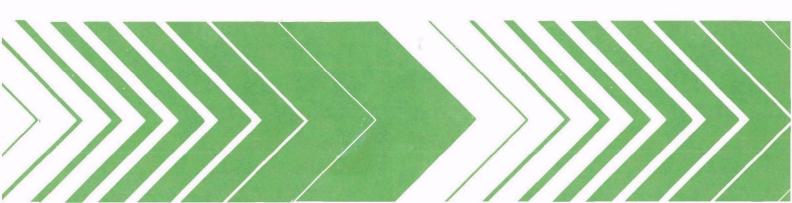
Research and Development



Assessing UST Corrective Action Technologies:

Site Assessment and Selection of Unsaturated Zone Treatment Technologies



ASSESSING UST CORRECTIVE ACTION TECHNOLOGIES:

Site Assessment and Selection of Unsaturated Zone Treatment Technologies

Ву

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FOREWORD

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

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

An area of major concern is the health impacts associated with uncontrolled releases of petroleum hydrocarbons from underground storage tanks. This document focuses on cleaning up soils contaminated with petroleum. It provides much needed assistance on how to make an informed selection of an effective soil treatment technology.

E. Timothy Oppelt, Director Risk Reduction Engineering Laboratory

ABSTRACT

A methodology is presented for evaluating the likely effectiveness of five soil treatment technologies at sites where petroleum products have contaminated the unsaturated zone. The five soil treatment technologies are: soil venting, biorestoration, soil flushing, hydraulic barriers, and excavation. The evaluation consists of a site assessment, selection of a treatment technology, and performance monitoring and follow-up measurements. The overall focus of the manual is on making a preliminary screening of what soil treatment technologies would likely be effective at a given UST site.

This manual identifies basic information about the subsurface environment and the released product that is needed for a site assessment. The reader is shown what information is needed and where it can be obtained; the manual also provides default values for some parameters if field data are not available or have not yet been collected.

Worksheets are provided to help the reader make a preliminary determination as to where in the unsaturated zone most of the petroleum product is likely to be, and further, how likely the petroleum is to move into and out of the three "phases" considered in this manual: 1) as contaminant vapors in the pore spaces of the soil; 2) as residual saturation trapped between soil particles; or 3) dissolved in pore water. Process descriptions, costs, advantages and disadvantages are provided for each soil treatment technology.

Factors that are critical to the successful implementation of each technology are presented and site conditions which are favorable for each factor are discussed.

Worksheets containing the relevent success factors are provided for each technology that assist the reader in determining if actual site conditions are favorable for a given technology. The worksheets can be compared to screen those technologies most likely to be effective.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

```
-- American Petroleum Institute
API
               -- biochemical oxygen demand
BOD
              -- Camp Dresser & McKee Inc.
CDM
              -- cubic feet per minute
CFM
               -- chemical oxygen demand
COD
               -- critical success factor
CSF
              -- U. S. Environmental Protection Agency
EPA
NAPL
             -- Non-aqueous phase liquid
              -- operation and maintenance
0&M
              -- EPA's Office of Research & Development
ORD
              -- EPA's Office of Underground Storage Tanks
OUST
UST
              -- underground storage tank
             -- centimeters per second
cm/sec
cPoise
             -- centipoise
               -- centimeters per day
cm/day
in/yr -- inches per year

g/cm³ -- grams per cubic centimeter

g/m³ -- grams per cubic meter

m²/g -- meters square per gram

mg/L -- milligrams per liter

mm Hg -- millimeters of mercury

liters per kilogram
               -- liters per kilogram
L/kg
```

SYMBOLS

```
°C<sub>2</sub>
             -- degrees Celsius
             -- centimeters squared
cm<sup>*</sup>
             -- gallon
gal
            -- feet
ft
             -- degrees Kelvin
٥K
             -- month
mo
             -- year
yr
             -- percent
            -- concentration of contaminant in soil [cm3/cm3]
            -- concentration of contaminant in pore water [mg/]]
            -- soil/water partitioning coefficient
            -- octanol/water partitioning coefficient
           -- indicates alkaline or acid conditions in log units
           -- refractory index
```

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SECTION 1

INTRODUCTION

BACKGROUND

Cleaning up releases from underground storage tanks (USTs) typically involves using several corrective strategies. Short-term emergency measures can involve actions to control acute safety and health hazards such as potential explosions. Examples of emergency measures include draining and removing tanks. After the imminent danger has been addressed, longer term corrective actions involve cleaning up petroleum product that has entered the subsurface environment. Petroleum product in the subsurface may be trapped between soil particles in the unsaturated zone, floating on the water table, or dissolved in groundwater in the saturated zone.

The focus of this manual is on long-term strategies for cleaning up petroleum product in the unsaturated zone. Unlike groundwater treatment technologies — where theories, equations and performance issues are well understood — soil treatment has only recently received widespread attention. The science associated with soil treatment technologies is not as well documented or understood as that associated with water treatment technologies. Despite this uncertainty, soil contamination must always be addressed, and some kind of soil cleanup is typically necessary when a spill occurs.

Removing petroleum hydrocarbons from the unsaturated zone can involve several technologies. Each technology varies with respect to the constituents removed and the method of removal. Also, each technology is most effective and efficient when applied under specific conditions. These conditions, herein called "critical success factors," are specific to each treatment technology.

This manual identifies and describes the critical factors that help characterize the contaminants that were released and the physicochemical properties that determine their movement in air, soil and water. It also identifies and describes the hydrogeologic parameters that are important to developing an understanding of how subsurface conditions will affect treatment performance. Further, this manual provides a framework for proceeding from site assessment to identification and evaluation of soil treatment technologies that can be effective in cleaning up a site.

PURPOSES OF THIS MANUAL

The purposes of this manual are: 1) to provide assistance to local and state decision—makers on how to assess site conditions in the unsaturated zone at a site where a petroleum product release has occurred; and 2) to present methods for evaluating various soil treatment technologies at a given site to determine their potential effectiveness. The manual describes: 1) what information is needed in a site assessment;

how to obtain that information; 3) how that information can be used to determine where in the unsaturated zone most of the released product is likely to be located; and 4) which of five soil treatment technologies considered in this manual are likely to be effective in removing petroleum products from the unsaturated zone at a given site.

The manual directs the user toward final selection of a treatment technology rather than presenting a methodology that results in selection of one best technology; and its value may lie as much in identifying which technologies are not likely to be effective as in identifying those that are. The user is provided with a framework for better understanding complex subsurface conditions and identifying key issues in selecting an appropriate soil treatment technology.

A good understanding of the conditions in the unsaturated zone is essential when selecting an appropriate soil treatment technology. One way to gain this understanding is to conduct a site assessment. The term site assessment, as used here, refers to a desktop analysis of basic hydrologic, geologic, and chemical data obtained from the literature, previous experience at similar sites, and some basic, easy-to-get field measurements collected at the site of interest. It is important to distinguish between a site assessment and a site characterization, which consists of a more rigorous and comprehensive field testing program and can include monitoring wells, sampling soil gas, and collecting soil samples for precise parameter determinations.

Though not as accurate as a site characterization, a good site assessment includes enough information to adequately answer the following questions:

- What was released? Where? When?
- Currently, where in the unsaturated zone is most of the petroleum product likely to be?
- How much petroleum product is likely to be present in different locations and phases?
- How mobile are the constituents of the contaminant, and where are they likely to travel and at what rate?

This manual helps the user answer these questions prior to conducting extensive field studies at the site. Often, a site assessment based on estimates of important parameters is sufficient to gain a relative understanding of the potential effectiveness of a given technology at a given site. This manual does not eliminate the need for site-specific measurements of important parameters since there is no substitute for accurate, site-specific, field data. However, it is possible to combine actual measurements with literature values for other parameters (for which no field data are presently available) to make qualitative assessments of site conditions, and to assess which corrective action technologies are likely to work. Prior to any final decisions, site-specific measurements should, of course, be made.

APPROACH AND ORGANIZATION

The intended primary users of this manual are state and local field and regulatory personnel. Contractors and other parties who have responsibility for selecting or reviewing corrective action plans for cleaning up the unsaturated zone may also find the manual useful. The manual presents a simplified approach to evaluating a site and does not require a highly technical background.

Figure 1 shows the three main components of the approach: 1) site assessment: 2) technology selection; and 3) monitoring and follow-up measurements. The leftmost column of Figure 1 contains questions which pertain to the boxed text immediately to their right. These questions provide the focus for each step in the site evaluation process. Each of the main components is briefly discussed below.

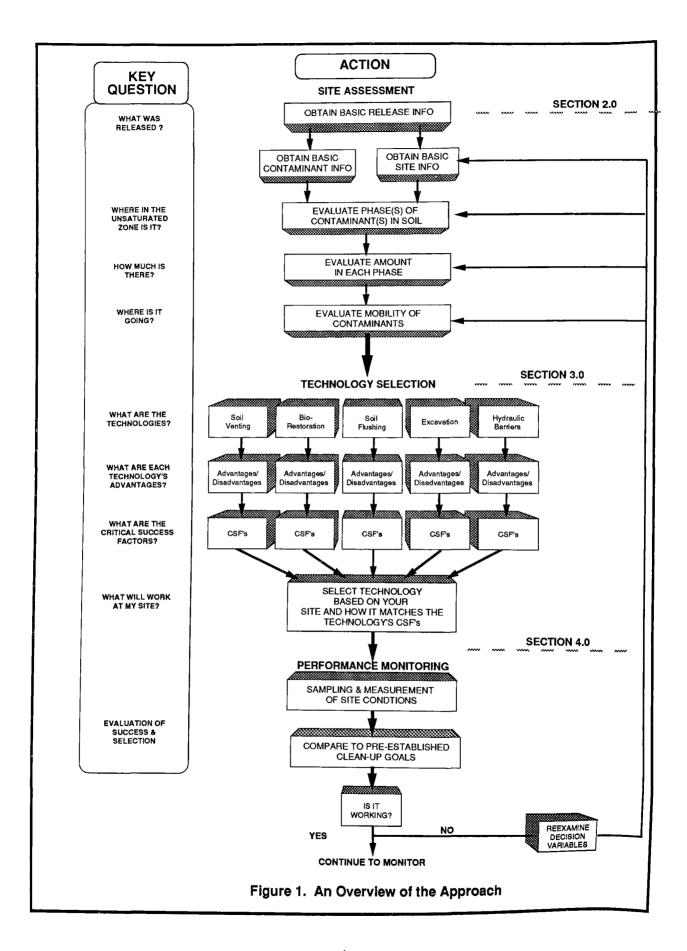
Site Assessment

In Section 2 the reader will be shown what data are helpful in developing a working hypothesis about subsurface conditions and how those data can be obtained. Some information is release-related (e.g., what was released and when) and is assumed to be readily available. Other important information may be less easily obtained, such as hydrogeologic characteristics of the site or the physical and chemical properties of the contaminant. For these data, the manual provides assistance in measuring and/or estimating values to be used in the assessment.

The data collected in the initial stages of the assessment are used to gain an understanding of the behavior of the contaminant in the subsurface. When dealing with the unsaturated zone, the data are primarily used to determine the mobility of the contaminant and what phase(s) it is likely to be in. Mobility of petroleum product in the unsaturated zone is related to: 1) the potential for the various phases of contaminant to move through the subsurface; and 2) the potential for the petroleum product to change from one phase into another. Most treatment technologies rely on mobilizing the contaminant by physically moving the contaminant through the suburface or by causing transformation from one phase to another, or both. Understanding the likely subsurface behavior of the contaminant is therefore very important in evaluating the effectiveness of a given technology.

Selection

In Section 3, the general understanding of subsurface contaminant behavior developed in Section 2 is used to help evaluate the five treatment technologies presented in this manual: 1) soil venting (including vacuum extraction); 2) biorestoration; 3) soil flushing; 4) excavation; and 5) hydraulic barriers. An overview of each technology is presented to familiarize the reader with the basic principles of how the technology works, and their major advantages and disadvantages.



Critical success factors are listed for each technology. These critical success factors, or CSFs, are incorporated into worksheets with which the user can systematically evaluate each technology. The worksheets are completed using the information collected in the site assessment stage, and a relative comparison of the alternatives can be made. Not all CSFs are equally important when evaluating a particular technology at a particular site and the importance of a particular CSF can vary depending on site conditions. Because of this, persons with some knowledge of hydrogeology and experience at site assessment should be consulted before final selection of a remedial action is made.

It should be noted that the selection process presented in this manual is scientifically based. Final selection of a soil treatment technology will also be affected by other criteria such as regulatory restrictions and time available to clean up the site. The cost of implementing a technology is another factor that often plays a significant role in final selection, but it is not considered here.

Performance Monitoring & Follow-Up Measurements

After a technology (or technologies) is selected and implemented, it is important to track its performance and monitor its effectiveness during cleanup activities. Section 4 discusses parameters that should be monitored and how these parameters should be measured (i.e., what types of samples are needed). Monitoring and follow-up are essential because of the uncertainty about subsurface conditions. If a technology's performance is poor, the field data and site assessment, including inherent assumptions, should be re-examined. Poor cleanup performance might be due to a misinterpreted or incomplete site assessment or an incorrect selection of the technology. This feedback loop is an important step in the entire cleanup process.

LIMITATIONS

Users of this manual should be aware of several significant limitations regarding its content and its precision:

- Estimates are for Relative Assessments One of the manual's purposes is to provide estimates of how much of the release is likely to be in each phase in the unsaturated zone, and which technologies are more likely to be effective. The screening of technologies should be reviewed in relative terms rather than an absolute endorsement of one particular technology.
- Not for Emergency Response It is assumed that all necessary emergency responses have been taken, that the source of the release (e.g., tank or supply line) has been identified and repaired, and that proper notification of government agencies (local, state and federal) has taken place.
- <u>Unsaturated Zone Coverage Only</u> This technical assistance document addresses site assessment and corrective action for contamination in the unsaturated zone only. Guidance is not provided for contamination of the saturated zone. In some instances, an

assessment of the unsaturated zone might proceed regardless of potential or actual groundwater contamination, but it should not be assumed that the groundwater is uncontaminated. The presence of a floating contaminant layer on the water table, or a contaminant plume in the groundwater, may ultimately affect the selection of the unsaturated zone corrective action or actions. Integrated guidance for site assessment, corrective action, and evaluation for both the unsaturated and saturated zones contamination is not addressed in this document.

- Focus on Petroleum Hydrocarbons as Contaminants Because petroleum products comprise most of the materials stored in USTs, they are the focus of this manual. Special focus is given to gasoline, primarily in example calculations. This implicit focus does not preclude the use of this report for other types of chemical contaminants, although it clearly is best suited for organic liquids.
- Focus on In Situ Treatment Other than excavation, all technologies discussed in the manual are in situ treatment * techniques. After a contaminated soil has been excavated, the soil can also be treated above ground using many of the same techniques described for in situ applications (e.g., biodegradation can be promoted in the excavated soil). These techniques are only briefly discussed in this manual.

^{* &}lt;u>In Situ</u> treatment means treatment of the soils in place, i.e., they are not dug up. The excavation of contaminated soils usually adds significant expense to a site remediation and also can raise complicating legal questions.

SECTION 2

HOW TO CONDUCT A SITE ASSESSMENT

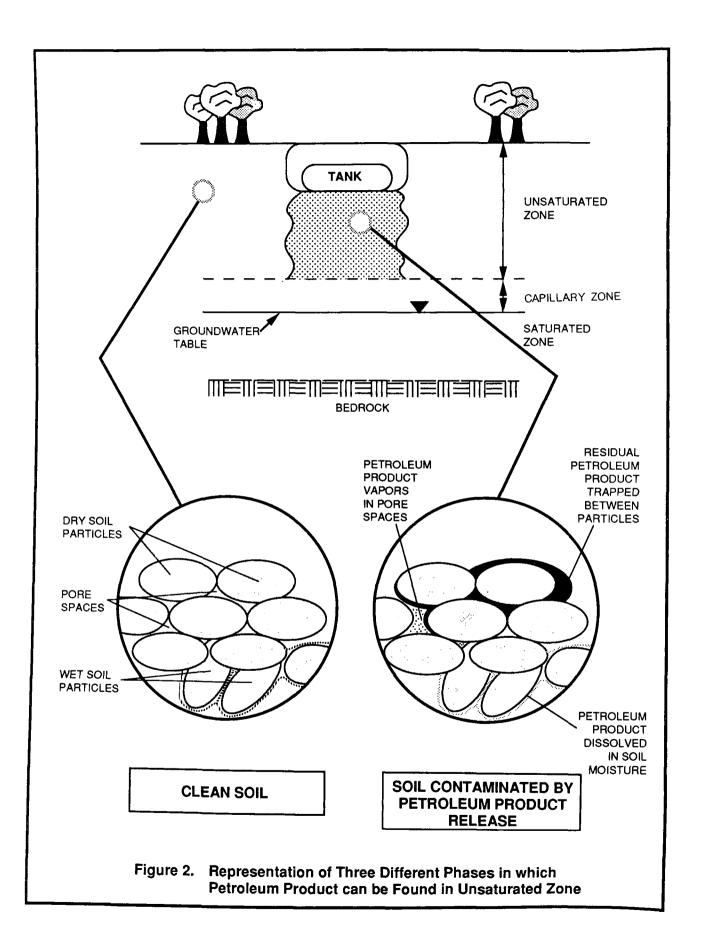
INTRODUCTION

To choose an effective clean-up technology for soils contaminated by petroleum, it is necessary to collect and interpret certain basic information about both the released product and the subsurface environment. At a minimum, the following questions should be addressed:

- What contaminants were released? Knowledge of the type of product released, its physical and chemical properties, and its major chemical constituents is required. The physical and chemical properties of the product can provide valuable insight into subsurface behavior.
- Where is the petroleum product currently? Different soil treatment technologies may be appropriate depending on how the petroleum product is distributed within the unsaturated zone, i.e., as a vapor in soil gas, as a residual liquid, or dissolved in pore water;
- How much petroleum product is in each phase? In the time period immediately after a release (weeks to months) most of the product will exist as a residual liquid. With time, however, significant fractions will volatilize (enter the vapor phase) and dissolve in existing pore water or infiltrating rain water. For old releases, the residual liquid phase may be nearly non-existent or transformed into a more viscous, gummy material.
- Where is the petroleum product going? Also important in the site assessment is an estimate of the mobility of the contaminant. Mobility affects not only the potential areal extent of a release (as the contaminant moves away from the release point), but also the potential effectiveness of any in-situ treatment scheme that depends on mobilizing the contaminants in order to remove them (e.g., vacuum extraction).

These four questions provide a framework for the types of information that should be collected. While additional information is not essential to making a preliminary decision regarding the corrective action, more information can often improve the selection process.

The guidelines contained in this manual are based on research done for EPA's Risk Reduction Engineering Laboratory (RREL) office in Edison, New Jersey. The report summarizing that research identified as many as 13 different conditions under which petroleum product could be found in the subsurface (EPA, 1988a). For simplicity, this manual assumes that petroleum product in the unsaturated zone exists only in three phases as shown on Figure 2: 1) as contaminant vapors in the pore spaces (vapor



phase); 2) as residual liquid trapped between soil particles (liquid phase); or 3) dissolved in the pore water that surrounds soil particles (dissolved phase). For recent petroleum product releases (less than 1 year old) most of the petroleum product is likely to be in the residual liquid phase rather than vapor and dissolved phases.

A distinction is made here between bulk product and the individual constituents that make up the bulk product. Examples of bulk product include automotive gasoline, No. 2 fuel oil, and jet fuel. These bulk products, in turn, are composed of hundreds of individual constituents, each with its own set of chemical properties. These individual constituents dissolve in water and evaporate at rates that are somewhat different than the rate of the bulk product. (The chemical properties of the bulk product tend to be a composite of the chemical properties of its individual constituents.) Default values are provided in this manual for the chemical properties for some typical bulk products and their individual constituents.

The following subsections are structured to correspond to the questions listed above. In each subsection, only the information that is basic and essential for this manual is listed. An informed and successful screening of corrective actions can be made using this information.

GATHERING RELEASE INFORMATION

A site assessment begins with basic information about the release itself, which may be obtained by asking the questions listed in Table 1. Answering these questions provides a starting point for understanding the mobility and phase distribution of the product in the subsurface. For most above-ground spills, the answers to the questions in Table 1 are usually easy to obtain. However, if the questions in Table 1 cannot be readily answered, additional field sampling and testing will be needed to start off the site assessment. This manual assumes the answers to these questions have been obtained.

One of the basic questions in Table 1 is: What contaminants were released? Petroleum products include a variety of fuel types, each with different physical and chemical properties. In addition, each fuel type is a mixture of many constituent compounds which have properties that can be quite different from those of the mixture. Different fuel types and compounds behave differently in the subsurface in terms of such things as their evaporation and dissolution into and out of the various phases (vapor, pure liquid, dissolved in water); their transport through the unsaturated zone; and their potential to biodegrade into simpler compounds. A contaminant's physical and chemical properties must be known to make a judgment about its mobility (e.g., "Will this contaminant spread quickly and reach the water table?"), its partitioning ("Will this contaminant vaporize and pose explosion hazards?") and its degradation potential ("Will this contaminant be biodegraded easily in the unsaturated zone?"). These factors are an important part of the technology selection process.

TABLE 1. BASIC RELEASE INFORMATION ASSUMED TO BE KNOWN

INFORMATION NEEDED

What contaminants were released?

How much was released?

- What was the nature of the release (quick spill/slow leak)?
- How long since the release?

How was the release detected?

WHY INFORMATION IS IMPORTANT

- Physical and chemical properties differ for each contaminant, leading to varying phase partitioning, mobility, and degradation characteristics for each contaminant.
 Corrective action selection is tied to these characteristics.
- The amount released directly affects the phases in which the contaminant may be found.
- Phase partitioning and mobility of the released contaminant are both affected by the nature of the release. As a result, selection of appropriate corrective actions may differ for quick spills versus leaks over extended period of time.
- Contaminants "weather" over time, that is, change in composition due to processes such as degradation, volatilization, and natural flushing from infiltrating rainfall. This change in composition directly affects the physical and chemical properties of the bulk contaminant.
- May provide insight into above questions and areal extent and distribution of contamination in the subsurface.

0

A related question is: <u>How much petroleum product was released?</u> Knowing the volume spilled can help the user evaluate whether the contaminant has reached the saturated zone and estimate the level of contamination in the unsaturated zone.

The time since release is important because the composition and properties of the released material changes over time; volatile compounds evaporate, soluble constituents dissolve in infiltrating rainwater, and some constituents biodegrade. These biochemical changes that occur over time are called "weathering." Weathering can result in contamination with dramatically different chemical concentrations than that originally released. In general, constituents with low molecular weights will move away from the source more quickly over time (either through volatilization or natural flushing by infiltrating rainwater); the more stable and less mobile constituents (typically, high molecular weight compounds) remain near the source longer.

GATHERING SITE-SPECIFIC INFORMATION

Site-specific information pertains primarily to the hydrologic and geologic characteristics of the site. Historic hydrologic data is typically available through state or local climatology offices or through the local United States Geological Survey (USGS) office. Geologic characteristics can vary greatly, even over short distances, making accurate estimates of soil parameters difficult without collecting numerous and expensive field data. For a site assessment, as opposed to characterization, representative geologic data such as can be found at the local USGS office may suffice to gain a relatively good understanding of the subsurface.

Table 2 lists site-specific data that are needed to conduct a site assessment. Again, Table 2 does not list all data that could be useful in an assessment, but rather lists the <u>essential</u> data needed to assess the site. In many cases additional data or measured data could improve the precision of the findings although, as will be shown, they may not be necessary to make a first-cut choice of corrective action technology.

This manual provides default values — obtained via tables, figures, and other data — for many of the parameters. These default values enable users of this manual to make estimates of the critical parameters on a timely basis for a preliminary site assessment. (An example of the use of these default values is given in Appendix A.) Estimated values however, should eventually be validated on a site-by-site basis through a carefully designed sampling program that would naturally take place when a corrective action is implemented.

Collecting field samples is covered extensively in many other publications and is not discussed in detail in this manual. A Compendium of Superfund Field Operations (EPA, 1987b) describes proper sampling procedures to ensure the collection of meaningful data. EPA (1988a) describes various techniques to determine eight key parameters needed for a site assessment:

TABLE 2. SITE-SPECIFIC PARAMETERS TO GATHER

| PARAMETER (UNITS) | DEFAULT SOURCE | IMPORTANT FOR DETERMINING: |
|--|---|---------------------------------|
| Soil Porosity (%) | Table 3, Figure 4 | Mobility, Phase |
| Particle Density (g/cm ³) | Table 3 | Mobility, Phase |
| Bulk Density (g/cm ³) | Table 3 | Mobility, Phase |
| Hydraulic Conductivity (cm/sec) | Table 3 | Mobility, Phase |
| Air Conductivity | Table 3 | Mobility, Phase |
| Permeability (cm ²) | Table 3 | Mobility, Phase |
| Soil Moisture Content (%) | Figure 4 | Mobility, Phase |
| Local Depth to Groundwater (f | Easy to Measure or the Site or Local records | rough Phase |
| Soil Temperature (^o C) | Figure 3 | Mobility, Phase |
| Soil pH | Measure | Bacterial Activity |
| Rainfall, Runoff, and Infiltration Rate (cm/day) | Local precipitation and evaporation records | Mobility, Phase, Composition |
| Soil Surface Area (m ² /g) | Table 4 | Mobility, Phase |
| Organic Content (%) Composition | Measure | Mobility, Phase, |
| Fractures in Rock | Local Records | Mobility |

- depth to groundwater;
- soil temperature
- moisture content;
- particle size distribution;
- bulk density;
- saturated hydraulic conductivity;
- unsaturated hydraulic conductivity, and
- residual saturation.

