected from same contaminated sections of stratigraphic interval for comparison to earlier samples from same locations and depths.

### Evaluation Criteria

The evaluation sampling described above provides evidence needed to assess the enhanced aerobic bioremediation system performance. This evidence requires examination and interpretation to confirm enhanced aerobic bioremediation system effectiveness and whether system modifications may be warranted. A discussion of these data and how system performance can be interpreted is provided below. In particular, an evaluation of performance is examined from the following two broad enhanced aerobic bioremediation system requirements:

- Oxygen delivery and distribution
- Aerobic biodegradation

Each of these is described in more detail in the following paragraphs.

**Oxygen Delivery and Distribution.** Performance sampling may indicate that the enhanced aerobic bioremediation system is meeting design specifications for oxygen delivery and distribution if the data show the following:

- Vadose zone air sampling suggests that there are negligible losses of supplied oxygen to the atmosphere

- Oxygen is being delivered to the subsurface at the mass delivery rate required by the design

- Dissolved oxygen levels in groundwater samples collected across the target treatment area have been elevated to concentrations of 2 mg/L or more and reduction/oxidation conditions are uniformly in the aerobic range ( greater than or equal to 750 mV)

If the performance monitoring data suggest that one or more of these conditions is not met, the system may not be meeting the requirements of the design and system adjustments or modifications may need to be made. As previously discussed, the remedial system design should include contingency planning that explores performance deficiency scenarios and identifies possible solutions.

Oxygen delivery deficiencies can normally be overcome by adjusting system flow rates or upgrading equipment capacities. However, occasionally, oxygen delivery rates may be limited by the capacity of the subsurface to absorb and/or transport the delivered oxygen mass. This may occur if an infiltration system component becomes hydraulically overloaded by the infiltration rates needed to meet the design oxygen delivery objectives. Also, groundwater could become over-saturated with dissolved oxygen at injection points requiring oxygen delivery rates to be reduced to avoid off-gassing losses of oxygen to the atmosphere. In both cases, additional infiltration or injection points could readily be added to the system to expand the oxygen delivery capacity to design-specified levels.

Loss of oxygen to the unsaturated zone and ultimately the atmosphere removes this supply of oxygen available to biodegrading microorganisms. One way to limit oxygen losses without decreasing application rates is to add application points with proportionally less oxygen delivered to each location. Another approach is to alternate the supply of oxygen to various locations in the contaminated zone, allowing existing levels of oxygen to dissipate before introducing oxygen again.

Perhaps the most challenging performance problem occurs when an enhanced aerobic bioremediation system is unable to restore and maintain aerobic conditions in a portion or multiple portions of a contaminated area. Oxygen distributed from delivery points can fail to reach target contaminated areas for many reasons:

# High biological oxygen demand in the delivery point vicinity
# Elevated soil organic content
# Low permeability heterogeneous soils
# Low hydraulic gradient and groundwater flow

Possible remedies to the performance problem include adding additional oxygen delivery points, increasing oxygen delivery rates, or enhancing hydraulic gradients and groundwater flow.

**Aerobic Biodegradation**. Successful oxygen delivery and distribution is probably the most important performance measure for an enhanced aerobic bioremediation system. However, this is only part of the performance. The second part requires confirmation that enhanced in-situ biodegradation of the petroleum contaminants is occurring as a result of, and at rates anticipated by, the enhanced aerobic bioremediation design. Performance monitoring that suggests that an enhanced aerobic bioremediation system is operating effectively includes the following.

# Decreasing dissolved and sorbed petroleum contaminant concentrations (i.e., gradual reduction of subsurface petroleum mass consistent with design expectations).

# Production of carbon dioxide in the subsurface, as evidenced by baseline and subsequent vadose zone sampling and field analyses. Carbon dioxide production in the saturated zone may also be evaluated by sampling groundwater and analyzing the groundwater for total inorganic carbon.

- Significantly increased microbial activity in the contaminated area as suggested by comparison of baseline and subsequent microbial population plate counts.

If only one or two of these conditions exist, there may not be enough evidence to conclude that bioremediation is a significant contributor to contaminant reduction or to conclude that the enhanced aerobic bioremediation system is effective. For example, apparent contaminant reductions in dissolved and sorbed phases could occur as a result of groundwater advection and dispersion or simply because of natural fluctuations in water levels. Or, if hydraulic manipulation (engineered hydraulic gradients) of the groundwater is part of the enhanced aerobic bioremediation system, apparent contaminant reductions could result from dilution or separation of the groundwater from the contaminated soil (e.g., if the water table is depressed below the contamination). In this case, contamination levels in groundwater could rebound to near preexisting concentrations if the hydraulic controls are turned off and groundwater re-contacts the contaminated soil.

The appearance of significant levels of carbon dioxide subsequent to enhanced aerobic bioremediation system activation is a good indicator of enhanced biological activity. However, if elevated carbon dioxide levels in the unsaturated zone are unable to be detected, this does not necessarily mean that microbial activity has not been enhanced. Carbon dioxide entering the vadose zone may be diluted by pore space air exchanges with the atmosphere, operation of vapor control systems, and other means, making it difficult to distinguish small differences in concentrations.

Possibly the most direct indication that enhanced aerobic bioremediation has increased the number of hydrocarbon degrading bacteria is observation of significantly increased populations of heterotrophic bacteria in the target treatment area. While larger populations of heterotrophic bacteria may not always translate to increased levels of petroleum hydrocarbon biodegradation, the increased number of bacteria over the baseline levels would serve as a strong indicator of biodegradation. If performance sample analyses detect intermediate degradation daughter products, this may be further evidence of contaminant biodegradation that has been enhanced.

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# Checklist: Can Enhanced Aerobic Bioremediation Be Used At This Site?

This checklist can help to evaluate the completeness of the corrective action plan and to identify areas that require closer scrutiny. In reviewing the corrective action plan, answer the following questions. If the answer to several questions is "no", request additional information to determine if the proposed enhanced aerobic bioremediation technology and approach will effectively accomplish the site cleanup goals within a reasonable period of time.

## 1. Site Factors

| Yes | No | |
|---|---|---|
| ☐ | ☐ | Is the soil hydraulic conductivity greater than $10^{-7}$ ft/s ? |
| ☐ | ☐ | Is the soil generally free of impermeable or low permeability layers that could retain significant petroleum contaminant mass and limit the bioavailability of this mass? |
| ☐ | ☐ | Does the soil profile of the contaminanted zone contain only limited natural organic material (e.g., layers of peat or humic material)? |
| ☐ | ☐ | Is the dissolved iron concentration in the site groundwater < 10 mg/L? |
| ☐ | ☐ | Have imminent likely excessive risks to human health or the environment (if any, associated with the petroleum contamination) been eliminated? |
| ☐ | ☐ | Does the state have specific permitting requirements? |

## 2. Enhanced Aerobic Bioremediation Design

| Yes | No | |
|---|---|---|
| ☐ | ☐ | Has the mass of petroleum hydrocarbons requiring biodegradation been estimated? |
| ☐ | ☐ | Has the mass of dissolved oxygen required to biodegrade the petroleum contaminants been estimated? |
| ☐ | ☐ | Can the proposed enhanced aerobic bioremediation approach deliver the necessary oxygen mass to the treatment area within the estimated cleanup time? |
| ☐ | ☐ | Is the capacity of the enhanced aerobic bioremediation treatment system sufficient to generate and deliver oxygen at the required design rate? |

| | | |
|---|---|---|
| o | o | Is the density and configuration of oxygen delivery points adequate to uniformly disperse dissolved oxygen through the target treatment zone, given site geology and hydrologic conditions? |

### 3. Written Performance Monitoring Plan

| **Yes** | **No** | |
|---|---|---|
| o | o | Will a comprehensive set of baseline sampling be performed prior to enhanced aerobic bioremediation system start-up? |
| o | o | Does the plan specifically exclude sampling from oxygen delivery wells when collecting data to evaluate enhanced aerobic bioremediation system performance? |
| o | o | Are monitoring wells adequately distributed between oxygen delivery locations to collect groundwater and soil vapor samples to evaluate the performance of the enhanced aerobic bioremediation system? |
| o | o | Does the written plan include periodically collecting soil samples from the contaminated interval(s) at locations between oxygen delivery locations? |
| o | o | Will the soil, soil vapor and groundwater samples be analyzed for the majority of the recommended performance monitoring parameters? |
| o | o | Will frequencies of performance monitoring generally correspond to those identified in Exhibit XII – 25? |

# Chapter XIII

# Chemical Oxidation

# Contents

# List of Exhibits

# Chapter XIII
# Chemical Oxidation

## Overview

Petroleum contaminant decomposition and in-situ destruction may be accomplished using chemical oxidation technologies. In contrast to other remedial technologies, contaminant reduction can be seen in short time frames (e.g., weeks or months). As discussed in this chapter, a variety of chemical oxidants and application techniques can be used to bring oxidizing materials into contact with subsurface contaminants to remediate the contamination. With sufficient contact time with the organic contaminants, chemical oxidants may be capable of converting the petroleum hydrocarbon mass to carbon dioxide and water and ultimately irreversibly reduce concentrations of petroleum hydrocarbons in soil and groundwater. While many of the chemical oxidants have been used in wastewater treatment for decades, only recently have they been used to treat hydrocarbon-contaminated groundwater and soil *in-situ*.

Chemical oxidation technologies are predominantly used to address contaminants in the source area saturated zone and capillary fringe. Cost concerns can preclude the use of chemical oxidation technologies to address large and dilute petroleum contaminant plumes. More frequently, chemical oxidation technologies are employed to treat smaller source areas where the petroleum mass is more concentrated. However, where excessive petroleum contaminant mass exists in the source area and where there is a significant thickness of mobile non-aqueous phase liquids (NAPLs), other remedial technologies (e.g., free product recovery) may need to precede chemical oxidation for the remediation to be safe and cost-effective.

Concurrent treatment of source area saturated and unsaturated zones usually requires the integration of chemical oxidation with other remedial technologies that target unsaturated zone contamination (e.g., soil vapor extraction). Frequently, soil vapor extraction, which is used to treat the unsaturated zone, is included as a component of chemical oxidation remedial solutions even if there is no specific need to treat unsaturated soils in the source area. Use of soil vapor extraction in conjunction with chemical oxidation can help alleviate safety issues associated with controlling and recovering off-gas containing volatile organic carbons (VOCs), oxygen, oxidants and other reaction byproducts that can be generated by various chemical oxidants.

As discussed in greater detail below, each chemical oxidant and application technology has advantages and disadvantages. Some oxidants are stronger than others, yet some weaker oxidants may persist in the subsurface, allowing longer contact times with the contaminants. Careful evaluation of the contaminants of concern is needed before selecting a chemical oxidation technology. Certain contaminants (e.g., benzene) that are frequently remedial drivers at petroleum UST release sites are unable to be readily chemically oxidized *in-situ* using some chemical oxidants (e.g., permanganate).

Understanding the site hydrogeologic conditions is important when considering chemical oxidation technologies because these conditions often determine the extent to which the chemical oxidants may come into contact with the petroleum contaminants. Chemical oxidants may not be able to penetrate low permeability homogenous soils or horizons in heterogeneous soils that contain the bulk of petroleum contaminant mass.

Soil reactivity with chemical oxidants is also important when considering the costs of the use of chemical oxidation. Excessive loss of a chemical oxidant that is reacting with organics in soil, instead of reacting with the contaminants, may preclude the use of the technology as an economically viable approach to site remediation. Different chemical oxidation technologies are most appropriate for particular hydrogeologic conditions. For example, Fenton’s Reagant may not be ideal for groundwater with high concentrations of carbonate. The carbonate ion preferentially scavenges the hydroxyl radicals created by Fenton’s Reagant reactions before they have a chance to react with the petroleum contaminants. By contrast, the presence of carbonate minerals in the geologic matrix has generally positive effects on permanganate oxidation.

Remedial strategies for petroleum UST sites that include a combination of active source zone treatment with enhanced natural attenuation outside the contaminant plume core may consider chemical oxidation technologies. Many chemical oxidation techniques also provide residual dissolved oxygen that is used by aerobic microorganisms to biodegrade contaminants. In addition, these technologies may also oxidize reduced electron acceptors (e.g., nitrogen to nitrate, sulfides to sulfate), which are then used by anaerobic microorganisms to biodegrade contaminants. For more information on enhanced aerobic remediation technologies, see "How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers” (EPA-510-B-95-007, 1995). For specific information on aerobic remediation technologies, see Chapter III, *Bioventing*, Chapter VIII, *Biosparging*, and Chapter X, *In-situ Groundwater Bioremediation*.

Exhibit XIII-1 summarizes the general advantages and disadvantages of chemical oxidation technologies.

Several chemical oxidants have been used to remediate petroleum contaminated UST sites. The most commonly used (and most effective) are Hydrogen Peroxide/Fenton's Reagent and Ozone. Sodium or Potassium Permanganate have been used, but experience with these compounds is more limited, although some recent bench-scale and field studies are showing promise.

## EXHIBIT XIII-1
## Chemical Oxidation
## Primary Advantages and Disadvantages

### Advantages

- Contaminant mass can be destroyed in-situ.
- Rapid destruction/degradation of contaminants (measurable reductions in weeks or months).
- Produces no significant wastes (VOC off-gas is minimal), except Fenton’s.
- Some oxidants (not Fenton’s) are capable of completely oxidizing MTBE (but production of degradation products may be problematic).
- Reduced operation and monitoring costs.
- Compatible with post treatment monitored natural attenuation and can even enhance aerobic and anaerobic biodegradation of residual hydrocarbons.
- Some oxidation technologies cause only minimal disturbance to site operations.

