Guide for Assessing and Remediating Petroleum Hydrocarbons in Soils

API PUBLICATION 1629
FIRST EDITION, OCTOBER 1993

STEP
Strategies for Today's
Environmental Partnership

American Petroleum Institute
1220 L Street, Northwest
Washington, D.C. 20005

Guide for Assessing and Remediating Petroleum Hydrocarbons in Soils

Manufacturing, Distribution and Marketing Department

API PUBLICATION 1629
FIRST EDITION, OCTOBER 1993

American Petroleum Institute

SPECIAL NOTES

1. API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.

2. API IS NOT UNDERTAKING TO MEET THE DUTIES OF EMPLOYERS, MANUFACTURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, NOR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.

3. INFORMATION CONCERNING SAFETY AND HEALTH RISKS AND PROPER PRECAUTIONS WITH RESPECT TO PARTICULAR MATERIALS AND CONDITIONS SHOULD BE OBTAINED FROM THE EMPLOYER, THE MANUFACTURER OR SUPPLIER OF THAT MATERIAL, OR THE MATERIAL SAFETY DATA SHEET.

4. NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANUFACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COVERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABILITY FOR INFRINGEMENT OF LETTERS PATENT.

5. GENERALLY, API STANDARDS ARE REVIEWED AND REVISED, REAFFIRMED, OR WITHDRAWN AT LEAST EVERY FIVE YEARS. SOMETIMES A ONE-TIME EXTENSION OF UP TO TWO YEARS WILL BE ADDED TO THIS REVIEW CYCLE. THIS PUBLICATION WILL NO LONGER BE IN EFFECT FIVE YEARS AFTER ITS PUBLICATION DATE AS AN OPERATIVE API STANDARD OR, WHERE AN EXTENSION HAS BEEN GRANTED, UPON REPUBLICATION. STATUS OF THE PUBLICATION CAN BE ASCERTAINED FROM THE API AUTHORING DEPARTMENT [TELEPHONE (202) 682-8000]. A CATALOG OF API PUBLICATIONS AND MATERIALS IS PUBLISHED ANNUALLY AND UPDATED QUARTERLY BY API, 1220 L STREET, N.W., WASHINGTON, D.C. 20005.

FOREWORD

This publication provides general information regarding site and release characteristics relevant to and methods for assessing and remediating soils contaminated with petroleum hydrocarbons released from underground or aboveground storage tanks. This publication is a companion document to API Publication 1628, *A Guide to the Assessment and Remediation of Underground Petroleum Releases.*

Throughout this standard, soft-conversion (calculated) units are provided in parentheses following actual units. Soft-conversion units are provided for the user's reference only.

API publications may be used by anyone desiring to do so. Every effort has been made by the institute to assure the accuracy and reliability of the data contained in them; however, the institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any federal, state, or municipal regulation with which this publication may conflict.

Suggested revisions are invited and should be submitted to the director of the Manufacturing, Distribution and Marketing Department, American Petroleum Institute, 1220 L Street, N.W., Washington, D.C. 20005.

CONTENTS

SECTION 6—CORRECTIVE-ACTION OPTIONS

SECTION 7—REFERENCES

Figures

Tables

Guide for Assessing and Remediating Petroleum Hydrocarbons in Soils

SECTION 1—INTRODUCTION

1.1 Purpose and Scope

This publication provides general information regarding the site and release characteristics relevant to and methods for assessing and remediating soils contaminated with petroleum hydrocarbons released from underground storage tank (UST) or aboveground storage tank (AST) systems and operations. It is designed to provide the reader with a basic understanding of the interaction between motor fuel and soils, the techniques for determining if petroleum hydrocarbons are present in the soil at a site, and the methods for quantifying the extent of hydrocarbons in the soil. Several conventional and proven technologies for treating soils containing hydrocarbons are discussed, and information for selecting one or more alternatives is provided.

In this publication, *petroleum hydrocarbons* and *motor fuel* include all grades of leaded and unleaded gasoline, kerosene, and diesel fuel that are commonly found at vehicle refueling facilities across the country. This publication primarily addresses the assessment and remediation of soils containing petroleum hydrocarbons in the unsaturated zone. The influence that groundwater fluctuation has on the lower portion of the unsaturated zone in specific situations is discussed briefly (see Section 2 for definitions and examples).

Whenever possible, the use of technical terms has been avoided; however, when such usage is necessary, the term is italicized and immediately defined in the text that follows.

1.2 Background and Organization

This document was developed to complement API Publication 1628, *A Guide to the Assessment and Remediation of Underground Petroleum Releases* [1], which focuses primarily on assessing and remediating petroleum releases that may impact groundwater.

This document contains six sections. The first two sections provide basic background information; Sections 3 through 6 are organized to reflect the common progression of events involved in identifying, assessing, and remediating soils that contain petroleum hydrocarbons.

The assessment and remediation of soils exposed to petroleum hydrocarbon releases involve the application of selected technologies to one or more of the following hydrocarbon phases:

a. Liquid phase, which includes residual hydrocarbons in soil (free product).
b. Dissolved phase in soil water.
c. Vapor phase.

Section 2 describes the physical and chemical properties of soils and hydrocarbon fuels, the characteristics of soils, and the interaction between petroleum hydrocarbons and soils. It also provides some fundamental information on how hydrocarbon phases behave in soils; such information is needed for properly assessing and confirming petroleum contamination and for effectively implementing corrective action. Section 3 presents an overview of emergency response and initial abatement. Section 4 presents a generic approach for conducting a site assessment. Section 5 discusses applicable sampling and analytical methods for use in the field or laboratory. Section 6 presents viable corrective-action options, including descriptions of in situ and aboveground corrective-action technologies such as soil vacuum extraction, bioremediation, land and thermal treatment, and other proven treatment alternatives for soils containing petroleum hydrocarbons.

1.3 Health and Safety Considerations

Appropriate safety precautions should always be taken at sites where soils are suspected of containing petroleum hydrocarbons. If a hazardous condition exists, the degree of hazard should be assessed so as to avoid physical harm to persons in the area. For example, if hydrocarbon vapors are generated from contaminated soil, the potential for explosion must be determined. The mixture of hydrocarbon vapors and oxygen could create explosive concentrations that are ignitable by a spark source, such as an electrical switch that is not designed to be intrinsically safe (explosion-proof).

Periodic field monitoring with combustible gas indicators and oxygen concentration meters should be conducted at any site where the potential for explosion or fire exists (see note). Explosive vapors from the volatilization of petroleum products in contaminated soil tend to be more dense than the surrounding air and can collect in an invisible layer near the ground, in excavations, or in confined spaces. Although a person can detect the presence of some vapors by smell, field monitoring by qualified personnel should be conducted for reliable identification and quantification (that is, the nature and extent) of the hazard. Because airborne concentrations of vapors can be affected by such variables as temperature, wind speed, rainfall, moisture, and work activities at a site, air monitoring should be repeated as site conditions and atmospheric conditions change.

Note: See Section 3 for a discussion of lower and upper explosive limits and flash points.

For further protection against fire or explosion, all potential ignition sources should be kept away from the area. Explosion-proof electrical equipment or air-powered tools should be used, and safe practices should be followed during the performance of any task that might create a hazardous atmosphere. For additional safety, potential sparking sources (for example, excavation equipment) should be operated upwind of the excavation, if possible.

The most serious immediate hazard, by far, is the threat of fire and explosion. However, the potential for exposure to constituents in motor fuels is another health and safety consideration. The Occupational Safety and Health Administration (OSHA) has developed regulations setting permissible limits for exposure to constituents; and guidelines for exposure have been developed by the National Institute for Occupational Safety and Health (NIOSH) [2] and the American Conference of Governmental Industrial Hygienists (ACGIH). Information on exposure limits for gasoline and the compounds listed in Table 1 can be found by consulting the latest editions of the Occupational Safety and Health Standards [3], and the ACGIH publication *Threshold Limit Values and Biological Exposure Indices for 1990–1991* [4]. Material safety data sheets (MSDS) from the manufacturer or supplier of the material, if identifiable, should also be reviewed.

The regulations and guidelines issued by OSHA, including Hazard Communication (HAZCOM) [5] and Hazardous Waste Operations and Emergency Response (HAZWOPER) [6]; the National Fire Protection Association (NFPA) [7]; NIOSH [2]; and ACGIH [4] should be used in the development of a site-specific safety program.

Table 1— Examples of Petroleum Constituents

Constituent
Benzene
Toluene
Ethyl benzene
Xylenes (ortho-, para-)
n-Butane
Pentane
n-Hexane
Cyclohexane
n-Heptane
Methylcyclohexane
Iso-octane
Tetraethyl lead (additive only)

1.4 Regulations and Codes

The U.S. Environmental Protection Agency (EPA) has promulgated regulations [8] establishing requirements for preventing, detecting, and reporting releases or suspected releases and for cleaning up releases from both new and existing UST systems, which are potential sources of hydrocarbon releases in soil. These regulations, Subtitle I of the Resource Conservation and Recovery Act (RCRA), became effective December 22, 1988. They apply to underground tanks in which petroleum substances are stored. For wastes that may be considered hazardous under RCRA, refer to 5.4.3 of this document.

States may develop their own comprehensive programs for preventing the occurrence of petroleum products in soils, groundwater, and surface water that are more stringent than the federal regulations. Consequently, a particular state or local jurisdiction may have specific reporting requirements for hydrocarbon releases, assessment results, analytical results, and remediation plans and progress. Permits may also be required for excavating, stockpiling, and treating soil containing petroleum hydrocarbons.

Details on specific state requirements can be obtained by contacting the appropriate state environmental regulatory agency or the state fire marshal. In some states (for example, California and Florida), county and local jurisdictions have developed their own ordinances, which may be more stringent than federal or state regulations.

1.5 Referenced Publications

A large body of reference material was assembled and used in developing this document. A list of relevant literature is presented in in Section 7. This reference list does not represent an exhaustive search but rather an accumulation of applicable and readily available information relating to the subject issues.

SECTION 2—INTERACTION OF HYDROCARBONS AND SOILS

2.1 Overview

A basic understanding of how hydrocarbons behave in different soils and hydrogeologic settings is necessary for effectively assessing and confirming the presence of petroleum and for implementing the appropriate corrective actions. The behavior of hydrocarbons in soils is governed by the physical and chemical properties of the hydrocarbon fuels and the characteristics of the soils through which these fuels migrate. This section briefly describes the characteristics of different soils and the physical and chemical properties of typical hydrocarbon fuels. It also addresses migration processes that influence the persistence and distribution of these fuels in soils.

2.2 Characteristics of Soils

For the purposes of this document, *soil* is defined as unconsolidated (loose) mineral and organic material that extends to bedrock. The soil matrix consists of air or vapor, water, and a variety of soil solids. *Soil solids* are composed of varying proportions of inorganic minerals and organic humic materials. The term *soil water* refers to water occurring in pore space between or on soil solids. The term *soil vapor* refers to the various gases that occupy the pore space between soil solids not occupied by soil water.

The distribution of water and air in soil is largely determined by the amount of available water and by the soil type, structure, and stratification. Figure 1 shows a static distribution of soil vapor and water in the subsurface when neither the vapor nor the water is in motion.

Two subsurface zones define the major distribution of soil vapor and water in the subsurface: the unsaturated zone and the saturated zone. The *unsaturated zone* extends from the ground surface to the top of the capillary fringe and contains soil vapor and a lesser amount of soil water. The *saturated zone* extends from the top of the capillary fringe to the bottom of the groundwater table. The spaces between soil solids in the saturated zone are filled with fluid. The term *groundwater* refers to all water in the saturated zone. The *capillary fringe* is the upper portion of the saturated zone, where groundwater moves upward from the groundwater table surface by *capillary forces* (resulting from surface tension and molecular attraction). The *groundwater table* is the surface along which the water pressure in the intergranular voids is equal to the local atmospheric pressure. The *water table* is a continuous surface that slopes from the recharge area of the water to the discharge area. The elevation of the water table fluctuates naturally throughout the year, and the fluctuation may range from a fraction of a foot to several tens of feet.

Fill material is often present in soil containing petroleum hydrocarbons. *Fill* is defined as any substance used to backfill previously excavated materials or topographically low areas. Fill materials commonly consist of soil, sand, gravel, or crushed rock.

Also present in the subsurface environment are biota (such as burrowing animals, plant roots, and microorganisms) and man-made structures (basements, utility service lines, and the like). An understanding of the interactions between these naturally occurring and man-made features and the movement of petroleum hydrocarbons is necessary for effectively assessing and remediating hydrocarbon-release sites.

2.2.1 SOIL CLASSIFICATION

The Unified Soil Classification System (USCS) is widely used in the United States. This system, which classifies soils according to their engineering properties, is based on soil texture, gradation, and liquid limit. The U.S. Department of Agriculture (USDA) has also developed a soil classification system based on physical, chemical, and biological properties. The USDA system uses such criteria as soil texture, soil structure, soil mineralogy, pH, salinity, and organic matter content. This system also addresses both surface and subsurface soil. The textural classes for these classification schemes are shown in Figure 2. The soil types range from clays to silts to sands, as shown at the three apexes of the textural triangles in Figure 2.

Despite the broad range of possible soil types, the actual soil types present at any particular site are frequently limited. Information on soil types present in specific areas is usually available from geologic reports and maps published by the U.S. Geological Survey (USGS) or from state geological surveys, logs of local drillers, and county soil survey reports published by the U.S. Soil Conservation Service (SCS).

2.2.2 PHYSICAL PROPERTIES OF SOILS

The physical properties of soils that strongly influence the behavior of petroleum hydrocarbon fuels are porosity, hydraulic conductivity, and the heterogeneity of these properties among different soil types. Porosity and hydraulic conductivity can vary within a soil. Large-scale differences in these physical properties can influence the multiphase transport of petroleum hydrocarbons.

2.2.2.1 Porosity

Porosity or *total porosity* is the ratio of the volume of void space in the soil to the total volume of soil material; it is expressed as a percentage. The following are typical total porosity values for different soils:

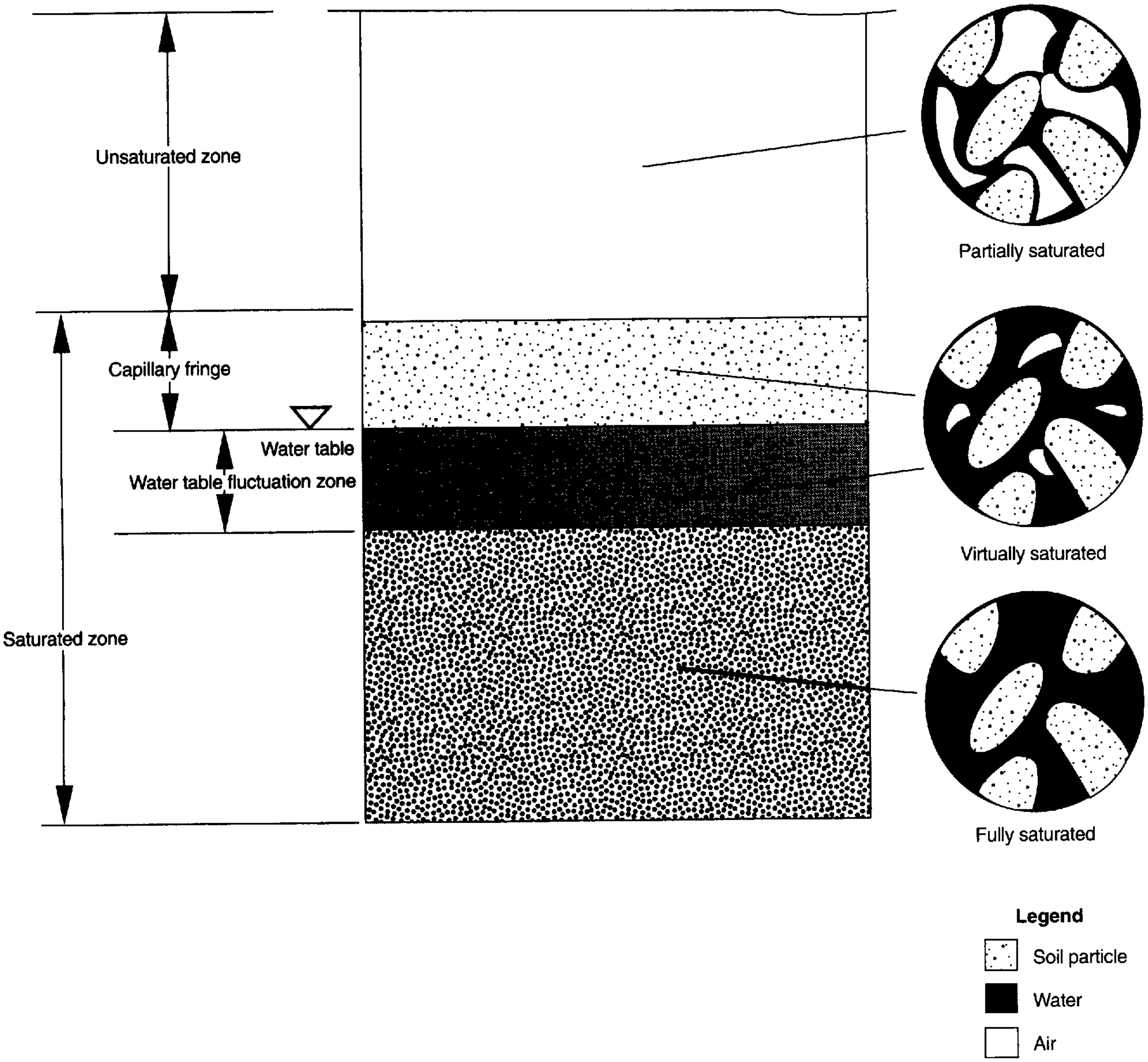
Soil Type	Range of Total Porosity
Well-sorted sand or gravel	25 to 40 percent
Sand and gravel, mixed	25 to 35 percent
Glacial till	10 to 20 percent
Clay	33 to 60 percent

Porosity depends on factors such as soil particle size and shape, the manner in which the soil particles are packed together, and sorting. The porosity of soil composed of well-rounded particles of equal size will be greater than the porosity of soil containing either angular or well-rounded particles of varying sizes. In the latter case, the smaller particles can fill in void space between the larger particles. The wider the range of sizes of soil particles, the lower the porosity.

Porosity is also affected by the shape of the particles in the soil. Spherically shaped soil particles pack together more tightly and exhibit less porosity than particles of other shapes, such as plates or rods. Clay particles, for example, vary in shape and do not tend to pack closely together. Thus, the total porosity of clays can be very high.