Site-specific data should be obtained whenever possible; however, if a quick initial assessment is desired it is often necessary to evaluate alternatives without the benefit of field data or when only incomplete data are available. In these cases, approximations may be useful. Tables 3 and 4 provide typical values for several of the parameters listed in Table 2 for various types of soil and rock. These tables can be used to select default values in the absence of measured values. Figure 3 gives generalized groundwater temperatures throughout the continental United States. An estimate of subsurface temperature can be made by interpolating between contour lines. Figure 4 provides water-holding properties by soil type. An estimate of the moisture content of a particular soil can be made by using a typical field capacity value from the from the range of values shown on Figure 4. Field capacity is an approximation of the amount of water retained in the soil spaces as infiltrating rainwater passes down through the formation, and is expressed as a percentage of the total soil volume. The sample problems provided in Appendix A refer to these tables and figures for representative values.

Other sources that can provide suitable estimates of these parameters include the USGS and the Soil Conservation Service (SCS). County extension offices may also offer another source of information, as hydrogeologic data is often categorized by county.

GATHERING CONTAMINANT-SPECIFIC INFORMATION

In addition to release-related and site-related information, a site assessment should include an understanding of the physical and chemical properties of the contaminants released. To a large extent, contaminant properties govern partitioning in the subsurface; what phase(s) it is likely to reside in, how it is likely to move away from the site, and whether it is likely to degrade significantly over time.

Table 5 lists contaminant-specific data that are needed to conduct a site assessment. For a preliminary site assessment, extensive field sampling and analysis is unnecessary to estimate values for contaminant-specific parameters. Instead literature values can be used to estimate contaminant-specific parameter values.

Looking at Table 5, the user can identify from the default source column where in the manual literature values for each parameter may be found. These values can be used in the assessment as will be demonstrated in the sample example in the Appendix. To illustrate, assume the liquid density of gasoline is needed. The user can locate liquid density in Table 5 and find that the default source is Table 7. Moving to Table 7, the typical value for automotive gasoline in the liquid density column is 0.73 g/cm3.

TABLE 3. PHYSICOCHEMICAL PROPERTIES OF ROCKS AND SOIL

| Rock/Soil Type | Porosity (%) | Particle Density (g/cm ³) | Bulk Density (g/cm ³) | Saturated Hyd. Cond (cm/sec) | Permeability (cm ²) | Air Conductivity (cm/sec) |
|--|---|--|---|---|---|--|
| UNCONSOLIDATED | | | | | | |
| Gravel Sand Loam Silt | 25-40 25-50 42-50 35-50 | 2.65 2.65 2.65 2.65 | 1.59-1.99 1.33-1.99 1.33-1.54 1.33-1.72 | 10 ⁻¹ - 10 ² 10 ⁻⁴ - 10 10 ⁻⁵ - 10 ⁻¹ 10 ⁻⁷ - 10 ⁻³ | 10 ⁻⁶ - 10- ¹ 10 ⁻⁹ - 10 ⁻⁵ 10 ⁻¹⁰ - 10 ⁻⁶ 10 ⁻¹² - 10 ⁻⁸ | 10 ⁻² - 10 10 ⁻⁵ - 10 ⁻¹ 10 ⁻⁶ - 10 ⁻² 10 ⁻⁸ - 10 ⁻⁴ |
| Clay | 40-70 | 2.25 | 0.68-1.35 | 10 ⁻⁷ - 10 ⁻³ 10 ⁻¹⁰ - 10 ⁻⁷ | 10 ⁻¹² - 10 ⁻⁰ 10 ⁻¹⁵ - 10 ⁻¹² | 10 ⁻⁰ - 10 ⁻⁸ |
| CONSOLIDATED | | | | | | |
| Sandstone Shale Granite Granite (fractured) Limestone Limestone (Karstic) Basalt (permeable) | 5-30 0-10 0-5 0-10 0-20 5-50 5-50 | 2.65 2.25 2.70 2.70 2.87 2.71 2.96 | 1.86-2.52 1.98-2.25 2.57-2.70 2.43-2.70 2.30-2.87 1.36-2.57 1.48-2.81 | 10 ⁻⁸ - 10 ⁻⁴ 10 ⁻¹¹ - 10 ⁻⁷ 10 ⁻¹¹ - 10 ⁻⁸ 10 ⁻⁶ - 10 ⁻² 10 ⁻⁷ - 10 ⁻⁴ 10 ⁻⁴ - 1 | 10 ⁻¹³ - 10 ⁻⁹ 10 ⁻¹⁶ - 10 ⁻¹² 10 ⁻¹⁶ - 10 ⁻¹³ 10 ⁻¹¹ - 10 ⁻⁷ 10 ⁻¹² - 10 ⁻⁹ 10 ⁻⁹ - 10 ⁻⁵ 10 ⁻¹⁰ - 10 ⁻⁵ | 10 ⁻⁹ - 10 ⁻⁵ 10 ⁻¹² - 10 ⁻⁸ 10 ⁻¹² - 10 ⁻⁹ 10 ⁻⁷ - 10 ⁻³ 10 ⁻⁸ - 10 ⁻⁵ 10 ⁻⁵ - 10 ⁻¹ |

Source: Adapted from Freeze and Cherry, 1979, and Krishnayya et al, 1988.

^{*} Air conductivity values at 10°C. Values are based on the ratio of hydraulic conductivity to air conductivity (K_r); where K_r= (viscosity of air/viscosity of water) (density of water/density of air)

TABLE 4. RELATIONSHIP BETWEEN DIAMETER OF PARTICLES AND SURFACE AREA

| Diameter of Particles (mm) | Description | Approximate Surface Area (m ² /g) |
|----------------------------|------------------|---|
| 1.0 - 2.0 | Very Coarse Sand | 0.001 - 0.003 |
| 0.5 - 1.0 | Coarse Sand | 0.003 - 0.005 |
| 0.25 - 0.5 | Medium Sand | 0.005 - 0.01 |
| 0.1 - 0.25 | Fine Sand | 0.01 - 0.03 |
| 0.05 - 0.1 | Very Fine Sand | 0.03 - 0.1 |
| 0.002 - 0.05 | Silt | 0.1 - 1 |
| <0.002 | Clay | >1 |
| | | |

Source: Adapted from Hillel, 1980

TABLE 5. CONTAMINANT SPECIFIC PARAMETERS TO GATHER

| PARAMETER (UNITS) | DEFAULT SOURCE | IMPORTANT FOR DETERMINING: |
|------------------------------------|----------------|------------------------------|
| Pure Vapor Pressure (mm Hg) | Tables 7,8 | Mobility, Phase |
| Water Solubility (mg/L) | Tables 7,8 | Mobility, Phase |
| Liquid Viscosity (cPoise) | Tables 7, 8 | Mobility |
| Liquid Density (g/m ³) | Tables 7, 8 | Mobility |
| Vapor Density (g/m ³) | Tables 7, 8 | Mobility |
| Soil Sorption Coefficient (L/kg) | Table 8 | Mobility, Phase |
| Refractory Index (ratio) | Table 9 | Degradation |
| Unweathered Composition (-)* | Table 6 | Mobility, Phase, Degradation |

^{*} Composition will change over time due to "weathering." See discussion in text.

APPROXIMATE TEMPERATURE OF GROUND WATER, IN DEGREES CELSIUS, IN THE CONTERMINOUS UNITED STATES AT DEPTHS OF 10 TO 25 M $\,$

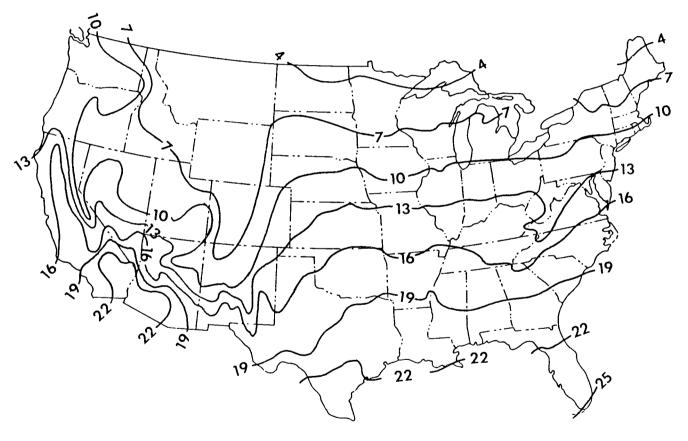
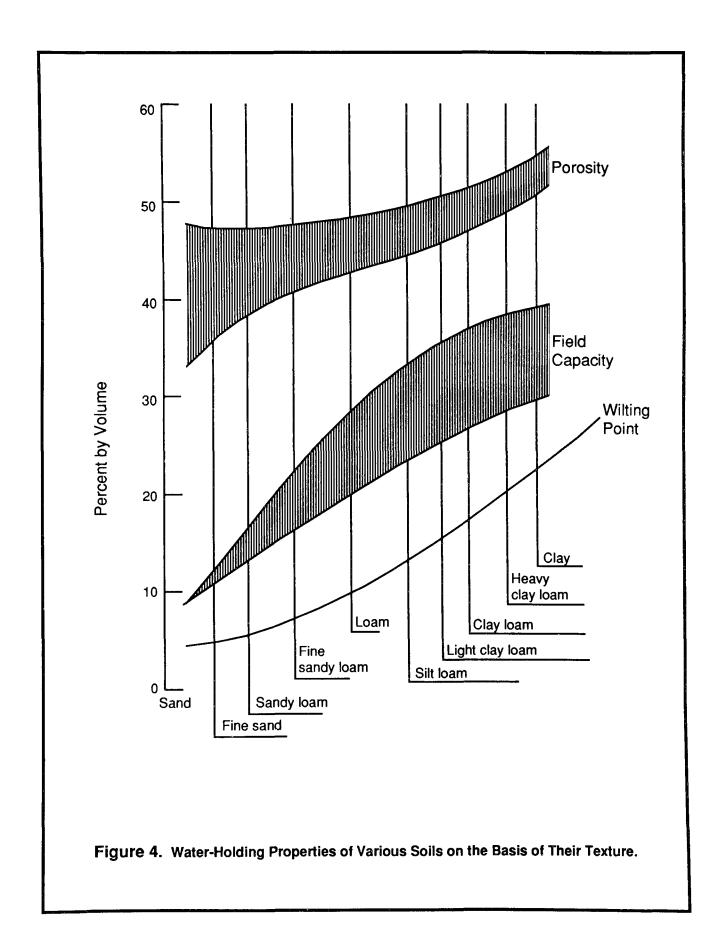


Figure 3. Groundwater Temperature in the United States (°C) at Depths of 10 to 25 m (from Heath, 1985)



Petroleum products are a mixture of many compounds. The physical and chemical properties of the constituents are different than those of the mixture. However, at most sites, evaluation will be based on the properties of the mixture rather than one or more constituents. This is particularly true of a preliminary assessment. The sample example in the Appendix of this manual evaluates contaminant mobility and phase partitioning based on properties of a mixture. However, an assessment that targets one or more constituents merits discussion.

There are, however, several reasons why individual constituents would be targeted during site assessment instead of the petroleum product mixture. Probably principal among these are: 1) natural weathering of the contaminants; and 2) focus on known health risks. Weathering is the process where a compound or mixture is reduced to simpler and/or fewer component parts over time. If a petroleum product has been in the subsurface for several years, the existing contaminant is likely to be significantly different than when originally released. In such a case, evaluation based on an understanding of the behavior of the original petroleum product could lead to selection of an ineffective remedial response.

The other reason to target individual constituents is to focus the assessment on a compound(s) which is thought to present the greatest potential threat. For instance, it may be desirable to select a remedial technology that is likely to be effective in removing benzene, a known human carcinogen and common constituent of gasoline. An understanding of how benzene behaves in the subsurface would be developed rather than an understanding of the behavior of the mixture.

Table 6 presents the unweathered composition of three common bulk hydrocarbon products. This list can be consulted to determine which constituents are likely to be in a given petroleum product and to estimate what percentage of the total product they represent.

Table 7 lists default values for various physical and chemical properties of common hydrocarbon mixtures; Table 8 provides similar information for individual hydrocarbon constituents. Contaminant-specific properties of petroleum product constituents in Table 8 are for pure compounds. These values may be different than would be found when a given compound is mixed with other organic compounds. For example, the water solubility of pure benzene is 1,780 mg/L, but in a gasoline/water mixture the dissolution of benzene is more likely to be in the 20 to 80 mg/L range.

Table 9 lists selected refractory index values for both hydrocarbon mixtures and individual constituents. The refractory index is a measure of the relative biodegradability of a compound.

EVALUATING CONTAMINANT PHASES IN THE UNSATURATED ZONE

Liquid petroleum products will partition into various phases when introduced to the subsurface. As mentioned previously, thirteen phases have been identified into which a contaminant can partition (EPA, 1988a). However, liquid contaminants released in the unsaturated zone will exist primarily in three physical phases: residual liquid contaminant, contaminants vapors, and contaminants dissolved in pore water.

TABLE 6. UNWEATHERED COMPOSITION OF THREE COMMON HYDROCARBON PRODUCTS

Selected Representative Concentrations (%w/w) 3 Hydrocarbon #2 Fuel Jet Fuel Representative **Automotive** Group Hydrocarbon Gasoline Oil JP-4 n-Alkanes 10.8 29.6 C4 n-Butane 4.8 7.0 0.12 C5 n-Pentane 4.5 1.06 1.9 C6 n-Hexane 12.9 2.21 2.0 C7 n-Heptane 0.2 2.3 3.67 C8 n-Octane 3.80 1.3 C9 2.25 n-Nonane 0.4 0.8 C10-C14 n-Decane 0.2 0.8 8.73 Branched Alkanes 59.5 18.8 C4 Isobutane 0.7 2.2 0.66 C5 Isopentane 8.6 17.3 C6 2-Methylpentane 4.6 9.7 2.27 C7 2-Methylhexane 8.3 5.48 1.4 C8 8.82 2,4-Dimethylhexane 1.8 16.7 C9 2,2,4-Trimethylhexane 1.2 2.7 3.36 C10-C14 2,2,5,5-Tetramethylhexane 2.6 1.35 0.5 3.2 13.7 Cycloalkanes C5 0.2 C6 Cyclohexane 1.0 3.9 2.40 C7 1.4 3.77 Methylcyclohexane 0.2 1,2,4-Trimethylcyclopentane 0.2 0.7 1.35 C8 7.5 1,1,3-Trimethylcyclohexane 3.21 1.6 Others 5.5 13.5 **Olefins** 0.9 C4 1-Butene C5 1-Pentene 1.3 3.3 8.0 1.8 C6 1-Hexene 2.5 7.5 Others 40.9 19.3 Mono-aromatics 4.4 0.50 0.9 Benzene Benzene 6.5 1.33 Toluene Toluene 4.0 5.6 8.8 0.07 2.32 m-Xylene **Xylenes** Ethyl benzene 1.2 1.4 0.03 0.37 Ethyl benzene 1,3,5-Trimethylbenzene 3.2 11.3 0.67 3.59 C3-benzenes 1,4-Diethylbenzene 2.1 2.6 0.88 3.98 C4-benzenes 1.6 5.2 Others

(Continued)

TABLE 6 (continued)

| TABLE 0 (COMMINGED | , | 1 | 2 | 3 |
|-----------------------------|-----------------------|------------|----------|----------|
| Hydrocarbon | Representative | Automotive | #2 Fuel | Jet Fuel |
| Group | Hydrocarbon | Gasoline | #2 1 doi | JP-4 |
| aroup | | Cacolino | | |
| Phenols | | | | |
| Phenol | Phenol | | 0.001 | |
| C1-phenols | o-Cresol | | 0.01 | |
| C2-phenois | 2,4-Dimethylphenol | | 0.02 | |
| C3-phenois | 2,4,6-Trimethylphenol | | 0.02 | |
| C4-phenols | m-Ethylphenol | | 0.01 | |
| Indanol | Indanol | | 0.001 | |
| indanoi | Illuation | | 0.001 | |
| Poly-aromatics | Fluorene | | 0.57 | |
| Nitro-aromatics | | | | |
| C1-Anilines | | | 0.003 | |
| C2-Anilines | | | 0.004 | |
| Complex Anilines | Quinoline | | 0.002 | |
| Di-aromatics | Naphthalene | 0.7 | 3.43 | 1.59 |
| Carboxylic Acids | Benzoic Acid | 0.7 | 0 | 1.55 |
| • | Bertzoic Acid | | U | |
| Saturated hydro- Carbons | | | | |
| C8 | n-Octane | | 0.05 | |
| C9 | n-Nonane | | 0.20 | |
| C10 | n-Decane | | 0.58 | |
| C11 | n-Undecane | | 0.98 | |
| C12 | n-Dodecane | | 1.14 | |
| C13 | n-Tridecane | | 1.20 | |
| C14 | n-Tetradecane | | 1.31 | |
| C15 | n-Pentadecane | | 1.42 | |
| C16 | n-Hexadecane | | 1.53 | |
| C17 | n-Heptadecane | | 1.51 | |
| C18 | n-Octadecane | | 1.31 | |
| C19 | n-Nonadecane | | 1.16 | |
| C20 | n-Eicosane | | 0.99 | |
| C21 | n-Heneicosane | | 0.51 | |
| C22 | n-Docosane | | 0.29 | |
| C23 | n-Tricosane | | | |
| | | | 0.15 | |
| C24 Pristane | n-Tetracosane | | 0.05 | |
| Phytane | | | 0.52 | |
| Waxes | | | 0.46 | |
| Base Compounds | | | | |
| Unknowns | | 6.6-13.8 | | |
| CHRIOWING | | 0.0-13.0 | | |
| | | | | |

NOTE: Blanks indicate the unavailability of data and do not indicate the absence of a particular compound from the hydrocarbon product.

SOURCES:

Column 1: Hoag et al, 1984; EPA, 1984; Ghassemi et al, 1984.

Column 2: ICF, 1984

Column 3: Smith et al, 1981.

TABLE 7. PHYSICOCHEMICAL PROPERTIES OF FIVE COMMON HYDROCARBON MIXTURES

| PRODUCT | LIQUID DENSITY (g/cm ³) | LIQUID VISCOSITY (cPoise) | WATER SOLUBILITY (mg/L) | VAPOR PRESSURE (mm Hg) | VAPOR DENSITY (g/m ³) |
|-------------------------------|---|---------------------------------|-------------------------------|------------------------------|---|
| Automotive Gasoline | (0.73) 0.72-0.76 [15.6] | (0.45) 0.36-0.49 [15.6] | (158) 131-185 [13-25] | (469) 263-675 [38] | 1950 |
| #2 Fuel Oil | (0.91) 0.87-0.95 | (1.56) 1.15-1.97 [21] | 3.2 | (14.3) 2.12-26.4 [21] | 109 |
| #6 Fuel Oil | (0.91) 0.87-0.95 | (254) 14.5-493.5 [38] | ~5 | (14.3) 2.12-26.4 [21] | 105 |
| Jet Fuel (JF-4) | 0.75 | 0.829 [21] | <300 | 91 | 400 |
| Mineral Base Crankcase Oil | 0.84-0.96 [15] | 275 [38] | insoluble | N/A | N/A |
| Air | | | | 760 | 1200 |
| Saturated Aqueous Vapor | 1 | 1 | | 17.5 | 17.3 |

N/A = Not Available

Note: All values for 20°C unless noted in brackets [].

Note: Values in parentheses are typical of the parameter ().

Note: Values for air and saturated aqueous vapor are included, where applicable, as a means of comparison.

Source: Compiled from various published and unpublished sources.

Table 8. Chemical Properties of Hydrocarbon Constituents

| Chemical Class | Representative Chemical | Liquid Density (g/cm. ³) @ 20°C | Liquid viscosity (cPoise) @ 20 ^o C | Water solubility (mg/L) @ 25 ⁰ C | Pure Vapor Pressure (mm Hg) @ 20°C | Vapor Density (g/m ³) @ 20 ⁰ C | Soil Sorption Constant (Koc) (L/kg) @ 25°C |
|----------------|----------------------------|---|--|--|---|---|---|
| n-Alkanes | | | | | | | |
| C4 | n-Butane | 0.579 | 0.177 | 61.1 | 1560 | 4960 | 250 |
| C5 | n-Pentane | 0.626 | 0.224 | 41.2 | 424 | 1670 | 320 |
| C6 | n-Hexane | 0.659 | 0.306 | 12.5 | 121 | 570 | 600 |
| C7 | n-Heptane | 0.684 | 0.409 | 2.68 | 35.6 | 195 | 1300 |
| C8 | n-Octane | 0.703 | 0.542 | 0.66 | 10.5 | 65.6 | 2600 |
| C9 | n-Nonane | 0.718 | 0.620 | 0.122 | 3.2 | 22.4 | 5800 |
| C10 | n-Decane | 0.730 | 0.740 | 0.022 | 0.95 | 7.4 | 13000 |
| Mono-aromatics | | | | | | | |
| C6 | Benzene | 0.885 | 0.638 | 1780 | 75.2 | 321 | 38 |
| C7 | Toluene | 0.867 | 0.580 | 537 | 21.8 | 110 | 90 |
| C8 | m-Xylene | 0.864 | 0.608 | 162 | 6.16 | 35.8 | 220 |
| C8 | Ethylbenzene | 0.867 | 0.666 | 167 | 7.08 | 41.1 | 210 |
| C9 | 1,3,5-Trimethylbenzene | 0.865 | 0.727 | 72.6 | 1.73 | 11.4 | 390 |
| C10 | 1,4-Diethylbenzene | 0.862 | 0.700 | 15 | 0.697 | 5.12 | 1100 |
| Phenols | | | | | | | |
| Phenol | Phenol | 1.058 | 12.7 | 438 | 0.529 | 2.72 | 110 |
| C1-phenols | m-Cresol | 1.027 | 20.8 | 26175 | 0.15 | 0.89 | 8.4 |
| C2-phenols | 2,4-Dimethylphenol | 0.965 | NA | NA | 0.058 | 0.39 | NA |
| C3-phenois | 2,4,6-Trimethylphenol | NA | NA | NA | 0.012 | 0.09 | NA |
| C4-phenois | m-Ethylphenol | 1.037 | NA | NA | 0.08 | 0.53 | NA |
| Indanol | Indanol | NA | NA | NA | 0.014 | 0.1 | NA |
| Di-aromatics | Naphthalene | 1.025 | NA | 31.7 | 0.053 | 0.37 | 690 |

NOTE: NA - Not availabe SOURCE: Compiled from various published and unpublished sources.

TABLE 9. REFRACTORY INDEX FOR COMMON HYDROCARBONS

RELATIVELY UNDEGRADABLE

| COMPOUND | RATIO |
|---|--|
| Butane Ethane Heptane Hexane Isobutane o-Xylene m-Xylene Ethylbenzene | ≥0 ≥0 ≥0 ≥0 ≥0 ≥0 <0.008 <0.008 <0.009 |
| | |

MODERATELY DEGRADABLE

| Gas oil (cracked) | ~0.02 |
|---------------------|---------|
| Gasolines (various) | ~0.02 |
| Mineral spirits | ~0.02 |
| Nananol | >0.033 |
| Undecanol | <0.04 |
| 1-Hexene | < 0.044 |
| Dodecanoi | 0.097 |

RELATIVELY DEGRADABLE

| p-Xylene | <0.11 |
|---------------------|---------------|
| Toluene | <0.12 |
| Jet fuels (various) | <u>~</u> 0.15 |
| Kerosene | ~0.15 |
| Range oil | <u>~</u> 0.15 |
| Naphthalene | <0.20 |
| Hexanol | <u>~</u> 0.20 |
| Octanol | 0.37 |
| Benzene | < 0.39 |
| Phenol | 0.81 |

Source: Adapted from Lyman et al, 1982

^{*}The refractory index is the ratio of BOD5 to COD

In addition to these three phases, petroleum products also become sorbed to soil particles in the unsaturated zone. This phase is also discussed in the manual, but to a lesser extent than the residual liquid, vapor, and dissolved phases.

The rate and degree of partitioning of the residual liquid into the vapor phase and dissolved phase depend on site-specific and contaminant-specific factors, as well as time. A contaminant's volatility (as measured by vapor pressure) is an indicator of how easily it will move into the air. A contaminant's solubility is a measure of how easily it will dissolve in water (including pore water).

Selecting a soil treatment technology will follow directly from an understanding of the phase in which most of the petroleum is to be found. As discussed in Section 3, certain corrective actions are more effective if most of the contaminants are located in one phase rather than another. The phase(s) in which the contaminants are found also affect the mobility of the contaminants.