### Disadvantages

- Potentially higher initial and overall costs relative to other source area solutions.
- Contamination in low permeability soils may not be readily contacted and destroyed by chemical oxidants.
- Fenton’s Reagant can produce significant quantity of explosive off-gas. Special precautions (i.e., SVE system) are required for appropriate implementation of remedial action involving Fenton’s Reagent/hydrogen peroxide.
- Dissolved contaminant concentrations may rebound weeks or months following chemical oxidation treatment.
- Dissolved contaminant plume configuration may be altered by chemical oxidation application.
- Significant health and safety concerns are associated with applying oxidants.
- May not be technically or economically able to reduce contaminants to background or very low concentrations.
- Significant losses of chemical oxidants may occur as they react with soil/bedrock material rather than contaminants.
- May significantly alter aquifer geochemistry; can cause clogging of aquifer through precipitation of minerals in pore spaces.

There has also been recent interest in and some field applications using sodium persulfate ($Na_2S_2O_8$) to oxidize organic contaminants or to reduce the oxidant demand of native soils before other oxidants are applied to the contamination. Some research has demonstrated that when mixed with ferrous iron as a catalyst, the sulfate free radical ($SO_4^-$) can be produced, which has an oxidation potential only slightly less than Fenton's Reagent. Field testing of this oxidant to date has primarily involved the destruction of chlorinated organics rather than petroleum hydrocarbons. Given the experimental status of this oxidant, it is not further described or discussed in this chapter.

A brief description of the three main petroleum hydrocarbon oxidants and associated application technologies is provided below. Exhibit XIII-2 compares the relative advantages and disadvantages of these chemical oxidation technologies.

### Hydrogen Peroxide and Fenton's Reagent

Hydrogen peroxide is a strong oxidant that can be injected into a contaminated zone to destroy petroleum contaminants. When injected to groundwater, hydrogen peroxide is unstable, and reacts with organic contaminants and subsurface materials. It decomposes to oxygen and water within hours of its introduction into groundwater generating heat in the process. Peroxide is typically shipped to a remediation site in liquid form at dose concentrations ranging from five percent to 50 percent by weight.

The reactivity of hydrogen peroxide can limit the extent to which it may be distributed in the subsurface before it decomposes. Injecting concentrations of hydrogen peroxide as low as 100 ppm (a small fraction of one percent) can cause oxygen concentrations in groundwater to exceed the solubility limit of oxygen in groundwater (typically 9-10 mg/L). When this occurs, oxygen gas is formed, and is lost in the form of bubbles that rise through the saturated zone to the water table and into the unsaturated zone.

Hydrogen peroxide is particularly effective when it reacts with ferrous iron ($Fe^{2+}$) to produce Fenton's Reagent. Ferrous iron may be naturally present in the subsurface soils and/or groundwater, or it can be added as a catalyst solution together with the hydrogen peroxide to produce this aggressive chemical reaction.

Hydrogen peroxide in the presence of ferrous iron ($Fe^{2+}$) reacts to form hydroxyl radicals ($OH\bullet$), ferric iron ($Fe^{3+}$), and hydroxyl ions ($OH^-$). The hydroxyl ions are very powerful oxidizers, and react particularly with organic compounds. The hydroxyl radicals break the petroleum hydrocarbon bonds of common petroleum constituents such as benzene, toluene, ethylbenzene, and xylene, as well as petroleum aromatic hydrocarbons (PAHs) and methyl tertiary butyl ether (MTBE), a common gasoline additive.

Fenton's Reagent requires soluble $Fe^{2+}$ to form OH•. This optimal reaction occurs under relatively low pH conditions (e.g., pH of 2 to 4). pH adjustment in the treatment area is often necessary to enable the oxidation process to proceed efficiently. This can be accomplished by either acidifying the hydrogen peroxide or by adding a chelating acid. Using a ferrous sulfate solution `simultaneously adjusts aquifer pH and adds the iron catalyst needed for Fenton's Reagent. Because of the low pH requirement, Fenton's Reagent treatment may not be efficient or effective in limestone geology or sediments with elevated pH levels or with significant capacity to buffer these reactions. In addition, reaction between hydrogen peroxide and ferric iron can consume hydrogen peroxide, reducing the effectiveness of the oxidant dose. The same effect may also occur in soils with high ferric iron content.

**Exhibit XIII-2**
**Chemical Oxidation Technologies Comparative Matrix**

| | Hydrogen Peroxide/ Fenton's Reagant | Permanganate | Ozone |
|---|---|---|---|
| **Advantages** | | | |
| Potential to complete remediation in shortest time | x | | |
| Capacity to oxidize MTBE and benzene | x | | x |
| No significant VOC off-gas produced by heat of reaction | x [1] | x | |
| Oxidizes over extended period, increasing possibility of contact with contaminants | | x | |
| Increases dissolved oxygen levels for potentially enhanced aerobic bioremediation | x | | x |
| Reduced health and safety concerns during application | | x [2] | |
| Can be applied using automated system | | | x |

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[1] If solid peroxide is injected below 10% strength, the heat of dilution is mitigated and VOC generation typically avoided.

[2] Note that sodium permanganate is often applied as a liquid at 40% strength, which poses a significant handling and explosion risk.

## Exhibit XIII-2
## Chemical Oxidation Technologies Comparative Matrix (continued)

| | Hydrogen Peroxide/ Fenton's Reagant | Permanganate | Ozone |
|---|---|---|---|
| **Disadvantages** | | | |
| Inability to effectively oxidize benzene or MTBE | | x | x |
| Increased risk of fugitive vapors entering building structures, utility conduits, particularly in absence of adequate vapor recovery technology (e.g., soil vapor extraction) | x | | x |
| Increased risk of plume reconfiguration | x | | x |
| Low permeability soil horizons less likely to be penetrated by oxidant over short injection period | x | x | x |
| On-site reactive chemical handling and storage required | x | x | x |
| On-site gas production and delivery equipment (e.g., ozone generator) required | | | x |
| Few petroleum remediation projects completed using this technology due to limited effectiveness | | x | |
| Possible production of unwanted compounds or by-products in the subsurface[3] | x | x | x |
| Potential to precipitate solids and clog aquifer pores | x | x | |

Fenton-like reactions produce the hydroxyl radical (OH•) which is one of the strongest oxidants, but the reaction proceeds so quickly that the radicals may not have sufficient time to come into contact with contaminant molecules so that they can be destroyed before the hydrogen peroxide decomposes. Also, some

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[3] Chemical oxidation may cause some may create some toxic or highly mobile secondary products. Ensure that analyses for potential secondary products are included in any corrective action plan that proposes the use of chemical oxidants.

contaminants may sorb so tightly to organic material in the soil that they are effectively protected from destruction.. This may be particularly true for sites with significant layers or lenses of low permeability that results from high clay content. In such cases, the oxidant may successfully address contaminants in more permeable layers or lenses of soil while leaving the bulk of the contamination that resides in the low permeability soils.

Difficulty in addressing contamination in low permeability soils may be alleviated to some degree by controlled pneumatic or hydraulic fracturing of the soil. However, engineered hydraulic fractures generally cannot be spaced more closely than about 5 feet, which means that chemical oxidants must still penetrate a substantial thickness of low permeability soil to come into contact with the contamination. Deep soil mixing with large diameter drill augers is the most effective method currently available to increase contact between adsorbed contaminants and the oxidants. In any case, long term post-injection monitoring of contaminant levels in groundwater is critical to evaluating the success of putting Fenton's Reagent into contact with adsorbed contaminants. If inadequate contact occurs, contaminant levels in groundwater samples will rebound as the adsorbed contaminant mass gradually (typically over months) bleeds back into groundwater.

Controlled oxidation is increasingly being practiced using solid peroxides, pH modifiers, and catalysts that promote the generation of free radicals. This new approach moderates the rate of dissolution and peroxide generation, which in turn controls that rate of reaction between peroxide and the petroleum contaminants. The use of slurried peroxides creates the opportunity to release oxidants and oxygen over a longer period, which can promote subsequent aerobic remediation.

“Modified” Fenton-type systems use pH-neutral and even higher pH conditions along with slurried solid peroxides and metallic or organo-metallic catalysts. The reaction of the oxidants with the catalysts generate hydroxyl radicals, which react with the organic contaminants within the subsurface. The advantage to this approach is the ability to use Fenton’s Reagent under neutral pH conditions, requiring no acidification of the aquifer. It leads to a mix of reducing and oxidizing reactions in the subsurface, which moderates the rate of dissolution and peroxide generation, which moderates the rate of reaction between the peroxide and the petroleum contaminants. This releases oxidants and oxygen over a longer period, and may promote subsequent aerobic remediation.

Fenton-like reactions are exothermic and can raise the temperature of groundwater, produce steam and generate significant pressures in the application area, particularly when the Fenton’s is added at strengths approaching 10-12%. Especially in deep vadose zones and in monitoring or injection wells where pressures may be elevated, Fenton’s-like reactions can lead to explosive conditions and present safety concerns that need to be promptly and effectively managed. In addition, migration of explosive vapors along preferential pathways may pose an explosion hazard.

Several incidents resulting in spontaneous explosions of subsurface vapors have occurred during Fenton's Reagent treatment of petroleum contaminated sites. Other incidences have involved VOC vapor migration and intrusion into buildings and contaminant plume expansion. To manage these risks, at a minimum, it is important before a chemical oxidation strategy is selected and implemented to:

- Locate pockets of high levels of petroleum contamination in the treatment area.
- Identify and evaluate preferential flow paths.
- Clear the area of subsurface utilities, basements or other enclosed spaces that could accumulate and transmit vapors.
- Ensure that no petroleum storage tanks or lines are in the treatment area.

During application of an oxidation technology, consider the following to manage risks:

- Use a field photo-ionization or flame ionization detector (PID/FID) and explosimeter to monitor for explosive conditions.

- Install and operate a soil vapor collection system during Fenton's Reagent treatment until such time it can be demonstrated that there is no significant threat.

- Use a heat probe to monitor subsurface temperatures. Hydrogen peroxide, for example, decomposes at temperatures above 65°C, so as reactions progress in the subsurface, it is important to control the temperature to ensure maximum efficacy of the oxidation process.

- Closely monitor hydrogen peroxide and catalyst injection into the treatment area and adjust levels based on field analyses of soil gas and groundwater samples.

- Consider hydraulically containing groundwater during the treatment process to minimize the possibility of the chemical reaction pressures expanding the contaminant plume. Note, however, that dissolved gases in groundwater often prevent this approach from being as effective as predicted.

Other safety concerns include those associated with storing and using concentrated hydrogen peroxide on site. Many applications of the technology have involved the storage and use of thousands of gallons of fifty-percent hydrogen peroxide. Skin burns and blindness can result from contact with this chemical at this concentration. Safety precautions include the use of skin protection and safety glasses during application of these chemicals. A shower and eye wash facility may need to be constructed for the duration of the application.

Hydrogen peroxide and catalyst solutions needed for Fenton's Reagent are usually added to the treatment area by pressure injection into one or more designated chemical oxidation injection wells, or gravity injection into one or more monitoring or other wells.

In pressure injection, compressed air is used to sparge the ferrous iron catalyst and relatively large volumes of peroxide solution (e.g., hundreds to thousands of gallons) into the contaminated soil and groundwater over a short period of time (e.g., days). The sparged air forces the chemical reactants down the injection well point(s) and out into the impacted saturated soil. This is an aggressive approach that poses inherent increased risks of VOC vapor production and migration as well as plume re-configuration. Plume re-configuration may occur because the zone of influence during injection is limited, and permeability decreases with application of the technology, which may create preferential flowpaths with continued injection. Operation of a soil vapor extraction system concurrently with oxidant injection is a sensible precaution.

In gravity injection, small volumes of reagents are gravity-fed into injection well(s) over a longer application period. The distribution and dissipation of the reagents in the saturated zone is largely controlled by the site hydrogeologic conditions. The gravity injection approach may reduce some of risks associated with chemical oxidation technologies. Additionally, given its prolonged application period, the oxidants may be able to penetrate into more of the lower permeability soils to address contaminants in these areas.

In both cases, multiple injection events, separated by extended periods of groundwater monitoring, may be required in order to approach cleanup objectives. Establishing which injection or application approach is likely to be most efficient or cost effective for a given site is challenging, given the recent emergence of this technology and the limited volume of scientifically defensible information that is currently available for the two basic application methods. Site-specific safety concerns may be a key determining factor of the most appropriate injection approach.

An additional benefit of hydrogen peroxide and Fenton's Reagent is the temporary increase of oxygen levels in and around the treatment area. The increased oxygen levels at the fringes of the treatment area can enhance naturally occurring aerobic biodegradation processes that reduce contaminant mass. While there may be concerns about oxidizing hydrocarbon-degrading bacteria in the chemical oxidation treatment area, many studies have shown that soil cannot be readily sterilized by Fenton's Reagent and that microbial populations rapidly rebound following chemical oxidation treatment. In addition to enhancing aerobic biodegradation, reduce nitrogen and sulfur are oxidized to nitrate and sulfate, which can be used by anaerobic microbes.

## Permanganate

Permanganate is emerging as a chemical oxidant that can be used to destroy petroleum and other organic compounds in soil and groundwater, and has successfully treated MTBE in recent laboratory and bench-scale studies. This oxidant is weaker than hydrogen peroxide. Its inability to oxidize benzene can lead to the early elimination of permanganate as a candidate for oxidation technology at petroleum cleanup sites.

However, permanganate has several advantages over other oxidants. It:

# Oxidizes organics over a wider pH range.
# Reacts over a prolonged period in the subsurface allowing the oxidant to more effectively permeate soil and contact adsorbed contaminants.
# Does not normally produce heat, steam and vapors or associated health and safety concerns.

Permanganate may be applied to sites as either potassium permanganate ($KMnO_4$) or sodium permanganate ($NaMnO_4$). Where cost dominates over engineering factors at a site, potassium permanganate is the preferred chemical form because it is more widely available, less costly, and is available in solid form, which facilitates transport and handling. Where other factors are more important, the liquid form of sodium permangante is preferable.