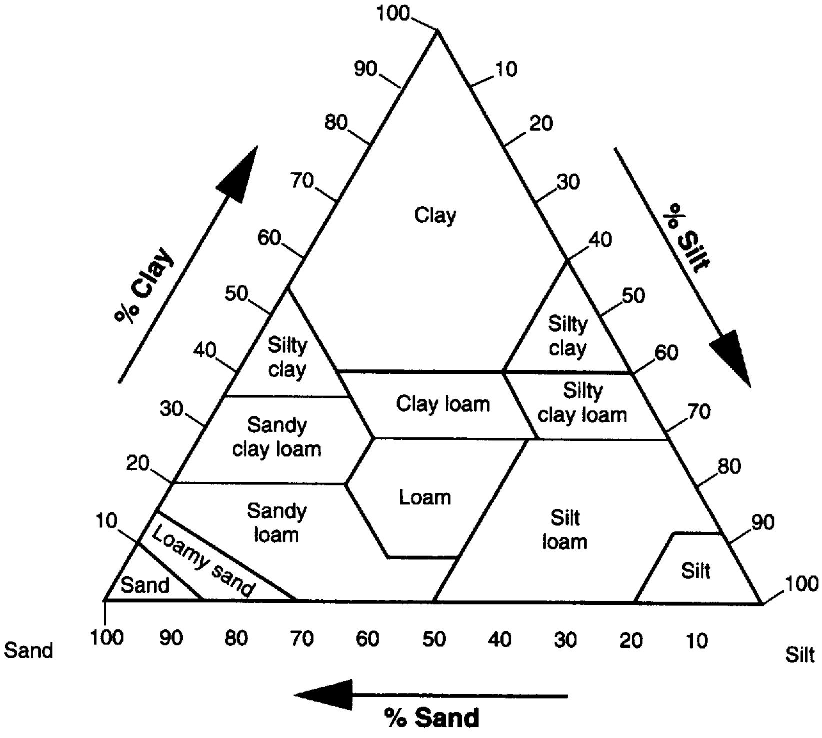
The preceding discussion assumes that all the intergranular void spaces of the soil material are interconnected, which is usually not the case. The term *effective porosity* refers to the ratio of the volume of interconnected voids through which fluid can flow to the total volume of the soil material.

(text continued on page 6)

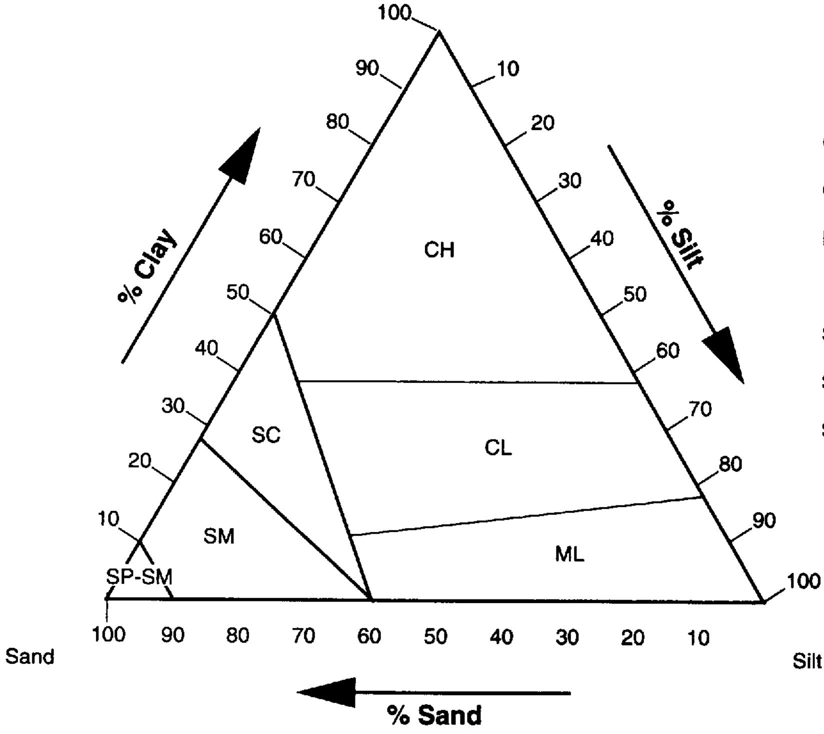


Source: Modified from API Publication 1628 [1].

Figure 1—Distribution of Water and Air in the Subsurface



USDA Soil Classification System



Legend

CH	Inorganic clays of high plasticity
CL	Inorganic clays of low to medium plasticity
ML	Inorganic silts and very fine sands, silty or clayey fine sands, or clayey silts with slight plasticity
SC	Clayey sands, sand-clay mixtures
SM	Silty sands, sand-silt mixtures
SP	Poorly graded sands or gravelly sands, little or no fines

Unified Soil Classification System (USCS)

Source: J. Dragun, *The Soil Chemistry of Hazardous Materials* [20].

Figure 2—Soil Textural Triangles for the USCS and USDA Soil Classification Systems

Although clays and some organic soils can have large total porosities, they generally have smaller intergranular voids and smaller effective porosities compared with coarser soil materials.

Fractures can develop in fine clayey soils and sediments, partly because of shrinkage due to drying. This phenomenon is known as *secondary porosity*. Secondary porosity can also develop by other means, such as animal burrows and root spreading.

Although the effective porosity of bedrock is generally low, bedrock near a land surface is usually fractured through one or several geologic processes. This fracturing permits the development of secondary porosity through which fluids can migrate. Secondary porosity can also result from dissolution of rock material by migrating groundwater, such as occurs in limestone or karst terrains.

2.2.2.2 Hydraulic Conductivity

Permeability is a measure of a soil's ability to transmit fluids. *Hydraulic conductivity* also is a measure of the soil material's ability to transmit fluid, but it is a function of the properties of the fluid passing through the soil material. Although the two terms are often used interchangeably, hydraulic conductivity is technically the more appropriate term and therefore used throughout this document.

Figure 3 presents ranges of soil hydraulic conductivity. These ranges apply to soil in which water is the primary interstitial or intergranular liquid. They may not be entirely applicable to soil or other materials in which the principal interstitial liquids are liquid-phase hydrocarbons.

The amount of soil water present and the characteristics and concentrations of constituents in bulk hydrocarbons can significantly influence the behavior of petroleum hydrocarbons in soil. For example, a near-surface soil that has a low moisture content and a high organic content will tend to retain the higher-molecular-weight constituents in a hydrocarbon release. Sorption of hydrocarbons on soil materials increases with a decrease in low moisture and an increase in organic content. This is discussed further in 2.3.2.

2.2.2.3 Soil Heterogeneity

Soil heterogeneity refers to the variation in the structure, stratification, type, and size of soil particles. Soil heterogeneity accounts for differences in porosity and hydraulic conductivity in or between different soil layers or horizons. These layers can consist of different soil types with significantly different porosities and hydraulic conductivities. For example, a soil profile at a site may consist of both clay-rich and sandy soil. The clay-rich soil layers could impede, or even confine, fluid migration; whereas the sandy soil layer would not.

The changes in different soil layers may be continuous and gradational (gradually changing soil types and structure), or discontinuous and well-defined. These soil layers may overlap with other soil types or form lenses with another soil layer. Soil layers may also be sloped in one direction, folded, or offset by fractures or expressions of bedrock faults. The configuration of these layers will influence pathways of migrating petroleum hydrocarbons. For example, a gasoline release could migrate downward through a sandy soil and travel along the downslope portion of an underlying impermeable clay layer. The presence of soil layers with low-hydraulic conductivity also promotes horizontal spreading of liquid hydrocarbons. Downward-moving fluids (water or liquid hydrocarbons) can accumulate, or perch, above these layers. These fluids will tend to migrate around laterally discontinuous perching layers and then continue their downward migration.

2.3 Characteristics of Petroleum Hydrocarbons

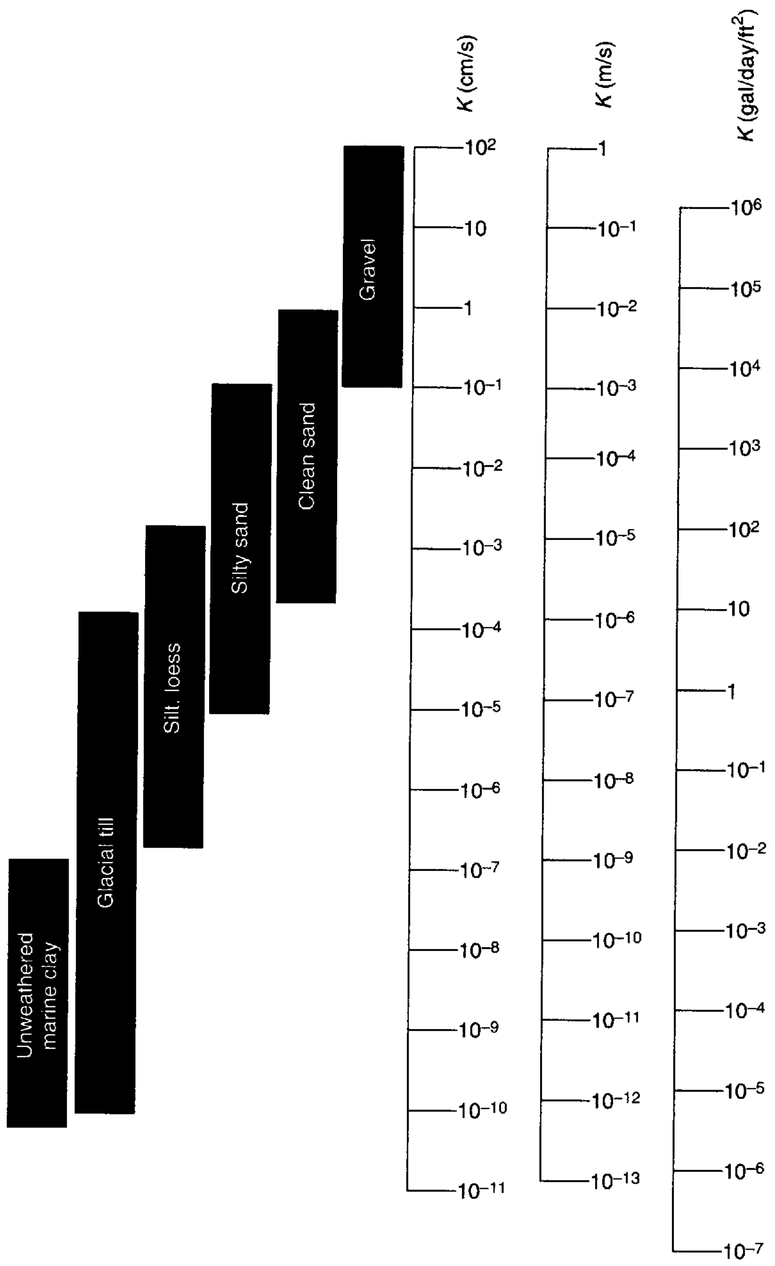
2.3.1 FUEL TYPES AND CONSTITUENTS

Petroleum hydrocarbon fuels consist of a complex mixture of organic compounds. Hydrocarbon fuels are formulated from several refinery streams to meet industry specifications for physical properties and desired performance standards. In addition to blended refinery streams, additives and blending agents are used to improve the performance and stability of the fuel. The hydrocarbons discussed in this section include gasolines and middle distillates such as diesel fuels, heating oil, kerosene, and jet fuels.

Gasolines are composed of numerous constituents (several hundred), the bulk of which are classified as either aliphatics or aromatics. *Aliphatic compounds* include constituents such as butane, pentane, and octane. *Aromatic compounds* include compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX). Some of the aromatic compounds, which can be useful indicators of the extent of hydrocarbons resulting from relatively recent releases, represent some of the more volatile and soluble compounds in gasoline and diesel fuels. Typically, gasolines are at least an order of magnitude more volatile (as indicated by vapor pressure) than diesel fuels (see Table 2).

The composition of gasoline blends varies with different locations and seasons. Although the variations in the bulk blends are not large, the sulfur, oxygen compounds, trace metals, and volatile constituent contents (such as BTEX) vary significantly (14 to 20 percent by weight) [9]. Seventeen districts in the United States are regularly surveyed by the U.S. Department of Energy (DOE) during the summer and winter of every year to compare the gasoline blends produced in the different districts. The apparent difference in distillation temperatures among the geographic locations is not large (see note). Nevertheless, significant differences do exist in the levels of sulfur, lead, and volatile constituents.

Note: Distillation temperatures are an American Society of Testing and Materials (ASTM) measure of gasoline quality.



Note: K = hydraulic conductivity; cm/s = centimeters per second; m/s = meters per second; gal/day/ft^2 = gallons per day per square foot.
Source: Modified from R. A. Freeze and J. A. Cherry, *Groundwater* [21].

Figure 3—Range of Values of Hydraulic Conductivity

Table 2—Properties of Oxygenates, Gasoline, and No. 2 Diesel Fuel

Property	Methanol	Ethanol	TBA	MTBE	Gasoline	No. 2 Diesel Fuel
Formula	CH_3OH	C_2H_5OH	$(CH_3)_3COCH$	$(CH_3)_3COCH$	C_4 to C_{12}	C_8 to C_{25}
Molecular weight	32.04	46.07	74.12	88.15	100–105	200 (approx.)
Density, lb/gal @ 60°F	6.63	6.61	6.59	6.19[j]	6.0–6.5	6.7–7.4[h]
Viscosity						
Centipoise @ 68°F	0.59[a]	1.19[a]	4.2 @ 78°F[a]	0.35[a]	0.37–0.44[b, c]	2.6–4.1
Centipoise @ –4°F	1.15[a]	2.84[a]	Solid[a]	0.60[a]	0.60–0.77[b, c]	9.7–17.6
Reid vapor pressure, psi	4.6[d]	2.3[d]	1.8[d]	7.8[e]	8–15[f]	<0.2
Flammability limits, Volume %						
Lower	7.3[d]	4.3[d]	2.4[d]	1.6[e, g]	1.4	1.0
Higher	36.0[d]	19.0[d]	8.0[d]	8.4[e, g]	7.6	6.0
Flash Point,						
Closed cup °F	52.0[d]	55.0[d]	52.0[d]	–14.0[d]	–45.0	165.0[h]
Water Solubility						
Volume % @ 70°F	100[i]	100[i]	100[i]	4.3[e]	trace	trace
mg/liter @ 20°–25°C	∞	∞	∞	48,000[k]	98–240[l]	2.7–3.2[l]

Note: psi = pounds per square inch; ∞ = completely water soluble.

[a] Design Institute for Physical Property Data, American Institute of Chemical Engineers, *Data Compilation Tables of Properties of Pure Compounds* [34].

[b] Calculated.

[c] SAE Recommended Practice J312 [37].

[d] API *Technical Data Book—Petroleum Refining* [36].

[e] ARCO Chemical Company, *Determination of Co-Extraction Effects of Oxygenated Fuels Including MTBE* [32].

[f] Petroleum Product Surveys, *Motor Gasoline* [27, 28].

[g] Department of Energy, "Status of Alcohol Fuels Utilization Technology for Highway Transportation: A 1981 Perspective" [33].

[h] Petroleum Product Surveys, *Diesel Fuel Oils* [31].

[i] *Handbook of Chemistry and Physics* [30].

[j] API Publication 723 [35].

[k] P. V. Cline *et al.*, "Partioning of Aromatic Constituents into Water from Gasoline and Other Complex Solvent Mixtures" [11].

[l] Shill, W. *et al.*, "The Water Solubility of Crude Oils and Petroleum Products" [38].

Source: Modified from API Publication 4261 [29].

Bulk blends of middle distillates such as diesel fuel and kerosene can contain as many as 500 individual constituents, most of which tend to be less volatile and less soluble than those in gasoline blends. The middle distillates also tend to have lower concentrations of aromatics such as BTEX (less than 1.5 percent by weight) [9]. Past releases of these middle distillates may no longer contain appreciable or detectable levels of aromatic compounds because these compounds may have volatilized over a period of time. This phenomenon should be considered when aromatic compounds are used as indicators of the presence of hydrocarbons in weathered motor fuels (including gasoline).

Additives and oxygenates are present in both gasolines and middle distillates. *Additives* consist of antioxidants, metal deactivators, and detergents, which make up less than 0.5 percent (by volume) of gasoline or diesel fuel. *Oxygenates* present in gasoline consist of octane enhancers such as alcohols (for example, ethanol) and ethers [for example, methyl-tertiary-butyl ether (MTBE)] and may constitute 10 percent by volume (or possibly higher) of some unleaded gasolines. MTBE was first used as an octane enhancer in 1979 in both unleaded and leaded gasoline. The use of MTBE has rapidly expanded since about 1983 and will become more prevalent in unleaded gasoline. Concentrations of additives and oxygenates also vary with geographic location and season. Because oxygenates and aromatic compounds are the most water-soluble constituents in gasoline, residual gasoline trapped in soil can release these soluble components to dissolve into water infiltrating through the unsaturated zone; consequently, they can migrate to and impact groundwater.

2.3.2 PHYSICAL AND CHEMICAL PROPERTIES OF HYDROCARBON FUELS

A number of properties of hydrocarbon fuels influence the mobility and retention of motor fuels in soil including density, dynamic viscosity, solubility, and vapor pressure. The *density* of a fluid is defined as the mass per unit volume. *Dynamic viscosity* is a measure of the resistance of a fluid to flow. Table 2 presents typical density and dynamic viscosity data for selected fuels and oxygenates. The density of hydrocarbon fuels is less than that of water, and this difference can have a significant effect on the flow and retention of hydrocarbon fuels in moist or water-saturated soil. An increase in temperature tends to lower both density and viscosity and can cause greater mobility of the hydrocarbon fuels in soil. However, small changes in viscosity will not significantly affect the mobility of some products in soil.

When hydrocarbons and soil come into contact with each other, the hydrocarbons can preferentially partition among soil water, soil vapor, and soil solids; or they can remain as free liquid in the free hydrocarbon phase. As stated earlier, hydrocarbon fuel blends are composed of as many as several hundred constituents. The extent to which these constituents partition among soil water, soil air, and soil solids depends on their individual properties. Table 3 presents water solubility and vapor pressure data and empirically derived sorption constants for selected hydrocarbon constituents.

The *solubility* of gasoline constituents is a measure of the degree to which a particular constituent can dissolve into water. The solubility data shown in Table 3 can be misleading because the concentration and water solubility of a specific constituent as part of a blend tend to be less than the concentration and solubility of the constituent alone in water. Hydrocarbon constituents with the highest solubilities are the light aromatics, such as benzene, toluene, ethylbenzene, and xylene. Gasoline oxygenates such as MTBE, ethanol, and methanol have solubilities more than two orders of magnitude higher than the solubilities of the light aromatics (refer to Table 2). As the relative concentration of a particular constituent in a hydrocarbon blend increases, the concentration of that constituent in water also increases [10][11]. *Vapor pressure* can be used to indicate the tendency of a liquid constituent to volatilize into a vapor phase. The extent of volatilization of liquid gasoline depends on the vapor pressures of its constituents; the higher the vapor pressure is, the greater the volatilization. The total vapor pressure of gasoline can be determined by summing the partial pressures of the individual constituents. The vapor pressure of gasoline constituents varies more than several orders of magnitude. As shown in Table 3, the lighter (lower molecular weight) constituents, such as isobutane, have the highest vapor pressure and volatility.

Vapor pressure depends greatly on temperature. For example, a hydrocarbon vapor pressure of 274 millimeters of mercury (Hg) at 68°F (20°C) would be reduced to 188 millimeters Hg at 50°F (10°C) and to 126 millimeters Hg at 32°F (0°C) [10]. Driving forces influencing vapor movement and local changes in vapor pressure include product temperature, density, and concentration gradients; barometric changes; and movement of infiltrating water.

Sorption refers to the bonding of a constituent onto the surface of a soil solid. When gasoline constituents are present in soil containing water, they will transfer or partition between the two phases (that is, liquid and dissolved phases) in proportion to their soil sorption constant values. In near-surface soil containing organic matter, sorption will increase in direct proportion to the organic content of the soil. As shown in Table 3, soil sorption constants vary more than two orders of magnitude, depending on the constituent and soil characteristics, including clay content. Only the highest molecular weight aliphatics (such as dodecane) tend to remain on the surface of a soil solid (also referred to as being strongly sorbed). Weakly sorbed constituents tend not to remain on the surface of a soil solid and thus are more easily transported by infiltrating water, which can ultimately impact groundwater.

2.4 Migration Processes

As shown in Figure 4, hydrocarbon constituents released into soil can exist in several phases. These phases are redistributed in the soil by various transfer and transformation processes. This subsection provides a brief overview of hydrocarbon phases and the processes that influence their mobility, retention, and degradation in soil.