Vapor analysis and soil sampling can be undertaken to determine in which phase most of the contamination resides. Typically, soil is analyzed for total hydrocarbon concentration, while soil gas is sampled for evidence of hydrocarbon vapors. General "rules-of-thumb" for determining the phase which contains most of the contamination are presented in Table 10.

TABLE 10. RULES OF THUMB FOR DETERMINING IN WHICH PHASE CONTAMINATION CAN BE FOUND

Evidence of residual liquid contamination:

- High concentrations (>1% by weight) of contaminants in several soil analyses; (i.e., petroleum product makes up >1% of the weight of the soil sample);
- High concentrations (>10% by volume) of pure chemical vapor density in several soil gas analyses (i.e. contaminant vapors are above 100,000 ppm).

Evidence of contaminant vapors:

- Presence of NALP;
- Significant concentrations in several soil gas analyses.

Evidence for pore water contamination:

- Significant concentrations of contaminants in several analyses of pore water or groundwater. Dissolved concentrations for typical petroleum product mixtures will generally be less than 100 mg/L;
- Presence of NAPL and a significant soil moisture content.

In the absence of site-specific sample data, it may still be possible to approximate the likelihood of having contaminants in three phases. Tables 11, 12, and 13 are provided here and may be used for this purpose. These tables provide a way to estimate the general likelihood of contamination being present in various phases by examining the range of values of several parameters. Parameters are grouped by release information, site-specific information, and contaminant-specific information. Each parameter and its importance is discussed below.

Release Information

The amount and rate of release will affect the probability of residual liquid being found in the unsaturated zone. Hydrocarbons will persist as bulk liquid longer for larger releases than for smaller releases, raising the likelihood of residual liquid for large release incidents. Some releases are quick spills with high rates of release while others are leaks where small amounts of product are released over a period of time. A slow rate of release results in conditions more suitable to transfer from residual liquid to other phases. Less residual liquid is likely for a slow leak than for a quick spill of similar volume.

The time since the release may also be important. More recent releases of petroleum would more likely result in a higher proportion of residual liquid being present in the unsaturated zone. The vapor and dissolved phases contain incrementally more of the contaminant mass for older releases. Older releases provide more opportunity for contaminants to volatilize and dissolve over time.

Site-Specific Information

A shallow depth to groundwater can result in more contaminants leaving the unsaturated zone than a site with a thicker unsaturated zone. Thus the greater the depth to groundwater, the greater the likelihood of finding significant amounts of contaminants in the unsaturated zone in all three phases.

A soil's hydraulic conductivity directly affects a contaminant's mobility, or ability to move away from the release site in the NAPL and dissolved phases; soil air conductivity affects the mobility of contaminant vapors. Air and hydraulic conductivity vary from formation to formation in much the same way, with formations of low hydraulic conductivity generally having low air conductivity as well. Low conductivity, either hydraulic or air, indicates a greater probability of finding contaminants in all three phases close to the release site.

A high <u>rainfall</u> infiltration <u>rate</u> can cause contamination to move from one phase to another. Some hydrocarbons will dissolve in the infiltrating rain water, thereby reducing the residual liquid portion of the contamination while increasing the amount of contaminant dissolved in pore water.

TABLE 11. LIKELIHOOD OF LIQUID CONTAMINANTS BEING PRESENT IN THE UNSATURATED ZONE



| FACTOR | UNITS | SITE OF INTEREST | INCREASING LIKELIHOOD | | |
|---------------------------------------|---------|---------------------|------------------------------|---|---|
| RELEASE- RELATED | | | | | |
| • Amount Released | gallons | | Small (<100) | Medium (100-1000) | Large (>1000) |
| • Rate Of Release | | | Slow Release | | Instantaneous Release O |
| • Time Since Release | months | | Long (>12) O | Medium (1 - 12) O | Short (< 1) O |
| SITE - RELATED | | | | | |
| ∙ Depth To Groundwater | meters | | Shallow (< 1) O | Medium (1-5) O | Dеер (>5) О |
| Hydraulic Conductivity | cm/sec | | High (>10 ⁻³) | Medium (10 ⁻⁵ -10 ⁻³) | Low (<10 ⁻⁵) |
| • Rainfall Infiltration Rate | cm/day | | High (>0.1) | Medium (0.05 - 0.1) | Low (<0.05) |
| Soil Temperature | °C | | Warm (>20) O | Medium (10 - 20) O | Cool (<10) O |
| Soil Sorption Capacity (Surface Area) | m²/g | | Low (<0.1) O | Medium (0.1 - 1) O | High (>1) O |
| CONTAMINANT- RELATED | | | | | - · · · · · · · · · · · · · · · · · · · |
| • Liquid Viscosity | сР | | Low (<2) O | Medium (2-20) O | High (>20) O |
| • Liquid Density | g/cm | | High (>2) O | Medium (1-2) O | Low (<1) O |
| Vapor Pressure | mm Hg | | High (>100) O | Medium (10-100) O | Low (<10) O |
| Water Solubility | mg/L | | High (>1000) O | Medium (100-1000) O | Low (<100) O |

TABLE 12. LIKELIHOOD OF CONTAMINANT VAPORS BEING PRESENT IN THE UNSATURATED ZONE



| FACTOR | UNITS | SITE OF INTEREST | INCREAS | NG LIKELIHO | OD |
|---------------------------------------|-------------------|---------------------|-----------------------------|---|-------------------------------|
| RELEASE- RELATED | | | | | |
| • Amount Released | gallons | | Small (<100) | Medium (100-1000) | Large (>1000) |
| | Ü | | 0 | 0 | 0 |
| • Rate Of Release | | | Slow Release | 0 : | instantaneous Release O |
| • Time Since Release | months | | Long (>12) O | Medium (1-12) | Short (< 1) O |
| SITE - RELATED | | | | | |
| ∙ Depth To Groundwater | meters | | Shallow (< 1) O | Medium (1-5) O | Dеер (>5) О |
| Air Conductivity | cm/sec | | High (>10 ⁴) | Medium (10 ⁻⁶ -10 ⁻⁴) | Low (<10 ⁻⁶) |
| • Rainfall Infiltration Rate | cm/day | · | High (>0.1) | Medium (.005-0.1) | O Low (<0.05) |
| • Soil Temperature | °C | | Cool (<10) O | Medium (10 - 20) O | Warm (>20) O |
| Soil Sorption Capacity (Surface Area) | m²/g | | Low (<0.11) O | Medium (0.1 - 1) O | High (>1) O |
| CONTAMINANT- RELATED | . #1 | | | | |
| • Liquid Viscosity | сР | | High (>20) | Medium (2-20) O | Low (<2) O |
| • Liquid Density | g/cm ³ | | High (>2) O | Medium (1-2) O | Low (<1) O |
| • Vapor Pressure | mm Hg | | Low (<10) O | Medium (10-100) O | High (>100) O |
| • Water Solubility | mg/L | | High (>1000) O | Medium (100-1000) O | Low (<100) O |

TABLE 13. LIKELIHOOD OF CONTAMINANTS DISSOLVED IN PORE WATER BEING PRESENT IN THE UNSATURATED ZONE



| FACTOR | UNITS | SITE OF INTEREST | INCREASING LIKELIHOOD | | |
|---------------------------------------|-------------------|---------------------|--------------------------|-------------------------------|----------------------------|
| RELEASE- RELATED | | | | | |
| • Amount Released | gallons | | Small (100) | Medium (100-1000) | Large (>1000) |
| | | | 0 | 0 | 0 |
| • Rate Of Release | | | Instantaneous Release | _ | Slow Release |
| - Mate of Melease | | | 0 | 0 | 0 |
| • Time Since Release | months | | Long (>12) O | Medium (1-12) O | Short (< 1) O |
| SITE - RELATED | | | , | | |
| Depth To Groundwater | meters | | Shallow (< 1) | Medium (1-5) | Deep (>5) |
| Moisture Content | % volume | | Low (<10) | Medium (10-30) | High (>30) |
| | | | 0 | 0 | 0 |
| • Soil Porosity | % volume | | Low (<20) O | Medium (20-40) O | High (>40) O |
| • Rainfall Infiltration Rate | cm/day | | Low (<0.05) | Medium (0.05-0.1) | High (>0.1) |
| Soil Sorption Capacity (Surface Area) | m²/g | | Low (<0.1) O | Medium (0.1-1) O | High (>1) O |
| CONTAMINANT- RELATED | | ; | | | |
| • Liquid Viscosity | сР | | High (>20) O | Medium (2-20) | Low (<2) O |
| • Liquid Density | g/cm ³ | | High (>2) O | Medium (1-2) O | Low (<1) O |
| • Vapor Pressure | mm Hg | | High (<100) O | Medium (10-100) O | Low (>10) O |
| • Water Solubility | mg/L | | Low (<100) O | Medium (100-1000) O | High (>1000) O |

The <u>soil temperature</u> also affects contaminants mobility. A contaminant's vapor pressure, and therefore the ease with which contaminants move into air spaces in soil, increases with increasing temperature. A greater percentage of the total amount of released contaminants is likely to be in the vapor phase in warmers regions or seasons. High soil temperatures also tend to reduce liquid viscosity, increasing ease of movement down through soil to the water table and out of the unsaturated zone. Other site-specific parameters relating to contaminant sorption on soils are described below.

Contaminant-Specific Parameters

A contaminant's vapor pressure and water solubility are indicators as to how easily liquid contaminants will move into air and water. Contaminants with high vapor pressures partition readily into the vapor phase; highly soluble contaminants dissolve readily. In each case, the amount of product remaining as residual liquid is lessened.

Viscosity, which decreases with increasing temperature, influences the mobility and phase partitioning of a contaminant. A highly viscous constituent is likely to remain in the liquid phase (perhaps sorbed to soil) rather than volatilize or dissolve. It will also remain in the unsaturated zone longer than a constituent with lower viscosity. On the other hand, a contaminant with a high liquid density may be more mobile and eventually move to the saturated zone, thus reducing concentration in the unsaturated zone.

The extent to which a contaminant will adhere or sorb to soil particles depends upon the phase it is in (liquid, vapor, or aqueous solution) and a variety of properties inherent to the contaminant. For liquid contaminants, interfacial tension (with water as well as with the soil matter) in conjunction with the pore size openings determines the capillary suction or holding force. For contaminant vapors, vapor pressure (which is primarily a function of the contaminants molecular weight and the soil temperature) is the important factor. The higher the partial pressure of a contaminant in the vapor phase, the greater will be the amount sorbed to the soil. For contaminants in aqueous solution, the soil sorption constant is used as the measure of the equilibrium distribution between sorbed and dissolved fractions of a contaminant. Understandably, the soil sorption constant is inversely proportional to the contaminants water solubility (i.e., the higher the solubility, the lower the degree of sorption). For soils with an organic carbon content (oc) greater than approximately 0.1 percent by weight, sorption from aqueous solution is almost completely controlled by the organic carbon, and the soil sorption constant is found to be proportional to the contaminant's octanol-water partition coefficient (Kow) (i.e., higher values of organic carbon or K lead to higher degrees of sorption). For soils with less than 0.1 percent organic carbon, the surface area of the soil often becomes the primary soil property affecting the degree of sorption from solution.

Tables 11, 12, and 13 are most useful when all the parameters are known; however, it is not necessary to know the value of every parameter to use the tables. In some cases, two parameters address similar

physical properties and can serve as substitutes for one another. For example, knowing that the rainfall infiltration rate is extremely low would make the water solubility less important in determining which phase predominates.

EVALUATING CONTAMINANT MOBILITY

The final step in a site assessment focuses on the mobility of the contaminants, both through the unsaturated zone and between phases. Many in-situ corrective actions depend on mobilizing contaminants (i.e., moving contaminants from one phase to another that can be more directly removed with a given treatment technology). For example, soil venting works to both transport vapor phase contaminants through the air spaces in the soil and transfer contaminants from the residual liquid and dissolved phases to the vapor phase. As clean (non-contaminated) air replaces the contaminant-saturated vapors that are removed, contaminants remaining as residual liquid will volatilize into the fresh air, seeking to re-establish equilibrium. As the process continues, more and more contaminant is mobilized from the residual liquid or dissolved phases into the vapor phase, where it can be captured by the soil venting system.

Different soil treatment technologies have different time frames for mobilization and for treatment, but all four in-situ technologies described in this report depend to some degree on the ability to mobilize the contaminants: venting will be successful if substantial amounts of vapor can be drawn through the soil; flushing and bioremediation both must move liquids through the unsaturated zone to reach the contaminants to be effective; and hydraulic methods are successful only if the contaminants can flow to the drain. Contaminant mobility is not important for excavation.

It is necessary to discuss the mobility of contaminants in the subsurface separately for each phase. The factors that control transport differ for each phase, as discussed below.

Residual Liquid Contaminant

The movement of bulk liquids in the unsaturated zone is dominated by three forces: gravity; pressure gradients; and capillary suction. Gravity exerts a direct, downward force, the magnitude of which depends only on the density of the contaminant. Pressure gradients generally result from infiltrating liquid (precipitation and contaminants), and most often act in the same direction as gravity. Capillary suction depends on the soil characteristics and the forces it generates act in all direction, although not equally.

In addition to these three major forces, other physical, chemical, and environmental factors can influence a liquid's mobility in the unsaturated zone (see Table 14). In Table 14, items are listed with both qualitative descriptors (high, medium and low), and corresponding quantitative ranges of values. Although the quantified ranges are somewhat subjective, they have been arranged so that the right-hand column indicates "high mobility" and the left-hand column "low mobility."

TABLE 14. FACTORS TO EVALUATE THE MOBILITY OF LIQUID CONTAMINANTS



| FACTOR | UNITS | SITE OF INTEREST | INCREASING MOBILITY | | |
|------------------------|-------------------|---------------------|-----------------------------|--|---|
| RELEASE RELATED | | | | | |
| • Time Since Release | Months | | Long (>12) | Medium (1-12) | Short (<1) |
| SITE - RELATED | <u> </u> | | 00 | 0 | 0 |
| Hydraulic Conductivity | cm/sec | | Low (<10 ⁻⁵) | Medium (10 ⁻⁵ - 10 ⁻³) | High (> 10 ⁻³) O |
| • Soil Porosity | % Soil Volume | | Low (<10) O | Medium (10-30) | High (> 30) O |
| Soil Surface Area | m² /g | | High (>1) O | Medium (0.1-1) O | Low (< 0.1) |
| Soil Temperature | ීර | | Low (<10) O | Medium (10-20) O | High (> 20) O |
| • Rock Fractures | _ | | Absent O | - 0 | Present O |
| Moisture Content | % Volume | | High (>30) O | Medium (10-30) O | Low (< 10) O |
| CONTAMINANT- RELATED | | | | | |
| • Liquid Viscosity | cPoise | | High (>20) O | Medium (2-20) O | Low (<2) O |
| • Liquid Density | g/cm ³ | | Low (<1) O | Medium (1-2) O | High (>2) O |

The site-related factors in Table 14 can vary with depth below the ground surface, particularly for hydraulic conductivity, soil porosity, and soil surface area. Often subsurface materials are deposited in layers, with each layer having different characteristics. For a preliminary site assessment, accurate data on the vertical soil profile may not be available and a best estimate of typical conditions throughout the unsaturated zone must suffice. If profile data are available, Table 14 can be completed for each distinct soil layer in the unsaturated zone using the appropriate soil-related data.

Using Table 14 to evaluate conditions at a site of interest, it is possible to get an understanding of the relative mobility of liquid contaminants at that site. If the preponderance of factors at a site fall in the right-hand column of Table 14, liquid contaminants would likely be more mobile and likely to migrate than if most factors matched those in the left-hand column. Where site-specific values are unavailable, default values can be used from the tables previously provided in this section.

One factor not listed in Table 14, yet likely to have an effect on liquid mobility, is whether the soil is "water-wet" or "oil-wet." This factor was not included because data are hard to find. Nonetheless, the reader should be aware of the following issues: "water-wet" soil describes the conditions where water preferentially coats the soil particles, effectively forming a barrier between the petroleum product and the soil particles. In this case, the contaminant viscosity and the interfacial tensions (IFTs) between the contaminant and water will control mobility. In "oil-wet" soils, where oil directly coats the soil particles, transport depends on the viscosity and the IFTs between the hydrocarbon and the soil. Because soil-hydrocarbon IFTs are stronger than soil-water IFTs, "oil-wet" scenarios often result in lower contaminant mobility.

Contaminant Vapors

Vapors are generally mobile in the unsaturated zone. The degree of mobility greatly depends on the air-filled porosity of the soil (the total porosity less that portion filled by water or liquid contaminants). Several other factors also influence vapor transport in the unsaturated zone as listed in Table 15.

Contaminants vapors may be mobilized (and subsequently removed) by several natural or induced processes or forces. These include:

- Bulk transport due to <u>pressure gradients</u> (e.g., gradients induced by vacuum extraction wells or by natural changes in barometric pressure);
- Bulk transport due to vapor density gradients (which could result, for example, if the contaminant vapor has a significantly different density than the soil air due to differences in molecular weight or temperature);

TABLE 15. FACTORS TO EVALUATE THE MOBILITY OF CONTAMINANT VAPORS



| FACTOR | UNITS | SITE OF INTEREST | INCREASING MOBILITY | | | |
|-----------------------|------------------|---------------------|-----------------------------------|-------------------------|-----------------------------|--|
| SITE - RELATED | | | | <u>.</u> | en enga ngang | |
| • Air Filled Porosity | % Volume | | Low (<10) O | Medium (10- 30) O | High (> 30) O | |
| - Total Porosity * | % Volume | | Lo w (<10) O | Medium (10- 30) O | High (> 30) O | |
| • Water Content * | % Volume | | High (> 30) | Medium (10- 30) | Low (< 10) | |
| Depth Below Surface | meters | | Deep (>10) O | Medium (2 - 10) O | Shallow (< 2) O | |
| CONTAMINANT- RELATED | | | | | | |
| • Vapor Density | g/m ³ | | Low (< 50) O | Medium (50-500) | High (>500) O | |

^{*} the total porosity less that fraction filled with water equals the air filled porosity

- In-situ generation of gases or vapors (e.g., vapors volatilizing from liquid contaminants or gases generated by microbial biodegradation of contaminants that force movement of vapors through the soil);
- Molecular diffusion due to concentration gradients.

The current scientific understanding of these process spans the range from well-documented to rudimentary and hypothetical. Molecular diffusion is perhaps, the best understood and the easiest to address experimentally and, hence, empirically. However, in some circumstances it may not be the most important process governing vapor mobility.

A soil with medium to high water-filled porosity will tend to retard vapor movement because of reduced air-filled porosity (less flow area) and because of absorption (dissolution) of vapors into the pore water. However, if one applies a vacuum extraction system — inducing soil gas flow — the soil will tend to dry out and this will increase vapor mobility over the treatment period.

Vapor density differences will be important only when liquid contaminant of sufficient volatility is present. For example, the density of air saturated with gasoline vapors (i.e, in contact with liquid gasoline) is about 1,950 g/m3 at 20°C; moist air has a density of about 1,200 g/m3 at 20°C. In the absence of other driving forces, heavier (contaminant containing) vapors should tend to migrate downward in the unsaturated zone. The driving force (density difference) will diminish as the vapors become more diluted (i.e., less dense).

Contaminants Dissolved in Pore Water

Table 16 lists factors that can help determine the relative mobility of contaminants dissolved in pore water in the unsaturated zone. In general, dissolved contaminants move with the pore water in which they are dissolved. The mobility of the pore water itself is dominated by the same factors that govern mobility of residual liquid contaminants: gradients, gravity, and capillary suction. As noted previously, contaminants dissolved in flowing pore water may be retarded (relative to the average water velocity) due to sorption on soil particles. The extent of sorption will increase with decreasing water solubility of the contaminant, and with increasing organic carbon content and/or surface area of the soil.

As with Table 14, the site-related factors in Table 16 may vary with depth. If information about the soil profile is available, Table 16 can be completed for each distinct soil group. Otherwise, a best estimate of actual conditions must be made to complete the preliminary assessment.

TABLE 16. FACTORS TO EVALUATE THE MOBILITY OF CONTAMINANTS IN PORE WATER



| FACTOR | UNITS | SITE OF INTEREST | INCREASING MOBILITY | | |
|------------------------------|----------|---------------------|----------------------------|--|-------------------------------|
| SITE RELATED | | | | | |
| · Hydraulic Conductivity | cm/sec. | | Low (10 ⁻⁵) | Medium (10 ⁻⁵ - 10 ⁻³) | High (> 10 ⁻³) |
| Moisture Content | % Volume | | Low (< 10) O | Medium (10 -30) O | High (> 30) O |
| • Rainfall Infiltration Rate | cm/day | | Low (< 0.05) | Medium (0.05-0.1) | High (>0.1) O |
| • Soil Porosity | % Volume | | Low (< 10) O | Medium (10 - 30) O | High (> 30) O |
| • Rock Fractures | _ | | Absent O | 10 | Present O |
| Depth Below Surface | meters | | Shallow (< 2) O | Medium (2 - 10) O | Deep (> 10) O |
| CONTAMINANT- RELATED |) | | | | |
| Water Solubility | mg/L | | Low (< 100) O | Medium (100 to 1000) O | High (>1000) O |

SECTION 3

TECHNOLOGY SELECTION

INTRODUCTION

This section describes five technologies used to remediate UST sites: soil venting (including vacuum extraction); biorestoration; soil flushing; hydraulic barriers; and excavation. The first four are in situ treatment methods, performed with the contaminated soil remaining in place. Alternatively, contaminated soil can be excavated. Excavated soil may be treated above ground, either on-site or at another location, or it may be landfilled without treatment. Above ground soil treatments include incineration, thermal stripping and other enhanced volatilization methods, soil washing, and biorestoration.

From an environmental viewpoint, in situ treatment is often preferred over excavation, but excavation is commonly employed because it can be implemented quickly, has been used widely, and also can present to a concerned public a timely response to the situation. Excavation, however, may not be desirable where large volumes of soil are contaminated or where excavation of the contaminated soil could undermine the foundations of existing structures. Bringing excavated soils to the surface is often accompanied by uncontrolled release of contaminant vapors. In situ methods afford a greater degree of control of these vapors.

Each of the five technologies is described herein and factors critical to the success of each are presented. These critical success factors (CSFs) are parameters that influence the likelihood of success of a particular method. For example, high contaminant volatility is a critical success factor for soil venting. These CSFs can be used to assess the likely effectiveness of each technology at a particular site. Finally, other advantages and disadvantages of each technology are discussed.

A worksheet has been provided for each soil treatment technology to help the user assess the likely success of the technology at a particular site. The CSFs important for that technology are listed. When completed, these worksheets provide insight as to which technologies are likely to be effective, and more importantly, which are not. The three right-hand columns of each worksheet provide ranges of values for the CSFs that suggest whether a technology is "less likely," "somewhat likely," or "more likely" to be effective. A column is provided for the user to write down the values for the CSFs at the site of interest. For each CSF, the user determines into which of the three "likelihood" ranges the site falls. most of the CSFs fall into the "less likely" column, another technology may be better suited to cleaning up the site. If the CSFs are fairly evenly distributed among the three columns, other factors can be considered that can help in the assessment (i.e., can a parameter be enhanced to increase the likelihood of success?). A more detailed example of how these worksheets are used is provided in the sample problem in the Appendix.

SOIL VENTING

Soil venting is a general term that refers to any technique that removes contaminant vapors from the unsaturated zone. Venting may be passive (with no energy input) or active. Passive venting, which is often used at sanitary landfills for methane gas removal, consists of perforated pipes sunk into the contaminated area that provide an easy path to the atmosphere. These vents sometimes have a wind-driven turbine at the outlet to provide a slight draft.

Active venting uses an induced pressure gradient to move vapors through the soil and is more effective than passive venting. Most common is vacuum extraction technology, where extraction wells are placed near the release site and a vacuum applied to the wells. Figure 5 shows such a system. The soil gas is drawn through the soil to the extraction well and brought to the surface. Positive-pressure injection wells may be employed to increase the removal rate. The use of plastic sheeting or other similar impervious layers at the ground surface may be required to avoid short circuiting of air flow.