When choosing potassium permanganate for application at a site, be aware of three properties that can cause concern to owner, operators or state regulators.

First, potassium permanganate is derived from mined potassium ores which, by their nature, typically contain salt and metal impurities (e.g., arsenic, chromium, lead). Depending on water quality criteria in the state in which the site occur and the quality and concentration of potassium permanganate used to oxidize the site contaminants, these impurities may generate concern. (This is also true of sodium permanganate, which is mined and processed in similar fashion.)

Second, potassium permanganate is used to produce pharmaceuticals and should be used and monitored carefully.

Third, potassium permanganate in flowable form contains silica, which can accumulate in wells and plug the screen.

As with other chemical oxidation technologies, the success of the use of permanganate relies heavily on its ability to come into contact with the site contaminants. The delivery mechanism must be capable of dispersing the oxidant throughout the treatment zone. To accomplish this, permanganate may be delivered in solid or liquid form in a continuous or cyclic application schedule using injection probes, soil fracturing, soil mixing, groundwater re-circulation or treatment fences.

Dissolved permanganate has been delivered to injection or re-circulation wells at concentrations ranging from 100 to 40,000 milligrams per liter (mg/L). Contaminated soils have been successfully oxidized through slurry injection, deep soil mixing or hydraulic fracturing using concentrated permanganate solutions ranging from 5,000 to 40,000 mg/L or up to 50 percent by weight solid permanganate.

In-situ permanganate reactions can yield low pH (e.g., pH 3) and high Eh conditions (e.g., +800 mV), which can temporarily mobilize naturally-occurring metals and metal contaminants that may also be present in the treatment area. The release of these metals from the aquifer formation, however, may be offset by sorption of the metals onto strongly sorbent $MnO_2$ solids that are precipitated as a byproduct of permanganate oxidation. In addition, high sodium permanganate concentrations can create sodium problems with clay permeability at the edges of the injection zone due to swelling clays and potential aquifer clogging. $Cr(OH)_3$ in soils may be oxidized to hexavalent chromium, which may persist for some time. This may generate concern if the aquifer is being used for drinking water. Questions remain about the mass of $MnO_4$ that is generated, and the effect, if any, the mass may have on subsurface permeability and remediation performance.

## Ozone

Ozone ($O_3$) is a strong oxidant with an oxidation potential about 1.2 times greater than hydrogen peroxide. It can be used to destroy petroleum contamination in-situ. Ozone, a gas, is typically generated on-site using a membrane filtration system and typically delivered to the subsurface through sparge wells. Delivery concentrations and rates vary, however, because of the high reactivity of ozone and associated free radicals. Ozone needs to be generated in close proximity to the treatment area, and sparge wells generally need to be spaced closely in the target remedial zone.

Ozone can also be injected into the subsurface in a dissolved phase. The gas may be transferred to the dissolved phase on-site by sparging upgradient water with ozone. Groundwater that is extracted upgradient from the area to be treated may be amended with ozone, then re-injected or re-infiltrated into the subsurface, where it transports the dissolved phase ozone and oxygen into the contaminated area. (Check with appropriate state groundwater authorities to learn whether groundwater re-injection is allowed in the state.) More commonly, gaseous ozone is injected or sparged directly into contaminated groundwater.

Typically, air containing up to five percent ozone is injected into strategically placed sparge wells. Ozone then dissolves in the groundwater, reacts with subsurface organics, and ultimately decomposes to oxygen. Ozone can oxidize site contaminants directly or through formation of hydroxyl radicals (OH•), strong nonspecific oxidants with an oxidation potential that is about 1.4 times that of ozone. It is capable of oxidizing BTEX constituents, PAHs, and MTBE (with limited effectiveness).

Heat and VOC vapors may be generated as a result of ozone sparging and the oxidation reactions when ozone concentrations are high. As a result, vapor control equipment (e.g., a soil vapor extraction and treatment system) is often needed to operate in conjunction with the ozone sparging system to capture and prevent the vapors from migrating to, entering and impacting subsurface utilities or nearby structures.

Ozone is also effective in delivering oxygen to enhance subsurface bioremediation of petroleum-impacted areas. Ozone is 10 times more soluble in water than is pure oxygen. Consequently, groundwater becomes increasingly saturated with dissolved oxygen as the unstable ozone molecule decomposes into oxygen molecules. About one-half of dissolved ozone introduced into the subsurface degrades to oxygen within approximately 20 minutes. The dissolved oxygen can then be used by indigenous aerobic hydrocarbon-degrading bacteria.

The oxidizing properties of injected ozone can temporarily suppress subsurface biological activity in the immediate injection area. However, this suppression has been found to be temporary, and sufficient bacteria survive in-situ ozonation to resume biodegradation once ozone has been applied. Additionally, aerobic bacteria along the fringes of the treatment area may thrive under the oxygen rich conditions produced during ozone treatment. Biodegradation enhancement is a primary benefit of this oxidation technology.

### Special Considerations for MTBE

As mentioned above, any of the three oxidation approaches may be applicable for remediating MTBE, either in the presence or absence of other gasoline hydrocarbons. Hydrogen peroxide and ozone addition have both been used on a number of MTBE-impacted field sites, with successes reported at many of them. The success of these techniques may be attributable to the combined effects of the oxidation, increased dissolved oxygen levels in the groundwater, and generated heat.

The available field data on these chemical oxidation projects for MTBE treatment is somewhat sparse. Some literature reports do not contain enough time-series sampling data on groundwater concentrations to ensure that the beneficial reductions of MTBE are not short-lived and that groundwater concentrations do not later rebound.

Very little published data exists on using permanganate on MTBE-impacted field sites, but recent laboratory batch testing looks promising. The method's ability to oxidize MTBE, but not benzene, may have application where an active remediation technology is desired for treating the MTBE, but the benzene is to be addressed by monitored natural attenuation. Further development and field confirmation of potassium permanganate's effectiveness for MTBE is needed.

With any oxidation method, the potential for creating unwanted intermediary products or other unwanted by-products always needs to be considered. In studies of aboveground oxidation of MTBE-impacted groundwater, the primary byproducts of concern were found to be acetone, tertiary butyl alcohol (TBA) and tertiary butyl formate (TBF), and bromate (for ozone-based oxidation). The possible in-situ formation of these by-products, as well as their potential fate and possible impacts, should be considered as part of any plan to conduct subsurface chemical oxidation of MTBE. Several laboratory studies that addressed the oxidation of MTBE-impacted water have indicated that combining ultraviolet light with hydrogen peroxide may oxidize MTBE more effectively, with fewer byproducts. Although the UV light requirement may render this application infeasible for in-situ chemical oxidation projects, the effectiveness of ex-situ treatment technologies may be enhanced.

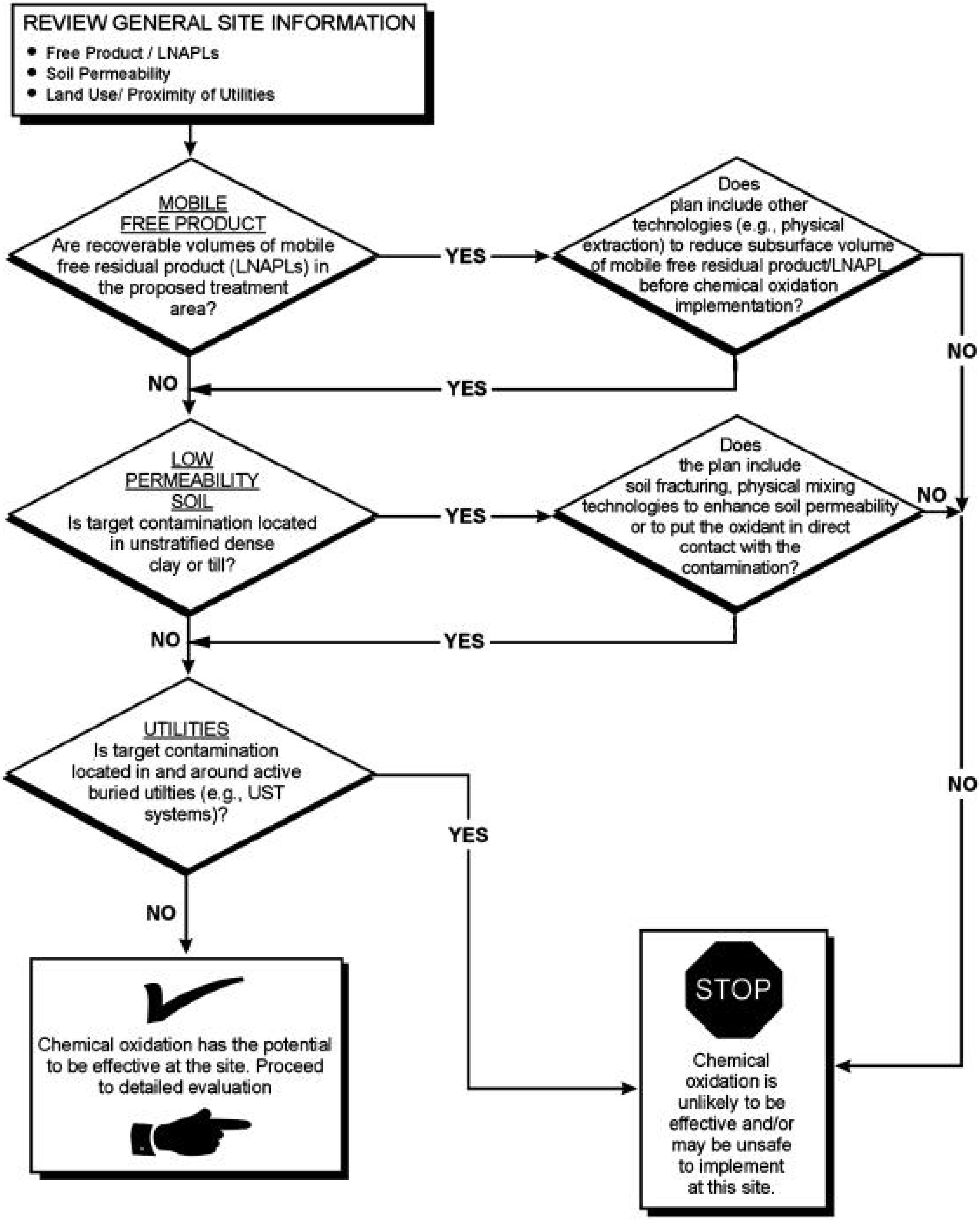
Another consideration for MTBE is whether chemical oxidation technologies can be cost effective for a highly soluble compound like MTBE and that is often found to exist in laterally extensive, mobile groundwater plumes. Chemical oxidation can be quite effective on the high hydrocarbon concentrations typically seen in groundwater and soils in source areas, but may not be applicable to the expansive, lower-concentration, dissolved-phase plumes often associated with MTBE-impacted sites.

## Chemical Oxidation Technology Effectiveness Screening Approach

The descriptions of the various chemical oxidation technologies in the overview should provide the basic understanding needed to move forward with evaluation of a corrective action plan that proposes to use chemical oxidation. To assist with evaluation of the chemical oxidation corrective action plan, a step-by-step technology effectiveness screening approach is provided in a flow diagram in Exhibit XIII-3. This exhibit summarizes the evaluation process and serves as a roadmap for the decisions to be made during evaluation of a corrective action plan that proposes chemical oxidation technologies. A checklist has been provided at the end of this chapter for use as a tool to both evaluate the completeness of the chemical oxidation corrective action plan and to focus attention on areas where additional information may be needed.

Note that the first step in this screening includes information that can only be gleaned from a thorough assessment of the site, such as soil permeabilities and the nature of the aquifer geology, including heterogeneity, the presence of preferred pathways, and other characteristics. Before embarking on the selection of a chemical oxidation technology, be sure that a complete, and preferably three-dimensional, delineation of the subsurface and contaminant plume has been conducted.

## Exhibit XIII-3
## Initial Screening for Potential Effectiveness of Chemical Oxidation



The evaluation process can be divided into the four steps described below.

- **Step 1: An initial screening of chemical oxidation effectiveness** allows quick determination of whether chemical oxidation should be considered as a remedial approach for the site.

- **Step 2: A detailed evaluation of chemical oxidation effectiveness** provides further screening criteria to confirm whether chemical oxidation is likely to be effective. First, extract from the corrective action plan certain site-specific data on the nature/extent of contamination, potential risk to human health/the environment, subsurface geology and hydrogeology, and other relevant site characteristics. Then, compare the site-specific data to the criteria provided in the Exhibit to assess whether chemical oxidation is likely to be effective.

- **Step 3: An evaluation of the chemical oxidation system design in the corrective action plan** allows determination of whether basic design information has been defined, necessary design components have been specified, the construction process flow designs are consistent with standard practice, and adequate feasibility testing has been performed.

- **Step 4: An evaluation of the operation and monitoring plans** allows determination of whether baseline, start-up and long-term system operation and monitoring are of sufficient scope and frequency and whether remedial progress monitoring and contingency plans are appropriate.

## Step 1: Initial Screening of Chemical Oxidation Effectiveness

This section allows you to perform an initial screening of whether chemical oxidation is likely to be an effective approach to remediate the petroleum-impacted areas at a site. Before selecting chemical oxidation as the preferred remedial approach, determine whether the corrective action plan has taken into account key site-specific conditions. In addition, evaluate several "bright lines" defining the limits of chemical oxidation overall viability as a remedial technology. These bright lines will assist in evaluating the corrective action plan and in determining the appropriateness of chemical oxidation as the site remedial solution. After establishing the overall viability of an chemical oxidation approach, basic site and petroleum contaminant information can be examined to further determine the expected effectiveness of chemical oxidation as the remedial choice.