2.4.1 HYDROCARBON PHASES

Hydrocarbon fuels released into soil consist of liquid, dissolved, and vapor hydrocarbon phases (see Figure 4). *Liquid-phase* hydrocarbons can exist in soil as relatively immobile residual liquids sorbed to soil particles and as free liquid in the pore space between soil solids. *Dissolved-phase* hydrocarbons can be present in soil water and as residual film on the surfaces of soil solids. *Vapor-phase* hydrocarbons can exist as components of soil vapor; however, hydrocarbon vapors may also condense and sorb onto soil solids or dissolve into soil water.

2.4.2 BEHAVIOR OF HYDROCARBON PHASES

A qualitative understanding of the behavior of hydrocarbon phases in soil is necessary for properly characterizing a hydrocarbon release and the extent of its spread, as well as for selecting and implementing effective corrective action. Subsections 2.4.2.1 through 2.4.2.3 discuss the overall behavior of liquid-phase, dissolved-phase, and vapor-phase hydrocarbons in soil. Detailed descriptions of specific transfer and transformation processes are beyond the scope of this publication.

2.4.2.1 Liquid-Phase Hydrocarbons

When hydrocarbon fuels are released into soil, a liquid-phase hydrocarbon will migrate downward by gravity and capillary forces. Some horizontal spreading occurs as the liquid-phase hydrocarbon migrates downward because of capillary forces and the differences in the hydraulic conductivities of each soil layer. The term *capillary forces* refers to forces influencing the rate of movement of a liquid phase in soil interstices or pore spaces. These forces depend on (a) whether the soil is initially wet with the water or liquid-phase hydrocarbon, (b) the physical and chemical properties of the liquid-phase hydrocarbon, and (c) the characteristics of the soil. The presence of soil layers with low hydraulic conductivity also promotes horizontal spreading of liquid-phase hydrocarbons in overlying soil

(text continued on page 12)

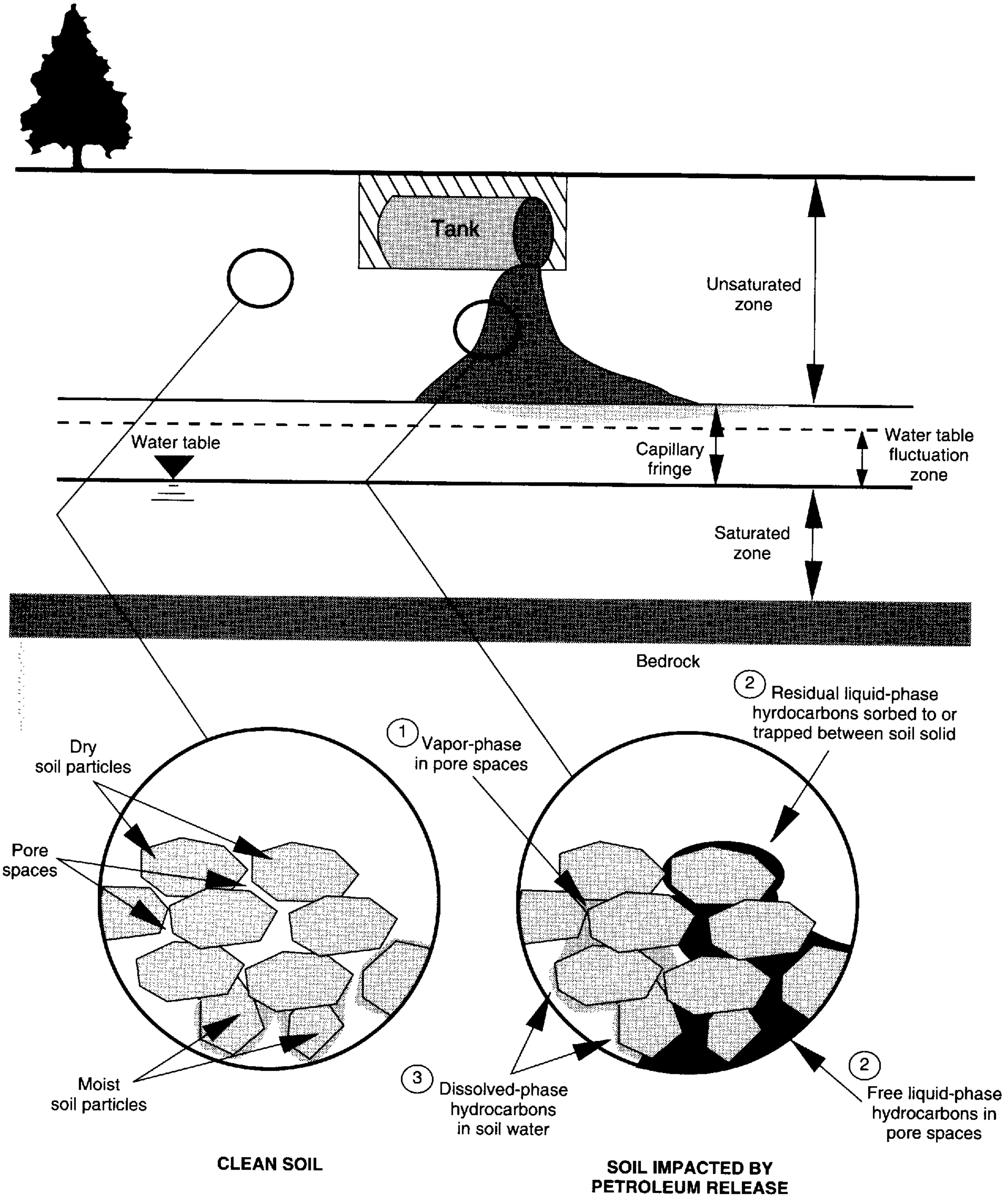
Table 3—Properties of Selected Hydrocarbon Constituents

Name	Empirical Formula	Molecular Weight	Water Solubility at 25°C (milligrams/ liter)	Vapor Pressure at 20°C (millimeters Hg)	Soil Sorption Constant K_{oc} (liters/ kilogram)
n-Butane	C_4H_{10}	58.12	61.4 (1 atm.)	1,560	490
Isobutane	C_4H_{10}	58.12	48.9 (1 atm.)	2,250	420
n-Pentane	C_4H_{12}	72.15	41.2	424	910
Isopentane	C_5H_{12}	72.15	48.5	575	880
1-Pentene	C_5H_{10}	70.14	148	531	460
n-Hexane	C_6H14	86.18	12.5	121	1,900
1-Hexene	C_6H_{12}	86.16	50	150	910
2-Methylpentane	C_6H_{14}	86.18	14.2	172	1,500
Cyclohexane	C_6H_{12}	84.16	59.7	77.6	960
Benzene	C_6H_6	78.11	1,780	75.2	190
n-Heptane	C_7H_{16}	100.20	2.68	35.6	4,300
2-Methylhexane	C_7H_{16}	100.23	2.54	51.9	3,200
Methylcyclohexane	C_7H_{14}	98.19	15	36.2	1,800
Toluene	C_7H_8	92.14	537	21.8	380
n-Octane	C_8H_{18}	114.23	0.66	10.5	8,200
2, 4-Dimethylhexane	C_8H_{18}	114.23	1.5	23.3	5,200
Ethylbenzene	C_8H_{10}	106.17	157	7.08	680
m-Xylene	C_8H_{10}	106.17	162	6.16	720
2, 2, 4-Trimethylhexane	C_9H_{20}	0.8	11.3	11.3	8,700
1, 3, 5-Trimethylbenzene	C_9H_{12}	120.20	72.6	1.73	940
2, 2, 5, 5-Tetramethylhexane	$C_{10}H_{22}$	142.29	0.13	6.47	14,000
1, 4-Diethylbenzene	$C_{10}H_{14}$	134.22	15	0.697	2,900
Dodecane	$C_{12}H_{26}$	170.3	0.005	0.075	88,000

Notes:

1. Many values, including all K_{oc} values, are estimated by using empirically derived relationships.
2. Hg = Mercury; atm. = atmosphere.

Source: Modified from W. Lyman, "Environmental Partitioning of Gasoline in Soil/Groundwater Compartments" [10].



Note: 1 = vapor phase; 2 = liquid phase (free and sorbed); 3 = dissolved phase.

Figure 4—Representation of Three Different Phases in Which Hydrocarbons Can Be Found in the Saturated Zone

layers with higher hydraulic conductivity. Downward-moving fluids (water or liquid-phase hydrocarbons) can accumulate, or perch, above these low-conductivity layers. As shown in Figure 5, these fluids will tend to migrate around laterally discontinuous impermeable soil layers and then continue their downward migration. After the major portion of the liquid-phase hydrocarbon has passed, some of it remains behind, trapped by capillary forces. This is known as *residual saturation*. This trapped or residual liquid-phase hydrocarbon acts as a source of contaminants that will dissolve into water and volatilize into soil vapor. Consequently, the dissolved- and vapor-phase hydrocarbons emanating from the residual liquid-phase hydrocarbons can potentially impact groundwater or pose a safety hazard to the surface or subsurface structures. Table 4 presents approximate ranges of residual hydrocarbon concentrations in the unsaturated zone for different types of petroleum products and soils.

Several variables will determine the extent to which a liquid-phase hydrocarbon plume migrates laterally and vertically and whether or not the liquid-phase hydrocarbons reach the groundwater. These variables include the volume and rate of release, the hydraulic conductivity of individual soil horizons within the vertical soil profile, the depth to groundwater, and the adsorptive characteristics of the soil. A high-volume liquid hydrocarbon release with a rapid leak rate will tend to exceed the sorptive capacity of the soil; if the hydraulic conductivity of the soil is sufficiently large, the release will tend to spread laterally and impact a larger volume of soil and possibly groundwater.

A detailed discussion of the behavior of liquid hydrocarbons at the capillary fringe and in groundwater can be found in API Publication 1628 [1]; such a discussion is beyond the scope of this document. The fluctuation of the groundwater table, however, significantly influences the distribution of hydrocarbons and the ability to assess and remediate them within the zone of fluctuation.

Water table fluctuations can promote vertical spreading, trapping, and dissolution of liquid-phase hydrocarbons. Liquid-phase hydrocarbons associated with the capillary fringe will move with a lowering of the water table and leave residual liquid in the expanded unsaturated zone. When the water table rises again, most of the residual liquid-phase hydrocarbons previously drawn down with the water table will be retained below the groundwater table. If a large-volume release has saturated the soil pore space below a groundwater table, only the mobile quantity of liquid-phase hydrocarbons that is not trapped will move upward with a subsequent rise in the water table. Lighter constituents in the residual liquid-phase hydrocarbons that are trapped below the groundwater table can dissolve in the groundwater. Fluctuations of 3 feet to 10 feet (0.9 meters to 3 meters) or more in groundwater levels are not uncommon, particularly during remedial activities. Thus, during a moderate release under these conditions, a significant volume of liquid-phase hydrocarbons (tens or hundreds of gallons) could become trapped below the water table and serve as a long-term source of dissolved-phase hydrocarbons that impact groundwater quality.

2.4.2.2 Dissolved-Phase Hydrocarbons

Dissolved-phase hydrocarbons result from contact between subsurface water, liquid-phase hydrocarbons, and (to a lesser degree) vapor-phase hydrocarbons. The amount of hydrocarbon present in the dissolved phase depends largely on the degree of mixing between the water and the hydrocarbon phases and the solubility coefficients of specific hydrocarbon constituents in a fuel blend. Liquid-phase gasoline constituents that readily dissolve into water include oxygenates (ethanol, methanol, and MTBE), phenols, and simple aromatic hydrocarbons (benzene, toluene, and xylenes). These constituents have high-solubility coefficients, and they tend to dissolve preferentially into water more readily than do hydrocarbon constituents with low-solubility coeffi-

Table 4—Ranges of Residual Liquid Hydrocarbon Concentrations in the Unsaturated Zone

	Gasolines			Middle Distillates			Fuel Oils		
Medium	(gal/ft^3)	(l/m^3)	(mg/kg)[a]	(gal/ft^3)	(l/m^3)	(mg/kg)[a]	(gal/ft^3)	(l/m^3)	(mg/kg)[a]
Coarse gravel	0.02	2.5	950	0.04	5.0	2,200	0.07	10.0	4,900
Coarse sand and gravel	0.03	4.0	1,500	0.06	8.0	3,500	0.12	16.0	7,800
Medium to coarse sand	0.06	7.5	2,800	0.1	15.0	6,500	0.22	30.0	15,000
Fine to medium sand	0.09	12.5	4,700	0.2	25.0	11,000	0.37	50.0	24,000
Silt to fine sand	0.15	20.0	7,600	0.3	40.0	17,000	0.60	80.0	39,000

Note: gal/ft^3 = gallons per cubic foot; l/m^3 = liters per cubic meter; mg/kg = milligrams per kilogram.

[a] Estimate assumes an earth material bulk density of 1.85 grams per cubic centimeter (gm/cm^3) and liquid hydrocarbon densities of 0.7, 0.8, and 0.9 gm/cm^3 for gasolines, middle distillates, and fuel oils, respectively.

Source: Modified from J. W. Mercer and R. W. Cohen, "A Review of Immiscible Fluids in the Subsurface: Properties, Models, Characterization, and Remediation" [39].

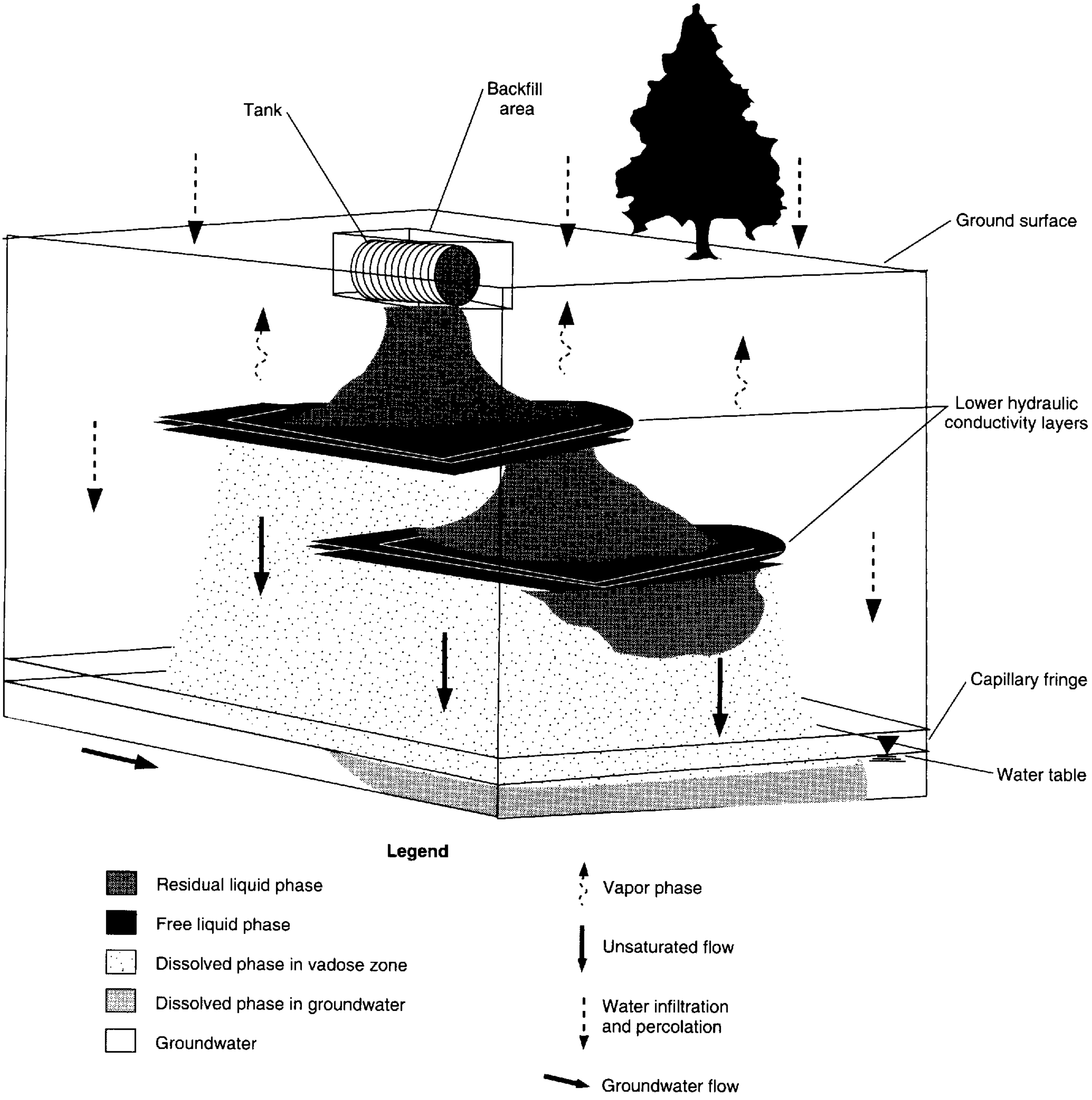


Figure 5—Schematic of Behavior of Hydrocarbon Phases in Soils

cients (see Table 3). Vapor-phase constituents, which typically consist of simple aliphatic (alkanes) and aromatic compounds (see 2.4.2.3), can also dissolve into water.

The processes of advection and hydrodynamic dispersion control the movement of dissolved-phase hydrocarbons in groundwater. *Advection*, the process by which chemical constituents are transported by groundwater movement, can vary widely depending on the hydraulic conductivity of the soil. *Hydrodynamic dispersion* is a measure of the tendency of a chemical constituent to spread in directions other than those attributable exclusively to groundwater movement. Natural degradation can also influence the movement of dissolved-phase hydrocarbons and limit transport in groundwater and soil.

The effect of hydrodynamic dispersion is to dilute the hydrocarbon concentrations within the dissolved hydrocarbon plume. Hydrodynamic dispersion is caused by the mechanical mixing of constituents during advection and chemical diffusion. Dispersion due to chemical diffusion is minimal and occurs principally under relatively static conditions with very low hydraulic conductivities and flow velocities. For the purposes of this document, *chemical diffusion* can be defined as a movement of constituents in the absence of bulk flow. Dispersion due to *mechanical mixing* processes caused by the motion of water in soil is the primary transport mechanism. Hydrodynamic dispersion, therefore, is largely the result of mechanical mixing. For example, a large influx of infiltrating water in soil containing petroleum hydrocarbons can increase the mechanical mixing and thus the dissolution and hydrodynamic dispersion of hydrocarbons in the soil.

Differences or large variations in the composition of the hydrocarbon blend can result in a large variation of dissolved constituent concentrations in water. For example, aromatic hydrocarbon concentrations in water can vary over one order of magnitude depending on the composition of the gasoline [11]. The range in concentrations of aromatic constituents in water, shown in Table 5, reflects the range of equilibrium concentrations that may be found in groundwater directly in contact with gasoline.

2.4.2.3 Vapor-Phase Hydrocarbons

Vapor-phase hydrocarbons result principally from the volatilization of free liquid-phase hydrocarbons present in the unsaturated zone. Vapor-phase hydrocarbons can also volatilize from residual liquid-phase hydrocarbons and, to a lesser degree, from dissolved-phase hydrocarbons in soil water. In vapors from a fresh gasoline release, the high-vapor-pressure, lower molecular weight constituents (for example, butane or pentane) typically account for 75 percent to 85 percent of the hydrocarbons in the vapor phase in equilibrium with fresh gasoline. A hydrocarbon release that is relatively older and more weathered than fresh gasoline will contain lower concentrations of volatile constituents, and thus the remaining liquid would have a lower vapor pressure.