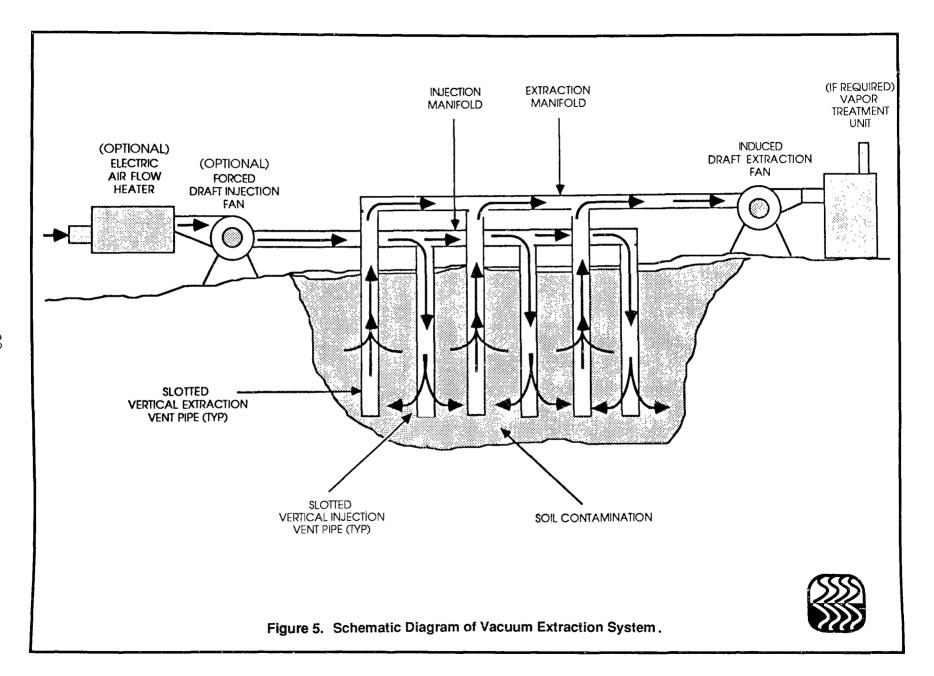
The contaminant-saturated vapors that are removed from the unsaturated zone may require treatment prior to discharge to the atmosphere, depending on local air-discharge restrictions. Granular activated carbon (GAC) can be used to capture contaminants prior to discharge; catalytic combustion is also used. One recent proposal involves passing the vapors through an acclimated biofilter bed, where the contaminant vapors are biodegraded (CDM, 1988).

Theoretical Factors

Venting removes vapor-phase contaminants from the unsaturated zone. As discussed in Section 2, contaminants exist primarily in three phases in the unsaturated zone: vapor; liquid; or dissolved in pore water. Venting is most effective on contaminants that exist predominantly in the vapor phase, or are easily volatilized.

Venting removes contaminant vapors trapped in soil air spaces, but also affects, to a limited extent, residual liquid contaminant and dissolved contaminants. Hydrocarbons typically are found in all three phases, and an equilibrium is established, with a certain fraction existing in each phase. The portion found in each phase depends on both the particular compound and the local conditions. If conditions change, the equilibrium will shift, and contaminants will transfer between phases until equilibrium is re-established.

For example, the removal of contaminant-saturated air by vacuum extraction causes an equilibrium shift. As clean (non-contaminated) air replaces the contaminant-saturated vapor that is removed, contaminants remaining as a residual liquid contaminant and those dissolved in pore water will volatilize into the fresh air, seeking to re-establish equilibrium. As this process continues, more and more of the liquid and dissolved contaminants will volatilize and be removed, eventually leading to a decrease in the overall in situ contaminant concentration. Vacuum



extraction is sometimes known as "in situ stripping" due to the similarity of the governing processes of vacuum extraction to those that govern air stripping.

The success of a vacuum extraction program depends both on the properties of the contaminants and the properties of the soil. Of particular importance are three equilibrium relationships: 1) the contaminant—air equilibrium, described by the contaminant's partial vapor pressure; 2) the equilibrium between contaminant dissolved in pore water and the soil vapor, described by the contaminant's Henry's law constant; and 3) the equilibrium between the contaminant dissolved in pore water and contaminant adsorbed to soil particles, described by the soil—sorption constant (K_{ac}).

Table 17 lists CSFs for soil venting. Among the most important are contaminant vapor pressure and soil—sorption capacity. As the table shows, compounds with high vapor pressures are "more likely" to be removed by vacuum extraction than those with low vapor pressure. Course materials, such as sand and gravel, which have low soil sorption coefficients (i.e. surface area), are also "more likely" to be amenable to vacuum extraction than fine—grained materials like clay or silt. Each of the remaining CSFs can be evaluated similarly to provide a preliminary screening of the suitability of soil venting at the site of interest.

The water solubility of each contaminant will also affect the success of venting, although this factor is relatively less important than those listed above. Highly soluble compounds may tend to exist predominantly dissolved in pore water, with less in the vapor phase. Vacuum extraction tends to dry out the soil, however, and over time dissolved contaminants will likely volatilize and be removed.

Soil properties also greatly influence the success of soil venting. Air conductivity is an important parameter to consider in soil venting. Soils with low air conductivity, such as clay, restrict the movement of vapors through the soil and towards wells. Contaminants can still be removed from soils with low air conductivity by soil venting, but the process requires more closely spaced wells or a greater vacuum. Increasing the vacuum creates a greater pressure gradient through the soil formation, increasing the rate of movement of contaminated vapors through the air spaces in the soil. By increasing the number of wells per unit area, the average distance contaminant vapors must travel to be captured by the system is decreased, thereby increasing the productivity of the system.

Most soils have preferential flow paths that are responsible for much of the soil's permeability. These flow paths result from things such as root intrusions, shrinking/swelling, wetting/drying, and uneven settling of the formation. They can prevent the vapors from coming into intimate contact with all of the contaminated soil, thus decreasing the effectiveness of the technique.

Other important properties include soil temperature and moisture content. The ambient temperature of the soil has a strong effect on the volatility of the contaminant. As temperature rises, vapor pressure and Henry's constant rise dramatically; Munz and Roberts (1987) report that for

TABLE 17 WORKSHEET FOR EVALUATING THE FEASIBILITY OF SOIL VENTING BEING EFFECTIVE AT YOUR SITE



| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
|---|----------|---------------------|-----------------------------------|---|------------------------------------|
| SITE RELATED | | | | | |
| Dominant Contaminant Phase | Phase | | Sorbed to soil | Liquid O | Vapor O |
| Soil Temperature | °C | | Low (< 10) O | Medium (10 - 20) | High (> 20) |
| • Soil Air Conductivity | cm/sec. | | Low (< 10 ⁻⁶) O | Medium (10 ⁻⁶ -10 ⁻⁴) O | High (> 10 ⁻⁴) O |
| • Moisture Content | % volume | | Moist (> 30) | Moderate (10 - 30) O | Dry (< 10) O |
| Geological Conditions | | | Heterogeneous O | 0 | Homogeneous O |
| Soil Sorption Capacity Surface Area | 2 m/g | | High (> 1) O | _ 0 | Low (< 0.1) O |
| • Depth to Ground Water | meters | | Low (<1) O | Medium (1-5) O | High (>5) O |
| CONTAMINANT- RELATED | | | | | |
| Vapor Pressure | mm Hg | | Low (< 10) O | Medium (10 to 100) O | High (> 100) O |
| • Water Solubility | mg/L | | High (> 1000) O | Medium (100 - 1000) O | Low (< 100) O |

OTHER CONSIDERATIONS

- Cost is from \$15 to \$60 per cubic yard.
- · Effictiveness decreases after several months of treatment.
- Capable of removing thousands of gallons.
- · Air emissions will likely need to be treated with GAC.
- · Treatment can be done on-site
- Care must be taken to avoid explosions because vapors are concentrated
- Cleanup takes time so that this technology is not appropriate when emergency response is needed

each rise of 10°C in temperature, Henry's constants increase by a factor of 1.6. While higher temperatures increase contaminant volatility, higher temperatures lower the air conductivity of the soil. However, the effects of temperature on volatility far outweigh its effect on air conductivity, and soil venting would be expected to be more successful in areas where soil temperature is high. In some cases, air is heated prior to injection to raise subsurface temperatures and increase volatilization. Figure 3 shows groundwater temperatures for the continental United States. Values from this table can be used as surrogate values for soil temperature.

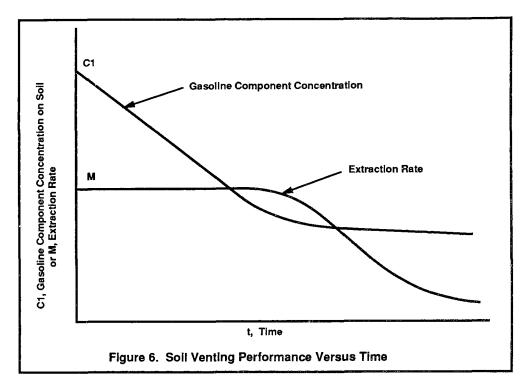
The moisture content has two effects on the soil. First, because soil with a high water content has relatively less air-filled porosity, higher water content leads to a lower air conductivity and therefore a lower removal rate. Second, pore water can absorb (dissolve) contaminants from the vapor phase, which serves to retard the removal of contaminant vapors. This is especially true of contaminants with low vapor pressures and low Henry's constants. Dry soil is thus better suited to in situ stripping than wet soil. The vacuum extraction process tends to dry out the soil; over time the air conductivity will increase and the dissolved contaminants will volatilize, both of which tend to increase the degree of removal.

Other Factors

Cost. In general, soil venting is a relatively inexpensive technique compared to other alternatives, especially when large volumes of soil must be treated. The capital costs of venting consist basically of the extraction and monitoring well construction, one or more centrifugal blowers and housing, pipes, valves, fittings, and other hardware, and electrical instrumentation. Operations and maintenance costs consist of labor, power, maintenance, and monitoring. Venting wells constructed of two-inch diameter slotted PVC pipe cost approximately \$20 per linear foot (0.3 m) for a 20-foot depth. Vacuum pump sizing depends on local soil conditions and the volume to be treated. A pump capable of removing 40-50 cubic feet (1.2 to 1.8 cubic meters) per minute (CFM) at 1.5 inches (3.8 cm) of water ranges in price from \$500-\$2000; larger pumps may cost up to \$4,000. Operating costs vary depending on time operation and local utility rates. One EPA study (1987d) reported the actual costs of soil venting at a Florida site to be \$106,000 (capital) and \$68,000 (annual O&M). Air treatment, if necessary, would have more than doubled costs. These figures correspond to roughly \$20 to \$60/yd³ (\$25 to \$78/m³). Other costs reported in the literature range from \$15-20/yd³ (\$20 to 26/m³), exclusive of air emission control (Anastos et al., 1986). Air emission control via GAC is usually assumed to double the total capital cost of the cleanup.

Time Scale. Soil venting programs are relatively easy to implement, and may be installed and started in two to four weeks. This time is devoted to determining the extent of contamination, designing the system, acquiring pumps and piping, and installing the equipment.

A venting program is typically operated for six to twelve months. The removal rate is usually highest at the beginning of the program (once the vacuum is established) and falls off after the most volatile contaminants are removed (see Figure 6). Volatilization from dissolved and sorbed contaminants then becomes rate-limiting, and the system's effectiveness may decline dramatically.



The following figures for total hydrocarbon removal versus time were reported in one study (EPA, 1987d):

| DAYS SINCE. | TOTAL POUNDS OF HYDROCARBON | DAYS SINCE | TOTAL POUNDS OF HYDROCARBON |
|-------------|--------------------------------|------------|-----------------------------|
| START | EXTRACTED | START | EXTRACTED |
| 1 | 182 | 66 | 18,996 |
| 3 | 2,880 | 97 | 21,229 |
| 10 | 8,728 | 123 | 22,050 |
| 33 | 16,402 | | |

These data show that the amount of recovered petroleum product decreases dramatically following several months of operation.

"Pulsed venting" may result in better removal at lower cost. This method refers to periodic shutdown of the vacuum system. During this time, contaminant vapor concentrations increase as equilibrium is re-established. Resumption of the vacuum extraction system following this shutdown will then remove this vapor more efficiently. However, it should be noted that the total length of time needed to remove the contaminant with pulsed venting may be longer.

BIORESTORATION

In situ biorestoration of the unsaturated zone is a process where oxygen and nutrients are added to contaminated soil to promote the breakdown of contaminants by naturally occurring microorganisms (usually bacteria). In some cases, specially acclimated, commercially available, bacteria may also be introduced to the subsurface, but this is not a common procedure. Bacteria capable of biodegrading petroleum hydrocarbons are

commonly found in subsurface soils. Natural breakdown of petroleum hydrocarbons is likely to occur whenever they are introduced to the subsurface, but without the addition of nutrients and oxygen biodegradation occurs very slowly.

Many Superfund cleanups have used biorestoration for cleanup, and this technique is now being used at UST sites. The effectiveness in removing hydrocarbons to low levels is site-specific, and some situations are not suitable for this technique. When applicable, biorestoration is often a cost-effective alternative to other treatment schemes and has the added advantage of transforming organic pollutants to less toxic end products rather than transferring them to another phase.

Biodegradation of hydrocarbons can occur aerobically (in the presence of oxygen) or anaerobically (without oxygen). Experimental data indicate that aerobic processes are far more effective than anaerobic processes, but recent a recent study (Major et al, 1988) suggests that the effectiveness of anaerobic biodegradation may approach that of aerobic processes under the right conditions. However, the focus of this manual is on the more well documented aerobic processes.

For a successful biorestoration program, an adequate supply of oxygen and nutrients must be available to the bacteria throughout the zone of contamination. This is usually accomplished by adding nutrient—enhanced water to the unsaturated zone through infiltration basins at the ground surface or through recharge wells. The water used to transport the nutrients can also work to dissolve sorbed contaminants and transport them to the water table. If the groundwater below the site has already undergone treatment, the contaminants and nutrients could recontaminate the groundwater if not properly contained. A pumping well can be installed to control local groundwater flow and recirculate water to the unsaturated zone. To increase efficiency, biorestoration of the unsaturated zone can be implemented in conjunction with treatment of groundwater. Biorestoration and air stripping are two groundwater treatment methods compatible with biorestoration of the unsaturated zone.

Although the biorestoration method described here is in situ above-ground equipment is required. At a minimum, an above-ground mixing tank is required to add nutrients and oxygen to the water being introduced to the unsaturated zone. The tank is also used as temporary storage of recirculated water, where additional bacteria can be grown and the organic content of the water can be reduced. Care must be taken when introducing nutrient laden water to the subsurface so that none of the treated water escapes the capture zone of the recovery well. Figure 7 shows a typical biorestoration system.

Theoretical Considerations

The careful addition of nutrients like oxygen, nitrogen and phosphorous can improve conditions for the biological breakdown of petroleum constituents to simple, non-toxic end products. What to add and how much is difficult to predict because of the many factors that influence the biodegradation process. To increase the likelihood of a successful biorestoration program at a particular site, pilot studies using samples collected at the site should be conducted to determine the appropriate nutrient additives and the required application rate.

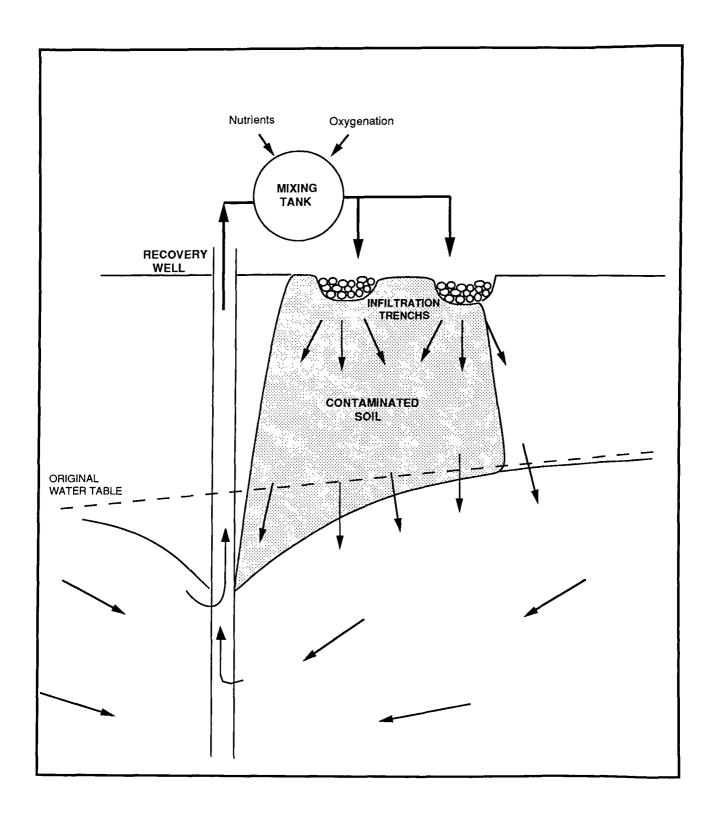


Figure 7. Schematic Diagram of a Biorestoration System for the Unsaturated Zone

Three general mechanisms are used by microbes to catabolize (break down to simpler substances) hydrocarbons: 1) aerobic respiration; 2) anaerobic respiration; and 3) fermentation (EPA, 1986). Aerobic respiration is typically the most rapid and most complete degradation process, and avoids the problematic end products (e.g., hydrogen sulfide) that result from anaerobic respiration. Petroleum hydrocarbons are composed of hydrogen and carbon and, under ideal conditions, the end products of (aerobic) biodegradation are carbon dioxide, water, and biomass. Under less than ideal conditions (i.e., inadequate oxygen supply, lack of nutrients, etc.), less complete degradation may take place resulting in only partial breakdown of the hydrocarbons. If conditions can be enhanced, more complete biodegradation can take place. The fact that biodegradation can transform a contaminant to a non-toxic or less-toxic end product is a major advantage this technique holds over other cleanup methods. The other techniques serve only to concentrate, disperse, or relocate the contaminants, and further treatment or handling is usually required.

Naturally occurring soil microorganisms are capable of degrading many chemicals compounds, including many petroleum constituents. More than 200 different soil microbes have been identified as being capable of assimilating petroleum (EPA, 1988c). Although it is not possible to predict with certainty whether a certain compound will be degraded at a specific site, the refractory index (RI) indicates a compound's susceptibility to degradation. The RI, a ratio of the BOD₅ (5-day biochemical oxygen demand) to the COD (chemical oxygen demand), predicts the likelihood of biodegradation for a compound (Lyman et al., 1982). For gasoline constituents, phenol, benzene, and toluene are all ranked as "relatively degradable" (see Table 9). In general, petroleum hydrocarbons are degradable in most natural settings.

The factors affecting the appropriateness and potential effectiveness of biorestoration for a particular site may be divided into three broad classes: 1) the susceptibility of the contaminants to biodegradation; 2) the various environmental factors at the site; and 3) the site hydrogeology. The biodegradability of the contaminants, discussed above, is the primary factor influencing the choice of biorestoration; situations where the contaminants of concern are relatively undegradable would not be appropriate for this treatment. Fortunately, many petroleum products are relatively degradable.

There are many site-specific environmental factors that affect the feasibility of biorestoration as a treatment alternative (EPA, 1985). These factors include, among others:

- available oxygen concentration
- appropriate levels of macronutrients, and micronutrients
- redox potential
- soil pH
- degree of water saturation
- soil temperature
- competition, predators, presence of toxins
- concentration of contaminants
- hydraulic conductivity of soil

The oxygen concentration is the single most important ingredient in a successful biorestoration program. Although biodegradation may continue to occur anaerobically, the lack of oxygen severely limits the rate of cleanup. Oxygen may be introduced to the subsurface in several ways. Air sparging pumps air (and oxygen) through slotted wells into the unsaturated zone. Hydrogen peroxide can be introduced through recharge wells or infiltration trenches and can result in available oxygen levels of up to 250-400 mg/L in the groundwater, compared to about 10 mg/L of oxygen by air sparging (Raymond, 1987). Conner (1988) reported that a vacuum extraction system resulted in increased microbial activity. In addition to oxygen, soil microbes also require macronutrients (nitrogen and phosphorous) and micronutrients to survive and prosper. These nutrients are typically added in order to facilitate biodegradation.

Soil moisture content and contaminant solubility in water are also important factors because the most rapid biodegradation occurs in the dissolved contaminant phase. Biodegradation is usually limited by the solubility of a compound in water, as most microorganisms either inhabit soil moisture or need moisture to acquire nutrients and avoid desiccation (EPRI, 1988). Moisture content between 50 and 80 percent of the water holding capacity is considered optimal (Bossert and Bertha, 1984). Soils with moisture content in this range promote adequate dissolution of contaminants and contain sufficient air voids to supply oxygen. However, the addition of aerated water to the soils reduces the need to maintain air voids in the soil.

Although most biodegradation takes place in the dissolved phase, sorbed contaminants are also biodegraded but at a much slower rate. Microbes inhabiting pore water can serve to partially breakdown sorbed compounds, increasing their likelihood of dissolution. Once dissolved, the compounds can be more readily biodegraded.

The concentration of contaminant dissolved in water affects biodegradation. If too low, bacteria may favor another competing food source; if too high, the contaminant may be toxic to the bacterial population. Aerobic bacteria are typically used for organic concentrations between 50 and 4,000 mg/L (Nyer, 1985). For in situ treatment, organic concentrations as low as 10 mg/L may be sufficient. Dissolved petroleum hydrocarbons are unlikely to be found at concentrations as high as 4,000 mg/L.

Slightly alkaline soil pH is optimal for biodegradation, but anything in the range of 6.0-8.0 is considered acceptable. Most soils are slightly acidic and neutralization may be required at some sites. The temperature of the soil environment will also affect the rate of degradation. Warmer temperatures generally result in higher rates of degradation. While biodegradation has been shown to occur over a wide temperature range, the range of 20°-35°C seems optimal but is typically above the normal subsurface temperature range. Also, microbes generally have a low tolerance for severe temperature changes as are experienced in northern regions.

A knowledge of the hydraulic conductivity of the soil, and the site hydrogeology in general, is also important in assessing the feasibility of biorestoration for a particular site. Even when all other factors are positive, in situ biorestoration will not be successful if a low hydraulic conductivity prevents the added nutrients and oxygen from contacting the zone of contamination. The residence time should be short enough so that the oxygen concentration is sufficient throughout the site for microbes to degrade all of the organic compounds. Also, the geochemistry of the subsurface could inhibit adequate mixing if reactions (such as metal oxide precipitation) clog the soil. The soil microbes themselves may clog the soil and decrease the hydraulic conductivity.

Table 18 lists the critical success factors for biorestoration. By comparing the parameters at the site of interest to those in this table, a general understanding can be obtained of the suitability of biorestoration at that site. A preponderance of CSFs that match the rightmost column would indicate that biorestoration is likely to be effective at that site.

Other Factors

Cost. The costs of biorestoration for the unsaturated zone vary widely and are difficult to quantify and compare. Also, most reported costs refer to cleaning up groundwater rather than the unsaturated zone. One estimate (Olsen et al., 1986) gave costs of \$60 to \$123 per cubic yard (\$78 to \$160 per cubic meter). Unit costs for larger volumes are generally lower due to economies of scale.

Time Scale. A biorestoration program can be set up relatively quickly, but it may take several weeks to several months for the microbes to become adjusted and start significant degradation if the contaminant release is recent, or if non-indigenous bacteria are used. The system may need to be "fine-tuned" (i.e., varying the levels of oxygen and nutrients added) to operate efficiently. The start of a biorestoration program may be delayed due to the drilling of injection and extraction wells, the design and procurement of construction of the oxygenation equipment, and the need for injection permits.

It is difficult to estimate the length of time it will take to clean up a particular site with biorestoration or even obtain accurate measurements to determine the degree of contaminant removal once remediation has begun. Studies show that the length of cleanup is generally six months to two years, although some sites may take more or less time. As with other methods, the removal rate typically will decrease with time, assuming the contaminant concentration decreases over time.

Other Advantages/Disadvantages. This method has several other, non-scientific factors that may influence the use of this technology at UST release sites:

of the technologies discussed in the manual, in situ biorestoration is the least-understood. Although much research has been performed in recent years, the specific mechanisms, kinetics, and pathways by which compounds are degraded are not well-understood. The data base on many contaminants, such as gasoline constituents, remains

TABLE 18. WORKSHEET FOR EVALUATING THE FEASIBILITY OF BIORESTORATION BEING EFFECTIVE AT YOUR SITE



| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
|---------------------------------------|---------------|---------------------|----------------------------------|--|------------------------------------|
| RELEASE - RELATED | | | | | |
| • Time Since Release | Months | | Short (< 1) O | Medium (1 - 12) O | Long (> 12) O |
| SITE RELATED | | | | | |
| Dominant Contaminant Phase | Phase | | Liquid O | Vapor O | Dissolved O |
| Soil Temperature | °C | | Low (< 5) O | Medium (5 - 10) O | High (> 10) O |
| Soil Hydraulic Conductivity | cm/sec. | | Low (<10 ⁻⁵) O | Medium (10 ⁻⁵ -10 ⁻³) O | High (> 10 ⁻³) O |
| • Soil pH | pH Units | | (< 6 or > 8) | _ | (6 - 8) |
| | | | 0 | 0 | 0 |
| Molsture Content | % Volume | | Dry (< 10) O | Moderate (10 to 30) | Moist (> 30) O |
| CONTAMINANT- RELATED | | | | | |
| • Solubility | mg/L | | Low (< 100) O | Medium (100 to 1000) | High (> 1000) |
| Biodegradability Refractory Index | Dìmensionless | | Low (< 0.01) | Medium (0.01 to 0.1) | High (> 0.1) |
| • Fuel Type | | | No. 6 Fuel Oil (Heavy) | No. 2 Fuel Oil (Medium) | Gasoline/ Diesel (Light) |

OTHER CONSIDERATIONS

- Cost is from \$60 to \$125 per cubic yard.
- Completely destroys contaminants under optimal conditions
- Effectiveness varies depending on subsurface conditions
- Biologic systems subject to upset
- · Public opinion sometimes against putting more chemicals in ground
- · Difficult to monitor effectiveness
- · Minimizes health risk by keeping contaminants in ground and on site
- Takes long time to work-not for emergency response

weak. One problem is that soil hydraulic conductivity may be reduced at high growth rates of bacteria (microorganisms), inhibiting further progress. Research continues on many of these topics.