### Overall Viability

The following site conditions are considered to be the “bright lines” defining the general limits of chemical oxidation viability at a site. If review of the corrective action plan indicates that any of the following conditions exist, chemical oxidation is not likely to be a feasible or appropriate remedial solution for the site.

- **Free mobile product is present and the corrective action plan does not include other means for its recovery.** Chemical oxidation is not likely to cost-effectively address free product. Significant thickness and volumes of free product may need to be recovered using conventional approaches before oxidizing the residual hydrocarbons. For some chemical oxidation technologies, free product poses a safety issue, increasing chances of an explosion.

# **Utilities (active gas mains, petroleum USTs/piping, sewers, etc.) lie in the immediate vicinity of the treatment area.** Concerns associated with the heat, VOC vapors, elevated oxygen levels and potential corrosion that can occur from the induced chemical reactions during application of oxidants may preclude the use of this technology until the utilities can be removed or relocated. Potential risks associated with the use of chemical oxidation in the presence of buried utilities include explosion, combustion, and vapor intrusion into buildings.

# **The target contaminant zone is comprised of or includes unstratified dense clay.** With the low permeabilities inherent to clay or clay-rich soils, chemical oxidants cannot easily come into contact with the adsorbed contaminants. Without adequate contact, the petroleum contaminants will remain adsorbed to the low permeability soil, which often contains most of the contaminant mass, rendering remediation unsuccessful. Soil fracturing, use of slow reaction oxidants (e.g., permanganate) or multiple oxidant applications may be used to help bring the oxidants into contact with the contaminants, but technical and cost considerations may lead to consideration of other remedial approaches or technologies.

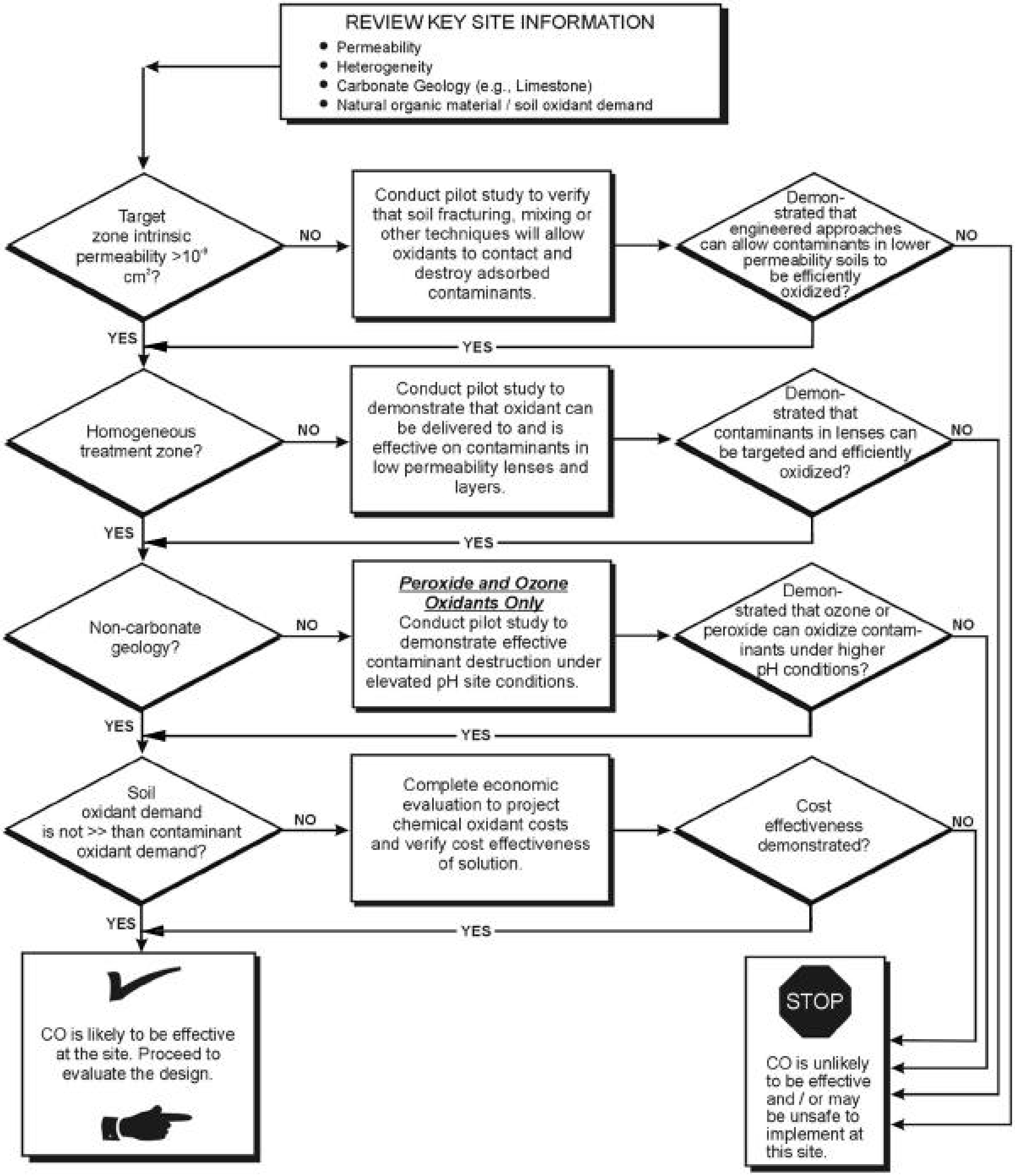
### Potential Effectiveness of Chemical Oxidation

Before performing a more detailed evaluation of chemical oxidation's potential remedial effectiveness and future success at a site, it is useful to review several key indicators. One key factor that influences the effectiveness of chemical oxidation at a site is soil permeability.

Chemical oxidation of contaminants in fine-grained soils, or in clays and silts with low permeabilities, is likely to be less effective than chemical oxidation of contaminants in coarse-grained soils (e.g., sand and gravels) because it is more difficult to effectively contact chemical oxidants with organic contaminants in low-permeability materials.

It is also important to determine whether the chemical oxidant that may be used to address site contaminants is able to readily oxidize the chemical constituents of concern. For example, permanganate cannot readily oxidize benzene or MTBE, which may be target contaminants. The detailed chemical oxidation effectiveness evaluation section of this chapter considers the oxidizing strength of various oxidants and the resistance of specific petroleum hydrocarbon constituents to oxidation. The flowchart in Exhibit XIII-4 outlines the factors that

# Exhibit XIII-4
# Detailed Screening for Potential Effectiveness of Chemical Oxidation



should be evaluated in the detailed screening for the use of chemical oxidation technologies.

### Step 2: Detailed Evaluation of Chemical Oxidation Effectiveness

If initial screening of the corrective action plan indicates that chemical oxidation may be feasible and potentially effective for the site, then a more detailed evaluation of the proposed chemical oxidation remedy should be performed to confirm this assessment. To help with this more detailed evaluation, this section covers a number of important site-specific characteristics influencing the potential effectiveness of chemical oxidation that were not considered or fully explored in your initial screening of the remedial approach. Additionally, this section provides a more detailed discussion of key contaminant characteristics influencing the potential effectiveness of chemical oxidation.

Key site and contaminant factors that should be explored in the detailed evaluation of chemical oxidation are listed in Exhibit XIII-5. The remainder of this section details each of the parameters described in Exhibit XIII-5. After reviewing and comparing the information provided in this section with the corresponding information in the corrective action plan, it should be possible able to evaluate whether chemical oxidation is likely to be effective at the site.

**Exhibit XIII-5**
**Key Parameters Used to Evaluate Chemical Oxidation Applicability**

| Site Characteristics | Constituent Characteristics |
|---|---|
| # Oxidant Demand Factors<br># Advective and Dispersive Transport Factors<br>– Intrinsic Permeability<br>– Soil Structure and Stratification<br>– Hydraulic Gradient<br>– Iron and Other Reduced Inorganic Compounds Dissolved in Groundwater | # Chemical Class and Susceptibility to Chemical Oxidation<br># Solubility Characteristics<br>– Solubility<br>– $K_{oc}$ Factor |

### Site Characteristics That Affect Chemical Oxidation

This section addresses three factors at a site that can affect the ability of chemical oxidants to treat petroleum-contaminated groundwater at a site:

- Oxidant Demand Factors
- Advective and Dispersive Transport Factors
- Constituent Characteristics Factors

Each of these factors is described in detail below.

**Oxidant Demand Factors.** Once introduced into the saturated zone, chemical oxidants and catalysts may be distributed by advection and dispersion to address the target treatment zone. Ideally, the oxidant concentrations are sustained from the point of application until the oxidants contact the contaminants. However, the concentrations of oxidant more typically decrease by dilution through mixing with subsurface pore water and through consumption via chemical reactions that are not related to the degradation of the target constituents of concern. The loss of oxidant due to subsurface reactions unrelated to contamination oxidation, often referred to as the natural oxidant demand (NOD), is a significant consideration in determining the economic viability of chemical oxidation and in engineering the appropriate oxidation application dose and approach.

NOD stems from reaction with organic and inorganic chemical species naturally present in the subsurface. Oxidants that react with the natural organic material (NOM) are lost and are, therefore, subsequently unable to react with the target contaminants. In certain soil types (e.g., peat), the NOM and therefore the NOD can be extremely high. Inorganic oxidant demand may exist if naturally-occurring reduced mineral species (e.g., ferrous iron) are present in the groundwater or saturated soils. These reduced compounds can also react with the oxidants to remove oxygen available for reaction with the target contaminants. Exhibit XIII-6 presents a sample of some common inorganic processes that consume oxygen and oxidants in groundwater.

NOD almost always exceeds contaminant oxidant demand. If insufficient doses of oxidants are not provided to satisfy both demands, the target contaminants may not be degraded to the desired level. Bench testing should be used to determine the NOD for the saturated zone.

**Exhibit XIII-6**
**Inorganic Oxidation Processes That Consume Dissolved Oxygen in Groundwater**

| Process | Reaction |
|---|---|
| Sulfide Oxidation | $O_2 + \frac{1}{2}HS \rightarrow \frac{1}{2}SO^{2-} + \frac{1}{2}H^+$ |
| Iron Oxidation | $\frac{1}{4}O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$ |
| Nitrification | $O_2 + \frac{1}{2}NH^{4+} \rightarrow \frac{1}{2}NO^{3-} + H^+ + \frac{1}{2}H_2O$ |
| Manganese Oxidation | $O_2 + 2Mn^{2+} + 2H_2O \rightarrow 2MnO_2\,(s) + 4H^+$ |
| Iron Sulfide Oxidation | $15/4O_2 + FeS_2\,(s) + 7/2H_2O \rightarrow Fe(OH)_3\,(s) + 2SO_4^{2-} + 4H^+$ |

Exhibit XIII-7 explores the theoretical oxygen demand of a number of petroleum hydrocarbon constituents common to petroleum UST cleanup sites. The exhibit outlines the stoichiometric reactions for the complete oxidation of the typical target hydrocarbons. In theory, oxygen levels of at least 3 to 3.5 times the amount of subsurface petroleum mass that needs to be removed to meet cleanup goals must be delivered to the groundwater and distributed over the planned remedial period.

**Exhibit XIII-7**
**Organic Compound Oxidation Stoichiometry**

| Petroleum Hydrocarbon | Oxidation Reaction | Oxygen Requirement (g $O_2$ per g Contaminant) |
|---|---|---|
| MTBE | $C_5H_{12}O + 7.5\ O_2 \rightarrow 5CO_2 + 6H_2O$ | 2.7 |
| Benzene | $C_6H_6 + 7.5\ O_2 \rightarrow CO_2 + 3H_2O$ | 3.1 |
| Toluene | $C_6H_5CH_3 + 9\ O_2 \rightarrow 7CO_2 + 4H_2O$ | 3.1 |
| Ethylbenzene | $C_2H_5C_6H_5 + 10.5\ O_2 \rightarrow 8CO_2 + 5H_2O$ | 3.2 |
| Xylenes | $C_6H_4(CH_3)_2 + 10.5\ O_2 \rightarrow 8CO_2 + 5H_2O$ | 3.2 |
| Cumene | $C_6H_5C_3H_7 + 12O_2 \rightarrow 9\ CO_2 + 6H_2O$ | 3.2 |
| Naphthalene | $C_{10}H_8 + 12O_2 \rightarrow 10CO_2 + 4H_2O$ | 3.0 |
| Fluorene | $C_{13}H_{10} + 15.5O_2 \rightarrow 13CO_2 + 5H_2O$ | 3.0 |
| Phenanthrene | $C_{14}H_{10} + 16.5O_2 \rightarrow 14CO_2 + 5H_2O$ | 3.0 |
| Hexane | $C_6H_{14} + 9.5\ O_2 \rightarrow 6CO_2 + 7H_2O$ | 3.5 |

A number of experiments and field tests have determined that site NOD is highly variable and not easily predicted. For example, NOD associated with permanganate application has been found to vary from two to over 100 mg $MnO_4^-$ per mg of total organic carbon (TOC) in the treatment area soil, and equal to or greater than the contaminant oxygen demand.

Oxidizing reactions associated with the NOD can produce solid precipitates that can accumulate in soil pore spaces. Particles may be produced by shearing off fragments of natural soil or by yielding reaction products (e.g., iron or manganese oxides). Permanganate oxidation results in the production of $MnO_2$ solids as a reaction product. These precipitates can potentially decrease soil permeability and remediation system function and performance; however, their effects in this regard have not been fully examined and are not well understood.

**Advective and Dispersive Transport Factors.** The site conditions affecting advection and dispersion of dissolved oxygen are:

# Intrinsic Permeability
# Soil Structure and Stratification
# Groundwater Velocity
# Iron and Other Reduced Inorganic Compounds Dissolved in Groundwater

Each of these conditions is described in detail below.