A portion of vapor-phase hydrocarbons can adhere to or be sorbed onto soil. Water vapor and hydrocarbon vapor compete for the same sorption sites on soil solids. In general, water can dramatically decrease the sorption capacity of a soil for vapor-phase hydrocarbons. In dry soil or soil with a very low moisture content, the amount sorbed is directly related to the surface area of the soil particles and the content of organic-matter. The available surface area for adsorption is decreased as the water content of the soil increases. Thus, a dry porous soil can sorb vapor-phase hydrocarbons more readily than a relatively wet soil. The sorbed hydrocarbons can be remobilized as dissolved-phase hydrocarbons by the influx of water percolating through the unsaturated zone.

The migration of vapor-phase hydrocarbons is controlled by many factors, including vapor pressure, vapor density, and concentration gradients leading to chemical diffusion; convection currents related to temperature gradients; barometric changes; and movement of infiltrating water. The soil type, permeability, heterogeneity, and moisture content can affect the temperature gradients that influence vapor pressure and volatilization.

Because the mechanisms that can affect the transport of hydrocarbon vapors are so varied, detailed discussion is beyond the scope of this publication. In general, however, vapor-phase hydrocarbons tend to follow more conductive pathways and migrate from areas of greater pressure to areas of lesser pressure. Hydrocarbon vapors are more dense than air; therefore, they can accumulate in buildings, sewers, underground telephone vaults, and other structures open to the

Table 5—Variations in Gasoline Composition and Aqueous-Phase Concentrations of Fuel Components in Gasolines

	Gasoline Composition Weight %			Aqueous-Phase Concentration, mg/l		
Constituent	Average	Minimum-maximum	Standard Deviation	Average	Minimum-maximum	Standard Deviation
Benzene	1.73	(0.7–3.8)	0.68	42.6	(12.3–130)	18.9
Toluene	9.51	(4.5–21.0)	3.59	69.4	(23–185)	25.4
Ethyl benzene	1.61	(0.7–2.8)	0.48	3.2	(1.3–5.7)	0.8
m/p-Xylene	5.95	(3.7–14.5)	2.07	11.4	(2.6–22.9)	3.8
o-Xylene	2.33	(1.1–3.7)	0.72	5.6	(2.6–9.7)	1.8
n-Propyl benzene	0.57	(0.13–0.85)	0.14	0.4	(0.1–3)	0.1
3, 4-Ethyl toluene	2.20	(1.5–3.2)	0.40	1.7	(0.8–3.8)	0.3
1, 2, 3-Trimethyl benzene	0.8	(0.6–1.1)	0.12	0.7	(0.2–2)	0.2

Note: mg/l = milligrams per liter.
Source: Copyright 1991 American Chemical Society [11].

atmosphere. Because vapor-phase hydrocarbons generally have the potential to move rapidly, they can be used to detect a release that has occurred and should be monitored for explosive vapor concentrations.

In summary, a release of petroleum hydrocarbons in soil initially consists mostly of a liquid-phase hydrocarbon plume. As the release ages, constituents in the liquid phase will volatilize into the vapor phase, dissolve into water, and remain sorbed to the soil. Consequently, these mobile free liquid-phase, dissolved-phase, and vapor-phase hydrocarbons tend to become more distinct and separate over time. In many instances, these phases are located as discrete bodies or plumes that can preferentially migrate in different directions. In the assessment of a site where a release has occurred, these different hydrocarbon-phase plumes in soil must be recognized relative to their potential to impact groundwater. The liquid-phase and dissolved-phase hydrocarbons pose the greatest threat to groundwater quality, whereas vapor-phase hydrocarbons near the surface have the potential to pose an explosive hazard.

SECTION 3—EMERGENCY RESPONSE AND INITIAL ABATEMENT

3.1 Overview

At sites where a hydrocarbon release is suspected or has recently been discovered or where the impacts of a past release have just become evident, an emergency response and/or initial abatement of the release may need to be conducted. Emergency response actions are initiated when a release is discovered that poses an immediate and serious threat to public health and safety and to the environment. Initial abatement is conducted to minimize further impacts to the environment until long-term remediation can be initiated. There is not always a clear distinction between the activities conducted for emergency response and initial abatement. Generally these operations are conducted concurrently, and a specific activity implemented for emergency response may also help in conducting the initial abatement. This section addresses the activities that may be conducted for emergency response to and initial abatement of spills and releases resulting in soil contamination.

3.2 Emergency Response and Initial Abatement Activities

The objective of an emergency response and initial abatement is to identify and control existing or potential hazards. Safety is paramount in an emergency response situation. Hazardous conditions generally consist of the following three types:

a. Fire and/or explosion hazard, posed by petroleum hydrocarbon vapors that are concentrated in the explosive range.
b. Vapor inhalation hazard, posed by petroleum hydrocarbon vapors accumulating in subsurface structures (such as in basements and crawl spaces) and near the ground surface (such as backfill pits and surface areas near excavated tanks).
c. Ingestion hazard, posed by water or soil containing dissolved- or liquid-phase hydrocarbons.

These hazards are addressed at a newly discovered hydrocarbon release by the following:

a. Identifying and stopping the release source (includes evacuating tank contents, removing the tank system from service, repairing piping and tanks, and other activities).
b. Identifying potentially affected areas.
c. Controlling product vapor to mitigate fire, explosion, and other immediate safety hazards (to reduce vapor concentrations below the lower explosive limit).
d. Controlling liquid hydrocarbons (includes recovering or removing liquid hydrocarbons from surface spills, sumps, subsurface drains, utility lines, and other conduits).
e. Notifying appropriate state and local regulatory agencies.

Identifying the release source is discussed in 4.3.1 of this document. The remaining items are addressed in the following subsections.

3.2.1 IDENTIFYING AFFECTED AREAS

As part of the emergency response and initial abatement, all areas that could be affected by the release or spill should be examined. Areas that should routinely be checked include underground utilities, water wells, nearby surface waters, and adjacent properties. Underground utilities can include sanitary sewers, storm sewers, water lines, gas lines, septic systems, electric power lines, and other conduits. The depth, location, and materials in the backfill around the utility line should be evaluated to determine if hydrocarbon vapors or liquids have migrated through these conduits. Water wells and nearby surface waters that possibly have been impacted may exhibit a sheen, odor, or bad taste, indicating the presence of liquid- or dissolved-phase hydrocarbons. For surface waters, the discharge point for storm drainage systems, creeks, springs, streams, and rivers may be affected and provide a preferential migration pathway.

3.2.2 VAPOR CONTROL

It is important to determine if vapors pose a health and safety threat on and off a hydrocarbon release site. Migration of hydrocarbon vapors off-site can readily occur when a release has intersected an underground utility trench.

Most liquid petroleum products are flammable, and many are volatile. The combination of these properties makes the production of explosive vapor likely. Flammable vapor-phase hydrocarbons can accumulate to explosive concentrations in confined or poorly ventilated areas. The following are ranges of hydrocarbon vapor concentrations in air that are capable of supporting combustion when ignited:

Hydrocarbon	Concentration
Automotive gasoline	1.4 to 7.6 percent by volume (depending on grade)
Aviation fuel (JP-4)	1.3 to 8.0 percent by volume
Diesel fuel	1.0 to 6.0 percent by volume

The lower end of the range for each fuel is generally referred to as the *lower flammable limit* (LFL) [the lower explosive limit (LEL)]. Similarly, the upper end of the range is called the *upper flammable limit* (UFL) [upper explosive limit (UEL)]. Below the LFL, the concentration (percent by volume in air) of explosive vapors present is too lean to support combustion. Above the UFL, the concentration of explosive vapors is too rich and the oxygen concentration is too lean to support combustion. The preceding values represent nonoxygenated fuels. The effect of additives in oxygenated fuels on the LFL and UFL is unknown, but UFL values for specific additives (for example, methanol and ethanol) can be as high as 19 to 36 percent by volume (LFL values range from 1.6 percent for MTBE to 7.3 percent for methanol; see Table 2).

Combustible gas indicators (CGIs) or explosion meters are used to measure the percentage of the LEL in an atmosphere. When properly calibrated, the meter scale is 0 to 100 percent of the LEL (100 percent on the meter corresponds to 1.4 percent gasoline vapor by volume). The levels at which explosion or combustion can occur are relatively low and can easily be reached in either open areas or confined spaces. They also can be reached from either below the lower limit or above the upper limit. For example, immediate evacuation of an area and control of all sources of ignition are recommended when vapors reach approximately 50 percent of the LEL. When the vapor concentration is above the UEL, caution must be exercised when fresh air is introduced to concentrated hydrocarbon vapors because the mixture may then be within the explosive range (for example, when vapor is being vented from a UST using air).

Although lower explosive limits for most petroleum products are similar (1.4 percent for gasoline and 1.0 percent for diesel fuel; see Table 2), gasoline presents more of an explosion hazard than does diesel fuel because of the difference in flash points. The relative risk of explosions for different products also depends on their *flash points*, that is, the lowest temperature at which the vapors emitting from a liquid can support combustion. The flash point for gasoline is –45°F (–42°C), whereas diesel fuel has an approximate flash point of 125°F (52°C). Even though the flash point of diesel fuel is much higher than that of gasoline, diesel fuel vapors can still accumulate in confined spaces and constitute a potential hazard.

Vapor inhalation hazards posed by petroleum hydrocarbon vapors include displacement or depletion of available oxygen and exposure to potentially hazardous vapors. Oxygen levels should be monitored with an oxygen meter that measures the percentage of oxygen by volume (the safe breathing range is 19.5 to 21 percent oxygen; the air we breath is 21 percent oxygen). Exposure to potentially hazardous vapors is discussed briefly in 1.3.

Vapor may initially be detected in a structure by its characteristic odor or by using vapor monitoring devices such as a CGI. When an explosion threat exists, the following actions should be taken:

a. Take proper precautions to protect personnel exposed to the hazard.

b. Notify the local fire department so that trained personnel can evaluate the fire and explosion hazards.

c. Use trained personnel to test for explosive vapor concentrations.

d. Use properly calibrated and maintained equipment with an explosion-proof rating.

e. Prohibit smoking and eliminate all other sources of ignition (such as furnaces and hot water heaters).

f. Ventilate the enclosure to reduce concentrations.

g. Locate the vapor source and seal it off, if possible.

Ventilating vapor from an enclosed space reduces its concentration to below explosive limits. Ventilating involves moving air through the enclosed space to displace the vapor and permit its collection. It must be continued for as long as vapor remains in the enclosed space or has the potential to enter.

Selecting a method to ventilate an enclosed space will depend on the type of structure and the source of the vapor. For an aboveground structure, opening windows and doors and allowing natural airflow to dilute the vapors may be sufficient. An explosion proof electrical or air-powered exhaust fan or a water hose with the nozzle set in the spray position and discharging outward may be placed in a window to enhance natural ventilation. If the structure is entirely underground, ventilation probably will require using approved fans or blowers. Explosion-proof electrical equipment or air-powered equipment also must be used to avoid igniting the vapor.

The National Fire Protection Association (NFPA) discourages the use of fans to force air into a structure because enough oxygen could be provided to reach explosive levels [7]. Instead, NFPA recommends using explosion-proof fans to exhaust the air and vapor. Only passive fresh-air inlets should be used. Fans used in a sealed area will also draw in more vapors; proper air flow must be maintained during the ventilation process. Subsurface soil-venting systems may be used initially to control the entry of vapor into structures, and they may be used later in site remediation. Soil venting is discussed in Section 6.

3.2.3 LIQUID HYDROCARBON CONTROL

The more time that elapses between a hydrocarbon release and the beginning of corrective actions, the higher the potential for soil and groundwater contamination. Therefore, prompt installation of an appropriate liquid-hydrocarbon recovery system can limit the spread of liquid-phase hydrocarbons and reduce the long-term efforts required to remove and control other hydrocarbon phases.

Temporary trenches, drains, or sumps can be installed to intercept the flow of liquid hydrocarbons and to begin recovery at shallow depths. Probes with sampling capabilities can be driven or wells can be installed to investigate liquid hydrocarbons and to recover them at greater depths.

Single-pump or skimming systems are used for emergency recovery operations. Positive-displacement, suction-lift pumps can be rapidly deployed to recover hydrocarbons from shallow sumps or wells. Pumping equipment should meet pertinent safety requirements. The transfer equipment (pumps and hoses) and storage equipment (tanks and drums) must be compatible with the hydrocarbons being recovered. Vacuum trucks can be used for quick-response removal and transport of hydrocarbons from trenches, sumps, wells, or utility vaults. Pumping should be carefully evaluated and used only when sufficient understanding of subsurface characteristics will ensure that the pumping operation will not spread the contamination.

Water-disposal options may be limited. If water is not allowed to be disposed of in the sanitary sewer after water and hydrocarbon are separated, it can be stored temporarily until provisions are made for handling it. Regulatory requirements and emergency authority should be obtained from the responsible regulating agency.

Product recovery filters and canisters can also be used for liquid hydrocarbon recovery. These devices are inserted into monitoring or recovery wells, and liquid hydrocarbons entering the well collect in them. To be effective, the filters or canisters must be emptied on a regular basis.

Excavating soil heavily contaminated with liquid hydrocarbons is sometimes appropriate when one or more of the hazards listed in 3.2 are present. The decision to excavate depends on the nature of the hazard, the volume of the hydrocarbon released, the depth and area of liquid hydrocarbon penetration, and the ease with which soil can be removed and properly treated. Excavation may be a reasonable option if the depth of penetration is within the operating limits of a backhoe. Petroleum-contaminated soil may be flammable or combustible, and it can be a source of potentially explosive vapor. Care must be taken, both during and after excavation, to ensure that vapor or liquid from the soil is not allowed to accumulate in a confined area where it could pose a fire or explosion hazard. Soil stored on-site after excavation should be covered and stored in a bermed or otherwise contained area to prevent leached petroleum product from being released into surrounding soil, surface waters, or groundwater. Transporting and disposing of contaminated soil off-site must be handled in accordance with local and state regulations. Section 6 presents various treatment and disposal options for excavated soil containing petroleum hydrocarbons.

SECTION 4—SITE ASSESSMENT

4.1 Overview

A site assessment is initiated when petroleum hydrocarbon contamination is known or suspected to be present in the subsurface environment. An investigation may be triggered by any one or more of the following scenarios:

a. A release detection method (such as an external monitoring device, a tank tightness test, a discrepancy in the inventory control records) has indicated a possible failure of the UST system.

b. Visual evidence at the site (soil staining) or near the site (vapor in a basement, contaminated drinking water well) is found.

c. Contamination is suspected during the replacement or upgrade of a UST system (this typically involves excavation of part or all of the UST system).

d. A UST system is closed (a site assessment is required regardless of whether a release is suspected).

The overall objective of a site assessment is to determine if corrective action is needed and, if so, to provide sufficient information for selecting and implementing the most appropriate corrective action. This objective is achieved by determining the following:

a. The presence, nature, concentration, and extent of liquid-, dissolved-, and vapor-phase hydrocarbons in soils.

b. The source or sources of petroleum hydrocarbons and directions of migration.

c. The effect of hydrogeologic conditions on the hydrocarbon phases.

d. Receptors that could be adversely impacted by hydrocarbons (such as buildings with basements, underground utility trenches, water wells, and surface waters). (Receptor is defined in 4.3.4.)

e. The data required to select, design, implement, and monitor corrective actions.

Site assessments typically involve three general activities: gathering background information, implementing a subsurface investigation to determine release and site characteristics, and conducting an exposure assessment. Information generated from the site assessment is evaluated as it is being collected to determine the need for corrective action. Once sufficient information has been obtained, a corrective-action strategy can be developed during the early stages of the site assessment (before the full extent of hydrocarbon contamination is defined). Many site assessment activities can be conducted concurrently to expedite the assessment and to start corrective action as soon as possible.

This section presents some general guidelines and approaches for assessing the presence, source, and extent of hydrocarbons in soil at sites where a release of petroleum hydrocarbons has occurred. Specific methodologies for collecting and analyzing soil samples are discussed in Section 5. All sites have unique, site-specific problems that can generally be defined and addressed by the approaches described in this section and the methodologies described in Section 5. This publication focuses on the applicability of assessment methods and techniques for soil containing petroleum hydrocarbons. A more comprehensive discussion of sample collection techniques involving groundwater monitoring wells can be found in API Publication 1628 [1].

4.2 Gathering Background Information

The objective of gathering background information is to assess the nature and extent of the release from readily available records, reports, and interviews and to identify any relevant site characteristics that may affect the corrective action of soils containing petroleum hydrocarbons. The following are suggested information-gathering tasks:

a. Review engineering drawings (for example, foundation soil borings; as-built diagrams of the storage system; and number, size, and location of past and present tanks). Obtain and review available maps and geologic and hydrologic information for the area of the release. Sources of the latter data include the U.S. Geological Survey (USGS), state geological surveys, and the U.S. Soil Conservation Service (SCS).
b. Interview site personnel to determine how liquid hydrocarbons are stored, transported, monitored, and removed from the site.
c. Obtain available information on the location, type, and estimated quantity of petroleum product released and the duration of the release.
d. Investigate the history of previous land ownership and land use, both on and near the site; investigate previous tank precision tests, overfills, spills, and other incidents; and identify other possible sources of the hydrocarbon release into the soil.
e. Determine the locations and depths of all underground utilities, including sanitary sewers, storm sewers, water lines, gas lines, telephone cables, dry wells, septic systems, and power lines (because they may serve as routes for rapid offsite migration).
f. Identify potentially affected areas on and off the site, including underground utilities, nearest water wells, surface-water bodies, and residential properties; and determine the current uses of potentially affected groundwater and surface water bodies.

Information gathered through these activities will be used to help identify possible release sources, types of contaminants, migration pathways, and receptors. Furthermore, this information is critical for developing an appropriate and rational sampling plan.

4.3 Comprehensive Assessment

After sufficient background information has been obtained on the site and release characteristics, the subsurface investigation can be implemented to address the established data requirements. The primary objectives of the subsurface investigation are as follows:

a. To confirm the source and presence of petroleum hydrocarbons in soil.
b. To define the nature and three-dimensional extent of hydrocarbon phases in soil.
c. To understand the influence of hydrogeologic conditions on the fate and transport of hydrocarbons (see 4.3.3).
d. To provide the data required for the selecting and designing appropriate corrective-action options (see 4.3.4).

4.3.1 RELEASE AND SOURCE CONFIRMATION

The first objective of the site assessment is to confirm that a release has occurred. Identifying site-specific evidence that may indicate a release has occurred will be based on whether the site is currently active and how much information is known about past operations conducted at the site.

4.3.1.1 Confirming a Release

When a release is suspected at a site, the following types of evidence should be considered:

a. Reported or observed leakage.
b. Large product inventory variance or discrepancies.
c. Detection by release-detection systems.
d. Problems with the piping system.
e. Nuisance conditions (hydrocarbon vapors or liquids in basements, sewers, utility conduits, and other locations).

Product discrepancies can be identified by examining inventory control records. These records should be inspected for errors in measurement (such as stick measurements and stick gauges) and record keeping. Records should be examined for all USTs located at the site. Inventory control practices at retail outlets are described in API Recommended Practice 1621 [12].

Detecting vapor- or liquid-phase hydrocarbons by external and interstitial release detection systems may indicate failure of the tank system. External release detection devices may also respond to very small releases due to overfills and surface spills.

The majority of releases from UST systems are due to pipeline failure. Indications of a release from pressurized systems include activation of the line leak detector, loss of pressurization, or soil contamination adjacent to the piping. Failure of suction pipeline systems may be indicated by a loss of suction, hesitation or erratic delivery of product at the dispenser, failure of a functioning pump to pump liquid, or soil contamination next to the piping.