- The difficulty in measuring the degree of removal reinforces fears that contamination is not being removed. When soil venting is used, for example, it is possible to quantify pounds of contaminant extracted very easily; judging biorestoration's effectiveness, on the other hand, is more difficult.
- These disadvantages have sometimes led to reluctance among regulators to approve biorestoration as a cleanup method. As the technology becomes better understood, however, it is expected that this treatment technique will receive more favorable attention from those selecting and approving corrective action plans.

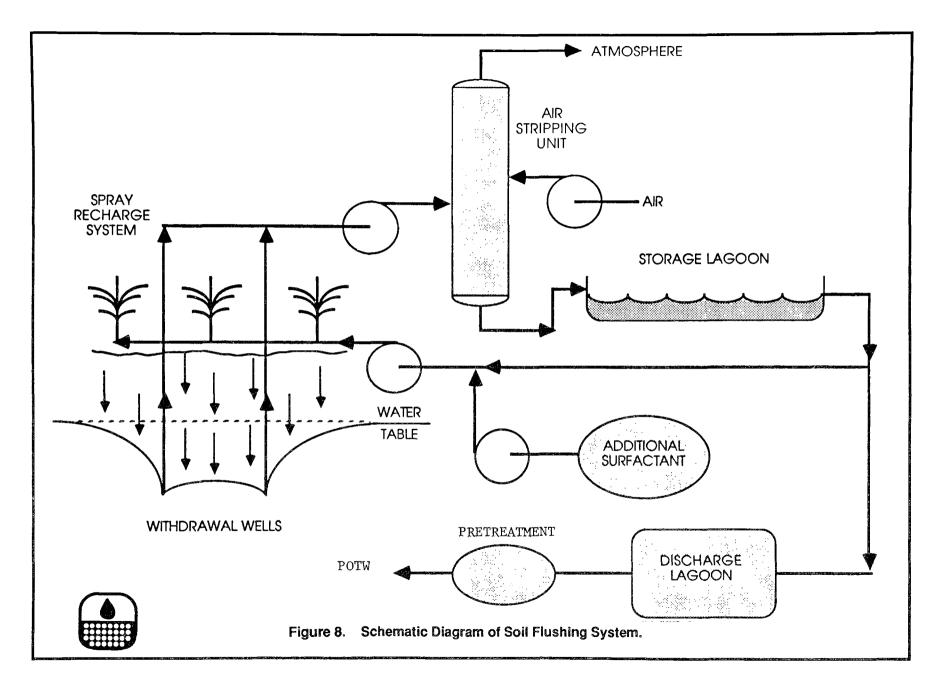
SOIL FLUSHING

Soil flushing refers to the <u>in situ</u> process where the zone of contamination is flooded with water or a water-surfactant mixture in order to dissolve the contaminants into the water or otherwise mobilize the residual contaminant to the water table. The contaminants are then brought to the surface for treatment by strategically placed extraction wells. The wells must be located such that the groundwater is completely controlled hydraulically, to ensure that the leached or mobilized contaminants do not escape once they reach the groundwater. This process may also be referred to as "ground leaching," "solvent flushing," or "extraction." Figure 8 shows a schematic diagram of a soil flushing system.

One soil flushing method removes contaminants by using water to dissolve the liquid, sorbed, or vapor contaminant. These processes are controlled by the contaminants' solubilities and Henry's law constants. Contaminants that are highly soluble in water, such as methanol, acetone, or phenol, are easily removed after only a few flushes with water. Other compounds, such as the gasoline additive tetraethyl lead or many of the major constituents in #6 fuel oil, are very insoluble and would not be solubilized to a high degree even after many flushes. The Henry's Law constant describes a contaminant's partitioning behavior between the vapor phase and liquid solution (how much contaminant exists in air versus how much exists in water). The introduction of large quantities of flushing solution will change the equilibrium of the vapor/liquid partitioning, and can result in some contaminant vapors being solubilized. A low Henry's constant is indicative of a tendency to exist in solution.

A second soil flushing method mobilizes contaminants existing as free product in the soil pores, and adsorbed to the soil. Contaminants found in these phases can be mobilized by the pressure gradient of the infiltrating flushing water. The viscosity and density of contaminants control the extent to which a compound may be mobilized as free product. This type of soil flushing would be expected to remove a greater portion of gasoline than heating oil or #6 fuel oil, because gasoline is less viscous then either of the other two petroleum products. Many of the constituents of gasoline are also more soluble than those of #6 fuel oil or heating oil and would be more readily mobilized in the dissolved phase as well. Tables 7 and 8 list the solubility, viscosity, density, and many other properties for many chemicals.

Similarly, compounds that are strongly sorbed to soil particles will not be as easily removed by flushing with water only. A compound's soil/water partitioning coefficient, K, may be used to identify the ease with which a compound will leave the soil. A compound's octanol/water coefficient, K, is more widely available and is often used as a surrogate for its soil/water coefficient. Organics with K, values less than 10, such as low-molecular weight alcohols and phenols, are very soluble, and can be leached from the soil by natural processes. Compounds with K values from 10 to 1000, such as low-to-medium molecular weight ketones, aldehydes, and aromatics, are somewhat amenable to flushing. Organics with K, greater than 1000 typically would require a surfactant (EPA, 1987a).



A surfactant is often added to the flushing water to help mobilize subsurface contaminants. Surfactants are natural or synthetic chemicals that have the ability to promote the wetting, solubilization, or emulsification of various organic chemicals. Many different types of surfactants are available, with varying properties; EPA (1986) provides an extensive summary of surfactant types and properties.

Surfactants can increase the "detergency" of an aqueous solution in three ways (EPA, 1986):

- Preferential wetting Surfactants can decrease the interfacial tension between the aqueous and solid phases (soil), allowing the water to preferentially wet the soil (resulting in a "water-wet" condition), thus displacing or partially displacing the contaminant.
- <u>Solubilization</u> Surfactants may enhance the solubility of certain contaminants.
- Emulsification Surfactants may enhance the emulsification -- or the dispersion of an insoluble organic phase within the aqueous phase -- of a contaminant.

In addition, organics that have been mobilized by surfactants are more accessible to biodegradation.

Local soil conditions also affect the likely effectiveness of soil flushing. Flushing is best suited to soils with a high hydraulic conductivity, such as gravel or sand. Soils with high silt and clay content impede movement of the flushing solution through the soils, resulting in less removal. Soils with high organic carbon content (especially those with more than 1% organic matter) and high clay content would tend to have stronger sorption characteristics and thus be less amenable to flushing. As with soil venting, the effectiveness of soil flushing depends on the degree to which all the contaminant is exposed to the flushing solution. Soils that are well-compacted may hold contaminants that are not reached by the leaching fluid. Preferential flow paths in the soil may also decrease the degree of intimate contact between the flushing solution and the contaminated soil, leading to decreased removal efficiencies.

A variation of the soil flushing process, known as "soil washing," takes place above ground in a reactor. Experience has shown that soil washing produces greater removal and better overall results than an in situ flushing system. By performing the washing ex situ (above ground), the leaching solution can more completely remove contaminants because the two major constraints of in situ flushing — low hydraulic conductivity and non-uniform contaminant contact due to preferred flow paths — are overcome. Although this discussion focuses on the in situ flushing process, many of the critical success factors apply to both soil flushing and soil washing. The site geology, however, will obviously be less important for above ground soil washing.

Table 19 lists the critical success factors for soil flushing. It can be used to evaluate whether soil flushing or washing will be effective at a particular site.

Other Factors

Experience. Actual field experience with in situ soil flushing for petroleum remediation is very limited, and thus data on effectiveness, costs and limitations are generally unavailable. The petroleum industry has experimented for several years with enhanced oil recovery, which uses surfactants to increase the production of an oil deposit. While similar, this experience is not directly applicable to soil cleanups.

Cost. Cost data are sparse. The Superfund site at Palmetto Wood, SC cited costs of \$3,710,000 (capital) and \$300,000 (annual O&M). These figures, on a unit basis, equal \$185/yd³ (\$240/m³) for capital costs, and \$15/yd³ (\$20/m³) annually for O&M. At Palmetto Wood, SC, soil flushing will be used to clean 20,000 yd³ (15,400 m³) of soil contaminated with metals (EPA, 1988b).

Other Advantages/Disadvantages. One principal drawback of soil flushing is the generation of large quantities of contaminated elutriate that requires treatment. Elutriate is the mixture of water, surfactants, and contaminants that is recovered in the soil flushing process. In some cases, the elutriate may be discharged to a local POTW, but often an on-site treatment must be devised. As with many other treatment methods, soil flushing requires that the groundwater flow pattern be well-defined to ensure complete recovery of the elutriate. If this is not the case, physical barriers such as slurry walls may be required. This technique also requires access to a source of water for flushing. Typically, groundwater is extracted, treated, and recycled as the flushing solution.

Site-specific factors that may limit the effectiveness of flushing include soils with pockets of low hydraulic conductivity. This limits the ability to pass large quantities of water through the contaminated soil. Many UST sites, especially those in urban settings, do not lend themselves to flushing due to nearby pipes and underground utilities. Soil flushing will be less effective at sites where the contaminants are relatively insoluble or tightly bound to the soil. The lack of an existing water supply may also be limiting.

The use of surfactants involves several considerations. The interactions of the surfactant with the biological, physical, and chemical properties of the unsaturated zone are typically uncertain, and must be determined at each site. For example, the addition of a surfactant containing sodium may lower soil permeability due to its reactive effect on the soil/sodium adsorption ratio (EPA, 1987b), which with time would decrease the effectiveness of this technique. The groundwater geochemistry also should be assessed for troublesome, naturally-occurring constituents prior to the addition of any surfactant. For example, hard water may render a surfactant ineffective. Soil type may also reduce a surfactant's effect. High clay content can cause chemical adsorption of the surfactant to the soil, thereby reducing available surfactant concentrations and limiting its effectiveness. Biological effects on the surfactant may also

TABLE 19. WORKSHEET FOR EVALUATING THE FEASIBILITY OF SOIL FLUSHING BEING EFFECTIVE AT YOUR SITE



| CRITICAL SUCCESS FACTOR | | | | | |
|--|---|-------------------|--------------|---|-----------|
| • Dominant Contaminant Phase Phase Vapor O O O O O O O O O O O O O O O O O O O | | UNITS | LESS | SOMEWHAT | MORE |
| - Dominant Contaminant Phase | SITE RELATED | | | A CANADA NO. | |
| Contaminant Phase | • Dominant | Phase | Vapor | Liquid | Dissolved |
| - Soll Hydraulic Conductivity cm/sec. | Contaminant Phase | 771430 | 0 | 0 | 0 |
| Conductivity | Soil Hydraulic | | | Medium (10 ⁻⁵ -10 ⁻³) | |
| - Soll Surface Area m²/g (>1) | Conductivity | cm/sec. | | , , | , , |
| - Carbon Content - Weight - Carbon Content - Weight - Carbon Content - Carbon C | - Soil Surface Area | m²/g | (>1) | (0.1 - 1) | (< 0.1) |
| CONTAMINANT- RELATED CONTAMINANT- RELATED | - Carbon Content | % Wei g ht | (> 10 %) | (1 - 10%) | (< 1%) |
| • Water Solubility mg/L Low (< 100) (< 1000) (>1,000) Medium (100 to 1000) (>1,000) High (>1,000) (>1,000) • Sorption Characteristics - Soil Sorption Constant L/kg High (>10,000) (>10,000) (>100-10,000) Low (< 100) (< 100) (< 100) (< 100) | Fractures in Rock | | | _ O | |
| • Water Solubility mg/L (<100) O O O O O O O O O O O O O O O O O O | CONTAMINANT- RELATED |) | | | |
| - Sorption Characteristics - Soll Sorption Constant - Vapor Pressure - Vapor Pressure - Vapor Pressure - Liquid Viscosity - Liquid Density - Liquid Density - Liquid Density - Liquid Constant - Liquid Characteristics (>10,000) (100-10,000) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) | Water Solubility | mg/L | (< 100) | (100 to 1000) | (>1,000) |
| • Vapor Pressure mm Hg (> 100) O (10 - 100) O (< 10) O • Liquid Viscosity cPoise High (>20) (2 - 20) (2 - 20) (2 - 20) O Low (< 2) O | Sorption Characteristics Soll Sorption Constant | L/kg | (>10,000) | (100-10,000) | (< 100) |
| • Liquid Viscosity cPoise (>20) (2-20) (<2) O O O • Liquid Density g/cm 3 Low Medium (1-2) (>2) | Vapor Pressure | mm Hg | (> 100) | (10 - 100) | (< 10) |
| • Liquid Density g/cm 3 (< 1) (1 -2) (> 2) | • Liquid Viscosity | cPoise | (>20) | (2 -20) | (< 2) |
| | • Liquid Density | g/cm ³ | (< 1) | (1 -2) | (> 2) |

OTHER CONSIDERATIONS

- Cost is from \$150 to \$200 per cubic yard.
- · Using surfactants may increase effectiveness
- Effluent requires separation techniques such as distillation, evaporation, centrifugation
- Most effective when used ex-situ (above ground)

be important. In some cases, a surfactant may biodegrade too quickly, reducing its exposure time to the contaminated soil. On the other hand, the surfactant should be degradable by the soil microbes at a slow rate so that surfactant buildup does not occur.

A general limitation of soil flushing is the inability at the present time to develop a method to separate the surfactant from the water, so that the surfactant can be recycled. Until the surfactant can be separated from the water, the high rates of surfactant consumption will limit the cost-effectiveness of soil flushing.

HYDRAULIC METHODS

Hydraulic methods include sumps, French drains, and other equipment and designs that allow for passive removal of accumulated free product from the unsaturated zone. This section does not address caps, slurry walls, or other physical barriers to flow, or technologies such as freezing, which although used in certain circumstances, typically are impractical at UST sites.

Hydraulic barriers are simple and relatively inexpensive, but do not remove contaminants to low levels. They are unlikely to be selected as a primary clean up option and might best serve as a means to easily collect some of the residual liquid in the unsaturated zone before implementation of another technology. For example, when a leaking UST is removed, the resulting excavated area might begin to accumulate residual liquid. The heavy machinery already on site could be used to enlarge or deepen the excavated area to promote further accumulation of product with little added effort.

Theoretical Considerations

Hydraulic methods create an area of high permeability in the unsaturated zone, allowing residual liquid contaminants to flow readily toward that permeable zone. Typically, a trench is dug into the contaminated soil and residual liquid will begin to seep into the trench. An impervious layer can be placed at the base of the trench to prevent re—infiltration of the product. As the product accumulates, it can be pumped out or removed manually, maintaining a gradient which facilitates further seepage into the trench. Figure 9 shows a typical drain system.

Hydraulic methods collect and remove only the mobile liquid and dissolved contaminants (and may serve as a passive venting system). Contaminants sorbed to soil particles or held as residual saturation are little affected by hydraulic methods and typically must be removed by other means. The method is best used in situations where the mobile phase — residual liquid and pore water — content is relatively high. Hydraulic methods are most effective for recent releases of significant quantities of contaminants at shallow depths.

Table 20 lists several CSFs for hydraulic methods. The single most important critical success factor is the amount of contaminant in the liquid phase. This method will not be effective unless significant quantities of liquid contaminant are in the soil. The CSFs from the site

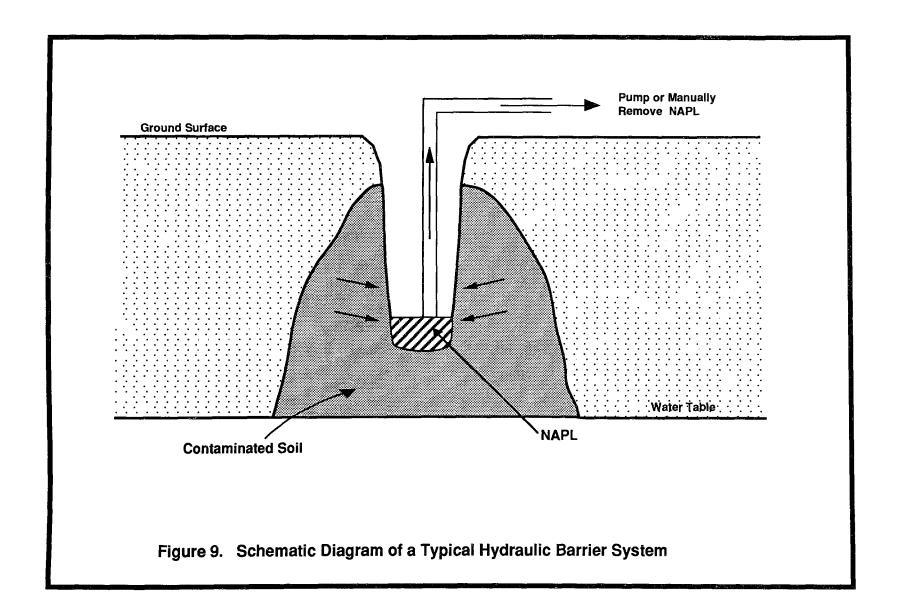


TABLE 20. WORKSHEET FOR EVALUATING THE FEASIBILITY OF HYDRAULIC BARRIERS WORKING AT YOUR SITE



| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
|---|----------|---------------------|------------------------------------|---|-----------------------------------|
| RELEASE - RELATED | | | | | |
| • Time Since Release | months | | Long (> 12 months) O | Medium (1 12 months) O | Short (< 1) O |
| Volume of Spill | gallons | | Small (<100) O | Medium (100 - 1000) O | Large (> 1000) O |
| SITE RELATED | | 1 | | ** | |
| Dominant Contaminant Phase | phase | | Vapor O | 0 | Liquid O |
| Soil Hydraulic Conductivity | cm/sec. | | High (> 10 ⁻³) O | Medium (10 ⁻⁵ -10 ⁻³) | Low (< 10 ⁻⁵) O |
| Soil Sorption Capacity Surface Area | m2/g | | High (> 1) O | Medium (0.1 - 1) O | Low (< 0.1) O |
| Carbon Content | % weight | | High (> 10%) O | Medium (1 10) O | Low (< 1) O |
| • Temperature | °C | | Low (<5) O | Medium (5 - 10) O | High (>10) O |
| Depth to Groundwater | meters | | High (>5) O | Medium (1 - 5) O | Low (< 1) O |
| CONTAMINANT- RELATED |) | V [*] | .26. | | |
| • Liquid Viscosity | c Poise | | High (> 20) O | Medium (2 to 20) O | Low (< 2) O |

OTHER CONSIDERATIONS

- Cost is from \$10 to \$90 per cubic meter.
- Only affects liquid portion of release—not portion sorbed to soil.
- Typically limited to shallow (<3 meters) depths.
- Not effective in removing contaminants to low levels.
- · Most effective when contamination is confined to small areas.
- Not effective for #6 fuel oil and other viscous fluids.
- Not effective if contamination is greater than 15 meters deep.

of interest can be entered on the worksheet for easy comparison to the preferred conditions to provide preliminary screening as to the likely effectiveness.

Other conditions may enhance or impede the effectiveness of hydraulic methods. Releases that are concentrated in small areas are more likely candidates for hydraulic barriers than releases that have spread over a large area. Releases of relatively immobile hydrocarbons such as #6 fuel oil are not amenable to this method. Also, releases that have moved a great distance below the surface are less amenable to this method because of limitations with excavation equipment.

Other Factors

Cost. Perhaps the most important variable is the depth of the drains. Two examples (EPA, 1987b) ranged in price from \$7.00/sq. ft. (\$75/sq. m.) to \$67-88/sq. ft. (\$720 - \$950/sq. m.), an order of magnitude difference. The first case involved a three-foot deep interceptor trench; in the second case, the trench was excavated to a depth of 12 - 17 feet (3.6 - 5.2 m).

EXCAVATION

Excavation is an alternative to the four $\underline{\text{in situ}}$ treatment methods. Excavated soil may be treated on site, treated $\overline{\text{off site}}$, or disposed of (landfilled) without treatment. Treated soil is sometimes placed back in the excavation at the site.

At present, excavating contaminated soil is more common than in situ treatment. Excavation, however, has many drawbacks not faced with in situ methods:

- Excavating contaminated soils allows uncontrolled release of contaminant vapors to the atmosphere, increasing exposure risks (EPA, 1989);
- Above- and below-ground structures -- buried utility lines, sewers and water mains, and buildings -- can pose real problems if contamination extends near or below the structures;
- Above-ground treatment methods tend to be more expensive than in situ methods;
- Disposal of contaminated soil is becoming increasingly difficult, and in some regulatory regions the soil is considered a hazardous waste;
- A source of backfill is required to fill the excavation.

Still, excavation is performed quite regularly. It is easy to undertake and may be done quickly; it is a well known technique; and it has the ability to remove most or all of the contamination from the site.

This report does not discuss in detail methods for treating excavated soil contaminated with hydrocarbons. A wide variety of methods may be used, including incineration, using soil as an aggregate in asphalt production, soil washing, enhanced volatilization, microbial degradation, and others. Short summaries of four above-ground treatment methods are presented later in this manual.

Table 21 lists the CSFs for excavation. The parameters from the site of interest can be compared with the CSFs on this table for a preliminary screening of the likely effectiveness of excavation.

Other Factors

Cost. The cost of excavation varies with the volume of soil to be removed, the type of equipment used, the cost of backfill, and the cost of treatment or disposal. EPA (1987b) quotes the costs on a volume and equipment basis: removal by backhoes costs between \$1.75 and \$5.00/yd³ (\$2.30 - \$6.50/m³), depending on the backhoe capacity; while dozers and loaders range from \$1.20 to \$4.50/yd³ (\$1.60 - \$5.90/m³). Backfill materials cost \$10-20/yd³ (\$13 - \$26/m³), depending on the distance transported. Transportation to disposal site may cost from \$0.50-\$1.00/yd³ (\$0.63 - \$1.30/m³) per mile transported. Landfill tipping fees are estimated at \$125-240/yd³ (\$163 - \$312/m³); these costs are expected to increase as landfill capacity becomes more limited. Total disposal costs can range from \$50 to \$300 or more per cubic yard (\$65 - \$390/m³).

Time Scale. This technique can be undertaken immediately, and is often used where urgent and immediate action is needed. The ability to respond quickly to a release is one of the main advantages that excavation enjoys over in situ methods. The soil and the associated contamination can be removed in only a few hours, rather than the several months it takes for the other methods described previously.

Disposal. Disposal of contaminated soils at landfills is becoming increasingly restricted by regulation, as well as being more expensive. Many states and localities now require disposal in secure landfills (which costs far more than if disposed at sanitary landfills). Also, landfill capacity is shrinking and sometimes poses an unexpected restriction.

ABOVE-GROUND TREATMENT METHODS

Because disposal of excavated soil is becoming increasingly difficult, treating excavated soil is becoming more attractive. Excavated soil may be treated on-site or off-site. This subsection briefly discusses various above-ground soil treatment methods that may be used for excavated soils. EPA (1988c) discusses in detail above-ground soil treatment technologies.

Incineration

Contaminated soil may be incinerated in rotary kilns, fluidized beds, or other systems. The systems may be either mobile units or fixed facilities. Both rotary kilns and fluidized beds are capable of destroying or removing 99 percent or more of the contaminants.

TABLE 21. WORKSHEET FOR EVALUATING THE FEASIBILITY OF EXCAVATION BEING EFFECTIVE AT YOUR SITE



| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
|---|------------------------|---------------------|---|-------------------------------|--|
| SITE RELATED | - | | | | da esta da est A esta da esta |
| Proximity of Above and Below Ground Structures | _ | | Buildings nearby Buried pipes and cables O | _ O | No nearby structures O |
| Volume of Soil Contaminated | Cubic Meters | | Large (> 1,000) O | Medium (100 -1,000) O | Small (< 100) O |
| Depth of Contamination | Meters From Surface | | Deep (> 5) О | Medium (1-5) O | Shallow (< 1) O |
| Proximity of Site to Traffic | _ | | Near O | | Far O |
| - Businesses | _ | | Near O | _ | Far O |
| - Disposal Site | | | Far O | | Near O |
| - Backfill Source | _ | | Far O | | Near O |

OTHER CONSIDERATIONS

- Cost is from \$50 to \$300 per cubic yard.
- Appropriate when urgent response is necessary
- Brings contaminants to surface, thereby increasing exposure risks
- · Significant amounts of surface area disturbed relative to depth excavated
- Requires suitable means of disposal. This is becoming increasingly difficult because some landfill operators consider petroleum-laden soil to be a hazardous waste.

Incineration capacity in the United States is rapidly becoming outpaced by demand. Additions to capacity typically face delays due to public opposition and the permitting process.