**Intrinsic Permeability**. Intrinsic permeability is a measure of the ability of soil to transmit fluids. Intrinsic permeability often decreases near injection wells or infiltration galleries. This is also commonly a result of the precipitation of carbonate species, such as calcite. In general, oxygen is more easily distributed in soils with higher soil permeabilities (e.g., sands and gravels) than in soils with lower permeabilities (e.g., clays or silts). Intrinsic permeability can be calculated from hydraulic conductivity measurements taken from on-site pump testing. Pump test or slug test-derived permeability ranges are representative of average hydraulic permeability conditions for heterogeneous conditions. Alternatively, intrinsic permeability can be estimated from soil boring logs and laboratory tests. Intrinsic permeability values obtained through empirical means are less accurate and result in a wider range of permeability estimates. In any case, derived permeabilities are only approximations of actual subsurface conditions and should be regarded as such in the evaluation of chemical oxidation as a remediation technology. Intrinsic permeability can vary over 13 orders of magnitude (from $10^{-16}$ to $10^{-3}$ cm$^2$) for the wide range of earth materials. Exhibit XIII-8 provides general guidelines on the range of intrinsic permeability values over which chemical oxidation is likely to be effective.

**Exhibit XIII-8**
**Intrinsic Permeability and Chemical Oxidation Effect**

| Hydraulic Conductivity (K) (in ft/sec) | Intrinsic Permeability (k) (in ft$^2$) | Chemical Oxidation Effectiveness |
|---|---|---|
| $K > 10^{-6}$ | $k > 10^{-12}$ | Effective to generally effective |
| $10^{-6} \leq K \leq 10^{-7}$ | $10^{-12} \leq k \leq 10^{-13}$ | Possibly effective; needs further evaluation |
| $K < 10^{-7}$ | $k < 10^{-13}$ | Marginally effective to ineffective |

It is important to note that the intrinsic permeability of a soil can decrease as chemical oxidation progresses. The most likely cause of reduced intrinsic permeability while implementing chemical oxidation is the precipitation of inorganic complexes that form during oxidation of reduced, naturally occurring mineral species such as ferrous iron. If the soil intrinsic permeability indicates borderline potential effectiveness (i.e., $10\text{-}9 \leq k \leq 10\text{-}10$), the geochemistry should be further evaluated. It may be necessary to determine the concentration of reduced inorganic species, primarily iron,  in the soil to assess whether subsurface flow pathways could become constricted by precipitation of inorganic compounds, such as ferric oxides.

**Soil Structure and Stratification.** Soils in a target treatment area are not uniformly permeable (i.e., heterogeneous), but rather have large-scale and small-scale variations in permeability (i.e., heterogeneous). Heterogeneity controls movement of fluids in the subsurface.  Soil heterogeneity plays a very important role in chemical oxidation technologies because oxidants and catalyst reagents introduced to the subsurface are distributed preferentially along higher permeability layers in the saturated soil.  For example, in a heterogeneous soil comprised of sand, silt and clay layers, oxidants may be effectively distributed through the sand layer to successfully reduce petroleum hydrocarbons there, but will be ineffectively delivered and distributed to the silt and clay layers. If the silt and clay layers are thick relative to the sand horizon and contain significant petroleum hydrocarbon mass, chemical oxidation technologies may be inefficient or ineffective.  In addition, the tendency for the development or enhancement of preferential flow paths may be increased by the addition of Fenton’s reagant or the use of ozone sparging.

Unless site soils are homogeneous, average soil intrinsic permeability may not adequately determine the viability of chemical oxidation approaches because discrete low permeability soil horizons may exist, and these horizons might contain a large fraction of the subsurface petroleum mass.   In most cases, it is prudent to evaluate petroleum mass distribution across all soil types to determine whether chemical oxidation is likely to be effective and will achieve cleanup objectives.  If select soil horizons containing hydrocarbon mass are not expected to be effectively treated using chemical oxidation, chemical oxidation may not be viable for the site.  For example, if 50 percent of the contaminant mass is contained and isolated in low permeability soil horizons, and the site cleanup goals is a 95 percent reduction in petroleum contaminant concentrations, then it is reasonable to conclude that the goal cannot be achieved using chemical oxidation.  However, in such circumstances, combining chemical oxidation with other technologies that enhance the permeability of low permeability horizons in the contaminated zone (e.g., soil fracturing) could be considered.  Or, alternatively, following source removal addition of peroxides could be employed to increase the rate of aerobic biodegradation to achieve remediation objectives.  For more information about enhanced aerobic bioremediation, refer to Chapter XII in this manual.

**Groundwater Velocity.**  Chemical oxidation technologies may rely on groundwater advection and dispersion to distribute oxidants and catalyst reagents in the subsurface.  Distribution of oxidants and reagents can be most readily accomplished under hydrogeologic conditions conducive to higher groundwater flow rates.  True groundwater velocity is referred to as the seepage velocity ($q_s$) and can be calculated from the equation at the top of the next page:

$$q_s = \frac{K(dh/dl)}{n_e}$$

where: dh/dl = aquifer hydraulic gradient (maximum difference in water table elevation or potentiometric surface (L)/distance between upgradient and downgradient measurement points (L)

K = hydraulic conductivity (L/T)

$n_e$ = soil effective porosity (dimensionless)

As the hydraulic gradient increases, groundwater velocity increases proportionately. This same relationship exists between groundwater velocity and soil permeability. Groundwater velocity is inversely proportional to soil porosity. As porosity increases, groundwater velocity decreases. When a significant hydraulic gradient exists, targeted delivery of oxidant to the contaminant zones may require injection and extraction wells.

In addition, transport of dilute dissolved contaminants is a function of advection, dispersion, and chemical and physical reactions. Advection refers to the movement imparted by flowing groundwater, and the rate of transport is usually taken to be equal to the *average* linear groundwater velocity. Hydrodynamic dispersion occurs as a result of molecular diffusion and mechanical mixing and causes the dissolved contaminant plume to spread out with distance from the source. Molecular diffusion is generally only significant when groundwater movement is very slow. Mechanical mixing occurs as groundwater flows through the aquifer matrix twisting around individual grains and through interconnected pore spaces at differing velocities. The movement of some dissolved contaminants may also be affected by chemical and physical reactions, such as sorption and biodegradation, which act to reduce the transport velocity and decrease concentrations in the plume.

**Iron and Other Reduced Inorganic Compounds Dissolved in Groundwater.** The effective intrinsic permeability of the saturated zone can be significantly reduced if the chemical oxidation treatment zone contains naturally elevated levels of reduced iron (e.g., ferrous iron, or $Fe^{2+}$) or other mineral species. For example, when dissolved iron is exposed to chemical oxidants, it may be oxidized to ferric iron ($Fe^{3+}$) oxide that can precipitate within the saturated zone and occlude soil pore space. On a large scale, this could reduce effective soil porosity, and oxidant delivery efficiency and availability. In such cases, decreases in soil porosity can be expected to occur closest to the oxidant delivery locations (i.e., near oxidant injection wells). Bench-scale tests may need to be performed to evaluate the inorganic NOD of the aquifer material and determine the feasibility of the remedial approach.

In addition to being considered in evaluating the potential effectiveness of chemical oxidation, hydraulic gradient can be an engineering design issue. If the gradient is not steep enough to provide adequate flow and oxidant transport through the contaminated zone, then certain engineering provisions (e.g., spacing application points more closely, creating artificial hydraulic gradients) can be added to the design to enhance oxidant distribution.

**Constituent Characteristics That Affect Chemical Oxidation**. It is important to evaluate the potential impacts of site contaminants on the performance of the proposed chemical oxidation approach. In particular, it is important to review how the chemical structure, chemical properties, concentrations and toxicities of the petroleum contaminants can influence remedial performance.

Petroleum products are complex mixtures of hundreds or even thousands of hydrocarbon chemical constituents, other chemical constituents and additives. Each of these constituents has a different atomic structure that determines, in part, how easily it may be chemically oxidized.

With the notable exception of benzene, most petroleum hydrocarbons have been demonstrated to be oxidized by all three primary chemical oxidants. Benzene is not readily oxidized by permanganate, and oxidation of MTBE has only been demonstrated to be oxidizable by permanganate at bench scale.

The two factors related to chemical classes, and their susceptibilities to chemical oxidation, are their solubility characteristics and their $K_{oc}$ values. Each is discussed in more detail below.

**Solubility Characteristics.** Solubility is the maximum concentration of a chemical that can be dissolved in water at a given temperature without forming a separate chemical phase on the water (i.e., free product). Most petroleum compounds have low solubility values, thus limiting the concentrations of contamination that can be dissolved in groundwater. The solubility values for petroleum hydrocarbons range over four orders of magnitude, as shown in Exhibit XIII-9.

Compounds with higher solubility values are generally smaller, lower molecular weight molecules (e.g., benzene). When spilled, these compounds exist in groundwater at higher relative concentrations and move more quickly through the aquifer than do compounds of higher molecular weights. Larger and higher molecular weight hydrocarbon molecules are generally less soluble in water; therefore, their dissolved concentrations in groundwater tend to be limited (e.g., naphthalene). Long-chain hydrocarbons are often saponified by chemical oxidation, making them more soluble, particularly in the presence of any free product.

**Exhibit XIII-9**
**Solubility Values and Organic Carbon Partition Coefficients For Select Petroleum Hydrocarbon Constituents**

| Compound | Molecular Weight (g/mol) | Solubility in Water (g/L) | Organic Carbon Coefficient ($K_{oc}$ - ml/g) |
|---|---|---|---|
| MTBE | 88 | 51 | 12 |
| Benzene | 78 | 1.79 | 58 |
| Toluene | 92 | 0.53 | 130 |
| Ethylbenzene | 106 | 0.21 | 220 |
| Xylenes (total) | 106 | 0.175 | 350 |
| Cumene | 120 | 50 | 454 |
| Naphthalene | 128 | 0.031 | 950 |
| Acenaphthene | 154 | .0035 | 4,900 |

Solubility is also an indicator of likely contaminant sorption onto soil. There is an inverse relationship between a chemical compound's solubility and its organic carbon partition coefficient ($K_{oc}$). A compound with a high solubility has a reduced tendency to adsorb to soil that is in contact with contaminated groundwater and may be more readily contacted by chemical oxidants. Conversely, contaminants with low solubility values will likely have an increased tendency to adsorb to soil that is in contact with contaminated groundwater and may be less readily chemically oxidized. Note that some compounds are less predictable in this relationship, such as cumene. Cumene has a strong ability to sorb to soils, despite its very high solubility. If cumene is a key target contaminant, chemical oxidation may not be the most appropriate technology for removing it from groundwater. The relationship between solubility and $K_{oc}$ is described in more detail below.

**$K_{oc}$ Factor**. When groundwater is contaminated by a petroleum UST release, the proportion of hydrocarbon mass in the soil is often far greater than that dissolved in groundwater. This is due in part to the low solubility thresholds for petroleum contaminants. However, another factor is the strong tendency for most petroleum hydrocarbons to adsorb to naturally occurring organic carbon material in the soils. This tendency along with the sheer mass of soil relative to groundwater in a contaminated area can lead to hydrocarbon mass distributions that are so unevenly distributed that they can make the mass in the dissolved-phase appear insignificant. Because of the high proportionate amount of contaminant mass in the adsorbed phase, it is important to understand the ability of the chemical oxidant to come into contact with the soil contamination.

$K_{oc}$ is a compound-specific property that helps define the equilibrium condition between organic carbon and the contaminant concentrations in an aqueous solution. Using site-specific soil organic carbon content data (i.e., fraction of organic content or foc), $K_{oc}$ can be used to determine the equilibrium contaminant concentrations between groundwater and soil below the water table. The typical organic carbon content in surface soils ranges from 1 to 3.5 percent. In aquifer soils, organic carbon content is an order of magnitude lower – from 0.1 and 0.01 percent – because most organic residues are either incorporated into the soil matrix or deposited on the surface.

Higher $K_{oc}$ and Kd values indicate that more contaminant mass is likely to be retained in soil, and therefore potentially less readily contacted by chemical oxidants. Conversely, lower $K_{oc}$ and Kd values indicate that lower contaminant concentrations will exist in equilibrium in soil for given concentrations in groundwater. A comparison of the solubility and $K_{oc}$ values for the sample group of petroleum hydrocarbons reveals the inverse relationship between the two parameters (i.e., compounds with higher solubility values have lower $K_{oc}$ constants).

In the absence of site-specific data that reveal the distribution of contaminant mass, solubility and $K_{oc}$ data can be used to obtain a general understanding of the likelihood that chemical oxidation is applicable at the site. Petroleum contaminants with high solubility limits and low $K_{oc}$ values are more likely to come in contact with chemical oxidants and to be destroyed by chemical oxidation technologies. When contaminant solubility constants are low and $K_{oc}$ values are high, chemical oxidants may not have adequate contact with the contaminants to effectively destroy contaminant mass, particularly in low permeability soils.

### Step 3: Evaluation of Chemical Oxidation Design

This section provides guidance on reviewing and evaluating a chemical oxidation remediation system's design. This section focuses on identifying and reviewing key elements of corrective action plans to help ensure they demonstrate a coherent understanding of the basis for the chemical oxidation system design**.** This section provides information on typical chemical oxidation technology components to help verify that the corrective action plan has included the basic equipment requirements for the remedial system.

It is assumed that it has already been verified, through the detailed technology screening process described in Steps 1 and 2, that chemical oxidation appears appropriate and is expected to be an effective cleanup approach, given site-specific conditions. If chemical oxidation effectiveness evaluation has not been completed, it is strongly recommended that this be done prior to evaluating the design.

Two important factors that need to be considered in evaluating the design of chemical oxidation treatment are (1) the design basis and (2) the site cleanup goals. Each of these factors is discussed in more detail below.