4.3.1.2 Confirming the Source

If it was not identified during emergency response activities, the source of contamination should be identified in the initial phase of the site assessment. It is extremely important to determine the release source at sites where a current leak may exist (that is, at operating UST facilities) to prevent further loss of product and to minimize environmental damage. It may not always be possible to verify the source of contamination. For example, a release due to past surface spills or overfills or to operation of UST systems no longer in existence may not be confirmed if records are not available regarding these types of incidents.

The source of contamination may be the result of on-site and/or off-site activities. If soil contamination cannot be attributed to any on-site sources, an evaluation of suspected off-site sources is conducted. The appropriate regulatory agency should be contacted to assist in this evaluation and to obtain access to the suspected off-site properties. In many cases, the regulatory agency will take responsibility for conducting sampling activities at off-site locations or require the off-site property owner to conduct a site investigation of the suspected source.

When a leak is discovered at an operating underground storage tank facility, the entire UST system must be evaluated to identify the exact location of the release. The tanks and associated piping should be precision tested or evaluated for leakage by approved methods for volumetric and nonvolumetric leak testing, inventory control, and external monitoring. If these test methods indicate a release, the UST system must be repaired or replaced to ensure that no further product is lost. Repair of the tank system will require excavation of the tank and/or piping backfill and possibly the soil surrounding the backfill. The amount of excavation should be minimized, where possible, to limit the volume of petroleum-contaminated backfill and soil that may require treatment and disposal.

Soil samples should be collected from the open excavation and either analyzed by on-site field measurement techniques or shipped off-site for laboratory analysis (see Section 5). If the water-table surface is within the tank backfill area, groundwater samples should also be collected for analysis. Depending on the results of soil and groundwater analyses, either no further action is warranted or a subsurface investigation is initiated to determine the lateral and vertical extent of contamination.

If no apparent on-site source of contamination is identified, all suspected off-site sources of petroleum hydrocarbons should be investigated. Off-site sources of contamination are more common in suburban and urban areas where UST facilities are in proximity or where a UST facility is located upgradient of another service station. The general source of off-site contamination migrating into the area of concern can be determined by collecting subsurface samples at the property boundaries.

4.3.2 SAMPLING STRATEGY

The initial phase of a site assessment is conducted to confirm a hydrocarbon release and to identify the source. A more extensive assessment is conducted to define the extent of vapor- and liquid-phase hydrocarbons in the soil. The sampling and analysis approach used to determine the lateral and vertical extent of contamination should be an extension of the sampling and analysis scheme used for conducting the initial phase of the assessment. The results of the initial assessment can be used to direct subsequent sampling and analysis activities, including determining the extent of multiphase hydrocarbons and quantifying the concentrations of petroleum hydrocarbon constituents.

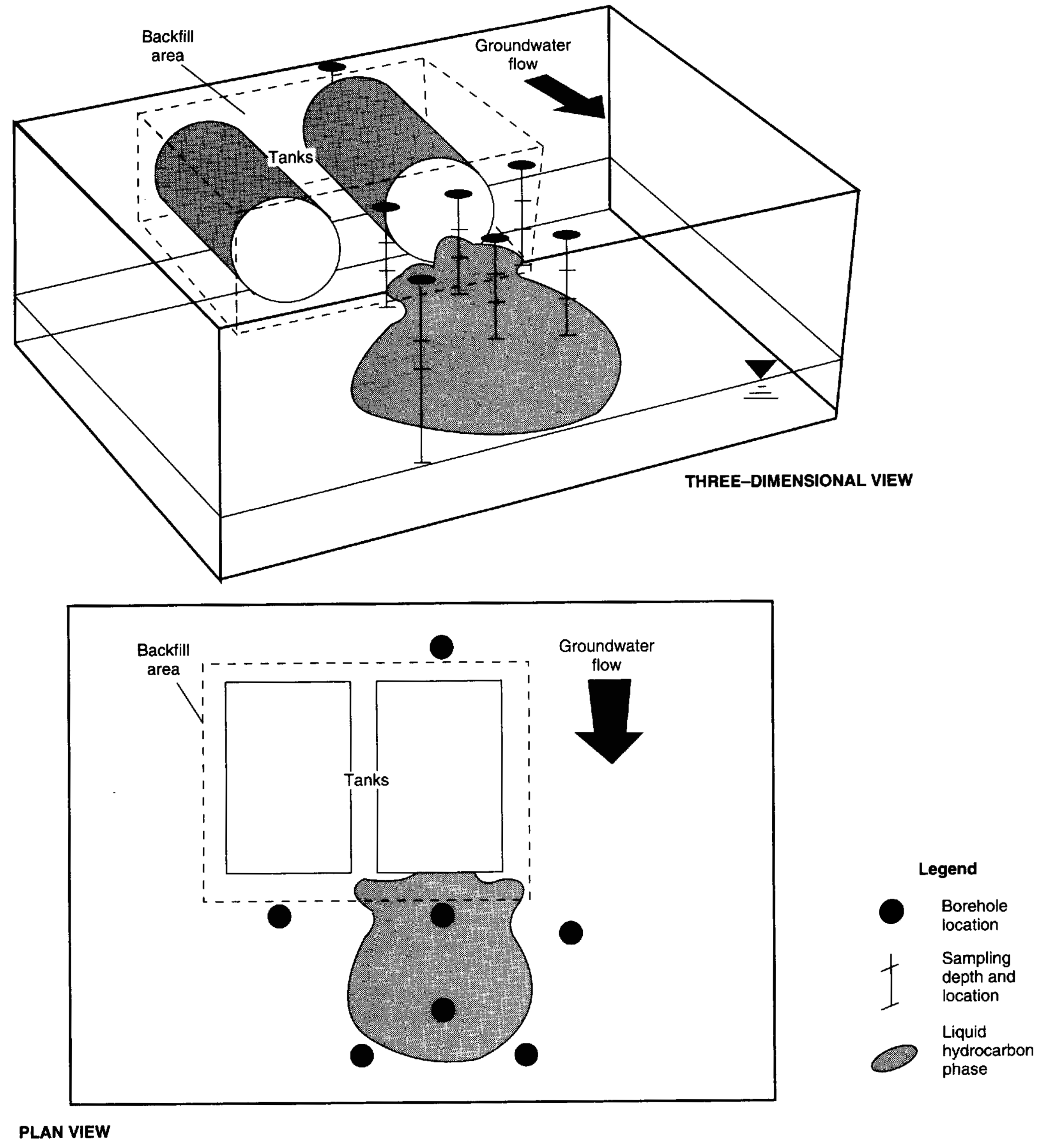
4.3.2.1 Determining Sample Locations

The approach used to determine sampling locations will vary depending on site- and release-specific factors. In general, when the source of contamination is known or is suspected of being limited to a specific area, sampling points are located relative to the suspected source (this is referred to as selective sampling). When there is no identifiable source or the contamination appears to be widespread, a grid or transect system is used to establish the sampling locations. These sampling strategies are shown in Figures 6 and 7, and are discussed below.

4.3.2.1.1 Selective Sampling

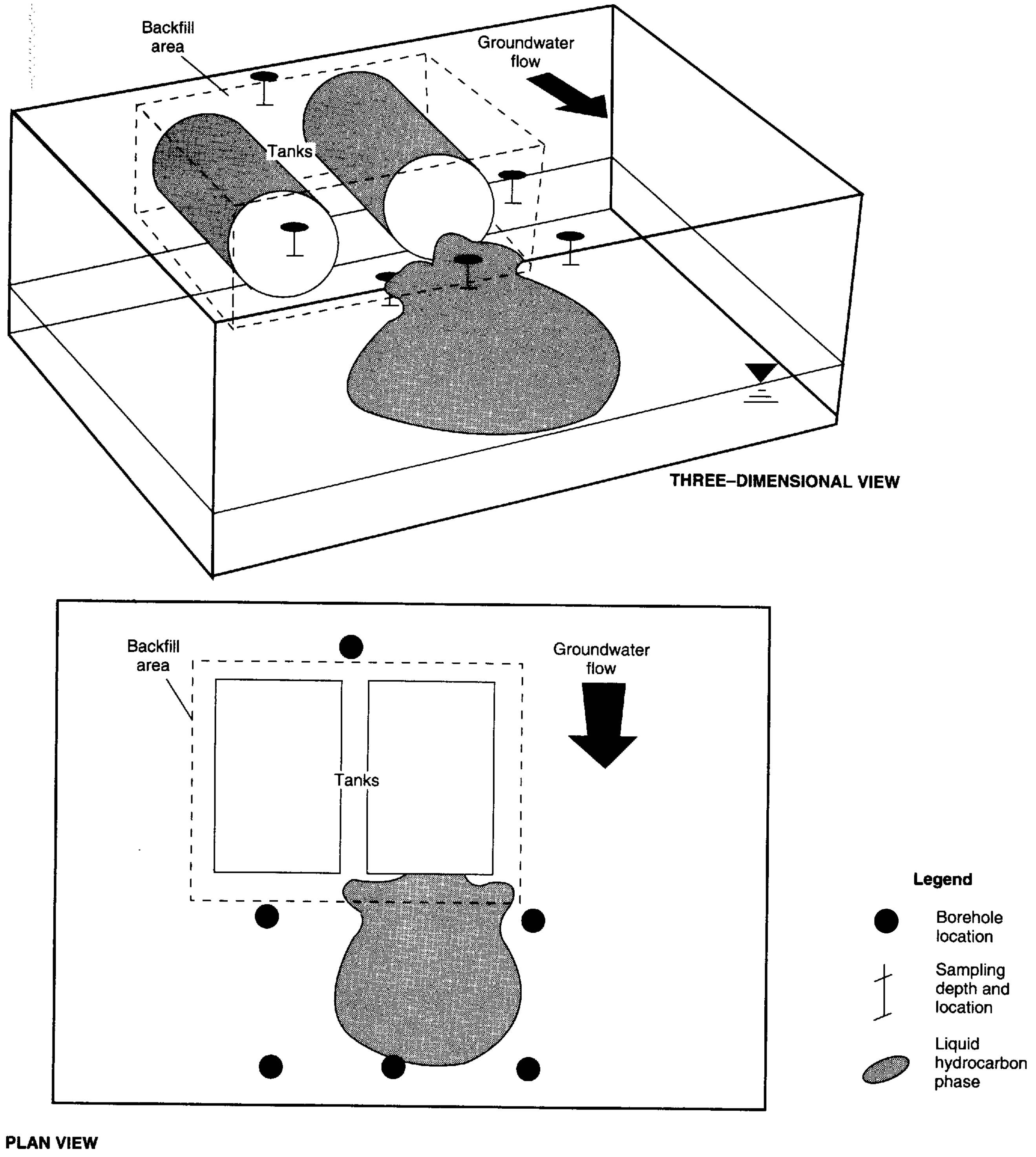
Select sampling locations are chosen based on known site and release conditions. Sampling points can be located close to the source of the known or suspected release and close to the suspected receptor (see Figure 6). They also can be used to delineate areas of high concentrations of petroleum hydrocarbons. For delineating the extent of a vapor- or liquid-phase hydrocarbon plume when the source is known, samples are initially collected close to the source. If hydro-

(text continued on page 22)



Note: This sampling scheme does not depict sample locations along pipelines or around dispensers.

Figure 6—A Simplified Schematic of Selected Sampling Locations



Note: This sampling scheme does not depict sample locations along pipelines or around dispensers.

Figure 7—A Simplified Schematic of Grid Sampling Locations

carbons are detected at the initial sampling points, the lateral extent of contamination is determined by collecting additional samples at succeedingly more distant locations in the suspected direction of migration until no hydrocarbons are detected. The vertical extent of contamination is defined by collecting samples at incremental depths [for example, at 5-foot (1.5-meter) intervals]. As soil samples are being collected, they are generally screened for the presence of volatile organic hydrocarbons using a portable field instrument (see Section 5). Vertical samples are collected until the groundwater table is reached or when contamination is no longer indicated by the field screening method. The reason for not collecting soil samples below the groundwater table is to prevent any contamination that may exist in the upper soil levels from reaching the groundwater.

Sampling points used to determine if a liquid-hydrocarbon release has migrated off-site are located at or near the site boundaries and downgradient from the source of the release. In the saturated zone, liquid hydrocarbons will tend to migrate in the direction of groundwater flow. Vapor-phase hydrocarbons migrate along preferential pathways in response to pressure and concentration gradients and not necessarily in the direction of groundwater flow. For example, at a site having silty clay soils, hydrocarbon vapors that intercept a utility line trench will preferentially move through the highly permeable trench backfill material, sands, or gravel. Soil vapors are often sampled and analyzed to help define the migration pathway of liquid hydrocarbon that has reached the water table.

4.3.2.1.2 Sampling Grids

Sampling grids are a network of sampling points located at predetermined intervals ranging from 10 feet (3 meters) to greater than 100 feet (30 meters) apart (see Figure 7). Grids may be used in the event a source area is not determined from the initial assessment. They may also be used to define the characteristics of any vapor-, liquid-, and dissolved-phase hydrocarbon plumes both near and far from a release. The interval between sampling points depends on the size of the site and the tank field, the proximity to the source, the hydrogeology of the site, and the number of samples to be collected for analysis. For example, on sites with relatively impermeable soils, released product may not migrate far from the tank field.

Depth profiling is also conducted when using sampling grids. If an area of contamination is found, the vertical extent of hydrocarbons can be determined by collecting samples at increasing depth intervals. Avoid introducing contaminants to lower elevations during sampling.

4.3.2.2 Determining the Extent of Contamination

To determine the lateral and vertical extent of hydrocarbon phases present in soil, a three-dimensional assessment is conducted. This can be accomplished by using several different site assessment approaches, including soil vapor surveys and soil sampling and analysis. Soil and soil vapor samples that have been collected may be analyzed using either field measurement techniques for on-site sample analysis or EPA laboratory methods for off-site analyses (see Section 5). Field measurements can be used to make immediate decisions while at the site, whereas off-site laboratory analyses should be used for more rigorous analytical requirements. For example, field measurements can be used to confirm the presence and source of a release, and laboratory analyses can be used during later assessment activities (for example, a closure site assessment). The choice of analytical methods or techniques is based on the required confidence level of the data produced by each method and the data quality objective of the assessment.

For many investigators, the proper interpretation of the data provided by these analytical methods is critical to characterizing and understanding site conditions. Proper interpretation of results recognizes the limitations of each method used and makes allowances for the implications of such limitations. The performance considerations for both field and laboratory analytical techniques are discussed further in Section 5.

4.3.2.2.1 Soil Vapor Survey

A soil vapor survey (SVS) is a technique used to help define the presence and extent of vapor-phase hydrocarbons. The source or sources of vapor-phase hydrocarbons detected by this method may include the following:

a. Liquid hydrocarbons present in the soil or on the groundwater table.
b. Residual hydrocarbons in the soil.
c. Dissolved hydrocarbons in the groundwater that volatilize due to shifts in equilibrium.

This technique involves the insertion of a small-diameter [less than 1 inch (25.4 millimeters) in diameter], hollow-core sample probe into the subsurface. A soil vapor sample is actively withdrawn through the probe and analyzed on-site using a portable photoionization detector (PID), flame ionization detector (FID), or gas chromatograph (GC). Care should be taken to purge enough vapor from the system prior to sampling to ensure that actual soil gas is analyzed. Depending on source depth and soil permeability, soil gas surveys may not always be effective.

Soil vapor sample locations are often determined using a grid system. Based on site-specific factors, vapor samples are collected at a predetermined depth [typically less than 5 feet (1.5 meters) below the ground surface] and above the groundwater table surface. Though generally used only to define the lateral extent of contamination, some UST investigators conduct vertical soil vapor sampling at selected sample points. This sampling is performed at sites where contamination is suspected of being confined to the upper soil material or at sites where impermeable clay layers may exist. Soil vapor samples are collected beneath the suspected area of contamination or below the clay layer to determine whether or not contamination has migrated vertically.

Soil vapor measurements cannot be used to quantify the amount of petroleum hydrocarbons in soil or groundwater. The results of soil vapor measurements provide qualitative information on hydrocarbon concentrations in soil vapor only, and these results should be interpreted relative to other soil vapor sampling points.

4.3.2.2.2 Soil Sampling

Soil sampling and analysis is the primary method used to define the vertical and lateral extent of contamination. One or more of the following techniques can be used to collect soil samples:

a. Drilled boreholes.
b. Driven or placed probes (for example, a geoprobe or cone penetrometer).
c. Hand auger or corers.
d. Grab sampling from excavated soils (test pits).

The sampling locations can be selected to help confirm the presence of hydrocarbons and to determine an apparent release source (if not already known). For example, if a release is suspected from a tank field at a particular site, a select or limited number of samples can be collected as follows:

a. At either end of the tank field in or adjacent to the backfill area.
b. At different depths to construct a depth profile.

Analyses of these soil samples can be conducted on-site by various field measurement techniques, or they can be properly preserved and shipped to an off-site laboratory for analysis (see Section 5). The limited number of samples collected from select locations and analyzed during an initial assessment can generally be used to determine if petroleum hydrocarbons are present and, if so, to develop an appropriate sampling and analysis scheme for defining the nature and extent of their presence in the soil.

Because a potential exists for small flash-type explosions at or near soil borings that have penetrated hydrocarbon locations, proper precautions should be taken to avoid having explosive sources (such as smoking or welding operations) near soil borings. The locations of underground utilities (gas, water, electrical, and sewerage) should be determined before any boring or drilling activity is begun. Soil boring drilling locations should be probed by hand to a depth of at least 5 feet (1.5 meters) before sampling operations begin.

4.3.3 FATE AND TRANSPORT CRITERIA

It is important to evaluate the extent (both laterally and vertically), direction, and rate of petroleum hydrocarbon migration at a release site. This information will determine the degree of remediation needed and selection of appropriate and effective corrective-action technologies.

The hydrogeologic characteristics of a site that will affect the potential mobility and transformation of the hydrocarbons in the soil should be evaluated during the site assessment. The site characteristics that are important in evaluating the migration of contaminants in soils include the following:

a. *Porosity* is the percentage of total soil volume not occupied by solid particles. Sandy soil, for example, may have a lower porosity than either silty or clayey soils. Typically, determining porosity does not require a lab analysis but can be established based on field documentation.
b. *Permeability* strongly influences the rate of movement of hydrocarbon fuel through the soil. Generally, the size of the pore will be proportional to the fluid flow through the pore space. A small increase in grain size will frequently result in a large increase in flow. Also, soils with low permeability tend to retain more fluid than those with higher permeability.
c. *Hydraulic conductivity*, which indicates the ease with which water will flow through the soil, depends on the porosity of the soil, the grain size, the degree of consolidation and cementation, and other soil factors.
d. *Depth to groundwater* can affect the attenuation capacity of soil and the time it takes for petroleum hydrocarbons to migrate to groundwater.
e. *Moisture content* can determine the wetting characteristics and the influences of pore/water exchange on the migration of vapor-phase hydrocarbons in soil.
f. *Organic carbon content* can greatly affect the retention of organic pollutants—the greater the fraction (by weight) of organic carbon, the greater the adsorption of organics. The amount of clay can also increase the adsorption capacity for organics.

Release factors that are important in evaluating the fate and transport of a hydrocarbon release (liquid, vapor, and dissolved phases) include the magnitude (or total volume), the depth (vertical and horizontal extent), and the timing (or age) of the release.