Incineration costs vary significantly with soil type and the contaminant characteristics. One estimate (EPA, 1988c) cited costs of \$200 to $$640/yd^3$ (\$260 - $$832/m^3$) for 20,000 yd³ (15,400 m³) of soil. Smaller quantities of soil would likely have higher unit incineration costs.

Soil Washing

Soil washing is the term used herein to refer to the aboveground process whereby contaminants are removed from soil via a leaching medium, typically water. Soil washing and soil flushing differ only in that soil flushing is an in situ process while soil washing is ex situ.

Above-ground washing has many advantages over soil flushing. The 'most important limitation of flushing — a soil's low hydraulic conductivity — does not constrain washing. The mixing of the leaching solution and contaminated soil in a countercurrent reactor also results in a much higher degree of contact between the soil and leaching material, which results in greater removal rates. Leaching soil aboveground also removes the possibility of contaminating underlying aquifers, which could result if the soil flushing was operated improperly.

The effectiveness of this process depends on several factors, but the most important are sorption of the contaminants to the soil, the solubility of the contaminant's constituents, and the presence of clay and silt in the soil.

Contaminants such as creosote coal—tars have very high sorptive characteristics. Such tightly—bound contaminants are difficult to remove by flushing or washing. Highly soluble contaminants are more easily removed by the leaching liquid than are insoluble contaminants. Finally, soil with high clay or silt content will impede contaminant—soil separation and thus decrease the effectiveness of this method.

The cost of soil washing has been reported (EPA, 1988b) to range from $$150-200/yd^3$ ($$195-$260/m^3$) for the processing costs alone (excluding excavation and disposal costs).

Enhanced Volatilization

Enhanced volatilization refers to any process or technique that removes contaminants from soil by increasing the volatilization rate, either by heating the contaminants or increasing the exposure to uncontaminated air. EPA (1988c) discussed four specific enhanced volatilization techniques: mechanical volatilization; enclosed mechanical aeration; low temperature thermal stripping; and pneumatic conveyer systems. Of these four types of systems, thermal stripping was reported to be most effective.

Rototilling disturbs the surface of the soil to a depth of about one foot, thereby increasing the access of fresh air to the soil. Soil may then be excavated and the underlying soil rototilled, so that successive iterations result in volatilization of contaminants from soils from greater depths. Enclosed mechanical aeration systems employ pug mills or rotary drums to increase the turbulence in the reactor, thereby increasing air/contaminant contact and, thus, removal. Low temperature thermal stripping systems are similar to mechanical aeration systems but, in addition, heat is added to increase the volatilization rate. Pneumatic conveyers use both increased temperature and high velocity air flow to remove contaminants. All of the systems capture the volatilized contaminants.

Enhanced volatilization methods have not been widely used in full-scale applications. Pilot-scale studies have predicted removal efficiencies of up to 99.99 percent based on post-aeration soil sampling. Of course, removal efficiencies would be higher for more volatile contaminants.

Cost data for these systems are scarce. EPA (1988c) estimated that actual processing costs for less than 10,000 yd 3 (7,700 m 3) of soil would exceed \$275/yd 3 (\$210/m 3).

SUMMARY

Table 22 presents a summary of the critical success factors for the four <u>in situ</u> treatment methods and excavation. This table is comprehensive in that it includes all the CSFs from Tables 17 through 21. Table 22 provides the preferred conditions for each technology.

Table 22 includes only the objective (scientific) factors that could affect the choice of technologies at a specific site. Economic, political, regulatory, and other potentially controversial factors, not listed on Tables 17 through 21, often are as important as these objective factors. Therefore, this summary table is useful for direct comparison of the technologies on the grounds of technical feasibility only. When potential treatment technologies have been narrowed to those that appear technically feasible, other considerations (cost, public perception, etc.) will likely affect the final selection.

| CRITICAL SUCCESS FACTORS | UNITS | SOIL VENTING | BIO- RESTORATION | SOIL FLUSHING | HYDRAULIC Barriers | EXCAVATION |
|-----------------------------|---------------------------|---------------------------|---------------------------|---------------------------|--------------------------|---------------|
| RELEASE - RELATED | | | | | | |
| TIME SINCE RELEASE | months | _ | Long (12) | _ | Short (< 1) | _ |
| VOLUME OF SPILL | gailons | _ | - | _ | Large (>1000) | Small (< 100) |
| VOLUME SOIL CONTAMINATED | m ³ | Large (>1000) | | - | _ | Smail (<100) |
| SITE - RELATED | | | | | | |
| HYDRAULIC CONDUCTIVITY | cm/sec | High (>10 ⁻³) | High (>10 ⁻³) | High (>10 ⁻³) | Low (<10 ⁻⁵) | _ |
| SOIL TEMPERATURE | •℃ | High (>20) | High (>20) | | _ | _ |
| SOIL SORPTION CAPACITY | L/kg | Low (<100) | | Low (<100) | _ | _ |
| SOIL MOISTURE CONTENT | % | Low (<10) | High (>30) | _ | | _ |
| SUFFICENT 0XYGEN/NUTRIENTS | _ | - | Sufficient | - | _ | - |
| SOIL pH | pH units | _ | 6.0 - 8.0 | - | _ | _ |
| DOMINANT CONTAMINANT PHASE | Vapor Dissolved liquid | Vapor and/ or Liquid | Dissolved | Dissolved and/ or Liquid | Liquid | _ |
| SOIL CARBON CONTENT | % | Low (<1) | _ | Low (<1) | Low (<1) | <u> </u> |
| DEPTH TO GROUNDWATER | meters | Deep (>15) | | Shallow (< 3) | Shallow (< 3) | Shallow (< 3) |
| PROXIMITY TO STRUCTURES | | | _ | | _ | Far |
| PROXIMITY TO LANDFILL | | | | _ | | Near |
| CONTAMINANT - RELATED | | | | | | |
| CONTAMINANT SOLUBILITY | mg/L | Low (< 100) | High (>1000) | High (>1000) | | |
| VAPOR PRESSURE | mm Hg | High (>100) | | Low (< 10) | | <u>—</u> |
| BIODEGRADABILITY | Refactory Index | <u> </u> | High (>0.1) | | | <u></u> |
| VISCOSITY | cPoise | | | Low (< 2) | Low (< 2) | |
| DENSITY | 3 g/cm | Low (<1) | | High (> 2) | | |
| FUEL TYPE* | | Light | Light | | | |

^{*} e.g., "Light" = Gasoline, "Heavy" = #6 Fuel Oil

TABLE 22. SUMMARY OF CRITICAL SUCCESS FACTORS FOR OPTIMUM PERFORMANCE

SECTION 4

MONITORING AND FOLLOW-UP MEASUREMENTS

INTRODUCTION

Once the most feasible soil treatment technologies have been screened, field samples should be collected before final selection of a corrective action technology and final design. Field samples are used to verify soil and site conditions and to confirm assumptions that have been made regarding the subsurface. It is always prudent to collect soil samples and corings prior to making a large investment in a particular technology.

The important parameters identified in this manual provide targets for field sampling. For example, air conductivities greater than 10^{-4} cm/sec suggest a better chance that soil venting would likely be effective. It is wise to measure this important parameter in the field before proceeding with final design. After site conditions are confirmed with the field data, or at least better understood, final selection and design can proceed.

Specifying Cleanup Goals

Cleanup goals are established based on the extent of the site specific health threat posed by the release. Once established, cleanup goals will determine what treatment technology is ultimately needed, how quickly the release needs to be cleaned up, and what removal efficiencies are required. If an uncontrolled petroleum release poses a significant health threat, then more urgent action will be needed. Hydraulic barriers and/or soil venting may be installed to contain the release and control vapors if immediate action is warranted. If the health threat is not immediate, then soil treatment technologies such as biorestoration that require more time, but tend to destroy rather than relocate hydrocarbons, may be preferred.

Selecting Design Criteria

Once the cleanup goals have been set and the treatment technologies selected, the next step is to develop the design criteria for the treatment technology. Treatment technologies remove contaminants at varying rates, and some contaminants may not be removed at all. A treatment technology is usually designed to remove one or more specific constituents to a specified level that is often set to conform to regulatory standards. Performance is then evaluated by measuring the concentrations of each contaminant of concern, and comparing those levels to cleanup goals.

Relative contaminant concentrations will change over time depending on their chemical properties, so it is possible that different contaminants will be used for design and for tracking performance at different stages of the cleanup. Benzene, toluene, ethylbenzene and xylene (BTEX) are often used for design criteria and performance monitoring, especially for gasoline releases. These chemicals are aromatics and make up a significant portion of petroleum products (as much as 20% by weight in gasoline). Based on present knowledge, the toxicity of the BTEX compounds is orders of magnitude greater than the other natural petroleum constituents. They are also typically more soluble and mobile than other constituents. Of the aromatics, benzene is of greatest concern since it is a known human carcinogen. Benzene is also one of the more soluble and volatile aromatics. It is almost always detected in the subsurface when a gasoline UST release occurs. When measuring vapors, it is common to monitor BTEX and the alkanes, total hydrocarbons (which includes all the aromatics) or total volatiles.

With time, aromatics dissolve in water (solubilize), evaporate into air (volatilize), and biodegrade until they cannot be detected. The contaminants likely to remain are more complex, less soluble, and less volatile than the aromatics. "More complex" constituents are constituents that have greater molecular weights and more complex molecular structures. They may eventually break down into simpler molecules. Constituents that are more complex than the simple aromatics (like BTEX) include certain additives like tetraethyl lead.

There are many different additives found in petroleum products, some of which can pose significant health risks. It may be desirable to include an additive in the design criteria or performance monitoring, but only on a site by site basis after specific additives have been identified. Often there will be little evidence to suggest the additive does or does not present a health risk.

MONITORING PERFORMANCE AND PROGRESS

Once a technology has been selected, designed and installed, it is essential that the performance of the treatment system be continually evaluated to ensure that it is operating effectively. If a technology is performing poorly, it may be due to an improper design arising from an incomplete site assessment.

It may be necessary to re-examine the data that were collected for the site assessment (see Figure 1) and collect more data to enhance the site assessment. Design modifications may be warranted if the understanding of site conditions changes appreciably.

Monitoring the treatment performance not only helps to evaluate how effectively the technology is working, but also how the overall cleanup is progressing. The results of the performance monitoring can be combined with other information to track the overall progress of the cleanup.

Soil Venting

Typically, gas concentrations at the wells are measured in the form of total hydrocarbons or total volatiles. Gauges can be placed on each of the extraction wells to monitor the vacuum pressure and extraction rate. Knowing the gas (or air) extraction rate and the concentration of the

contaminants in the gas, the total pounds of contaminants removed can be estimated. This can be compared with the estimate of total petroleum product released to the environment to estimate how much product remains in the subsurface.

Once soil gas concentrations begin to taper off, it should not be assumed that the cleanup is over. Soil gas concentrations take time to build up as shown in Figure 10. Once the vacuum is shut off, it is likely that soil gas concentrations will increase again as equilibrium between the soil vapor and liquid contaminants and dissolved contaminants is re-established. Concentrations can often reach their original levels after venting is stopped. Long-term monitoring is needed to ensure that as much petroleum as possible has been recovered.

Biorestoration

In most cases, soil samples are collected and analyzed for the constituents of concern. Carbon dioxide concentrations can be measured to determine how much biological activity is occurring (aerobic biodegradation produces carbon dioxide as one of its end products). Because biorestoration can fail, it is important to collect additional samples and analyze the availability of oxygen, nutrients, pH, redox potential, and microbial populations to make sure that suitable conditions are maintained.

Soil Flushing

Leachate is analyzed for the specific contaminants of concern or for groups of constituents like total hydrocarbons, with results reported as weight of contaminant per volume of fluid. Knowing the volume of fluid that has been processed, it is possible to estimate the total amount of petroleum recovered.

Hydraulic Barriers

Contaminants are primarily recovered as residual liquid in this method. The volume or mass of fuel is typically measured directly and compared with estimates of total product released. However, the hydraulic barrier method is not effective as a complete solution and is unlikely to be the primary clean up technology. Product recovery by this method can probably be discontinued when the rate of additional product recovered by the system decreases to the point where long time periods are required to allow significant amounts of product to be recovered.

Excavation

The purpose of excavation is to remove the contaminated soil until concentrations in the remaining soil are below the cleanup criteria, until excavation is no longer feasible, or until a stage is reached where other remediation technologies are more appropriate. There are several approaches to determine when a criteria level has been reached. Soil gas concentrations in the excavation can be measured to determine whether they exceed the cleanup criteria.

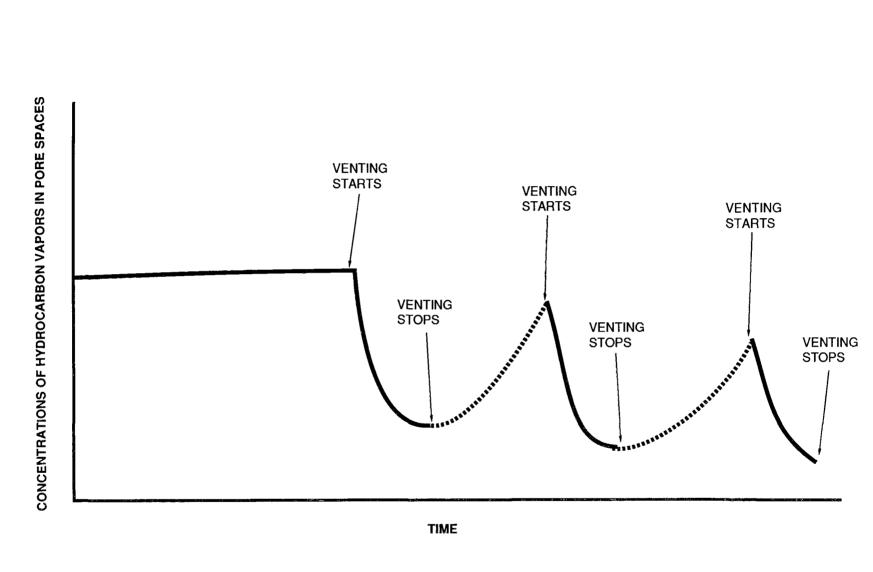
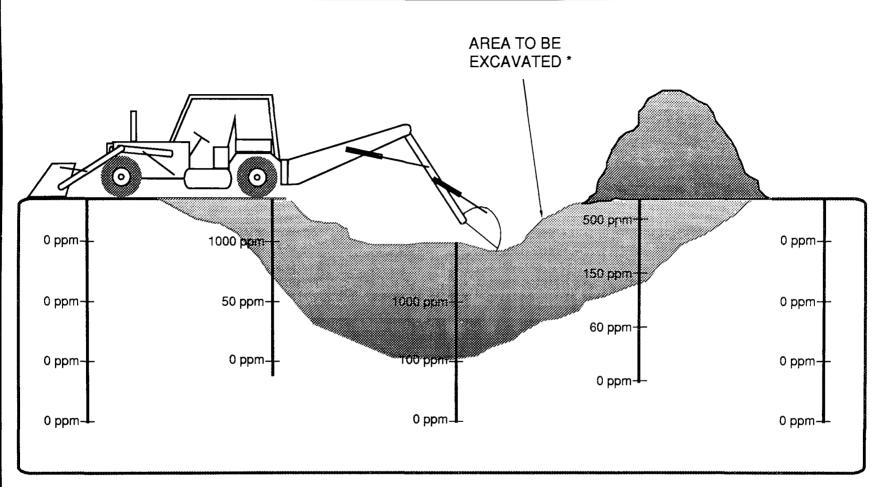


Figure 10. How Concentrations of Hydrocarbon Vapors Change During Soil Venting.



An alternative approach, and a more accurate one, would be to measure hydrocarbon concentrations in the soil both vertically and spatially in the soil matrix (see Figure 11). The area needed to be excavated can be interpolated from the vertical profiles (a cleanup level of 100 ppm of total hydrocarbons was assumed in Figure 11).



* A CLEANUP LEVEL OF 100 PPM OF TOTAL HYDROCARBONS HAS BEEN ASSUMED

Figure 11. Determining Area to be Excavated Using Hydrocarbon Concentrations

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APPENDIX A

HOW TO USE THIS MANUAL: A SAMPLE PROBLEM

This manual discusses the selection of an appropriate corrective action for contamination in the unsaturated zone. The purpose of this appendix is to help the user apply this information to actual situations. Although the case study that is presented is hypothetical, it represents events and conditions likely to occur during an actual contaminant release. The user is guided through a step-by-step process to help narrow the range of treatment technologies. As stated earlier, this manual does not address emergency measures required in response to a leaking UST. It is assumed that these measures have been completed prior to the selection process.

There are many, sometimes complex, factors to consider during the selection process. To accurately assess the conditions at a site, and therefore, select the best corrective action, field sampling and analysis is required. In addition, a degree of engineering judgment and scientific interpretation of the collected information is needed. Therefore, it is important to understand that a corrective action should not be selected based solely on information provided in this manual. Preliminary conclusions from this manual should be reviewed by experienced engineers and hydrogeologists and validated with actual field data.

This manual is set up to aid in the selection of a corrective action; it can be used as a tool to assess the feasibility of a proposed corrective action or provide a quick preliminary assessment of the various alternatives. For these purposes, it is not necessary to conduct extensive field studies or perform detailed investigations to use this manual. Information provided in the text of this report along with information readily available through resources such as local EPA, USGS or state environmental offices can be used to assess the relative merits of different corrective actions in a comparatively short time and at minimal cost.

The case study presented is hypothetical. Many assumptions were made concerning various factors or parameters associated with the selection process. Because of this, it is more a quick preliminary screening than an actual detailed selection process. Where possible, estimates for the different parameters were obtained from information in the text. For other parameters, it was assumed that some simple field tests were conducted to estimate their value. The source of information for all parameters is identified.

An important consideration in attempting to select a corrective action is whether to base the analysis on the characteristics of the contaminant mixture or one or more "targeted" constituents. In this sample problem and in most real-world cases, the analysis will be based on the hydrocarbon mixture, particularly if the release is recent. However, it is unlikely than one corrective action will be best suited for removing every constituent. After a preliminary assessment has identified the most promising technologies, it may be prudent to check their effectiveness at

removing selected contaminants of concern. This can be fairly easily accomplished using the worksheets provided since most of the input to the worksheets would be the same as for the initial assessment, the only new input being contaminant-specific parameters.

DESCRIPTION OF THE CASE

The setting of the case study is a northeastern, suburban community with a population of about 50,000. A rapid release of 500 gallons of gasoline occurred due to rupture of an UST in June. Authorities were immediately notified. The release occurred at a gasoline station near a relatively busy intersection. There are several homes and small commercial businesses in the proximity of the gasoline station.

DESCRIPTION OF THE METHODOLOGY

Step 1: Collect Information About the Release

The first step after emergency response action is to conduct a site investigation. The release-related information necessary to initiate the investigation is listed in Table 1. For this example, the following is known:

- 1(a) The contaminant is automotive gasoline.
- 1(b) The volume of contaminant released was estimated to be 500 gallons. The release was due to rupture of an UST by heavy machinery.
- 1(c) The nature of release was a quick spill.
- 1(d) The spill was immediately detected by workers at the gasoline station.
- 1(e) The spill occurred one month ago.

In addition to the above information, it was determined that none of the contaminant was recovered during the initial emergency response to the spill. The gasoline quickly infiltrated into the soil at the site.

Step 2: Collect Information About the Site

Table 3 (p.14) lists parameters necessary to characterize the site. Table 4 (p.15) presents estimates of various physical and geological parameters related to the unsaturated zone. For this example, all of the site-related parameters were estimated from readily available information.

To estimate many of the site-specific parameters, soil type must be known. USGS and Soil Conservation Service geologic maps of the area show the subsurface to be predominantly sand and gravel to a depth of 6 meters (20 feet). A single shallow well was installed and the depth to groundwater was estimated to be 5 meters (16 feet). Once the soil type is known, the remaining site-specific parameters may be estimated:

- 2(a) Porosity = 35 percent (Average for sand and gravel from Table 3, p.14)
- 2(b) Particle Density = 2.65 g/cm³ (Average for sand and gravel from Table 3)
- 2(c) Bulk Density = 1.75 g/cm^3 (Average for sand and gravel from Table 3)
- 2(e) Permeability = 10^{-4} cm² (Average for sand and gravel from Table 3)
- 2(f) Depth to Groundwater Table = 5 m (16 feet). This value was assumed to be measured. Often depth to groundwater can be obtained from local sources such as USGS records.
- 2(g) Soil Moisture Content = 10 percent. This value was obtained from Figure 4 (p. 17) for the sand soil type using field capacity as an estimate of moisture content.
- 2(h) Soil Surface Area = $0.005 \text{ m}^2/\text{g}$. This value was obtained from Table 4 (p. 15) for the medium to coarse sand soil type.
- 2(i) Rainfall Infiltration Rate = 0.14 cm/day. Infiltration rates can usually be obtained from local sources such as the USGS. In this case, an approximation of 50 percent of total daily rainfall for the northeastern U.S. (0.28 cm/day) was assumed for the infiltration rate. It is important to identify actual rainfall occurrences within the last month or two, particularly for recent spills. This will show whether historic data reflects what has actually happened at the site. In the northeast, rainfall patterns are quite consistent throughout the year and historic data is assumed adequate for the assessment. Also, paved areas should be noted because infiltration may be reduced significantly.
- 2(j) Soil temperature = 8°C. Soil temperature was estimated from Figure 3 (p.16) for the northeastern U.S. and could also be easily measured.
- 2(k) Organic Content = 0.2%. The organic content of a soil is difficult to estimate without collecting and analyzing soil samples. Because the organic content of a sand and gravel soil type is usually relatively low, a value of 0.2 percent (near the low end of the scale) was assumed for this example. Ordinarily, the organic content of a soil must be determined from field samples.
- 2(1) Soil pH = 5.5 This parameter can easily be measured through a simple field analysis. For this example, a pH value of 5.5 was assumed.

2(m) The presence of rock fractures in the subsurface can be estimated from readily-available local geographic information. It is assumed that there are no rock fractures in this case study.

Step 3: Collect Information About the Contaminants

Table 5 (p. 18) lists contaminant-specific parameters. The specific table or tables from which a particular parameter value may be estimated is also presented in Table 5 in the default source column.

In step 1(a), the released contaminant was determined to be automotive gasoline. For a preliminary site assessment, properties of the bulk product rather than individual constituents are used. Estimates for the parameters found in Table 5 for gasoline are as follows:

- 3(a) Vapor pressure = 469 mm Hg (Average from Table 7, p.21)
- 3(b) Water Solubility = 158 mg/L (Average from Table 7)
- 3(c) Viscosity = 0.45 cPoise (Average from Table 7)
- 3(d) Liquid Density = 0.73 g/cm³ (from Table 7)
- 3(e) Vapor Density = 1.950 g/m^3 (Average from Table 7)
- 3(f) *Soil Sorption Constant = 38.1 L/kg (from Table 8, p.22)
- 3(g) Refractory Index = 0.02 (From Table 9, p.23)

Values for the parameters in Steps 3(a) through 3(e) could as easily been obtained for a constituent of gasoline by using Table 6 (p.20) and Table 8 (p.22). Table 6 lists major constituents of various petroleum products and Table 8 lists parameter values for many of the constituents. The remainder of the assessment would be carried out as will be done for the bulk product. A technology that looked promising at removing the bulk product could be checked to see if it was equally effective in removing a contaminant of concern.

NOTE: *Information on Soil Sorption Constant for a gasoline mixture is not readily available. Sorption characteristics of a substance are related to its molecular weight. In order to provide an estimate of the Soil Sorption Constant for gasoline, a constituent of gasoline for which the constant was known and which is similar to gasoline in molecular weight was used. The molecular weight of benzene (78 g/mole) is similar to the molecular weight of gasoline (approximately 100 g/mole). Also, benzene is a known human carcinogen. Therefore, by substituting the Soil Sorption Constant of benzene for that of gasoline, a reasonable approximation is made and the analysis is better focused on a known health threat.

All the information collected in Steps 1(a) through 3(g) can be used to complete the worksheets provided in this manual. To illustrate, Tables A-1 through A-11 are presented here with the appropriate information filled in. Additional copies of all blank worksheets are provided at the back of this manual.

Step 4: Evaluate Contaminant Phase Distribution (Tables A-1 to A-3)

Once a site investigation has been conducted and site-specific and contaminant-specific information has been assembled, an evaluation of the contaminant phase distribution should be made.

A <u>qualitative</u> evaluation of phase distribution can be accomplished by determining the likelihood of the contaminant being in one of the three phases: residual liquid, vapor, or dissolved in pore water. Table 11 (p.26), Table 12 (p.27) and Table 13 (p.28) can be used to demonstrate the likelihood of each phase being present as discussed in Section 2 of the manual.

For this example, Tables 11, 12, and 13 have been used as worksheets to determine the likelihood of the contaminant being present in any one of the three phases and are included as Tables A-1, A-2, and A-3 in the case study. As shown in the worksheets, there is no dominant pattern indicating that a majority of the contaminant would be present in any one phase. It is likely that some portion of the contaminant exists in each phase. Because the spill was recent, it is likely most of the contaminant is in the residual liquid phase, and this is assumed in the assessment.