## Design Basis

A review of the corrective action plan should find consistency between site characterization work and information that is presented as the basis for the chemical oxidation design in the corrective action plan. It is important that during the chemical oxidation effectiveness evaluation a reviewer has a solid understanding of the nature and extent of the site-specific petroleum constituents of concern, including an understanding of the contaminant phases present and the relevant site chemical, physical, and biological properties. When preparing and reviewing the corrective action plan design, it is important to understand the site geology and hydrogeology, and the risks associated with the contamination. These data, which should have been developed and interpreted as part of the site characterization effort, serve as the foundation for the remedial system design.

While site characterization data provide the core raw materials for the design, further refinement is often needed and useful. For example, while the site characterization work may identify potential human or ecological receptors that may be exposed to contamination, specific cleanup goals may not have been established. In such cases, the specific remedial goals would need to be developed and identified in the corrective action plan through one or more established approaches. These approaches may include adopting state-published cleanup standards, developing site-specific risk-based standards acceptable to the state, or employing other state-specific and approved methods.

A corrective action plan may also include the results and interpretation of follow-up studies completed after the original site characterization. The need for such studies is often identified after a review of the site characterization shows that additional information is needed to complete the remedial system design. For example, the site characterization may suggest that one or more of the constituents of concern is believed to be marginally degradable, either chemically or biologically, and the level of expected degradation is difficult to predict from the existing data.

Examples of typical information expected to be developed during the site characterization, or as a result of follow-up studies that should be completed to support the basis for the technology selection and design of the corrective action plan, are summarized in Exhibit XIII-10.

## Cleanup Goals

The evaluation of alternative remedial approaches and the subsequent design of the selected approach are strongly influenced by the cleanup goals that the remediation program must achieve. Often, preliminary goals identified during the site characterization evolve as a better understanding of site conditions and potential receptors is attained. However, owing to their importance to remediation planning and design, the cleanup goals should be fully evolved and solidified in the corrective action plan.

These goals usually provide the end-point concentrations for petroleum constituents in soil and groundwater that are acceptable to state or other regulatory agencies. These cleanup thresholds could be goals that represent any of the following:

- Health-based numeric values for petroleum chemical constituents published by the respective regulatory agency.
- Cleanup goals developed and proposed by the contractor specifically for the contaminated site.
- Goals derived from site-specific risk assessment involving contaminant fate and transport modeling coupled with ecological and human-health risk assessment.

Additional project goals that may be regulatory requirements include hydraulic control of the contamination, a cleanup time frame, or other performance goals established in the corrective action plan. Regardless of the cleanup goals and how they are established, the state-sanctioned goals should be noted in the corrective action plan and recognized as a fundamental basis for the technology selection and design.

The cleanup goals presented in the corrective action plan answer important questions about the viability of the selected remedial approach and the adequacy of the remedial design. The critical question is, Can the cleanup concentration goals be economically met by the designed chemical oxidation approach? It is important to understand how much oxidant will be consumed by NOD reaction, and how much will be lost attempting to permeate low permeability soils, in order to weigh the economics and technical feasibility of the approach. Multiple applications of the chemical oxidants may be required in order to accomplish the site objectives. Many logistical, political, risk-related, and cost issues are associated with successive attempts to oxidize the site contamination, and should be considered when such a proposal is put forth in a corrective action plan. Verification that the target petroleum constituents of concern can be chemically oxidized by the oxidant of choice should be completed.

## Exhibit XIII-10
## Chemical Oxidation Design Basis Factors

| Design Basis Factor | Source(s) of Design Information |
|---|---|
| **Cleanup Goals**<br># Target contaminant levels (soil and groundwater)<br># Remediation timeframe<br># Plume control<br># Others | Receptor survey, pre-design exposure or risk assessment analyses (potentially including numerical modeling), or state requirements. |
| **Geology**<br># Uniformity (homogeneity, heterogeneity)<br># Stratigraphy (vertical profile of sand, silt, clay, etc.)<br># Geochemistry (reduced mineral content, organic content, mineral demand for ferrous iron, sulfite, nitrite, dissolved oxygen, etc.)<br># Bedrock (description, depth, strike, dip, fracturing, etc.)<br># Soil permeabilities | Site characterization, soil borings, well installations, sampling and analysis, and site observations.<br>Local geologic studies. |
| **Hydrogeology**<br># Depth to groundwater<br># Groundwater elevation and gradient<br># Aquifer/water bearing unit class (confined, unconfined, perched, bedrock, etc.)<br># Hydraulic parameters (conductivity, transmissivity, storativity, effective porosity, etc.)<br># Geochemistry (aqueous demand for ferrous iron, sulfite, nitrite, dissolved oxygen, etc.)<br># Modeling (simulation of groundwater flow and effects of manipulation of hydraulic head) | Site characterization, well gauging, aquifer pump testing, data analyses, and local hydrogeologic studies. |
| **Petroleum Contamination**<br># Target chemical constituents<br># Concentrations of other contaminants that can consume oxygen<br># Mass estimates (adsorbed, dissolved, liquid and vapor phases)<br># Extent (vertical and lateral)<br># Fate and transport characteristics (solubility, partition coefficients)<br># Vapor pressure and Henry's law constant for contaminants, especially if these contaminants are driven into the vapor phase by the remediation process<br># Modeling (simulation of contaminant transport under various scenarios) | Soil, groundwater and other media sampling/laboratory analysis, review of published data on contaminants and data interpolation and analysis.<br>Materials Safety Data Sheets can provide this information. |

## Chemical Oxidation Technology Selection

With the design basis established in the corrective action plan, it is now possible to review the corrective action plan to confirm that the proposed candidate chemical oxidation technology is a reasonable site-specific choice. Depending on project-specific circumstances, there may be a few chemical oxidation technologies equally viable and appropriate for a site. Alternatively, site-specific or project-specific circumstances may suggest that one of the chemical oxidation technologies would address the on-site contamination far better than any of the others.

Exhibit XIII-2 presented a comparative summary of each of the chemical oxidation technologies. These factors can be used to help evaluate the appropriateness and feasibility of the chemical oxidation approach outlined in the corrective action plan. Other differences among alternative chemical oxidation technologies can also help to distinguish their most appropriate application(s). Two characteristics that can be useful in evaluating the feasibility and appropriateness of a proposed chemical oxidation technology are (1) oxygen production for enhancement of aerobic biodegradation, and (2) chemical oxidation potential. Each of these is described in more detail below.

**Oxygen Enhanced Biodegradation and Chemical Oxidation Potential.** Another distinguishing characteristic of some chemical oxidation technologies is their ability to impart oxygen to the groundwater, which enhances aerobic biodegradation of contaminants while chemically oxidizing petroleum contaminants. In particular, both ozone and hydrogen peroxide are strong oxidizers. During their decomposition, these oxidizers may also generate the hydroxyl radical, an even more powerful chemical oxidizer of organic compounds. As these chemical oxidants react in the subsurface, oxygen is produced which may help enhance aerobic biodegradation processes occurring along the fringes of the treatment area. These chemical oxidation technologies not only chemically oxidize the contaminants in the treatment area but also provide oxygen to promote biodegradation of petroleum contamination. In addition, chemical oxidants can oxidized ferrous iron minerals to ferric iron, and transform other reduced forms to oxidized forms that anaerobic microbes can use.

Ozone and hydrogen peroxide can help to fully or partially chemically oxidize the recalcitrant subsurface petroleum contamination while providing oxygen for in-situ bioremediation of the contamination. Either of these technologies may be applied to sequentially treat the contamination via oxidation, followed by bioremediation, or configured for concurrent treatment relying on oxidation for core treatment with bioremediation as the treatment approach in the peripheral reaches of the plume.

**Exhibit XIII-11**
**Relative Power of Chemical Oxidants**[4]

| Compound | Oxidation Potential (volts) | Relative Oxidizing Power ($Cl_2$ = 1.0) |
|---|---|---|
| Hydroxyl Radical | 2.8 | 2.1 |
| Sulfate Radical | 2.6 | 1.9 |
| Ozone | 2.1 | 1.5 |
| Hydrogen Peroxide | 1.8 | 1.3 |
| Permanganate | 1.7 | 1.2 |
| Chlorine Dioxide | 1.5 | 1.1 |
| Chlorine | 1.4 | 1.0 |
| Oxygen | 1.2 | 0.90 |
| Bromine | 1.1 | 0.80 |
| Iodine | 0.76 | 0.54 |

However, both ozone and hydrogen peroxide are non-selective with respect to reaction with subsurface organic material. If naturally occurring organic materials (e.g., humic substances) are present in the site subsurface, injected ozone or infiltrated hydrogen peroxide may be lost through the oxidation of these organics, leaving fewer of the oxidants available to react with (and oxidize) the petroleum contaminants. The relative oxidizing power of the chemical oxidants may also be helpful in determining the most appropriate chemical oxidant for site conditions. Exhibit XIII-11 shows that the hydroxyl radical (Fenton's Reagent), ozone, hydrogen peroxide and permanganate, in order of decreasing oxidation strength, are among the strongest chemical oxidizers.

## Design Components

Although the design elements of alternative chemical oxidation technologies can vary, Exhibit XIII-12 describes common ones. Several of the more important elements are discussed below to assist with evaluation of the corrective action plan. Each of the major headings in the exhibit above is discussed in more detail below.

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[4] Note that these compounds are provided for comparative purposes only. Many of these compounds are not typically used for in-situ chemical oxidation.

### Exhibit XIII-12
### Common Chemical Oxidation Remediation Design Elements

- Oxidant and Catalyst Delivery Design
  - Theoretical oxidant mass requirement
  - Natural oxidant demand estimates
  - Application delivery rate
  - Number and depth of application points/position
  - Equipment

- Permit Requirements and Thresholds
  - Underground injection/well installation
  - Groundwater (wastewater) discharge
  - Air (soil vapor) discharge

- Performance Monitoring Plan
  - On-going distribution of oxidants
  - Reduction in contaminants (adsorbed and dissolved phases)

- Contingency Plan
  - Inadequate oxidant distribution
  - Lower-than-expected petroleum mass reduction rates
  - Excessive contaminant migration
  - Build-up of excessive recalcitrant petroleum constituents
  - Fugitive (soil vapor) emissions
  - Difficult-to-treat/fouling of treated wastewater discharge
  - Aquifer clogging with precipitates or biomass

**Oxidant Application Design** should be based primarily on contaminant mass reduction requirements, site characteristics and cleanup goals. Oxidants need to be applied at concentrations and total mass levels that satisfies both the NOD and the oxidant demand of the petroleum hydrocarbons. Note that state regulations may either require permits for oxidant or catalyst injection or prohibit them entirely.

**Permit Requirements and Thresholds** should be identified in the design so that the system can be constructed to comply with permit requirements and constraints. Depending on the specific chemical oxidation technology and the state in which the site is located, permits may be required for underground injection, treated groundwater discharge (to sanitary or storm sewer, or air (soil vapor) discharge. Several federal, state and local programs either directly manage or regulate aquifer remediation wells (ARWs). Many of these programs require permits for underground injection of oxygen. On the federal level, management and regulation of these wells fall primarily under the underground injection control program authorized by the Safe Drinking Water Act (SDWA). Some states and localities have used these authorities, as well as their own, to extend the controls in their areas to address concerns associated with ARWs.

Aquifer remediation injection wells are potentially subject to at least three categories of regulation. First, a state's underground injection control program (or in direct implementation states, the federal UIC program) may have jurisdiction over such wells. Second, in some states without UIC programs, the state's program for groundwater protection or national pollution discharge elimination system (NPDES) requirements may apply to remediation wells. Third, remediation wells may be regulated by federal and state authorities through Superfund programs, corrective action programs under RCRA, the UST program, or other environmental remediation programs. In the case of remediation programs, the regulatory requirements typically address the selection of aquifer remediation as a cleanup alternative and establish the degree of required cleanup in soil and groundwater, while deferring regulation of the injection wells used in the remediation to other programs.

**Performance Monitoring** should be accounted for in the form of a written data quality objective plan that can be used to objectively evaluate chemical oxidation system performance. The monitoring plan should outline a data quality objective process that defined the criteria that the data collection should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision error for the study, and how many samples to collect, balancing risk and cost in an acceptable manner. It should describe the approaches and methods that will be used to evaluate chemical oxidation system effectiveness in each of the following:

- Delivering the oxidant and catalyst to the subsurface.
- Distributing the oxidant throughout the contaminated area.
- Reducing adsorbed and dissolved phase petroleum concentrations.
- Achieving other performance requirements consistent with site-specific cleanup goals.
- Confirming chemical oxidation effectiveness through long-term monitoring.

**Contingency Plans** should also be prepared as part of the remedial design. The design should anticipate low-likelihood problems and potentially changing environmental conditions, as well as outline specific response actions that may be taken. Examples include response actions to take if performance monitoring data indicate any of the following:

- Inadequate oxidant distribution
- Inadequate permeation of low permeability soil zones
- Low petroleum mass reduction rates
- Excessive contaminant migration
- Recalcitrance of constituents
- Production of excessive fugitive emissions
- Rebound in contaminant levels measured during long term post-application monitoring
- Evidence of oxidant moving in wrong direction

## Components of Chemical Oxidation Systems

Having briefly covered factors that affect the selection and design of a particular chemical oxidation technology and the critical elements that should be included in the corrective action plan chemical oxidation design, it is now appropriate to discuss major components of various chemical oxidation systems. This discussion should help in the evaluation of the corrective action plan chemical oxidation design.

Exhibit XIII-13 summarizes some of the major equipment components associated with each of the more common chemical oxidation technologies. Note that this exhibit continues across three pages. Depending on which chemical oxidation technology has been selected in the corrective action plan, a subset of these major system components should be presented and discussed and schematically depicted (e.g., process flow diagram) in the corrective action plan. The design should relate capacities of these equipment components to design requirements (e.g., required oxidant production and delivery rates).