The quantity and rate of a release can sometimes be estimated from site operating records and other available sources but often is never known. The quantity of fuel released to the soil and the rate of release can affect the extent of its migration. Each soil type has a specific sorptive capacity to retain liquid hydrocarbons. If the sorptive capacity is exceeded (and the hydraulic conductivity is sufficiently large), hydrocarbons will tend to migrate more readily through the soil pore space toward the groundwater. Thus, smaller releases may be completely adsorbed by the soil and confined to a discrete area. Larger releases are more likely to result in free liquid hydrocarbons impacting a larger volume of soil and possibly reaching the water table.

The depth to which a release can migrate depends on many factors, including the source and volume of the material released, the amount of water infiltrating the soil, how long ago the release occurred, and the chemical and physical properties of the product and the soil. In porous homogeneous soil, liquid-phase hydrocarbons tend to move directly downward through the unsaturated zone. Lateral movement generally occurs through dispersion and diffusion. However, changes in the hydrogeologic properties of the soil (structure or composition) with depth and the presence of zones of seasonally saturated soil, fractures, or other features can cause liquid-phase hydrocarbons to spread horizontally for some distance before migrating downward.

The length of time that has passed since a release occurred can affect the extent of migration and the chemical composition of the hydrocarbons released. Recent releases tend to be more concentrated within the original boundaries of the release, whereas older releases are more likely to have migrated a considerable distance from their origin. Fuel constituents having low molecular weights (more volatile and soluble) move away from the source via volatilization or dissolution by rainwater infiltration. More stable compounds (heavier molecular weights) will remain near the source for a longer period. In a process called weathering, the relative chemical composition of the product may change with time following a release into the soil environment. Processes responsible for this change include volatilization, dissolution, and degradation. Degradation of petroleum hydrocarbons in soil may occur as the result of the metabolic processes of a wide variety of microorganisms or through chemical processes.

The duration and frequency of a release can affect the amount of product released to the soil and how long the contaminants remain in the soil. A single-episode release may move as a discrete "pulse" of different petroleum hydrocarbons through the soil, whereas an intermittent or continuous release may result in a situation in which petroleum hydrocarbons exist at varying distances from the source or have undergone considerable volatilization and weathering. Hydrocarbon vapor concentrations vary with distance from the hydrocarbon source.

4.3.4 EXPOSURE ASSESSMENT

An exposure assessment is conducted to predict possible migration routes and to identify areas where a hydrocarbon release may have an impact on human health or the environment. In an exposure assessment, all available information must be integrated to determine the movement of all hydrocarbon phases towards potential receptors. An *exposure pathway* is a surface or subsurface route of exposure that may allow the migration of liquid-, vapor-, or dissolved-phase hydrocarbons to a receptor. Figure 8 shows potential exposure pathways that may exist at a site. The pathways for liquid- and vapor-phase hydrocarbons in the subsurface environment are dictated by natural soil conditions and geologic barriers and conduits, as well as by man-made structures and infrastructures.

A *receptor* can be defined as a person or location that is directly impacted by the migration of hydrocarbons. Generally receptors can be classified as either human or environmental (for example, vegetation or aquatic life).

Whether emanating from petroleum hydrocarbon trapped in soil or floating on or dissolved in the water table, hydrocarbon vapors tend to migrate along the paths of least resistance and towards areas of lower pressure. Although vapor migration can be halted by buried structures, vapors will readily follow other more convenient pathways through backfill materials surrounding structures such as water, sewer, and utility lines. Vapors can enter structures through drains or cracks in foundations and accumulate in basements.

If a facility is located over or near public water supplies or private wells, the possibility that any amount of released oil could affect water quality is likely to be a concern. Nevertheless, attention to sites in industrialized areas or in areas that rely on remote water supplies should not be minimized.

The constituents of concern encountered in hydrocarbon releases typically include benzene, toluene, xylenes, and lead. Benzene and toluene are mobile constituents that readily partition into vapor- and dissolved-phase hydrocarbons. Lead occurs in free liquid and residual hydrocarbons sorbed to soil particles and leached into dissolved-phase hydrocarbons. Caution should be exercised in using lead as an indicator of contamination, because it can already exist in soil material. The use of lead as an indicator of contamination will decrease as the production of leaded gasoline is phased out and sites with a history of petroleum product contamination are remediated.

Present and future potential exposure pathways and receptors should be identified, and the impact of these pathways and receptors on site use should be evaluated. The assessment of exposure pathways and receptors may include constructing a map of the distribution of hydrocarbon phases and all potential pathways; developing a conceptual understanding of the migration of liquid, vapor, and dissolved hydrocarbon phases beneath and near to the release site; and evaluating the migration rates and concentrations of mobile hydrocarbon phases reaching potential receptors.

Data collected in the site assessment are used to develop a conceptual understanding of how the various hydrocarbon phases are migrating from the source area. The factors that should be considered include the following:

a. Volume released.
b. Adsorptive capacity of the soil.
c. Presence of perching horizons and interconnected void spaces.

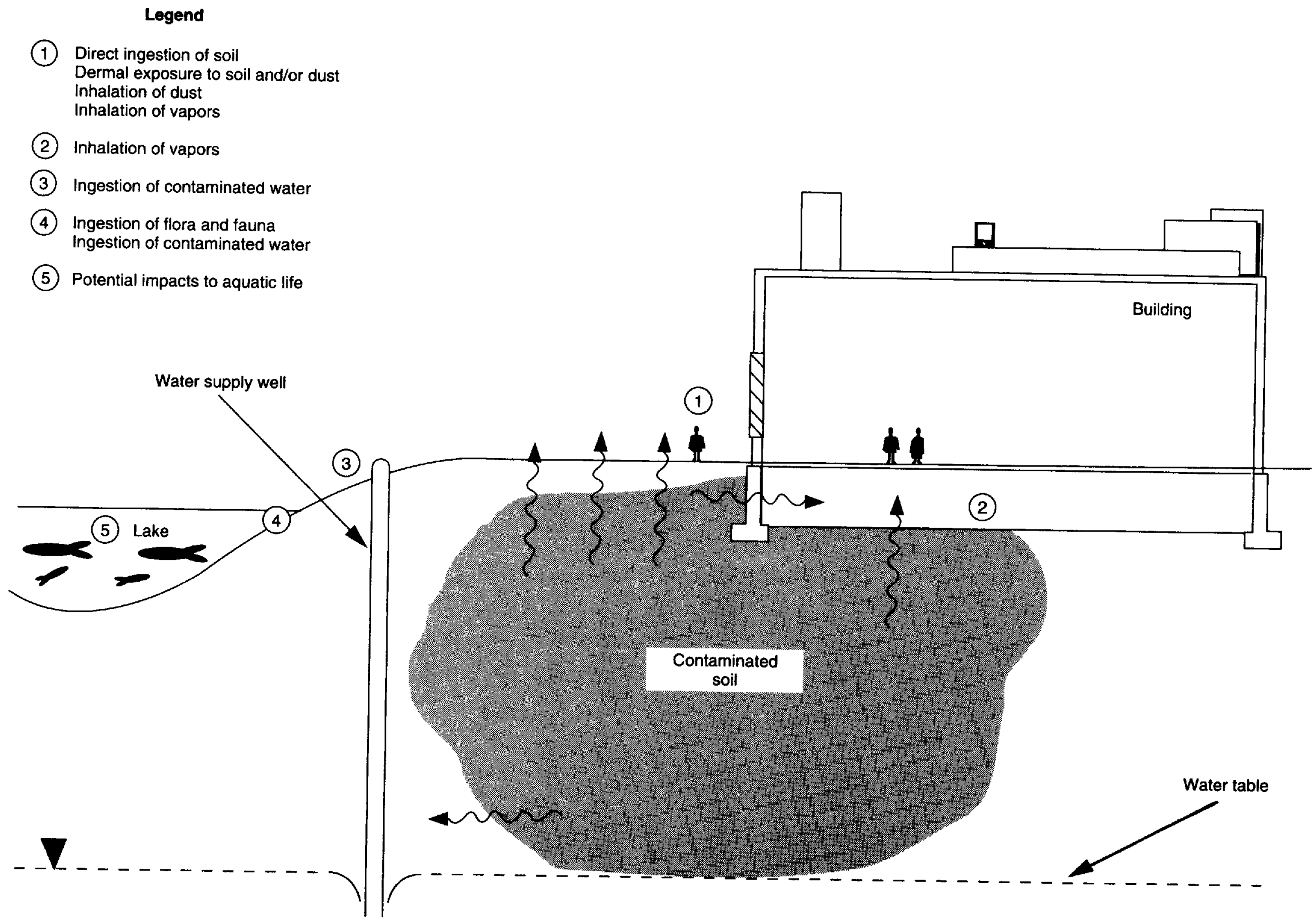


Figure 8—Examples of Potential Exposure Pathways

d. Relative ability of the soil to allow migration of dissolved- and vapor-phase hydrocarbons and free liquid hydrocarbon fluids.
e. Rates and directions of groundwater movement.
f. Processes such as dispersion, advection, and degradation that dilute concentrations and limit the area of the hydrocarbon impacted zones.

The potential for petroleum contaminated soils to act as a long-term source of groundwater contamination should be considered. Computer models are available to predict the impact of residual hydrocarbons in soil on groundwater quality. These analytical models use information collected during the site assessment to determine if groundwater will be impacted and, if so, to estimate the arrival time and approximate concentration of a contaminant at a given receptor (that is, monitoring well). A monitoring network capable of delineating the contaminant plume can be established to verify the model being used. The model can then be refined based on the monitoring data. These models can be very useful in (a) determining the need for corrective action, (b) establishing cleanup goals and time frames, and (c) selecting and designing appropriate corrective actions.

4.3.5 SITE CHARACTERIZATION FOR CORRECTIVE-ACTION SELECTION

If an initial site assessment reveals the need for corrective action, a comprehensive site investigation plan should be designed that includes developing an information base that will allow the investigator to select, design, and implement appropriate and effective corrective actions. Determining the feasibility of alternative corrective actions requires a thorough understanding of the contaminant and site characteristics. For the majority of cleanup technologies currently in use or newer technologies that are becoming more widely accepted, the site and release characteristics listed in Table 6 are used to evaluate applicability of alternative technologies. Soil characteristics were previously discussed in Sections 2 and 4. Contaminant characteristics are defined in Section 2. Site criteria that should be evaluated during the site assessment for specific corrective-action technologies are discussed in Section 6.

Not all corrective-action technologies are evaluated using only the soil and contaminant characteristics listed in Table 6. In situ bioremediation (both passive and active) relies on biological processes in subsurface soils to degrade and transform petroleum hydrocarbon constituents to nontoxic compounds. Other subsurface soil characteristics that need to be evaluated to determine the applicability of this technology at a particular site include oxygen, carbon dioxide, and methane concentrations; pH; temperature; and nutrient status (nitrogen and phosphorus). These parameters relate to how well the subsurface environment will support microbial populations that will degrade petroleum hydrocarbon constituents.

Table 6—Soil and Release Characteristics

Soil Characteristics	Contaminant or Release Characteristics
Soil type	Unweathered composition
Porosity (by visual estimation)	Soil sorption capacity
Permeability to air	Density (liquid and vapor)
Hydraulic conductivity	Viscosity
Moisture content (varies over time)	Solubility
Depth to groundwater	Vertical distribution in soil
Soil heterogeneity	Vapor pressure
	Toxicity
	Safety parameters (LEL, UEL, FP, IP)

Note: LEL = lower explosive limit; UEL = upper explosive limit; FP = flash point; IP = ionization potential.

SECTION 5—SAMPLING AND ANALYSIS TECHNIQUES

5.1 Overview

Soil sampling and analysis are the principal components of the subsurface investigation conducted as part of the site assessment process. The objectives of soil sampling and analysis are to determine the following:

a. The presence, concentration, and extent of hydrocarbons in soil.
b. The source or sources and directions of hydrocarbon migration.
c. The effect of soil characteristics and subsurface structures on the migration of liquid- and vapor-phase hydrocarbons.
d. The potential of hydrocarbon phases in soil to have an adverse impact on groundwater and receptors and outlets (such as basements and utility lines).
e. The data required to decide whether corrective action is needed and, if so, to select an appropriate corrective-action approach.

This section describes soil sampling techniques and methods for conducting both on-site field analyses and currently used off-site laboratory analyses to address the preceding objectives. This section also discusses performance considerations for on-site field analyses and off-site laboratory analyses.

The initial step in a sampling and analysis program is developing a plan that identifies and defines both field activities and, if used, laboratory procedures. Planning is essential to ensure that soil samples are properly collected, representative of site conditions, properly documented and transported, and correctly analyzed. The plan should include procedures for collecting the sample, handling and preserving it, and tracking it from the field to the laboratory. The plan should also identify and assure selection of appropriate types of analyses and methods for performing chemical analysis of the samples. It should further assure that appropriate field and laboratory quality assurance/quality control (QA/QC) procedures are conducted as part of the data quality objectives (see Section 4). Note that several state regulatory programs have specific procedures for soil sampling and analysis.

The planning of field activities and the selection of sampling and analysis techniques should be based on the background information gathered during the initial assessment. For example, estimates regarding the location and depth of borings can be based on background information such as local geology, soil types, hydraulic conductivity, depth to groundwater, and source and volume of release. The number of samples required will depend primarily on how much information is already available, the suspected extent and severity of the release, the site soil and hydrogeologic conditions, and the data quality objectives of the subsurface investigation.

5.2 Soil Sampling Techniques

Several techniques are available for collecting soil samples for both on-site field analyses and off-site laboratory analyses. Under many circumstances, the same sampling technique can be used for either. Soil sampling techniques differ depending on the depth at which the sample is collected, the size or volume of sample required, the hydrocarbon phase being sampled, and the need to maintain the integrity of the soil sample.

5.2.1 SOIL SAMPLE COLLECTION

A wide range of techniques is available for soil boring and sampling. The sampling techniques used to collect samples for measuring hydrocarbon releases in soil differ substantially depending on the following:

a. Type of soil being sampled.
b. Anticipated sampling depths.
c. Soil sampling capabilities.
d. Equipment availability.
e. Cost.

Table 7 presents a list of methods for boring and collecting soil samples. Generally, samples taken from excavated soil or from the upper 3 to 5 feet (0.9 to 1.5 meters) of soil can be collected with simple tools such as trowels, shovels, spatulas, or manual soil borers. Soil samples are relatively easy to remove from an open corer.

Hydrocarbons that have migrated away from the source often require tools such as tube samplers and augers. Manually operated tools are normally useful to a depth of 3 to 5 feet (0.9 to 1.5 meters), depending on the soil type. Below this depth, hydraulically or mechanically driven equipment is generally needed.

Augers provide one of the simplest methods for collecting soil samples. The required equipment is simple and readily available. Auger borings are made by rotating and advancing the auger device to the desired depth in the soil, withdrawing the device from the hole, and removing the soil. The depth of auger investigations is usually limited by groundwater depth, soil characteristics, and the equipment used. Augers can be used both for bringing up disturbed soil samples and for advancing holes so other types of sampling devices can be used.

Both hand-operated and machine-operated augers are available in various sizes. Figure 9 shows three types of hand augers. Hand-operated augers, which consist of a spiral cutting blade that transports soil cuttings upward, are generally used to a depth not exceeding approximately 5 feet (1.5 meters).

Machine-operated augers are driven by a motor (sometimes handheld, but usually rig-mounted). After the auger is attached to a drilling rod, the rod is rotated and pressed downward to penetrate the soil. Two common types of machine-operated augers are hollow-stem augers and solid-stem augers. A typical hollow-stem auger is illustrated in Figure 10.

Hollow-stem augers have a continuous-flight cutting blade around a hollow metal cylinder; the cylinder may be plugged to prevent soil from entering it. The auger sections, or "flights," come in 5-foot (1.5-meter) lengths and have outside diameters of about 7 to 18 inches (178 to 457 millimeters) and inside diameters of 3.5 to 12 inches (89 to 305 millimeters). Soil samples can be collected from the inside opening of the auger without withdrawing it from the hole. If the plug is removed, a small tube or drive sampler can be driven into the soil not yet penetrated by the auger flight; this produces a relatively undisturbed soil sample. Solid-stem augers do not have an inner barrel; therefore, they must be withdrawn to obtain each sample.

Two common sampling devices used in connection with the auger are the split spoon and the conventional thin-walled tube sampler. These tools work well in soils that contain sufficient clay or are cohesive enough for the material to remain stable during sample collection and retrieval. The split-spoon sampler is a thick-walled tube that is split in half longitudinally and can be separated to reveal the soil sample. Another version of the split spoon is the Modified California Sampler. This is a split spoon that contains several brass sleeves with metal fingers to retain less cohesive sandy soils.

Table 7—Basic Soil Sampling Techniques

Boring and Sampling Methods	Normal Hole Diameter	Maximum Depth	Average Time Per Hole	Advantages	Disadvantages
Trowels, spatulas, shovels	Variable	< 1 foot (< 0.3 m)	Fast	Wide availability. Does not require specialized equipment.	Limited depth. Sample is moderately to severely disturbed.
Hand augers	4 in. (100 mm)	5 ft (1.5 m)	Fast with suitable soil conditions	Wide availability. Minimal soil disturbance.	Limited depth. Not recommended for gravel-rich soil. Slow in hard soil.
Hollow-stem augers	4–12 in. (100–305 mm)	100–150 ft (30–46 m)	Fast with suitable soil conditions	Versatile in a variety of soils. Other sampling devices can be used while auger is in place. Dry soil samples from split spoon and tube can be obtained. Caving is controllable.	Moderate sample disturbance. Boulders of bedrock not easily penetrated. Overhead clearance limitations.
Split-spoon samplers	6 in. (152 mm)	Only limited by drilling rig	Moderate to fast with suitable soil conditions	Moderate to fast soil disturbance. Suitable for collecting samples from cohesive soils. Undisturbed sample.	Less suited for loose soil or soil with coarse gravel. Used in conjunction with drilling rig.
Modified California Sampler				Useful with more sandy soils.	
Tube samplers (Shelby Tube)	6 in. (152 mm)	Only limited by drilling rig	Moderate to fast with suitable soil conditions	Obtains undisturbed sample for determining soil characteristics. Suitable for collecting samples from cohesive soils.	Less suitable for loose soil or soil with coarse gravel.
Cone penetrometer/ drive probes	2 in. (51 mm)	30–150 ft (9–46 m) depending on the probe used	Moderate to fast with suitable soil conditions	Used to map soil characteristics. Collects soil and water samples. Minimal site disturbance. Can obtain relatively undisturbed samples.	Not suited for soils with a high density of rock. Many techniques do not allow for collection of soil sample; some require drill rigs.
Test pits	15 ft (4.6 m)	15–20 ft (4.6–6.1 m)	Moderate to fast	Used to examine soil type and structure. Easily excavated.	Caving can be a severe problem. Limited depth. Greater explosion hazard when excavating into hydrocarbons. Safety of leaving holes open.

Note: in. = inches; ft = feet; m = meters; mm = millimeters.

The thin-walled tube sampler (also known as a push tube or a Shelby tube) is a cylinder typically constructed of stainless steel or brass. Both types of samplers are placed at the bottom of a clean dry hole and driven into the hole without rotation either manually or by power equipment.

Other investigative and sampling techniques that have gained popularity in recent years are the cone penetrometer and hydraulically or mechanically driven probe samplers. The standard cone penetrometer has a 60-degree apex cone tip at the end of a friction sleeve containing strain gauges, an inclinometer, and a pressure transducer (see Figure 11). The typical driven probe sampler has a probe or piston tip, and a protected sleeve on the tube is retracted for soil or groundwater sampling (see Figure 12). The cone tip or probe tip is attached to a series of push rods that are driven into the ground by a truck-mounted hydraulic jacking system. A special truck or van is used to house, transport, and deploy the driven probe sampler or the cone penetrometer.