Step 5: <u>Determine Contaminant Mobility</u> (Tables A-4 to A-6)

The mobility of contaminants in each of the phases is influenced by different factors. For this reason, each phase is addressed separately.

Residual Liquid Mobility. The relative degree of mobility can be estimated through use of Table 14 (p. 31). The table is set up the same as Tables 11, 12, and 13. Table A-4 shows values from this case study. As can be seen, the factors are distributed throughout the three right-most columns, indicating likely migration from the residual liquid phase.

<u>Vapor Mobility</u>. Table 15 (p. 33) can be used to estimate vapor phase mobility in the same manner that Table 14 demonstrated residual liquid phase mobility. Table A-5 presents the results from the case study. It shows that three of the five factors fall within the middle range of mobility and two fall within the high range. The worksheet indicates the vapor phase of the contaminant is relatively mobile.

<u>Dissolved Mobility.</u> Mobility of the contaminant dissolved in pore water can be estimated through the use of Table 16 (p. 35). Table A-6 presents the factors determined from the case study. The majority of the factors indicate that there is a potential for a high degree of dissolved contaminant mobility.

TABLE A-1. LIKELIHOOD OF LIQUID CONTAMINANTS BEING PRESENT IN THE UNSATURATED ZONE



| FACTOR | UNITS | SITE OF INTEREST | INCREASING LIKELIHOOD | | |
|---------------------------------------|---------|---------------------|------------------------------|---|-----------------------------|
| RELEASE- RELATED | | | | | |
| Amount Released | gallons | 500 | Small (<100) O | Medium (100-1000) | Large (>1000) |
| • Rate Of Release | | instantaneous | Slow Release | 0 | Instantaneous Release |
| • Time Since Release | months | one | Long (>12) O | Medium (1 - 12) ● | Short (< 1) O |
| SITE - RELATED | | | | | |
| ∙ Depth To Groundwater | meters | 5 | Shallow (< 1) O | Medium (1-5) ● | Deep (>5) O |
| Hydraulic Conductivity | cm/sec | 10-2 | High (>10 ⁻³) | Medium (10 ⁻⁵ -10 ⁻³) | Low (<10 ⁻⁵) |
| • Rainfall Infiltration Rate | cm/day | 0.14 | High (>0.1) | Medium (0.05 - 0.1) | Low (<0.05) |
| Soll Temperature | °C | 8 | Warm (>20) O | Medium (10 - 20) | Cool (<10) |
| Soil Sorption Capacity (Surface Area) | m²/g | 0.005 | Low (<0.1) | Medium (0.1 1) O | High (>1) O |
| CONTAMINANT- RELATED | | | | | |
| • Liquid Viscosity | сР | 0.45 | Low (<2) | Medium (2-20) O | High (>20) O |
| • Liquid Density | g/cm | 0.73 | High (>2) O | Medium (1-2) O | Low (<1) |
| Vapor Pressure | mm Hg | 469 | High (>100) | Medium (10-100) | Low (<10) O |
| • Water Solubility | mg/L | 158 | High (>1000) O | Medium (100-1000) ● | Low (<100) O |

TABLE A-2. LIKELIHOOD OF CONTAMINANT VAPORS BEING PRESENT IN THE UNSATURATED ZONE



| FACTOR | UNITS | SITE OF INTEREST | INCREASING LIKELIHOOD | | |
|---|---------|---------------------|----------------------------------|---|-----------------------------|
| RELEASE- RELATED | | : | | . | |
| • Amount Released | gallons | 500 | Small (<100) | Medium (100-1000) | Large (>1000) |
| • Rate Of Release | | Instantaneous | Slow Release | O | Instantaneous Release |
| • Time Since Release | months | one | Long (>12) O | Medium (1-12) ● | Short (< 1) O |
| SITE - RELATED | | | | | |
| Depth To Groundwater | meters | 5 | Shallow (< 1) O | Medium (1-5) ● | Deep (>5) O |
| • Air Conductivity | cm/sec | 10-3 | High (>10 ⁴) ● | Medium (10 ⁻⁶ -10 ⁻⁴) | Low (<10 ⁻⁶) |
| • Rainfall Inflitration Rate | cm/day | 0.14 | High (>0.1) ● | Medium (.005-0.1) O | Low (<0.05) O |
| • Soll Temperature | °C | 8 | Cool (<10) | Medium (10 - 20) O | Warm (>20) O |
| Soil Sorption Capacity (Surface Area) | m²/g | 0.005 | Low (<0.11) | Medium (0.1 - 1) O | High (>1) O |
| CONTAMINANT- RELATED | | | | | |
| • Liquid Viscosity | сР | 0.45 | High (>20) O | Medium (2-20) O | Low (<2) ● |
| • Liquid Density | g/cm | 0.73 | High (>2) O | Medium (1-2) O | Low (<1) |
| • Vapor Pressure | mm Hg | 469 | Low (<10) O | Medium (10-100) O | High (>100) |
| Water Solubility | mg/L | 1,950 | High (>1000) ● | Medium (100-1000) O | Low (<100) O |

TABLE A-3. LIKELIHOOD OF CONTAMINANTS DISSOLVED IN PORE WATER BEING PRESENT IN THE UNSATURATED ZONE



| FACTOR | UNITS | SITE OF INTEREST | INCREASING LIKELIHOOD | | | |
|---------------------------------------|-------------------|---------------------|---------------------------|---------------------------|-----------------------|--|
| RELEASE- RELATED | | | | | | |
| Amount Released | gallons | 500 | Small (100) | Medium (100-1000) | Large (>1000) O | |
| • Rate Of Release | | Instantaneous | Instantaneous Release | _ O | Slow Release | |
| • Time Since Release | months | one | Long (>12) O | Medium (1-12) | Short (< 1) O | |
| SITE - RELATED | | | | | | |
| Depth To Groundwater | meters | 5 | Shallow (< 1) O | Medium (1-5) ● | Deep (>5) O | |
| • Moisture Content | % volume | 10 | Low (<10) O | Medium (10-30) ■ | High (>30) | |
| • Soil Porosity | % volume | 35 | Low (<20) O | Medium (20-40) | High (>40) O | |
| • Rainfall Infiltration Rate | cm/day | 0.14 | Low (<0.05) O | Medium (0.05-0.1) | High (>0.1) | |
| Soil Sorption Capacity (Surface Area) | m²/g | 0.005 | Low (<0.1) | Medium (0.1-1) O | High (>1) O | |
| CONTAMINANT- RELATED | | | | | | |
| • Liquid Viscosity | сР | 0.45 | High (>20) O | Medium (2-20) O | Low (<2) | |
| • Liquid Density | g/cm ³ | 0.73 | High (>2) O | Medium (1-2) O | Low (<1) | |
| Vapor Pressure | mm Hg | 469 | High (<100) ● | Medium (10-100) O | Low (>10) O | |
| Water Solubility | mg/L | 158 | Low (<100) O | Medium (100-1000) ● | High (>1000) O | |

TABLE A-4. FACTORS TO EVALUATE THE MOBILITY OF LIQUID CONTAMINANTS



| FACTOR | UNITS | SITE OF INTEREST | INCREAS | ING MOBILITY | |
|------------------------|-------------------|---------------------|----------------------------------|---|-------------------------------|
| RELEASE RELATED | | | | | |
| • Time Since Release | Months | one | Long (>12) O | Medium (1-12) ■ | Short (<1) |
| SITE - RELATED | | | | | |
| Hydraulic Conductivity | cm/sec | 10-2 | Low (<10 ⁻⁵) O | Medium (10 ⁻⁵ - 10 ⁻³) O | High (> 10 ⁻³) |
| • Soil Porosity | % Soil Volume | 35 | Low (<10) O | Medium (10-30) O | High (> 30) ● |
| Soil Surface Area | m²/g | 0.005 | High (>1) O | Medium (0.1-1) O | Low (< 0.1) |
| Soll Temperature | ౪ | 8 | Low (<10) | Medium (10-20) O | High (> 20) O |
| • Rock Fractures | _ | Absent | Absent • | - o | Present O |
| Moisture Content | % Volume | 10 | High (>30) O | Medium (10-30) | Low (< 10) O |
| CONTAMINANT- RELATED | | | | | |
| • Liquid Viscosity | cPoise | 0.45 | High (>20) O | Medium (2-20) O | Low (<2) |
| • Liquid Density | g/cm ³ | 0.73 | Low (<1) | Medium (1-2) O | High (>2) O |

TABLE A-5. FACTORS TO EVALUATE THE MOBILITY OF CONTAMINANT VAPORS



| FACTOR | UNITS | SITE OF INTEREST | INCREASING MOBILITY | | | | | | |
|---------------------|------------------|---------------------|---------------------------------------|--------------------------------|-----------------------------|--|--|--|--|
| SITE - RELATED | | | | | | | | | |
| Air Filled Porosity | % Volume | 25 | Low (<10) O | Medium (10- 30) ● | High (> 30) O | | | | |
| - Total Porosity * | % Volume | 35 | Low (<10) O | Medium (10- 30) O | High (> 30) ● | | | | |
| • Water Content * | % Volume | 10 | High (> 30) | Medium (10- 30) ● | Low (< 10) | | | | |
| Depth Below Surface | meters | 5 | Deep (>10) O | Medium (2 - 10) ● | Shallow (< 2) O | | | | |
| CONTAMINANT- RELATE | 0 | | · · · · · · · · · · · · · · · · · · · | ÷ | , | | | | |
| • Vapor Density | g/m ³ | 1,950 | Low (< 50) O | Medium (50-500) | High (>500) ● | | | | |

 $^{^{\}star}$ the total porosity less that fraction filled with water equals the air filled porosity

TABLE A-6. FACTORS TO EVALUATE THE MOBILITY OF CONTAMINANTS IN PORE WATER



| FACTOR | UNITS | SITE OF INTEREST | INCREASING MOBILITY | | |
|------------------------------|----------|---------------------|---------------------------------|--|-------------------------------|
| SITE RELATED | | | | | |
| Hydraulic Conductivity | cm/sec. | 10-2 | Low (10 ⁻⁵) O | Medium (10 ⁻⁵ - 10 ⁻³) | High (> 10 ⁻³) |
| Moisture Content | % Volume | 10 | Low (< 10) O | Medium (10 -30) | High (> 30) O |
| • Rainfall Infiltration Rate | cm/day | 0.14 | Low (< 0.05) O | Medium (0.05-0.1) O | High (>0.1) ● |
| • Soil Porosity | % Volume | 35 | Low (< 10) O | Medium (10 - 30) O | High (> 30) |
| Rock Fractures | _ | Absent | Absent | 0 | Present O |
| Depth Below Surface | meters | 5 | Shallow (< 2) O | Medium (2 - 10) | Deep (> 10) О |
| CONTAMINANT- RELATED | | | | | |
| • Water Solubility | mg/L | 158 | Low (< 100) O | Medium (100 to 1000) | High (>1000) O |

Step 5 results suggest that conditions are conducive for the contaminants to move into and out of each phase. Because it is a relatively new release, most of the product is likely to still be in the liquid contaminant phase. Site conditions are such that liquid contaminants can move easily into both the vapor and dissolved phases. These results have implications for cleanup, as discussed below.

Step 6: Evaluate Soil Treatment Technologies

The information gained from the previous steps which can be useful in selecting possible corrective actions. Section 3 presents a detailed description of the five types of corrective actions which are discussed in this manual. Included in the description of the various corrective actions are some of the unique factors that may need to be addressed before final selection can be made.

In this step, each of the corrective actions will be evaluated for their likelihood of success in removing the contaminant of concern, in this case gasoline. Tables 17 through 21 list a unique set of critical success factors (CSFs) for each corrective action. These worksheets can help determine the likely effectiveness of each technology of a particular site. Copies of the worksheets are provided here as Tables A-7 through A-11 for use in the evaluation process. Additional copies of all worksheets are provided at the back of the manual.

Because of the unique character of each site analysis, the worksheets will not always indicate whether a particular technology will likely succeed or fail. Typically, some CSFs will indicate a high degree of success while others will indicate the opposite. For this reason, it is better to complete each worksheet and conduct a comparative analysis between technologies, identifying one or more which are more likely to succeed.

The information required to complete the worksheets is available from the steps outlined earlier. Information for determining the CSFs not already introduced is presented below.

- Proximity of Above and Below Ground Structures as was described initially in the case study, there are several businesses proximate to the release site. Also, because the site is close to a relatively busy intersection, buried cables and pipes are likely to exist in the area.
- Volume of Contaminated Soil a rough estimate of this CSF is obtained by multiplying the depth to groundwater by an approximation of the surface area over which the release occurred. From Step 2(f), the estimated depth of contaminated soil is about 5 yd (4.6m). The ground surface area exposed to contamination was estimated to be approximately 25 yd² (21 m²). Volume = 5 yd (4.6 m) x 25 yd² (21 m²) = 125 yd³ (97 m³)

TABLE A-7. WORKSHEET FOR EVALUATING THE FEASIBILITY OF SOIL VENTING BEING EFFECTIVE AT YOUR SITE



| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
|---|-----------|-------------------------|-----------------------------------|--|------------------------------------|
| SITE RELATED | | | | | |
| Dominant Contaminant Phase | Phase | 1:01:1 | Sorbed to soil | Liquid | Vapor |
| | | Liquid | 0 | • | 0 |
| • Soil Temperature | °C | 8 | Low (< 10) | Medium (10 - 20) O | High (> 20) O |
| Soil Air Conductivity | cm/sec. | 10-3 | Low (< 10 ⁻⁶) O | Medium (10 ⁻⁶ -10 ⁻⁴) O | High (> 10 ⁻⁴) ● |
| Moisture Content | % volume | 10 | Moist (> 30) O | Moderate (10 - 30) | Dry (< 10) O |
| • Geological Conditions | _ | Assumed Heterogenems | Heterogeneous • | 0 | Homogeneous O |
| Soil Sorption Capacity Surface Area | 2 m /g | 0.005 | High (> 1) O | 0 | Low (< 0.1) ● |
| • Depth to Ground Water | meters | 5 | Low (<1) O | Medium (1-5) | High (>5) O |
| CONTAMINANT- RELATED | | | | | |
| Vapor Pressure | mm Hg | 469 | Low (< 10) O | Medium (10 to 100) O | High (> 100) |
| Water Solubility | mg/L | 158 | High (> 1000) O | Medium (100 - 1000) | Low (< 100) O |

- . Cost is from \$15 to \$60 per cubic yard.
- Effictiveness decreases after several months of treatment.
- Capable of removing thousands of gallons.
- · Air emissions will likely need to be treated with GAC.
- Treatment can be done on-site
- Care must be taken to avoid explosions because vapors are concentrated
- Cleanup takes time so that this technology is not appropriate when emergency response is needed

TABLE A-8. WORKSHEET FOR EVALUATING
THE FEASIBILITY OF BIORESTORATION
BEING EFFECTIVE AT YOUR SITE



| | | | | | , |
|---------------------------------------|---------------|---------------------|----------------------------------|--|------------------------------------|
| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
| RELEASE - RELATED | - 42 1 | | | | |
| • Time Since Release | Months | one | Short (< 1) O | Medium (1 - 12) | Long (> 12) O |
| SITE RELATED | | | | | |
| Dominant Contaminant Phase | Phase | Liquid | Liquid • | Vapor O | Dissolved O |
| • Soil Temperature | °C | 8 | Low (< 5) O | Medium (5 - 10) | High (> 10) O |
| Soil Hydraulic Conductivity | cm/sec. | 10-2 | Low (<10 ⁻⁵) O | Medium (10 ⁻⁵ -10 ⁻³) O | High (> 10 ⁻³) ● |
| • Soil pH | pH Units | 5.5 | (< 6 or > 8) | - 0 | (6 - 8) O |
| • Moisture Content | % Volume | 10 | Dry (< 10) O | Moderate (10 to 30) | Moist (> 30) |
| CONTAMINANT- RELATED | | | | | |
| • Solubility | mg/L | 158 | Low (< 100) O | Medium (100 to 1000) ● | High (> 1000) |
| Blodegradability Refractory Index | Dimensionless | 0.02 | Low (< 0.01) | Medium (0.01 to 0.1) | High (> 0.1) O |
| • Fuel Type | _ | gasoline | No. 6 Fuel Oil (Heavy) | No. 2 Fuel Oil (Medium) | Gasoline/ Diesel (Light) |

- Cost is from \$60 to \$125 per cubic yard.
- · Completely destroys contaminants under optimal conditions
- Effectiveness varies depending on subsurface conditions
- · Biologic systems subject to upset
- · Public opinion sometimes against putting more chemicals in ground
- · Difficult to monitor effectiveness
- · Minimizes health risk by keeping contaminants in ground and on site
- Takes long time to work-not for emergency response

TABLE A-9. WORKSHEET FOR EVALUATING
THE FEASIBILITY OF SOIL FLUSHING
BEING EFFECTIVE AT YOUR SITE



| | , | 35 | | | |
|----------------------------|---|---------------------|-----------------------------|---|-------------------------------|
| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
| SITE RELATED | | | | | |
| Dominant | Phase | , , , , | Vapor | Liquid | Dissolved |
| Contaminant Phase | , ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,, | Liquid | 0 | • | 0 |
| Soil Hydraulic | | 10-2 | Low (<10 ⁻⁵) | Medium (10 ⁻⁵ -10 ⁻³) | High (> 10 ⁻³) |
| Conductivity | cm/sec. | 70 | 0 | 0 | (> 10) |
| - Soil Surface Area | m²/g | 0.005 | High (>1) | Medium (0.1 - 1) | Small (< 0.1) |
| | | 0,005 | o' | 0 | (20.1) |
| - Carbon Content | % Weight | 0.2 | High (> 10 %) | Medium (1 - 10%) | Low (< 1%) |
| | | مے وں | 0 | 0 | (~176) |
| Fractures in Rock | _ | Absent | Present | | Absent |
| | | 7153611 | 0 | 0 | 9 |
| CONTAMINANT- RELATED |) | | | | |
| Water Solubility | mg/L | 158 | Low (< 100) | Medium (100 to 1000) | Hìgh (>1,000) |
| | | 150 | `0' | • | 0 |
| Sorption Characteristics | L/kg | 38 | High (>10,000) | Medium (100-10,000) | Low (< 100) |
| - Soil Sorption Constant | | 30 | Ö ′ | 0, | |
| Vapor Pressure | mm Hg | 469 | High (> 100) | Medium (10 - 100) | Low (< 10) |
| | | 701 | • | (0) | \O´ |
| • Liquid Viscosity | cPoise | 0.45 | High (>20) | Medium (2 -20) | Low (< 2) |
| | | 0.45 | 0 | 0 | • |
| • Liquid Density | g/cm ³ | 0.73 | Low (< 1) | Medium (1 -2) | High (> 2) |
| | J. 222 | 0,73 |) e | , O | O |
| | | | | | |

- Cost is from \$150 to \$200 per cubic yard.
- Using surfactants may increase effectiveness
- Effluent requires separation techniques such as distillation, evaporation, centrifugation
- Most effective when used ex-situ (above ground)

TABLE A-10. WORKSHEET FOR EVALUATING THE FEASIBILITY OF HYDRAULIC BARRIERS **WORKING AT YOUR SITE**



| CRITICAL SUCCESS FACTOR UNITS SITE OF INTEREST SUCCESS LESS LESS LESS LESS MORE LIKELY SUCCESS MORE LIKELY RELEASE - RELATED Time Since Release months On e. Long (s 12 months) Medium (1 - 12 months) Short (s 1) . Volume of Spill gallons 500 Small (s 100) Medium (100 - 1000) (s 1000) . Small (s 100) Dominant Contaminant Phase Description Conductivity Crm/sec. 10 - 2 High (s 10°3) Medium (10°5-10°3) Low (s 10°3) . Soil Sorption Capacity - Surface Area m2/g 0.005 High (s 10°3) Medium (0.1 - 1) Low (s 0.1) . Carbon Content % weight 0.2 High (s 10°4) Medium (1 - 10) (s 0.1) . Temperature °C 8 Low (s 0.1) High (s 10°4) Low (s 10°4) . Depth to Groundwater meters 5 High (s 20°4) Low (s 10°4) . Liquid Viscosity c Poise 0.45 High (s 20°4) Medium (1 - 10°4) Low (s 10°4) | | | | | | |
|---|----------------------|----------|--------|---|---------------------------------------|--|
| • Time Since Release months One Long (> 12 months) (1 - 12 months) Medium (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< 1) (< | | UNITS | | LESS | SOMEWHAT | MORE |
| • Time Since Release months One (>12 months) (1 - 12 months) (<1) | RELEASE - RELATED | | | | | |
| • Volume of Spill gallons 500 (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (<100) (< | • Time Since Release | months | one | (> 12 months) | | (< 1) |
| • Dominant Contaminant Phase Description Capacity - Carbon Content Carbon Content Medium (10-5-10-3) (2-10) (| • Volume of Spill | gallons | 500 | (<100) | | (> 1000) |
| Dominant Contaminant Phase Liquid O Medium (10.5-10.3) Low (<10.5) | SITE RELATED | | | | | |
| Soil Sorption Capacity - Surface Area m2/g 0.005 High (>1) (0.1 - 1) (0.1 - 1) (0.1 - 1) Low (<0.1) (<0.1) • Carbon Content % weight 0.2 High (>10%) (1 - 10) (1 - 10) (<1) | | phase | Liquid | | - 0 | Liquid |
| - Soli Sorption Capacity - Surface Area - Carbon Content - Carbon Conten | | cm/sec. | 10-2 | High (> 10 ⁻³) ● | (10 ⁻⁵ -10 ⁻³) | (< 10 ⁻⁵) |
| Carbon Content % weight O. 2. (> 10%) O O (1 - 10) O O (< 1) O O • Temperature • C 8 Low (<5) O O O O O O O O O O O O O O O O O O O | | m²/g | 0.005 | (> 1) | (0.1 - 1) | |
| • Temperature • C • C • C • C • C • C • C • | Carbon Content | % weight | 0.2 | (> 10%) | (1 - 10) | |
| . Depth to Groundwater meters | Temperature | °C | 8 | (<5) | | (>10) |
| • Liquid Viscosity c Poise 0.45 High Medium Low (< 2) | Depth to Groundwater | meters | 5 | (>5) | | (< 1) |
| c Poise 0, 45 (> 20) (2 to 20) (< 2) | CONTAMINANT- RELATED | | | | | e de la companya de l |
| | • Liquid Viscosity | c Poise | 0.45 | (> 20) | | |

- Cost is from \$10 to \$90 per cubic meter.
- Only affects liquid portion of release—not portion sorbed to soil.
 Typically limited to shallow (<3 meters) depths.
- · Not effective in removing contaminants to low levels.
- Most effective when contamination is confined to small areas.
- Not effective for #6 fuel oil and other viscous fluids.
- Not effective if contamination is greater than 15 meters deep.

TABLE A-11. WORKSHEET FOR EVALUATING THE FEASIBILITY OF EXCAVATION BEING EFFECTIVE AT YOUR SITE



| | | , | | | |
|---|------------------------|---------------------|--|-------------------------------|------------------------------|
| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
| SITE RELATED | | | | | |
| Proximity of Above and Below Ground Structures | _ | nearby | Buildings nearby Buried pipes and cables | _ O | No nearby structures O |
| Volume of Soil Contaminated | Cubic Meters | 97 | Large (> 1,000) O | Medium (100 -1,000) O | Small (< 100) |
| • Depth of Contamination | Meters From Surface | 4.9 | Deep (> 5) O | Medium (1-5) ● | Shallow (< 1) O |
| Proximity of Site to Traffic | _ | Near | Near | _ | Far O |
| - Businesses | _ | Near | Near • | | Far O |
| - Disposal Site | _ | Far | Far ● | | Near O |
| - Backfill Source | | Far | Far • | | Near O |

- Cost is from \$50 to \$300 per cubic yard.
- Appropriate when urgent response is necessary
- Brings contaminants to surface, thereby increasing exposure risks
- Significant amounts of surface area disturbed relative to depth excavated
- Requires suitable means of disposal. This is becoming increasingly difficult because some landfill operators consider petroleum-laden soil to be a hazardous waste.

• Proximity of Site to Disposal Site — this is important in that disposal costs of hazardous substances are expensive and are likely to become more so. For this case study, the assumption was made that an adequate disposal site was at a great enough distance to significantly increase the cost of the corrective action.

A review of the completed worksheets shows that soil venting and soil flushing are likely to be the most effective soil treatment technologies given the present understanding of the site. The worksheets for these technologies show numerous factors where success is "somewhat" to "more" likely. Site conditions may also be amenable to using a hydraulic barrier method to recover some residual liquid. The worksheet for biorestoration is inconclusive; none of the three "likelihood" columns definitively indicate success or failure of the method. Excavation at the site appears unlikely since most of the CSFs indicate success to be less likely. A brief analysis of the results of the worksheets for each technology is presented below.

Soil Venting — Site conditions are conducive for soil venting to be effective at this site. The worksheet suggests that effectiveness could be improved if soil temperature could be increased somewhat. Further, it was assumed that heterogeneous soil conditions exist. It would be prudent to collect soil borings to better define the substrata. If clay layers or lens exist at the site of interest, then the effectiveness of soil venting could be "short-circuited." The less permeable clay would tend to retard and restrict the movement of air and limit the distribution of nutrients throughout the contamination zone.