### Exhibit XIII-13
### Major Components of Chemical Oxidation Systems

| Component | Function |
|---|---|
| **Hydrogen Peroxide/Fenton's Reagent Injection Systems** | |
| Extraction Wells | Wells may be used to capture soil vapor generated by the oxidation process that may be heated and contain elevated levels of VOCs and oxygen (i.e., soil vapor extraction). Can also be used to help control groundwater flow during oxidant and catalyst delivery (i.e., groundwater extraction). |
| Injection Wells or Infiltration Galleries | Injection wells, infiltration galleries or a combination of these may be used to inject hydrogen peroxide catalyst solution, and compressed air for reagent contact with the treatment zone contaminants. Diluted peroxide and peroxide slurries can be injected via lance points. |
| Extraction, Injection, Transfer, and Metering Pumps and Tanks | Extraction, injection, transfer, and metering pumps may be used for various purposes including: transferring groundwater from and back into the ground; transferring extracted groundwater between different components of the treatment system; and metering hydrogen peroxide and catalyst into the infiltration system to maintain design concentrations. Note that pumps can be damaged by hydrogen peroxide and may need frequent replacement. |
| Blowers | Extraction blower(s) may be used to draw soil vapor from extraction wells to capture fugitive VOC vapors and oxygen. |

## Exhibit XIII-13
## Major Components of Chemical Oxidation Systems (continued)

| Component | Function |
|---|---|
| **Hydrogen Peroxide/Fenton's Reagent Injection Systems (continued)** | |
| Groundwater and Vapor Treatment Equipment | Extracted groundwater or soil vapor may be treated to remove petroleum hydrocarbons by various means such as: granular activated carbon adsorption, air stripping or others. |
| Instrumentation and Controls | Used to integrate and activate/deactivate system components. Help maintain the balance of flows consistent with the design and to safeguard against inadequate treatment or inappropriate discharges. |
| Monitoring Wells | Used to collect environmental samples analyzed in laboratories and field to evaluate on-going effectiveness of remediation. Groundwater well samples tested for peroxide and contamination to evaluate overall effectiveness of oxidant delivery/dispersal and the contaminant reductions over time. Long term monitoring of contaminant concentrations is essential to evaluating the effectiveness of the technology. |
| **Permanganate Injection Systems** | |
| Extraction Wells | Wells may be used to enhance hydraulic gradient across the treatment area so that permanganate can be more rapidly delivered to and put in contact with site contaminants. |
| Injection Wells or Infiltration Galleries | Injection wells, infiltration galleries or a combination of these may be used to inject permanganate or permanganate amended groundwater into the treatment zone. Upgradient injections of amended groundwater with downgradient extraction of groundwater may enhance the hydraulic gradient across the treatment zone, thereby accelerating permanganate delivery to the contamination. |
| Extraction, Injection, Transfer, and Metering Pumps and Tanks | Extraction, injection, transfer, and metering pumps may be used for various purposes including: transferring groundwater from and back into the ground; transferring extracted groundwater between different components of the treatment system; and metering permanganate into the infiltration system to maintain design concentrations. |
| Groundwater Treatment Equipment | Extracted groundwater may be treated to remove petroleum hydrocarbons by various means such as: granular activated carbon adsorption, chemical oxidation, air stripping or others. |
| Instrumentation and Controls | Used to integrate and activate/deactivate system components to maintain the balance of flows consistent with design and to safeguard against inadequate treatment or inappropriate discharges. |

## Exhibit XIII-13
## Major Components of Chemical Oxidation Systems (continued)

| Component | Function |
|---|---|
| **Permanganate Injection Systems (continued)** | |
| Lance Injection Points | Permanganate in slurry form may be injected into the subsurface over a grid using push-point technologies. |
| Large Diameter Auger Deep Soil Mixing | Permanganate may be mixed deeply into the contaminated soil and groundwater using large diameter augers in patterned drilling over contaminated areas. |
| Monitoring Wells | Used to collect environmental samples tested in laboratories and the field to evaluate on-going effectiveness of remediation. Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination indicates how effectively oxygen is being delivered/dispersed and contaminant reductions are occurring. |
| **Ozone Injection Systems** | |
| Sparging Wells | Used as a conduit to inject ozone into contaminated groundwater. The ozone is sparged near the base of the soil and groundwater petroleum contamination so that it may contact the contaminants and provide oxygen to the hydrocarbon degrading bacteria. |
| Air Compressing Equipment | Used to pressurize ambient air needed to generate ozone and to provide the pressure needed to inject the ozone beneath the water table. Oil-less compressors are preferred, because air compressor equipment must supply oil- and contaminant-free air to minimize in-line reactions with and pre-mature decomposition of ozone. |
| Ozone Generating Equipment | Used to generate ozone gas on-site, typically at concentrations of about 5%. |
| Soil Vapor Extraction/ Treatment Equipment (optional) | Used, if necessary, to control fugitive soil vapor ozone and volatilize organic compounds emissions in the unsaturated zone. May consist of low vacuum/flow blower to generate vacuum conditions in unsaturated zone and collect the vapors. Off-gas treatment may be necessary and may be accomplished using granular activate carbon, biofilters or other technologies. |
| Instrumentation and Controls | Used to integrate and activate/deactivate system components to maintain the balance of flows consistent with the design and to safeguard against inadequate treatment or inappropriate discharges. |
| Monitoring Wells | Used to collect environmental samples tested in laboratories and the field to evaluate on-going effectiveness of remediation. Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination indicates how effectively oxygen is being delivered/dispersed and contaminant reductions are occurring. |

While the sets of major equipment components used by the chemical oxidation technologies differ significantly, the use of wells by each different approach warrants recognition and further discussion. In particular, the orientation, placement, number and construction of this common design element is worthy of a brief review. wells or gravity-fed into vertical delivery wells. Additionally, hydrogen peroxide-amended groundwater can be re-infiltrated using either vertical or horizontal wells. Although vertical sparge wells are more common for ozone injection, horizontal sparge wells can be used. Permanganate amended groundwater can similarly be re-infiltrated using vertical wells, horizontal wells, infiltration trenches or combined approaches. Well orientation should be based on site-specific needs and conditions. For example, horizontal systems should be considered when evaluating sites that require re-infiltration of amended groundwater into shallow groundwater at high flow rates. They are also readily applicable if the affected area is located under a surface structure (e.g., a building), or if the thickness of the saturated zone is less than 10 feet.

**Injection, Extraction and Re-infiltration Wells.** Three important considerations are well orientation, well placement and number, and well construction.

- **Well Orientation.** Both horizontal and vertical wells can be used to treat subsurface petroleum releases with any of the various chemical oxidation systems. However, hydrogen peroxide and a catalyst (Fenton's Reagent) is most commonly injected into vertical sparge wells.

- **Well Placement and Number of Wells**. The number and location of wells are determined during the design to accomplish the basic goals of (1) optimizing reliable oxidant and catalyst delivery to the contaminated area, and (2) providing conduits to measure chemical oxidation system performance. For permanganate re-infiltration systems this typically means placing re-injection wells in the upgradient portion of the source area(s) while extracting groundwater from downgradient locations. This approach simultaneously provides an enhanced hydraulic gradient, which can accelerate oxidant distribution across the impacted area. The number, location and design of the extraction wells will largely be determined from site-specific hydrogeology, the depth(s) and thickness(es) of the contaminated area(s), and the results of field-scale pilot testing and hydraulic modeling. Note that well placement may need to be changed as remediation progresses, as wells often generate preferential flow paths over time.

Determining the number and spacing of the wells for ozone injection may also be determined through field-scale pilot testing. However, the following general points should be considered.

- # Closer well spacing is often appropriate in areas of high contaminant concentrations to enhance contaminant contact and oxidant delivery/distribution where the oxidant demand is the greatest.

- # Direct delivery of oxidant into the contaminated material using closer well spacings can deliver, disperse, and significantly decrease the treatment timeframe through groundwater advection/dispersion more quickly than oxidant delivery.

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

**Well Construction.** Chemical oxidation system wells are constructed of 1- to 6-inch diameter PVC, galvanized steel, or stainless steel pipe, although caution should be exercised in the use of stainless steel pipe in low-pH conditions. Ozone injection sparge wells have screened intervals that are normally 1-3 feet in length and situated within the contaminated zone. Injection sparge points must be properly grouted to prevent the oxidants from moving directly up the well annulus to the unsaturated zone rather than being forced into the contaminated aquifer (“short circuiting” of the injected oxygen) when horizontal injection oxidant exits along the entire screen length. Exhibit XIII-14 shows a cross-section typical ozone or hydrogen peroxide (Fenton's Reagent) sparge well.

Re-infiltration wells typically have screen lengths that extend from the base of the wells into the unsaturated zone. Groundwater extraction wells should ideally be screened in the saturated interval containing the greatest mass of hydrocarbons. Field-scale pilot studies and subsequent data analysis and hydraulic modeling can greatly assist one in determining the configuration and construction design of groundwater extraction and injection wells.

## Step 4: An Evaluation of the Operation and Monitoring Plan

### Remedial Progress Monitoring

Significant uncertainties associated with site conditions can remain even as remedial designs are completed and implemented. In the start-up period, these unknowns frequently can result in operations that vary from the original design. These variances often require adjustments to account for unforeseen conditions and to optimize system performance. Unfortunately, in many cases, the need for these adjustments can go unrecognized for a long time.

In some cases, the delay in recognizing that remedial system adjustments are necessary may be attributed to slow responses in subsurface conditions to the applied technology. Because these subsurface responses to the applied remedial technology can be delayed, there is often the tendency to give the remedial program more time to work (sometimes years) before making system modifications or adjustments. In other cases, the delay may stem from misuse or misinterpretation of site data, which can lead to the conclusion that the remedial system is performing well when it is, in fact, not. An example of this misuse is the practice of using groundwater analytical data from chemical oxidant delivery wells as an indicator of remedial progress. In this case, an assessment is biased by the localized effects of concentrated chemical oxidation in the immediate vicinity of the oxidant delivery wells, but does not provide an objective measure of the chemical oxidation system's ability to distribute the oxidant and contact the adsorbed contaminants throughout the treatment area.

However, at many sites remedial system or application operational efficiencies are not optimized simply because an adequate performance monitoring plan has either not been developed or has not been fully implemented. In such cases, the designed remedial system may be installed, implemented, and allowed to run its course with insufficient numbers or types of samples to determine whether the remedial system is performing in accordance with design expectations. The result of such monitoring approaches can be the discovery of a sub-standard or failed remediation program years after its implementation.

The previous section discussed the importance of developing a comprehensive remedial progress monitoring plan. This covers the topics that should be addressed in such a plan to ensure objective gauging of remedial system performance. Necessary optimization adjustments can be made early in the remediation program as well as throughout the duration of a chemical oxidation remedial program. The following section provides a focused discussion on evaluation sampling and chemical oxidation evaluation criteria that should be examined during review of a operations and monitoring plan that proposes to use chemical oxidation.

### Evaluation Sampling

Evaluation sampling is performed to gauge the effectiveness of the chemical oxidation program relevant to design expectations. Based on a comparison of the actual field sampling data to design and operational expectations, timely modifications to the system or operating procedures can be made to optimize the application of chemical oxidants early in the remediation program. Projects with regular performance reviews guided by the results of such sampling and monitoring programs have a greater chance of achieving the design remedial goals within desired timeframes and, potentially, at a lower cost.

Various environmental media are sampled to evaluate system performance. Groundwater, soil, and soil vapors from the treatment area and vicinity are commonly sampled to determine the degree to which the chemical oxidation program is meeting the basic objectives of the approach, including:

- Delivering oxidants to the treatment zone at required design rates.

- Distributing the oxidants across the target contaminated area to contact the contaminants.

- Reducing concentrations of petroleum hydrocarbons in soil and groundwater at design rates through chemical oxidation of the petroleum compounds.

Exhibit XIII-14 identifies those parameters that are commonly measured in groundwater, soil and soil vapor samples to help evaluate chemical oxidation progress and system performance. A brief description of the respective sampling frequencies and the relevance and significance of each parameter to the performance evaluation are also provided in the exhibit. A key element is the location(s) where performance evaluation sampling takes place relative to subsurface oxidant delivery points. As stated in the exhibit, performance evaluation samples should not normally be collected from oxidant delivery locations.