The ability to collect in situ groundwater samples has made the cone penetrometer a valuable tool for rapid, cost-effective sampling. Driven probe samplers similar to the cone penetrometer have been designed to collect discrete, relatively undisturbed soil samples. Special sampling piston tips can be used with either cone penetrometer testing (CPT) or other driven probes. A piston tip and rod is set into a sample tube on the end of the probe tip and then driven into the ground to the desired sampling depth. At the desired sampling interval depth, the piston stop is released to allow the piston to move freely as the sample is driven (see Figure 12). The driven sampling tube can collect an undisturbed sample 10 to 12 inches (254 to 305 millimeters) in length and 0.85 to 1 inch (21.6 to 25.4 millimeters) in diameter. The samplers should be cleaned after each sample is collected to prevent cross-contamination with residual materials from previous soil samples. The techniques for cleaning are discussed in 5.2.3.

One of the most common uses of the cone penetrometer is stratigraphic logging of soils. The penetrometer differentiates changes in soil horizons or strata by sensing changes in pore pressure as it moves deeper into the soil. Logs generated by CPT data are comparable to logs generated by field classifications and grain size distribution analyses of soils. Subsurface investigations performed by CPT methods are more rapid and more cost-effective than investigations in which conventional drilling methods are used. Under favorable conditions, it is possible to conduct 300 to 900 vertical feet (91 to 274 vertical meters) of soundings in one day. Costs are reduced because there are no drill cuttings or fluids to be contained for disposal and the small holes are easily grouted up if they do not collapse when the instruments are withdrawn. Lithologic descriptions produced by CPTs should always be correlated against at least one soil boring at every site. The use of CPTs as a screening tool allows more effective placement of observation wells. Caution should be exercised to prevent penetrating low-permeability zones, thus allowing vertical migration of product.

The cone penetrometer test can be used to determine various hydraulic parameters. Soil permeability, groundwater head, and water-bearing zones can be derived from the pore pressure data generated during the CPT run. As the push rods are driven into the ground, excess pore pressure is produced. When steady penetration is stopped, the excess pore pressure will decrease over time. This decrease of pore pressure over time provides the information needed to calculate the hydraulic conductivity. This method is not as accurate for clean sands and coarser materials because the excess pore pressure generated during penetration of these materials is dissipated almost as soon as it is produced.

In poorly to moderately consolidated soil or sediment, soil samples for residual liquid hydrocarbon analysis should be collected using hydraulically or mechanically driven probe samplers. Soil samples for residual hydrocarbon analysis should be collected from both above and below the water table. The depth to the water table and the presence of liquid hydrocarbons should be documented. These horizons may be evident from the texture, soil color, and odor of the soil. The presence of free liquid hydrocarbons in the soil boring is clear evidence that a free hydrocarbon plume has been penetrated.

5.2.2 SAMPLE HANDLING FOR ON-SITE ANALYSES

Soil samples collected for on-site analyses should be analyzed as soon as possible after collection to avoid the loss of volatiles. The amount of mixing, aerating, heating, or otherwise disturbing the sample should be minimized to prevent loss of any volatile organic compounds.

When the soil sample has been removed from the sampling device (such as a hand auger or soil corer), it is either immediately analyzed or transferred to a fixed-volume, sealed container for extraction, preservation, or head-space analysis. For some field measurement methods, soil samples are weighed before analysis. A sealed, reclosable container that has been weighed or tarred can be used during the weighing of the sample to minimize loss of volatile hydrocarbons. Some reclosable, airtight containers (for example, Tedlar® or polyethylene bags) also can be used to split samples for field and laboratory analyses or to dilute vapor samples systematically (referred to as a serial dilution) to circumvent effects that might influence field instrument response (see 5.3.1).

5.2.3 SAMPLE HANDLING AND PRESERVATION FOR LABORATORY ANALYSIS

When a soil sample is collected, chemical and physical changes can begin immediately. These changes include loss of volatile components, gas exchange, moisture loss, oxida-

(text continued on page 34)

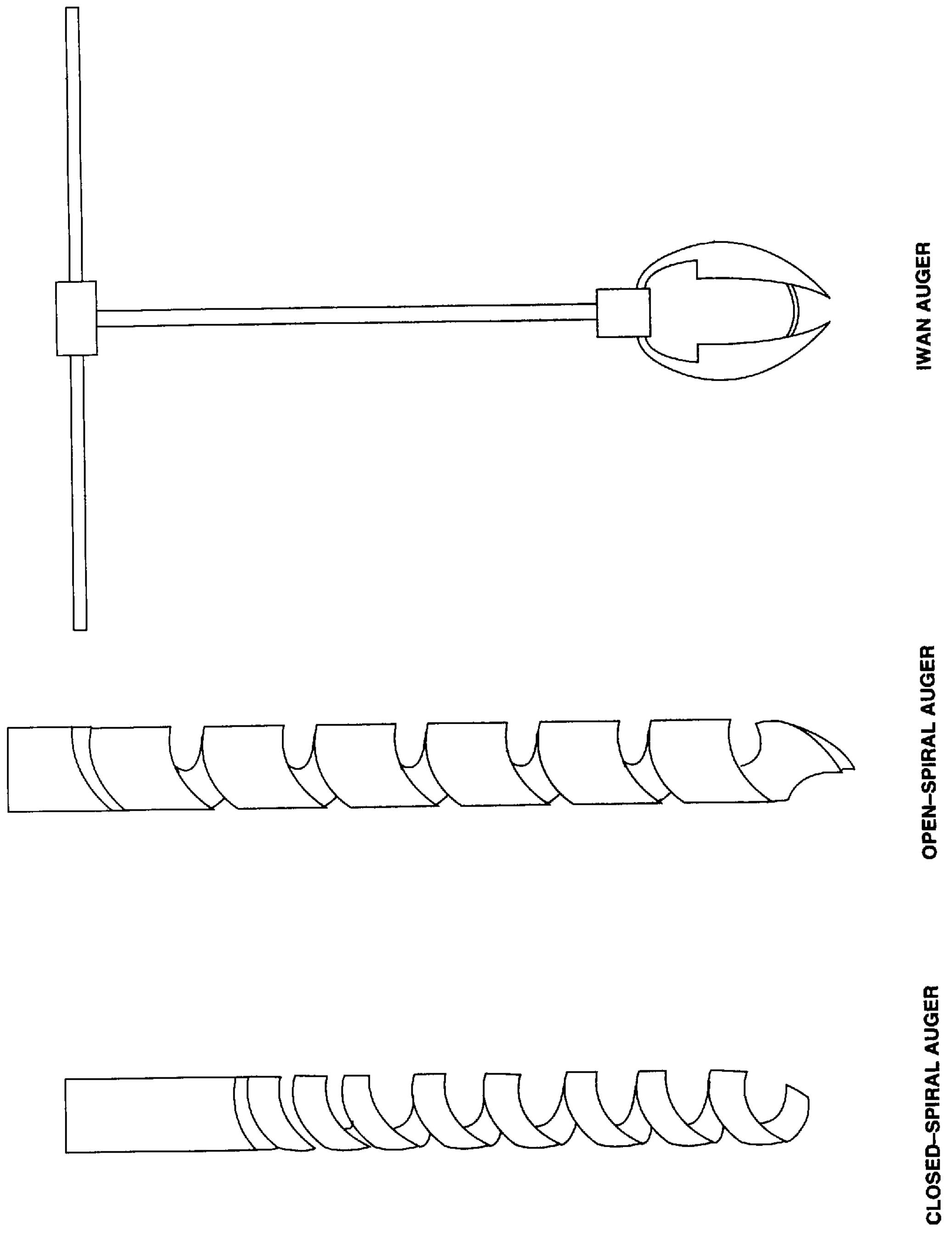
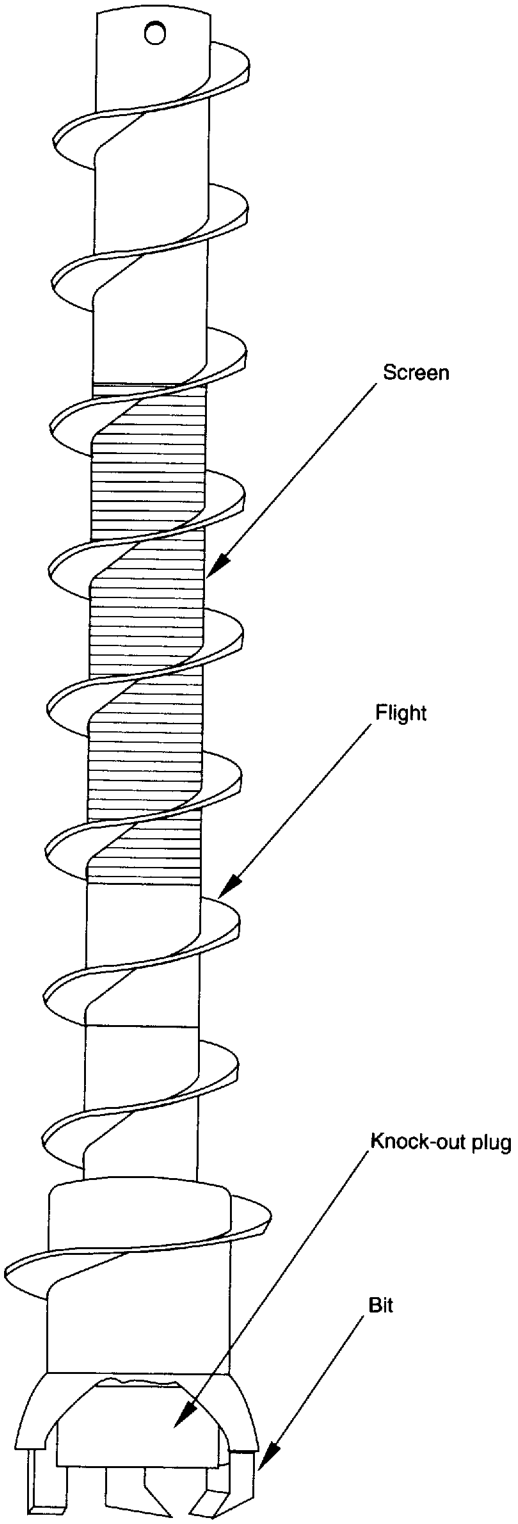
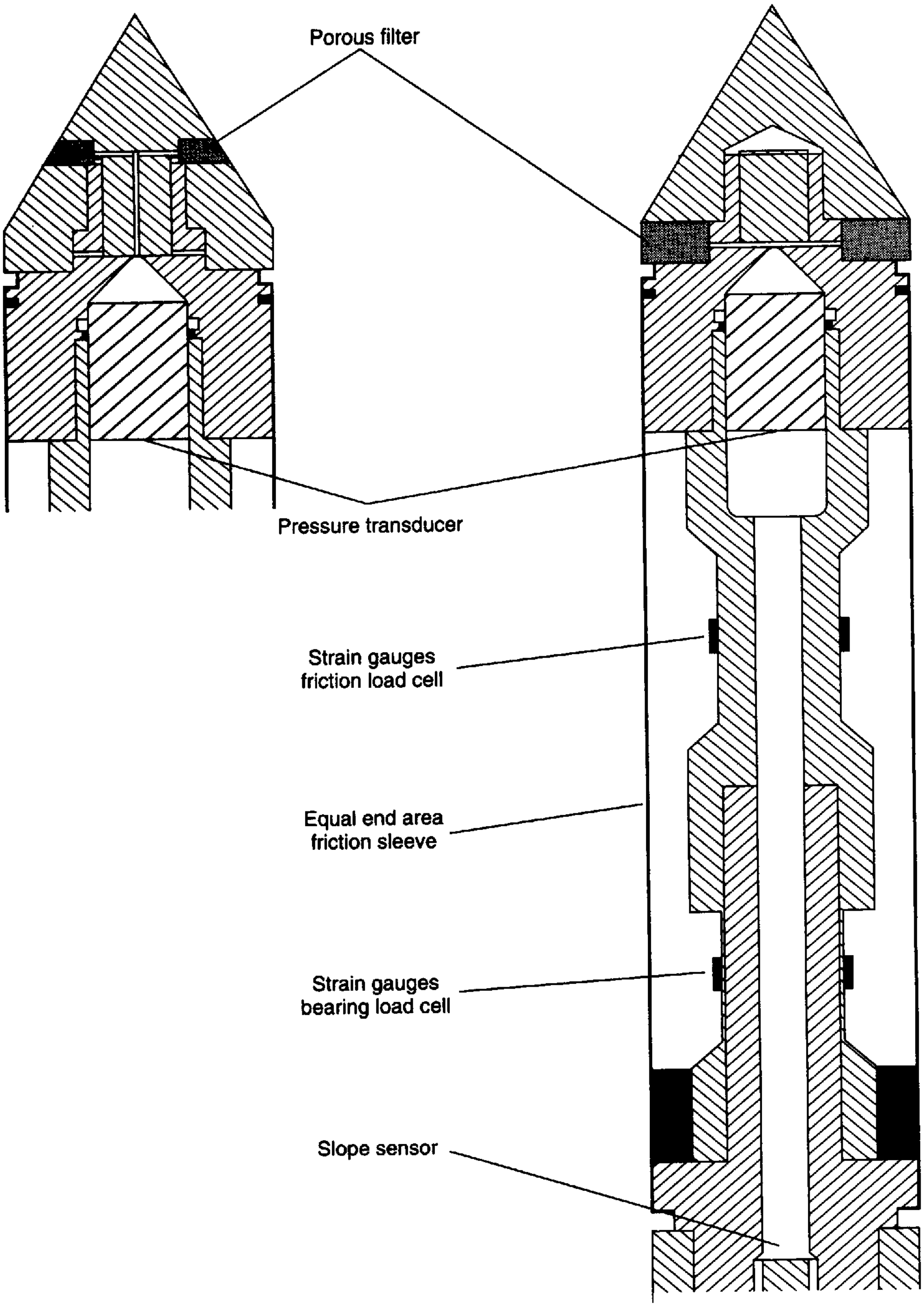


Figure 9—Three Types of Hand Augers



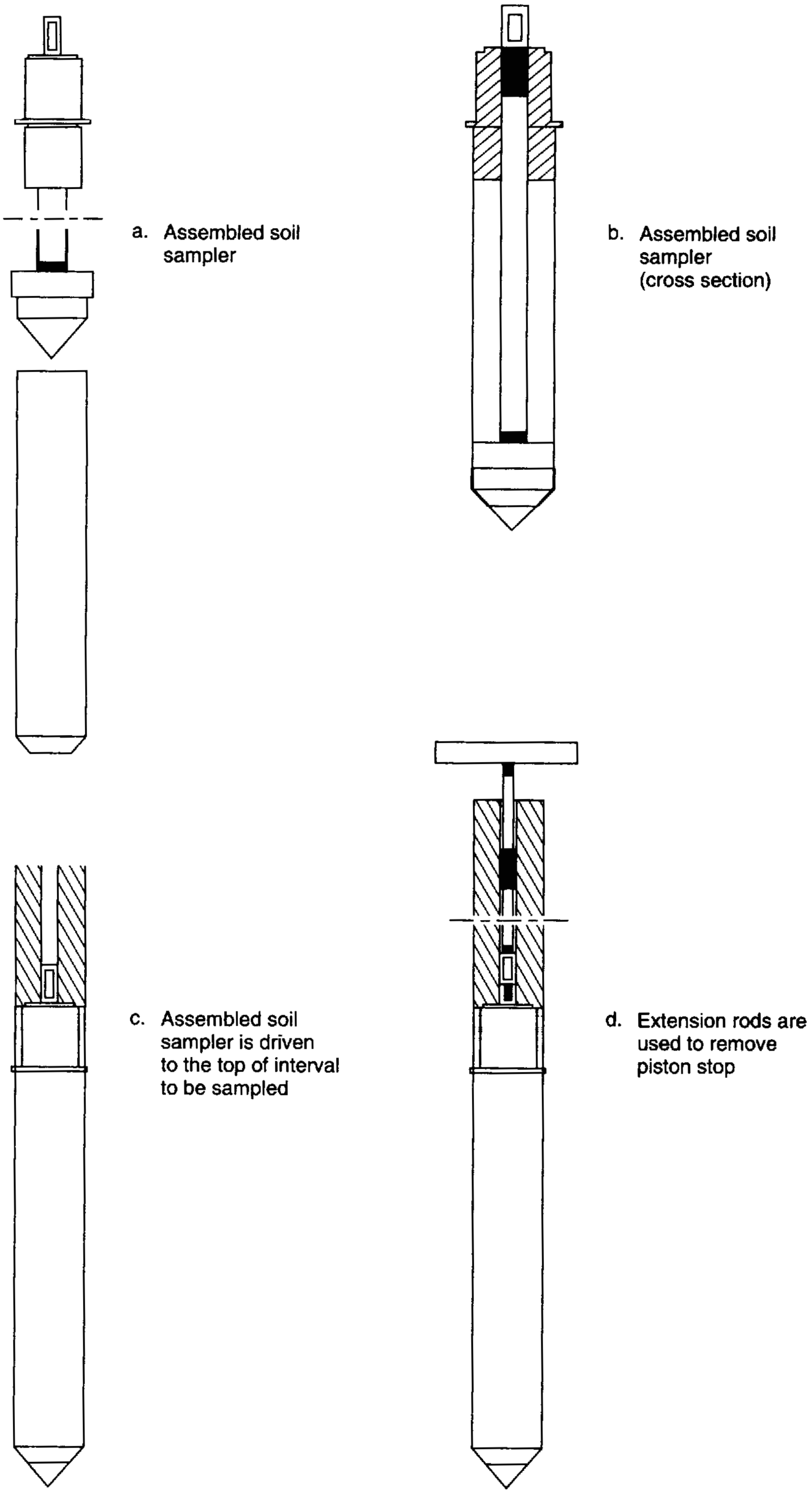
Source: EPA, *A Compendium of Superfund Field Operation Methods* [22].

Figure 10—Keck-Screened, Hollow-Stem, Continuous-Flight Auger



Source: B. Manchon, "Workshop: Introduction to Cone Penetrometer Testing and Groundwater Samplers" [23].

Figure 11—Schematic of a Cone Penetrometer



a. Assembled soil sampler

b. Assembled soil sampler (cross section)

c. Assembled soil sampler is driven to the top of interval to be sampled

d. Extension rods are used to remove piston stop

Source: Geoprobe Systems, Sales Brochure [24].

Figure 12—Schematic of a Driven Probe Sampler

tion, increased or decreased biological activity, and potential contamination of the sample. Therefore, appropriate measures must be taken to handle and preserve samples to minimize these effects.

Before collecting each sample, care should be taken to remove any residues of petroleum hydrocarbons from the sampling equipment to prevent cross contamination of the next sample. All equipment, liners, and small tools used to collect the samples must be decontaminated by specific scrubbing and washing procedures. Residual contamination can be rinsed with solvents, surfactants, and deionized water. These cleaning fluids should then be collected for disposal. The equipment should be air-dried before it is reused. Disposable plastic sampling equipment may also be used.

The collected sample should be immediately transferred to a proper, clean container. Various types of sample containers can be used to store soil samples. One of the best is a glass jar fitted with a polytetrafluoroethylene (PTFE) liner. If thin-walled tube samplers are used, the sample may be left in the cylinder. The sample container must be tightly capped as quickly as possible to prevent the loss of volatile components. The amount of headspace in a sample container should be minimized to limit any volatilization of hydrocarbons from the soil sample. The exterior of all sample containers should be cleaned before shipping to remove any residual material.