Biorestoration — Conditions at the site suggest that biorestoration might be effective if soil temperature and pH could be made more favorable. The relatively high hydraulic conductivity shows that oxygen and nutrients can be readily distributed throughout the contaminated zone to promote microbial activity. This option may be more desirable if used in conjunction with biorestoration of groundwater in the saturated zone, where addition of nutrient and oxygen laden water to the unsaturated zone could serve to flush contaminants down to the saturated zone as well as biodegegrade them.

Soil Flushing - Site conditions are such that soil flushing is likely to be highly effective at this site, although the density of the released petroleum is somewhat low. The solubility, on the other hand, is sufficiently high so that much of the contamination could be leached out of the soil.

Hydraulic Barriers — The worksheet suggests that site conditions are such that hydraulic barriers might be effective at this site. Because the spill was recent, much of the contaminant is likely to be in the residual liquid phase. If further analysis showed that a collection trench could be dug quickly and easily, some of the residual liquid could be recovered with minimal cost and effort.

Excavation - The worksheet suggests that excavation is not a suitable alternative at this site. Buildings and buried cables are nearby, and a disposal site for the excavated material is far away. Excavation could be undertaken at the site, but it would have to be done painstakingly. Other treatment technologies would be easier to undertake. However, if speed of clean-up is an overriding concern, excavation could prove to be a viable option.

GLOSSARY OF TERMS

Aerobic - in the presence of oxygen.

Anaerobic - in the absence of oxygen.

Biodegradation - a process by which microbial organisms transform or alter through enzymatic action the structure of chemicals introduced into the environment.

Biomass - The amount of living matter in a given area or volume.

- 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 between the soil grains.
- Capillary Suction process where water rises above the water table into the void spaces of a soil due to tension forces between the water and soil particles.
- Capillary Fringe The zone of a porous medium above the water table within which the porous medium is saturated but is at less than atmospheric pressure. The capillary fringe is considered to be part of the vadose zone, but not of the unsaturated zone.
- Consolidated Soil when a soil is subjected to an increase in pressure due to loading at the ground surface, a re-adjustment in the soil structure occurs. The volume of space between the soil particles decreases and the soil tends to settle or consolidate over time.
- Degradation Potential the degree to which a substance is likely to be reduced to a simpler form by bacterial activity.
- Dissolution Dissolving of a material in a liquid solvent (e.g., water).
- Elutriate the mixture of water, surfactants, and contaminants that is recovered during the soil flushing process.

Fermentation - the breakdown of complex molecules in an organic compound.

- Free Product a contaminant in the unweathered phase, where no dissolution or biodegradation has occurred.
- Field Capacity the percentage of water remaining in the soil 2 or 3 days after gravity drainage has ceased from saturated conditions.
- Henry's Law the relationship between the partial pressure of a compound and the equilibrium concentration in the liquid through a constant of proportionality known as Henry's Law Constant. See partial pressure.
- Hydraulic Conductivity the constant of proportionality in Darcy's Law relating the rate of flow of water through a cross-section of porous medium in response to a hydraulic gradient. Also known as the coefficient of permeability, hydraulic conductivity is a function of the intrinsic permeability of a porous medium and the kinematic viscosity of the water which flows through it. Hydraulic conductivity has units of length per time (cm/sec).
- Interfacial tension phenomena occurring at the interface of a liquid and gas where the liquid behaves as it if were covered by an elastic membrane in a constant state of tension. The tension is due to unbalanced attractive forces between the liquid molecules at the liquid surface.
- Liquid Density the amount of mass of a liquid per unit volume of the liquid.
- Mobility the ability of a substance to move into or out of a phase due to physical or chemical processes.
- Moisture Content the amount of water lost from the 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; in the vadose zone, moisture content ranges between zero and the porosity value for the medium. See porosity, vadose zone, saturated zone.
- Molecular Diffusion process where molecules of various gases tend to intermingle and eventually become evenly dispersed.
- Molecular Weight the amount of mass in a mole of molecules of a substance determined by summing the masses of the individual atoms comprising the molecule. One mole is equivalent to 6.02×10^{23} molecules.

- Partial Pressure the portion of total vapor pressure in a system due to one or more constituents in the vapor mixture.
- Particle Density the amount of mass of a substance per unit volume of the substance.
- Permeability a measure of a soils resistance to fluid flow.

 Permeability, along with fluid viscosity and density are used to determine fluid conductivity.
- Phase the physical form in which a substance is found. As discussed in this manual, the three major phases are liquid, vapor and dissolved in pore water.
- Porosity the volume fraction of a rock or unconsolidated sediment not occupied by solid material but usually occupied by water and/or air. Porosity is a dimensionless quantity.
- Pressure Gradient a pressure differential in a given medium, such as water or air, which tends to induce movement from areas of higher pressure to areas of lower pressure.
- Refractory Index a measure of the ability of a substance to be biodegraded by bacterial activity.
- Residual Saturation the amount of water or oil remaining in the voids of a porous medium and held in an immobile state by capillary and dead-end pores.
- Saturated Zone the zone of the soil below the water table where all space between the soil particles is occupied by water.
- Soil Sorption Coefficient a measure of the preference of an organic chemical to leave the dissolved aqueous phase in the soil and become attached or adsorbed to soil particles as organic carbon.
- Solubility the amount of mass of a compound that will dissolve into a unit volume of solution.
- Sorption a general term used to encompass the process of absorption, adsorption, ion exchange, and chemisorption.

- Surfactant natural or synthetic chemicals that have the ability to promote the wetting, solubilization, or emulsification of various organic chemicals.
- Unsaturated Zone the portion of a porous medium, usually above the water table in an unconfined aquifer, within which the moisture content is less than saturation and the capillary pressure is less than atmospheric pressure. The unsaturated zone does not include the capillary fringe.
- Vadose Zone the portion of a porous medium above the water table within which the capillary pressure is less than atmospheric and the moisture content is usually less than saturation. The vadose zone includes the capillary fringe.
- Vapor Density the amount of mass of a vapor per unit volume of the vapor.
- Vapor Pressure the equilibrium pressure exerted on the atmosphere by a liquid or solid at a given temperature. Also a measure of a substance's propensity to evaporate or give off flammable vapors. The higher the vapor pressure, the more volatile the substance.
- Volatilization the process of transfer of a chemical from the water or liquid phase to the air phase. Solubility, molecular weight, and vapor pressure of the liquid and the nature of the air-liquid/water interface affect the rate of volatilization. See solubility, vapor pressure.
- Water Content see moisture content
- Water Table the water surface in an unconfined aquifer at which the fluid pressure in the voids is at atmospheric pressure.
- Weathering the process where a complex compound is reduced to its simpler component parts, transported through physical processes, or biodegraded over time.

Blank Worksheets

TABLE A-1. LIKELIHOOD OF LIQUID CONTAMINANTS BEING PRESENT IN THE UNSATURATED ZONE



| FACTOR | UNITS | SITE OF INTEREST | INCREASING LIKELIHOOD | | |
|---------------------------------------|---------|---------------------------------------|------------------------------|---|-------------------------------|
| RELEASE- RELATED | | | | · · · · · · · · · · · · · · · · · · · | |
| Amount Released | gallons | | Small (<100) | Medium (100-1000) | Large (>1000) |
| • Rate Of Release | | | Slow Release | | Instantaneous Release O |
| - Time Since Release | months | | Long (>12) O | Medium (1 - 12) O | Short (< 1) O |
| SITE - RELATED | | | | | |
| Depth To Groundwater | meters | | Shallow (< 1) O | Medium (1-5) O | Deep (>5) |
| Hydraulic Conductivity | cm/sec | | High (>10 ⁻³) | Medium (10 ⁻⁵ -10 ⁻³) | Low (<10 ⁻⁵) |
| • Rainfall Infiltration Rate | cm/day | · · · · · · · · · · · · · · · · · · · | High (>0.1) | Medium (0.05 - 0.1) | Low (<0.05) |
| Soil Temperature | °C | | Warm (>20) O | Medium (10 - 20) | Cool (<10) O |
| Soil Sorption Capacity (Surface Area) | m²/g | | Low (<0.1) O | Medium (0.1 - 1) O | High (>1) O |
| CONTAMINANT- RELATED | | . " | | ¥ : | |
| • Liquid Viscosity | сР | | Low (<2) O | Medium (2-20) O | High (>20) O |
| • Liquid Density | g/cm | | High (>2) O | Medium (1-2) O | Low (<1) O |
| • Vapor Pressure | mm Hg | | High (>100) O | Medium (10-100) O | Low (<10) O |
| • Water Solubility | mg/L | | High (>1000) O | Medium (100-1000) O | Low (<100) O |

TABLE A-2. LIKELIHOOD OF CONTAMINANT VAPORS BEING PRESENT IN THE UNSATURATED ZONE



| FACTOR | UNITS | SITE OF INTEREST | INCREASING LIKELIHOOD | | |
|---|-------------------|---------------------|-----------------------------|---|-------------------------------|
| RELEASE- RELATED | | | | | |
| Amount Released | gallons | | Small (<100) | Medium (100-1000) | Large (>1000) |
| | | | 0 | 0 | 0 |
| • Rate Of Release | | | Slow Release | | Instantaneous Release O |
| • Time Since Release | months | | Long (>12) O | Medium (1-12) | Short (< 1) O |
| SITE - RELATED | | | et e j | | |
| Depth To Groundwater | meters | | Shallow (< 1) O | Medium (1-5) O | Dеер (>5) О |
| Air Conductivity | cm/sec | | High (>10 ⁴) | Medium (10 ⁻⁶ -10 ⁻⁴) | Low (<10 ⁻⁶) |
| • Rainfall Infiltration Rate | cm/day | | High (>0.1) | Medium (.005-0.1) | Low (<0.05) |
| • Soil Temperature | °C | | Cool (<10) O | Medium (10 - 20) O | Warm (>20) O |
| Soil Sorption Capacity (Surface Area) | m ² /g | | Low (<0.11) O | Medium (0.1 - 1) O | High (>1) O |
| CONTAMINANT- RELATED | | | | | |
| • Liquid Viscosity | сР | | High (>20) | Medium (2-20) | Low (<2) O |
| • Liquid Density | g/cm | | High (>2) O | Medium (1-2) O | Low (<1) O |
| Vapor Pressure | mm Hg | | Low (<10) O | Medium (10-100) O | High (>100) O |
| • Water Solubility | mg/L | | High (>1000) O | Medium (100-1000) O | Low (<100) O |

TABLE A-3. LIKELIHOOD OF CONTAMINANTS DISSOLVED IN PORE WATER BEING PRESENT IN THE UNSATURATED ZONE



| FACTOR | UNITS | SITE OF INTEREST | INCREASING LIKELIHOOD | | |
|---|-------------------|---------------------|-------------------------------|---------------------------|----------------------------|
| RELEASE- RELATED | | | | | |
| Amount Released | gallons | | Small (100) | Medium (100-1000) | Large (>1000) |
| • Rate Of Release | | | Instantaneous Release O | | Slow Release |
| • Time Since Release | months | | Long (>12) O | Medium (1-12) | Short (< 1) O |
| SITE - RELATED | | | | | |
| • Depth To Groundwater | meters | | Shallow (< 1) O | Medium (1-5) | Deep (>5) |
| • Moisture Content | % volume | | Low (<10) | Medium (10-30) | High (>30) |
| • Soil Porosity | % volume | | Low (<20) | Medium (20-40) | High (>40) |
| • Rainfail Infiltration Rate | cm/day | | Low (<0.05) O | Medium (0.05-0.1) | High (>0.1) O |
| Soil Sorption Capacity (Surface Area) | m²/g | | Low (<0.1) O | Medium (0.1-1) | High (>1) O |
| CONTAMINANT- RELATED | | | | | |
| • Liquid Viscosity | сР | | High (>20) O | Medium (2-20) O | Low (<2) O |
| • Liquid Density | g/cm ³ | | High (>2) O | Medium (1-2) O | Low (<1) O |
| Vapor Pressure | mm Hg | | High (<100) O | Medium (10-100) O | Low (>10) O |
| Water Solubility | mg/L | | Low (<100) O | Medium (100-1000) O | High (>1000) O |

TABLE A-4. FACTORS TO EVALUATE THE MOBILITY OF LIQUID CONTAMINANTS



| FACTOR | UNITS | SITE OF INTEREST | INCREASING MOBILITY | | | |
|------------------------|-------------------|---------------------|-----------------------------|--|------------------------------------|--|
| RELEASE RELATED | - | | | | | |
| • Time Since Release | Months | | Long (>12) | Medium (1-12) | Short (<1) | |
| SITE - RELATED | <u> </u> | | 00 | 0 | 0 | |
| Hydraulic Conductivity | cm/sec | | Low (<10 ⁻⁵) | Medium (10 ⁻⁵ - 10 ⁻³) | High (> 10 ⁻³) O | |
| • Soil Porosity | % Soil Volume | | Low (<10) O | Medium (10-30) O | High (> 30) O | |
| Soil Surface Area | m² /g | | High (>1) O | Medium (0.1-1) | Low (< 0.1) O | |
| Soll Temperature | °C | | Low (<10) O | Medium (10-20) O | High (> 20) O | |
| Rock Fractures | _ | | Absent O | 1 0 | Present O | |
| Moisture Content | % Volume | | High (>30) O | Medium (10-30) O | Low (< 10) O | |
| CONTAMINANT- RELATED | | | | | | |
| • Liquid Viscosity | cPoise | | High (>20) O | Medium (2-20) O | Low (<2) O | |
| • Liquid Density | g/cm ³ | | Low (<1) O | Medium (1-2) O | High (>2) O | |

TABLE A-5. FACTORS TO EVALUATE THE MOBILITY OF CONTAMINANT VAPORS



| FACTOR | UNITS | SITE OF INTEREST | INCREASING MOBILITY | | | | |
|-----------------------|------------------|---------------------|---------------------|-------------------------|-----------------------------|--|--|
| SITE - RELATED | | | | | | | |
| • Air Filled Porosity | % Volume | | Low (<10) | Medium (10- 30) | High (> 30) O | | |
| - Total Porosity * | % Volume | | Low (<10) O | Medium (10- 30) O | High (> 30) O | | |
| • Water Content * | % Volume | | High (> 30) | Medium (10- 30) | Low (< 10) O | | |
| Depth Below Surface | meters | | Deep (>10) O | Medium (2 - 10) O | Shallow (< 2) O | | |
| CONTAMINANT- RELATED | | | | | | | |
| · Vapor Density | g/m ³ | | Low (< 50) | Medium (50-500) | High (>500) O | | |

^{*} the total porosity less that fraction filled with water equals the air filled porosity

TABLE A-6. FACTORS TO EVALUATE THE MOBILITY OF CONTAMINANTS IN PORE WATER



| FACTOR | UNITS | SITE OF INTEREST | INCREASING MOBILITY | | |
|------------------------------|----------|------------------|----------------------------|---|------------------------------------|
| SITE RELATED | | | | | |
| • Hydraulic Conductivity | cm/sec. | | Low (10 ⁻⁵) | Medium (10 ⁻⁵ - 10 ⁻³) O | High (> 10 ⁻³) O |
| Moisture Content | % Volume | | Low (< 10) O | Medium (10 -30) O | High (> 30) O |
| • Rainfall Infiltration Rate | cm/day | | Low (< 0.05) O | Medium (0.05-0.1) | High (>0.1) O |
| • Soil Porosity | % Volume | | Low (< 10) O | Medium (10 - 30) O | High (> ³⁰) O |
| • Rock Fractures | _ | | Absent O | 0 | Present O |
| Depth Below Surface | meters | | Shallow (< 2) O | Medium (2 - 10) O | Deep (> 10) O |
| CONTAMINANT- RELATED | | | | | |
| • Water Solubility | mg/L | | Low (< 100) O | Medium (100 to 1000) O | High (>1000) O |

TABLE A-7. WORKSHEET FOR EVALUATING THE FEASIBILITY OF SOIL VENTING BEING EFFECTIVE AT YOUR SITE



| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
|--------------------------------|-------------|---------------------|------------------------------|---|-------------------------------|
| SITE RELATED | | | | | |
| Dominant Contaminant Phase | Phase | | Sorbed to soil | Liquid | Vapor |
| Containinant Filase | | | 0 | 0 | 0 |
| Soil Temperature | ပံ့ | | Low (< 10) | Medium (10 - 20) | High (> 20) |
| · | | | O O | 0 | `O´ |
| Soil Air Conductivity | cm/sec. | | Low (< 10 ⁻⁶) | Medium (10 ⁻⁶ -10 ⁻⁴) | High (> 10 ⁻⁴) |
| | | | \\o\ | (,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,, | Y O |
| Moisture Content | % volume | | Moist | Moderate (10 - 30) | Dry |
| | 78 VOIGITIO | | (> 30) O | O (10 - 30) | (< 10) O |
| • Geological | | | Heterogeneous | | Homogeneous |
| Conditions | | | 0 | 0 | 0 |
| Soil Sorption Capacity | 2 | | High | <u>—</u> | Low |
| - Surface Area | m/g | | (> 1) O | 0 | (< 0.1) O |
| | | | Low | Medium | High |
| Depth to Ground Water | meters | | (<1) O | (1-5) O | (>5) O |
| CONTAMINANT- RELATED | | | | | |
| Vanor Processes | | <u> </u> | Low | Medium (10 to 100) | High (> 100) |
| Vapor Pressure | mm Hg | | (< 10) O | (10 to 100) | (\$ 100) |
| Webs Oak bills | | | High | Medium | Low (- 100) |
| Water Solubility | mg/L | | (> 1000) O | (100 - 1000) O | (< 100) O |

- Cost is from \$15 to \$60 per cubic yard.
- Effictiveness decreases after several months of treatment.
- · Capable of removing thousands of gallons.
- · Air emissions will likely need to be treated with GAC.
- Treatment can be done on-site
- Care must be taken to avoid explosions because vapors are concentrated
- Cleanup takes time so that this technology is not appropriate when emergency response is needed

TABLE A-8. WORKSHEET FOR EVALUATING THE FEASIBILITY OF BIORESTORATION BEING EFFECTIVE AT YOUR SITE



| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
|---------------------------------------|---------------|---------------------|----------------------------------|--|------------------------------------|
| RELEASE - RELATED | | | | | |
| - Time Since Release | Months | | Short (< 1) O | Medium (1 - 12) O | Long (> 12) O |
| SITE RELATED | | | | | |
| Dominant Contaminant Phase | Phase | | Liquid O | Vapor O | Dissolved O |
| Soil Temperature | °C | | Low (< 5) O | Medium (5 - 10) O | High (> 10) O |
| Soil Hydraulic Conductivity | cm/sec. | | Low (<10 ⁻⁵) O | Medium (10 ⁻⁵ -10 ⁻³) O | High (> 10 ⁻³) O |
| • Soil pH | pH Units | | (< 6 or > 8) | - 0 | (6 - 8) O |
| • Moisture Content | % Volume | | Dry (< 10) O | Moderate (10 to 30) | Moist (> 30) O |
| CONTAMINANT- RELATED | | | | | |
| • Solubility | mg/L | | Low (< 100) O | Medium (100 to 1000) O | High (> 1000) O |
| Blodegradability Refractory Index | Dimensionless | | Low (< 0.01) O | Medlum (0.01 to 0.1) O | High (> 0.1) O |
| • Fuel Type | _ | | No. 6 Fuel Oil (Heavy) | No. 2 Fuel Oil (Medium) | Gasoline/ Diesel (Light) |

- Cost is from \$60 to \$125 per cubic yard.
- · Completely destroys contaminants under optimal conditions
- Effectiveness varies depending on subsurface conditions
- · Biologic systems subject to upset
- Public opinion sometimes against putting more chemicals in ground
- Difficult to monitor effectiveness
- · Minimizes health risk by keeping contaminants in ground and on site
- Takes long time to work—not for emergency response

TABLE A-9. WORKSHEET FOR EVALUATING THE FEASIBILITY OF SOIL FLUSHING BEING EFFECTIVE AT YOUR SITE



| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
|---|-------------------|---------------------|-----------------------------|---|------------------------------------|
| SITE RELATED | | | | | |
| • Dominant | Phase | | Vapor | Liquid | Dissolved |
| Contaminant Phase | | | 0 | 0 | 0 |
| Soil Hydraulic Conductivity | cm/sec. | | Low (<10 ⁻⁵) | Medium (10 ⁻⁵ -10 ⁻³) O | High (> 10 ⁻³) O |
| - Soil Surface Area | m²/g | | High (>1) O | Medium (0.1 - 1) O | Small (< 0.1) O |
| - Carbon Content | % Wei g ht | | High (> 10 %) O | Medium (1 - 10%) O | Low (< 1%) O |
| • Fractures in Rock | - | | Present O | 10 | Absent O |
| CONTAMINANT- RELATED | | | | : | |
| Water Solubility | mg/L | | Lo w (< 100) O | Medium (100 to 1000) O | High (>1,000) O |
| Sorption Characteristics Soil Sorption Constant | L/kg | | High (>10,000) O | Medium (100-10,000) O | Lo w (< 100) |
| Vapor Pressure | mm Hg | | High (> 100) O | Medium (10 - 100) O | Lo w (< 10) O |
| • Liquid Viscosity | cPoise | | High (>20) O | Medium (2 -20) O | Low (< 2) O |
| • Liquid Density | g/cm ³ | | Low (< 1) O | Medium (1 -2) O | High (> 2) O |

- Cost is from \$150 to \$200 per cubic yard.
- · Using surfactants may increase effectiveness
- Effluent requires separation techniques such as distillation, evaporation, centrifugation
- Most effective when used ex-situ (above ground)

TABLE A-10. WORKSHEET FOR EVALUATING THE FEASIBILITY OF HYDRAULIC BARRIERS WORKING AT YOUR SITE



| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY |
|---|----------|---------------------|------------------------------------|--|------------------------------|
| RELEASE - RELATED | | | - | | |
| • Time Since Release | months | | Long (> 12 months) O | Medium (1 12 months) O | Short (< 1) O |
| Volume of Spill | gallons | | Small (<100) O | Medium (100 - 1000) O | Large (> 1000) O |
| SITE RELATED | | | | | |
| Dominant Contaminant Phase | phase | | Vapor O | 0 | Liquid O |
| Soil Hydraulic Conductivity | cm/sec. | | High (> 10 ⁻³) O | Medium (10 ⁻⁵ -10 ⁻³) O | Low (< 10 ⁻⁵) |
| Soil Sorption Capacity Surface Area | m²/g | | High (> 1) O | Medium (0.1 - 1) O | Low (< 0.1) O |
| Carbon Content | % weight | | High (> 10%) O | Medium (1 10) O | Low (< 1) O |
| Temperature | °C | | Low (<5) O | Medium (5 - 10) O | High (>10) O |
| Depth to Groundwater | meters | | High (>5) O | Medium (1 - 5) O | Low (< 1) O |
| CONTAMINANT- RELATED | | | | | |
| • Liquid Viscosity | c Poise | | High (> 20) O | Medium (2 to 20) O | Low (< 2) O |

- Cost is from \$10 to \$90 per cubic meter.
- Only affects liquid portion of release—not portion sorbed to soil.
- Typically limited to shallow (<3 meters) depths.
- · Not effective in removing contaminants to low levels.
- · Most effective when contamination is confined to small areas.
- Not effective for #6 fuel oil and other viscous fluids.
- Not effective if contamination is greater than 15 meters deep.

TABLE A-11. WORKSHEET FOR EVALUATING THE FEASIBILITY OF EXCAVATION BEING EFFECTIVE AT YOUR SITE



| CRITICAL SUCCESS FACTOR | UNITS | SITE OF INTEREST | SUCCESS LESS LIKELY | SUCCESS SOMEWHAT LIKELY | SUCCESS MORE LIKELY | | | | |
|---|------------------------|---------------------|--|-------------------------------|------------------------------|--|--|--|--|
| SITE RELATED | SITE RELATED | | | | | | | | |
| Proximity of Above and Below Ground Structures | _ | | Buildings nearby Buried pipes and cables O | _ 0 | No nearby structures | | | | |
| Volume of Soil Contaminated | Cubic Meters | | Large (> 1,000) O | Medium (100 -1,000) O | Small (< 100) O | | | | |
| Depth of Contamination | Meters From Surface | | Deep (> 5) O | Medium (1-5) O | Shallow (< 1) O | | | | |
| Proximity of Site to Traffic | | | Near O | _ | Far O | | | | |
| - Businesses | _ | | Near O | | Far O | | | | |
| - Disposal Site | | | Far O | _ | Near O | | | | |
| - Backfill Source | _ | | Far O | | Near O | | | | |

- Cost is from \$50 to \$300 per cubic yard.
- · Appropriate when urgent response is necessary
- Brings contaminants to surface, thereby increasing exposure risks
- Significant amounts of surface area disturbed relative to depth excavated
- Requires suitable means of disposal. This is becoming increasingly difficult because some landfill operators consider petroleum-laden soil to be a hazardous waste.