### Exhibit XIII-14
### Common Performance Monitoring Parameters and Sampling Frequencies

| | **Sampling Frequency** | | | |
|---|---|---|---|---|
| **Analytical Parameter** | **Start-up Phase (7-10 days)** | **Remediation/ Post-Application Long-Term Monitoring Phase** | | **Purpose** |
| | ***Daily*** | ***Weekly to Monthly*** | ***Quarterly to Annually*** | |
| **GROUNDWATER**<br>*Samples should be collected from monitoring wells located in and around the treatment area and from extraction wells (if used). Samples should not be collected from oxidant delivery wells for evaluating system performance because they represent highly localized effects of the remediation program.* | | | | |
| Dissolved Oxygen | X | X | | Determines the effect of the oxidants on dissolved oxygen levels and potential to boost aerobic biodegradation as a secondary benefit. |
| Redox Potential | X | X | | Yields data on system's ability to increase the extent of aerobic subsurface environment. |

## Exhibit XIII-14
## Common Performance Monitoring Parameters and Sampling Frequencies (continued)

| Analytical Parameter | Sampling Frequency: Start-up Phase (7-10 days) | Sampling Frequency: Remediation/ Post-Application Long-Term Monitoring Phase | | Purpose |
|---|---|---|---|---|
| | ***Daily*** | ***Weekly to Monthly*** | ***Quarterly to Annually*** | |
| **GROUNDWATER (continued)**<br>*Samples should be collected from monitoring wells located in and around the treatment area and from extraction wells (if used). Samples should not be collected from oxidant delivery wells for evaluating system performance because they represent highly localized effects of the remediation program.* | | | | |
| pH | X | X | | Confirms pH conditions are stable and suitable for Fenton's Reagent, or identifies trends of concern. |
| $H_2O_2$, Ozone, or Permanganate | X | X | | Provides information on distances the oxidizing compounds are able to be transmitted by the remedial system before decomposing. |
| Petroleum COCs | | | X | Indicates remedial progress. |
| Degradation Daughter Constituents (e.g., TBA) | | | X | Could indicate incomplete oxidation process. |
| Water Table Elevations | X | X | | Determines if hydraulic conditions (groundwater flow) are consistent with design intent or if chemical oxidation has had an unanticipated affect on these conditions. |

## Exhibit XIII-14
## Common Performance Monitoring Parameters and Sampling Frequencies (continued)

| Analytical Parameter | Sampling Frequency: Start-up Phase (7-10 days) | Sampling Frequency: Remediation/ Post-Application Long-Term Monitoring Phase | | Purpose |
|---|---|---|---|---|
| | ***Daily*** | ***Weekly to Monthly*** | ***Quarterly to Annually*** | |
| **SOIL VAPOR**<br>*Samples should be collected from monitoring wells located in and around the treatment area that are screened in the unsaturated zone and from soil vapor extraction wells (if used). Samples should not be collected from oxidant delivery wells for evaluating system performance because they represent highly localized effects of the remediation program.* | | | | |
| Carbon Dioxide | X | X | | Provides evidence of chemical oxidation. |
| Oxygen | X | X | | Indicates potential losses of introduced oxygen through the unsaturated zone. |
| Volatile Petroleum Contaminants (Constituents) of Concern (COCs) | X | X | | Suggests residual sources in soil or fugitive emissions associated with the remedial effort. |
| Fugitive Ozone or Hydrogen Peroxide | X | X | | Determines losses of oxygen-yielding reagents delivered to the subsurface. |
| **SOIL**<br>*Samples should be collected from borings or using push point or drill rig sampling equipment in and around the treatment area. Soil samples should consistently be collected from same contaminated sections of stratigraphic interval for comparison to earlier samples from same locations and depths.* | | | | |
| Petroleum COCs | | | X | Provide a measure of remedial progress, contaminant mass reducions and the extent to which chemical oxidation of adsorbed contaminants is limited. |

The performance of the chemical oxidation system should be determined by the chemistry of soil and groundwater located between, around and downgradient of oxidant delivery locations rather than inside or in the immediate vicinity of the oxidant delivery points. Conditions inside or in the immediate vicinity of oxidant injection locations have been preferentially altered by chemical oxidation to destroy the petroleum contaminants. Therefore, data from these locations are not representative of the subsurface conditions that exist beneath most of the site. To understand the effect the chemical oxidation system is having on the subsurface conditions as a measure of its performance, samples of soil, groundwater and soil gas should be collected from alternate locations. In review of the performance monitoring plan in the corrective action plan, it should be verified that a sufficient number of sampling locations exist between oxidant application points to provide the necessary performance sampling data. A description of how these data may be used to evaluate the chemical oxidation system performance is provided below.

## Evaluation Criteria

The evaluation sampling described above provides the evidence needed to assess the chemical oxidation system performance. This evidence requires examination and interpretation to confirm chemical oxidation system effectiveness and whether system or application modifications may be warranted. A discussion of these data and how system performance can be interpreted is provided below. In particular, an evaluation of performance is examined from the following two broad chemical oxidation system requirements:

- Oxidant Delivery and Distribution
- Permanent Contaminant Mass Reduction and Attainment of Cleanup Goal

Each of these is discussed in more detail below.

**Oxidant Delivery and Distribution.** Performance sampling may indicate that the chemical oxidation system is meeting design specifications for oxidant delivery and distribution if the data show the following:

- Oxidant and catalyst are being delivered to the subsurface at the design mass delivery rate or design adjusted rate based on analysis of field monitoring data; and
- The oxidant and catalyst are detected in samples from the treatment area at the design concentrations.

If the performance monitoring data suggest that one or more of these conditions is not met, the system may not be meeting the requirements of the design, and system adjustments or modifications may need to be made. As previously discussed, the remedial system design should include contingency planning that explores performance deficiency scenarios and identifies possible solutions.

Oxidant delivery deficiencies may be overcome by simply adjusting system flow rates, upgrading equipment capacities or increasing oxidant dose concentrations. However, occasionally, oxidant delivery rates may be limited by the capacity of the subsurface to transport the delivered oxidant mass.

Perhaps the most challenging performance problem is when a chemical oxidation system or program is unable to deliver oxidants to a portion or multiple portions of a contaminated area. There are many ways that oxidants distributed from delivery points could fail to reach target contaminated area. These may include:

- Low permeability heterogeneous soils.
- Low hydraulic gradient and groundwater flow.

Possible remedies to the performance problem include adding additional oxidant delivery points; increasing oxidant delivery rates; increasing dose concentrations; or enhancing hydraulic gradients and groundwater flow.

**Permanent Contaminant Mass Reduction And Attainment of Cleanup Goal.** The effectiveness of a chemical oxidation program can only be determined after examining the reduction in contaminant mass, and after identifying whether the contaminant mass reduction is sufficient for the soil and groundwater to permanently meet cleanup standards.

It is not sufficient to simply review groundwater monitoring data collected during and weeks or even months after completing a chemical oxidation program. These data are often biased, reflecting the successful oxidation of the most readily contacted contaminants, predominantly contaminants in the most permeable soil zones. False positive evaluations of chemical oxidation program performance can result from reliance on short-term post-chemical oxidation application groundwater monitoring data. These false positive evaluations may become evident during long-term groundwater monitoring when contaminant levels rebound as untreated contaminant mass in the less permeable soil bleeds back out and re-contaminates the more permeable zones. Long term (e.g., months to years), post-chemical oxidation groundwater monitoring is needed to evaluate the effectiveness of a chemical oxidation program.

Program effectiveness may also be evaluated by estimating the mass of contaminants destroyed, which can be accomplished using sample analytical data. Provided that a sufficient number of soil samples are collected and analyzed for the treatment area, soil sampling using identical methods before and after implementation of a chemical oxidation program may indicate the volume of contaminant mass destroyed by the oxidants. Comparing the estimated actual mass destruction with the projected mass destruction (as predicted in the corrective action plan) will reveal the relative effectiveness the oxidant application program. If the contaminant mass destroyed is roughly the amount predicted during the design, the chemical oxidation program can be considered a success.

Should significantly more contaminant mass be destroyed than predicted, the program might be characterized as highly successful, but if significantly less contaminant mass is destroyed than predicted, it may be more accurately characterized as a failure. As the remediation program progresses, it may be necessary to review the project goals, particularly if the source has been effectively reduced (e.g., 70-90%), but significant contaminant mass remains in the associated plume. It may be necessary to perform a second phase of remediation (e.g., apply a different oxidant, move to monitored natural attenuation) to determine whether site cleanup has been achieved or is feasible.

The most direct measurement of the success of a chemical oxidation program is to determine whether the groundwater and soil remedial objectives have been met and can be sustained indefinitely following chemical oxidation treatment. Post-application monitoring should be conducted for a minimum of one year following chemical oxidation treatment to confirm that short-term reductions can be sustained, indicating that contaminant levels have been adequately reduced throughout the contaminated soil and groundwater.

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## Checklist: Can Chemical Oxidation Be Used At This Site?

This checklist can help you to evaluate the completeness of the corrective action plan and to identify areas that require closer scrutiny. As you go through the corrective action plan, answer the following questions. If the answer to several questions is “no”, you will most likely want to request additional information to determine if the proposed chemical oxidation technology and approach will accomplish the site cleanup goals.

### 1. Site Factors

| **Yes** | **No** | |
|---|---|---|
| o | o | Is the soil intrinsic permeability greater than $10^{-9}$ cm$^2$? |
| o | o | Is the soil generally free of impermeable or low permeability layers that could retain significant petroleum contaminant mass and limit the bioavailability of this mass? |
| o | o | Is the soil profile determined from geologic boring logs generally free of natural organic material (e.g., layers of peat or humic material)? |
| o | o | Is the soil temperature expected to be 10°C or higher during remediation? |
| o | o | Is the pH of site groundwater between 5 and 9? |
| o | o | Is the dissolved iron concentration in the site groundwater < 10 mg/L? |
| o | o | Have imminent likely excessive risks to human health or the environment (if any, associated with the petroleum contamination) been eliminated? |
| o | o | Does the state have specific permitting requirements? |

### 2. Chemical Oxidation Design

| **Yes** | **No** | |
|---|---|---|
| o | o | Has the mass of petroleum hydrocarbons requiring biodegradation been estimated? |
| o | o | Has the mass of dissolved oxygen required to biodegrade the petroleum contaminants been estimated? |
| o | o | Can the proposed chemical oxidation approach deliver the necessary oxygen mass to the treatment area within the estimated cleanup time? |
| o | o | Is the capacity of the chemical oxidation treatment system sufficient to generate and deliver oxygen at the required design rate? |
| o | o | Is the density and configuration of oxygen delivery points adequate to uniformly disperse dissolved oxygen through the target treatment zone, given site geology and hydrologic conditions? |

## 3. Permitting Issues

| Yes | No | |
|---|---|---|
| ☐ | ☐ | Does the state have specific permitting requirements? If so, are they addressed in the plan? |

## 4. Written Performance Monitoring Plan

| Yes | No | |
|---|---|---|
| ☐ | ☐ | Will a comprehensive set of baseline sampling be performed prior to chemical oxidation system start-up? |
| ☐ | ☐ | Does the plan specifically exclude sampling from oxygen delivery wells when collecting data to evaluate chemical oxidation system performance? |
| ☐ | ☐ | Are monitoring wells adequately distributed between oxygen delivery locations to collect groundwater and soil vapor samples to evaluate the performance of the chemical oxidation system? |
| ☐ | ☐ | Does the written plan include periodically collecting soil samples from the contaminated interval(s) at locations between oxygen delivery locations? |
| ☐ | ☐ | Will the soil, soil vapor and groundwater samples be analyzed for the majority of the recommended performance monitoring parameters? |
| ☐ | ☐ | Will frequencies of performance monitoring correspond to those identified in Exhibit XIII–14? |

# APPENDIX

## Abbreviations and Definitions

# Appendix
# 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:** in the presence of oxygen.

**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:** in the absence of oxygen.

**anisotropic:** the condition in which hydraulic properties of an aquifer are not equal when measured in all directions.

**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.

**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.

**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.

**empirical:** relying upon or gained from experiment or observation.

**entrained:** particulates or vapor transported along with flowing gas or liquid.

**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.

**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.

**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.

**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:** 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.

**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.

**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.

**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-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.

***in situ*:** in its original place; unmoved; unexcavated; remaining in the subsurface.

**indigenous:** living or occurring naturally in a specific area or environment; native.

**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.

**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.

**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 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.

**molecular diffusion:** process whereby molecules of various gases tend to intermingle and eventually become uniformly dispersed.

**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 anaerobes:** organisms for which the presence of molecular oxygen is toxic. These organisms derive the oxygen needed for cell synthesis from chemical compounds.

**obligate aerobes:** organisms that require the presence of molecular oxygen ($O_2$) for their metabolism.

**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.

**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.

**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.

**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.

**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.

**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:** 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.

**stratum:** a horizontal layer of geologic material of similar composition, especially one of several parallel layers arranged one on top of another.

**stratification:** layering or bedding of geologic materials (e.g., rock or sediments).

**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 desorption system:** refers to a thermal desorber and associated systems for handling materials and treated soils and treating offgases and residuals.

**thermal desorber:** describes the primary treatment unit that heats petroleum-contaminated materials and desorbs the organic materials into a purge gas or off-gas.

**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.

**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 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.

**unsaturated:** the characteristic of a carbon atom in a hydrocarbon molecule that shares a double bond with another carbon atom.

**upgradient:** it the direction of increasing potentiometric (piezometric) head.

**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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Glossary of Technical TermsThe following glossary is from OUST's publication: How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers. (EPA 510-B-95-007). This publication also describes 10 alternative technologies for remediation of petroleum releases. You can download PDF files of every chapter of the document (including two new chapters produced in 2004, but not represented in this glossary) at: http://www.epa.gov/swerust1/pubs/tums.htm.

Select the first letter of the term you are looking for from the list below, or scroll down the alphabetical listing. A key to return back to this spot is provided at the end of each section.
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A
abiotic: not biotic; not formed by biologic processes.
absolute viscosity: A measure of a fluid's resistance to tangential or shear stress. Also referred to as dynamic viscosity; see also viscosity. Units are usually given in centipoise.
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(n)H(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(n)H(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(n)H(2n-2).

ambient: surrounding; the surrounding environment and conditions.

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).

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## B

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: "British Thermal Unit"; the quantity of heat required to raise the temperature of one pound of water one degree Fahrenheit at 39 degrees 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.

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C

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.

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D

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.

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E

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) any of numerous proteins or conjugated proteins produced by living organisms and functioning as biochemical catalysts. (b) 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.
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.

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F

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.

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G

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.

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H

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(2)O(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(2)O] 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.

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I

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.

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K

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.

kow: see octanol/water partition coefficient.

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L

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.

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M

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.

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N

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.

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O

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 (Kow): 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 Kow, the more non-polar the compound. Log Kow is generally used as a relative indicator of the tendency of an organic compound to adsorb to soil. Log Kow 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.

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P

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: (1) 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. (2) 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.

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## R

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.

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## S

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 (used for SVE and bioventing) 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.

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T

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(3)O(10)[-5 charge] anion. Most common is sodium tripolyphosphate [Na(5)P(3)O(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.

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U

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.

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V

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.

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W

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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