After a sample is collected and transferred into a proper container, it should be labeled, placed in an ice chest, and kept at 39 °F (4°C) using blue ice or bagged ice for immediate shipment to the laboratory selected to perform the analysis. The ice cooler should be kept in a shaded area during the sample collection process.

Samples should be analyzed as soon as possible after collection because loss of volatile hydrocarbon constituents can result from biodegradation and volatilization during sample holding. The methods used to analyze a sample may specify the maximum holding time before analysis, which can range from 1 to 2 weeks. The analytical results of samples held for longer periods may not be considered valid.

After the sample is collected and identified, it should be handled in accordance with a prescribed chain-of-custody procedure that involves keeping records of the handling of a sample from its collection through its delivery to the laboratory. Such a procedure assures sample integrity and the technical defensibility of the analytical data. The sampler should initiate a chain-of-custody document after samples are collected, and the document should accompany the samples wherever they go. The document should be signed by all individuals collecting, relinquishing, and receiving samples.

Each sample container should be sealed in a manner that prevents it from being opened without breaking the seal. The label should contain the following information:

a. Sample number (unique to the person collecting the sample).
b. Location.
c. Date sampled.
d. Sampled by (signature).
e. Date seal broken.
f. Seal broken by (signature).

5.3 Field Analytical Techniques

Properly applied and performed field measurement techniques provide results more rapidly than laboratory analyses for making decisions on-site [13]. Because field measurements are proving to be useful, new and improved instruments and techniques are being developed. Performance information of currently available field techniques is presented in Table 8. Some of the advantages of field measurement procedures and instruments include the following:

a. Reliable qualitative and semiquantitative data become available at the site and can be used to make immediate decisions regarding the need for further assessment and ongoing remediation..
b. The lower cost of field measurements allows more sampling points to be included in the site assessment, which results in a more comprehensive set of data.
c. Immediate sample analysis reduces sample handling and eliminates sample storage, thus minimizing the loss of volatiles.

Some of the disadvantages of field measurement procedures and instruments include the following:

a. Depending on the procedure or instrument used, the results are semiquantitative or qualitative. (Note that portable gas chromatographs (GCs) can provide quantitative results.)
b. The age, degree of weathering, or type of petroleum hydrocarbons in a sample determines which field technique will be used. (Some techniques, such as headspace methods that are less sensitive to nonvolatile constituents, are not well suited for weathered products.)
c. Field techniques are subject to procedural errors that can affect the reliability of the results.
d. Several state underground storage programs currently do not accept field measurement results alone (that is, without laboratory results).

Although information collected by field measurement procedures can save time and money, many state and local agencies require laboratory analysis of soil to verify field information, to quantify BTEX and total petroleum hydrocarbon (TPH) levels, or to test for less volatile products (for example, diesel fuel).

Comparing results obtained by field measurement procedures and instruments with those obtained by laboratory analyses is difficult. As indicators of the presence of hydrocarbons, both techniques can provide useful results (given proper performance of the field technique). The types of results differ, however; most field procedures and instruments test for groups of constituents, whereas most laboratory methods can be selected to analyze for individual constituents or groups of constituents. Also, the different detectors used in the field do not always evaluate the same range of hydrocarbons as a lab method.

A significant variability factor also enters into comparisons of field and laboratory analyses. Field measurement methods can yield variable results because of variable instrument response, variable conditions in the outdoor environment, inconsistent protocol, detector limitations, and inappropriate calibration (see Table 8). Laboratory analyses can be significantly influenced by the sample collection method, holding time, and sample transport. For these reasons, it is important to have a well thought out QA/QC program to help eliminate external influences on analytical results.

Both field and laboratory analyses provide useful information for investigating a release. Field data are most reliable when obtained by a competent, well-trained field analyst using properly calibrated and maintained field instruments.

5.3.1 FIELD MEASUREMENT PROCEDURES

Collecting useful and reliable field measurement data depends on the selection of appropriate sampling devices and field measurement procedures. The field measurement procedures currently in use vary widely. Some procedures are very simple to conduct and are used to indicate contamination, whereas others are used to quantify the degree of contamination. The overall performance criteria and general types of procedures adapted from an EPA manual [13] are described in subsections 5.3.1.1 through 5.3.1.4 and presented graphically in Figures 13 through 17.

5.3.1.1 Active Soil Vapor Sampling and Analysis

Active soil vapor sampling and analysis is a method used to measure volatile hydrocarbon concentrations in a soil vapor sample that is collected in place, or in situ, by pumping or withdrawing the sample into a field instrument for analysis. These samples can be collected in the following ways:

a. Drilling or augering a borehole, inserting an instrument probe, and taking a reading.
b. Driving a hollow steel probe [typically less than 1 inch (25.4 millimeters) in diameter] into the soil, collecting a sample with a gas-tight syringe, and injecting the sample into a field instrument for analysis.
c. Driving a hollow steel probe into the soil and collecting the sample in a Tedlar® (or the equivalent) bag for analysis with a portable field instrument.
d. Performing sampling directly from the soil vapor probe (in-line sampling) with a portable analytical field instrument, such as a PID, a FID, or a GC.

Soil vapor collection techniques are presented in Figures 13 through 16. The level of skill needed by investigators depends on the type of procedure and analytical instrument being used.

Soil air permeability tests and depth profiles should be performed as part of a soil vapor survey to assess the influence of permeability, stratigraphy, and moisture content on the soil

Table 8—Summary of Soil and Soil Vapor Field Measurement Procedures and Analytical Instrument Performance

Procedure	Measuring Device	Lower Detection Limits for Gasoline[a]		Estimated Time for Collection and Analysis (in minutes)
		Soil and Water	Soil Vapor	
Drager tube				5
General headspace analysis[b]	FID/PID/colorimetric detector tube GC	10's–100's ppm ppb	10's–100's ppm ppb	 10–20
Polyethylene bag sampling system	FID/PID colorimetric detector tube GC	1 ppm 10's–100's ppb	1–100's ppm ppb	10–20 20
Extraction-colorimetric procedure	N/A	Soil: 1 ppm Water: 0.1 ppm	N/A	Soil: 45–60 Water: 10–15
Soil vapor	FID/PID/colorimetric detector tube GC	N/A N/A	10's–100's ppm ppb	10–30 15–35

Notes: FID = flame ionization detector; PID = photoionization detector; GC = gas chromatograph; ppm = parts per million; ppb = parts per billion; N/A = not applicable.
[a] Determined by spiked field standards.
[b] General headspace analysis refers to dynamic and static headspace analysis.

vapor sampling results and to assist in survey interpretations. Soil vapor survey results provide qualitative information on the type and concentration of vapor-phase hydrocarbons, and the results should be interpreted by evaluating the level of hydrocarbons relative to those at other vapor sampling points. At certain sites, the relative concentrations of constituents (alkanes and aromatics) in the soil vapor may be used to determine if the vapor-phase hydrocarbon plume is weathered and its distance from the source. Interpretation of soil vapor sampling results should consider site characteristics such as high-clay or organic matter content and moisture percentage.

5.3.1.2 Passive Soil Vapor Sampling and Analysis

Passive soil vapor sampling and analysis involves using a buried accumulator device (shown in Figure 17) to collect a sample that represents the total mass of vapor accumulated over the time the device was in place. Compounds adsorbed to the sampling device are measured using a desorption procedure followed by mass spectrometry analysis in a laboratory.

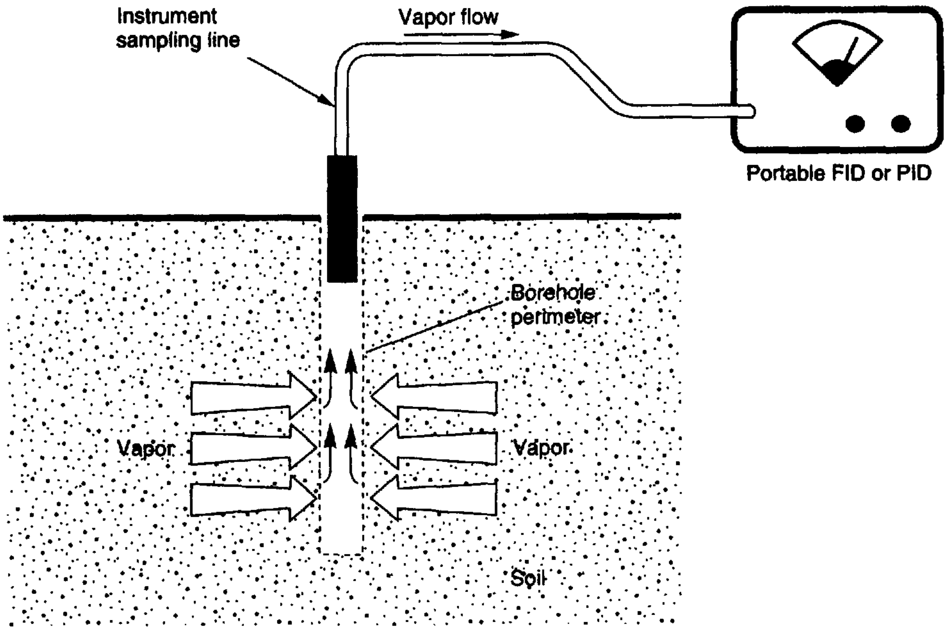
Advantages of this technology are its simplicity, ruggedness, ease of installation, and relatively low cost. Disadvantages include longer sampling analysis periods and potential interference from high background concentrations near the land surface. A major limitation is that results are not reported as concentrations that can easily be compared with other data.

5.3.1.3 General Headspace Analysis of Soil

Headspace analysis of soil involves collecting a soil sample, placing it in an airtight container such as a volatile organics analysis (VOA) vial or larger glass container, and analyzing the headspace vapor above the soil sample with a portable analytical instrument (see 5.3.2). High soil moisture and high levels of organics and clay in the soil can limit the amount of volatile hydrocarbons that will volatilize into the container headspace. Concentrations of volatile constituents are lower in soils containing weathered petroleum hydrocarbons compared with soils containing fresh releases because the volatile constituents decrease in varying degrees over time. Headspace analysis of soil provides qualitative results that can be used as a general indicator of the presence of hydrocarbons.

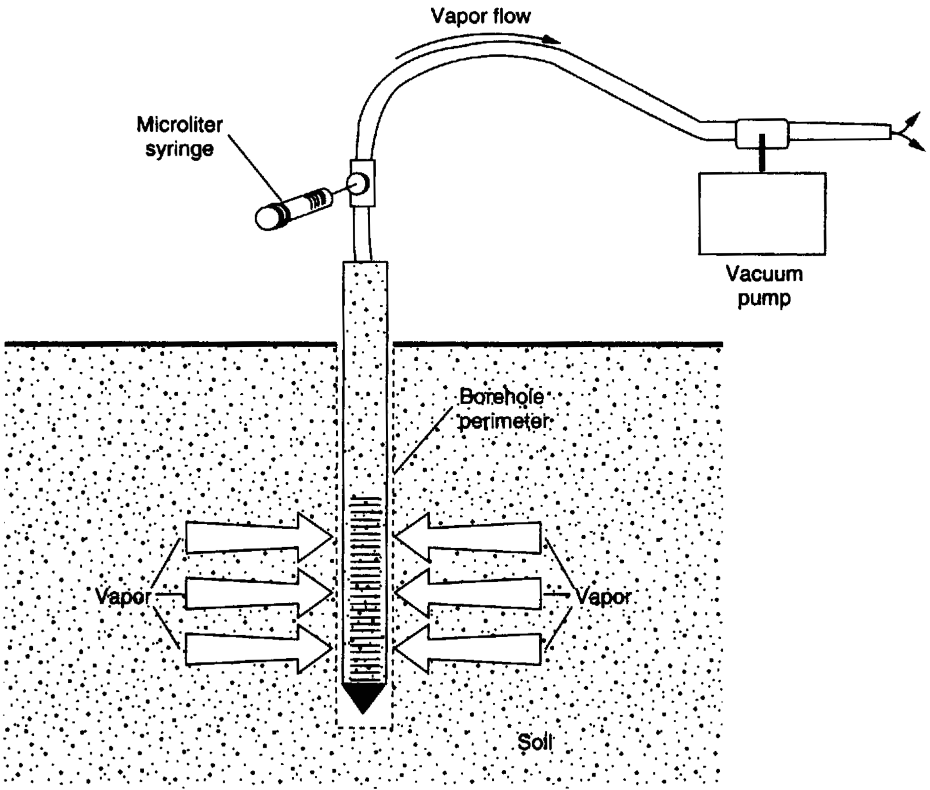
Dynamic headspace analysis of soil by using a polyethylene freezer bag system involves collecting a soil sample, placing it in a reclosable freezer bag, adding water, and then agitating the sample to release vapors in the bag. The vapor concentration in the bag headspace is measured using an analytical field instrument (see 5.3.2). Measured concentra-

(text continued on page 40)

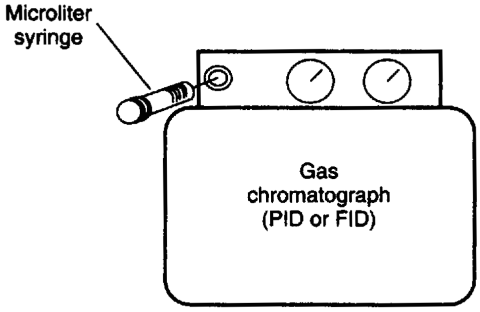


Note: PID = portable photoionization detector; FID = flame ionization detector.
Source: Modified from EPA, *Field Measurements: Dependable Data When You Need It* [13].

Figure 13—Collection and Analysis of Soil Vapor in a Borehole Using a Portable PID or FID



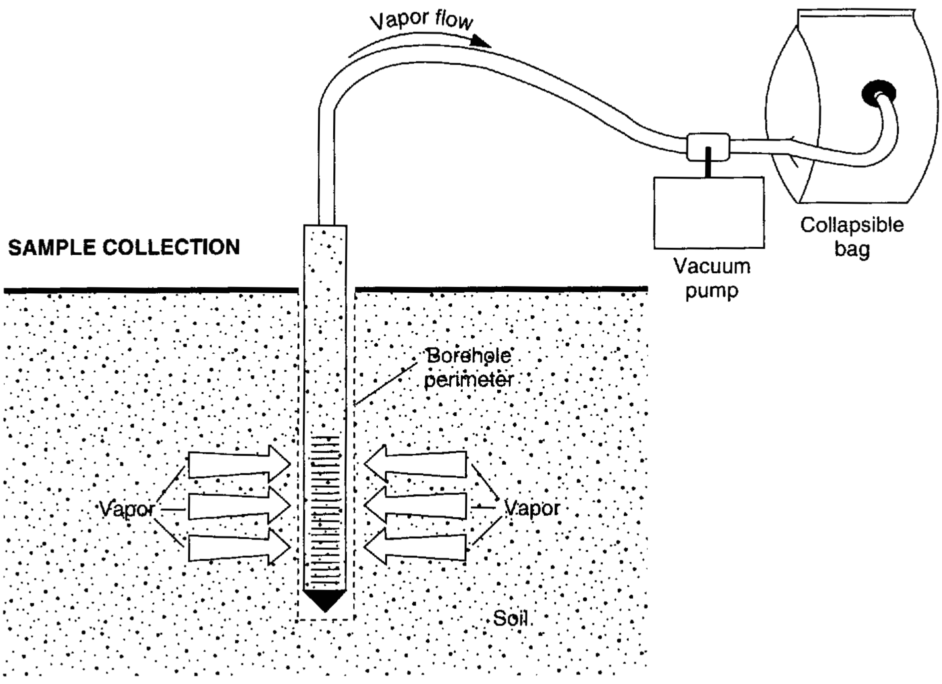
Step 1: Sample collection with a syringe



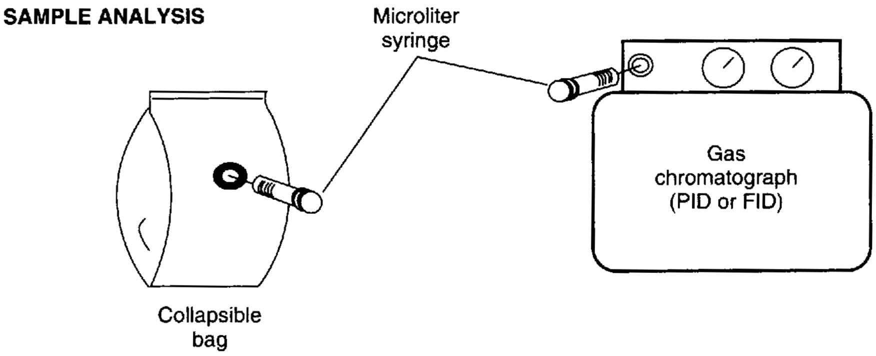
Step 2: Sample analysis by GC

Note: GC = gas chromatograph; PID = portable photoionization detector; FID = flame ionization detector.
Source: Modified from EPA, *Field Measurements: Dependable Data When You Need It* [13].

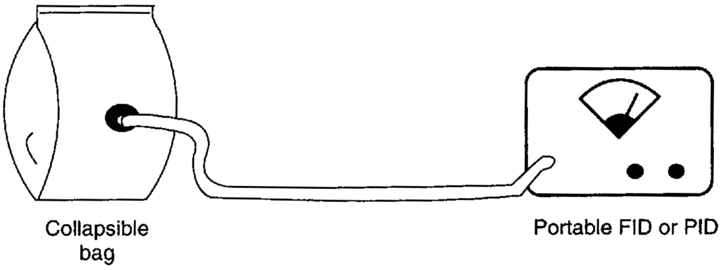
Figure 14—Soil Vapor Collection by Syringe and Analysis by GC



Collect sample in a collapsible container



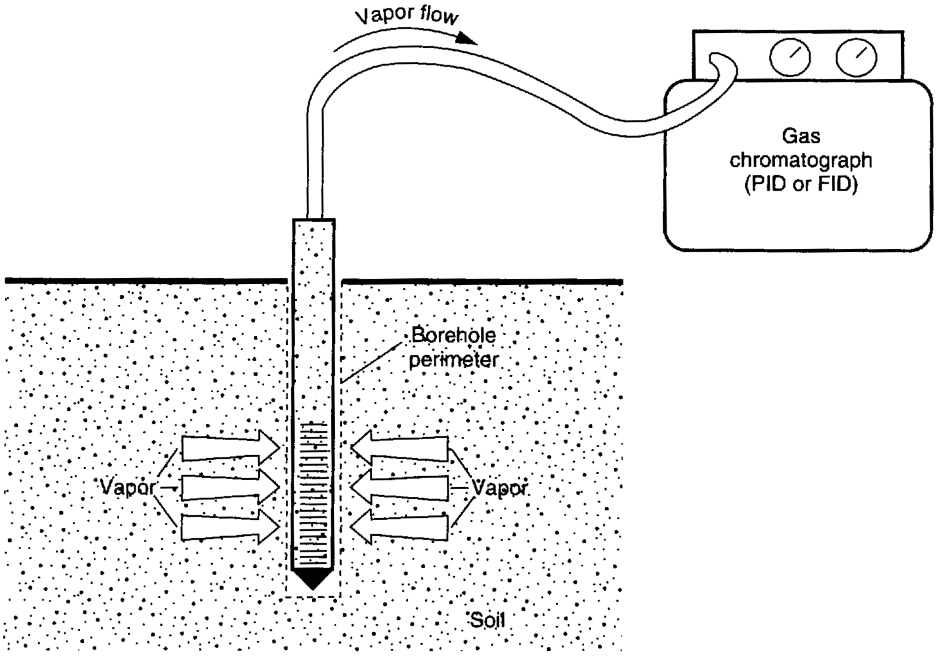
Alternative 1: Withdraw a vapor sample from bag with syringe and analyze on the GC



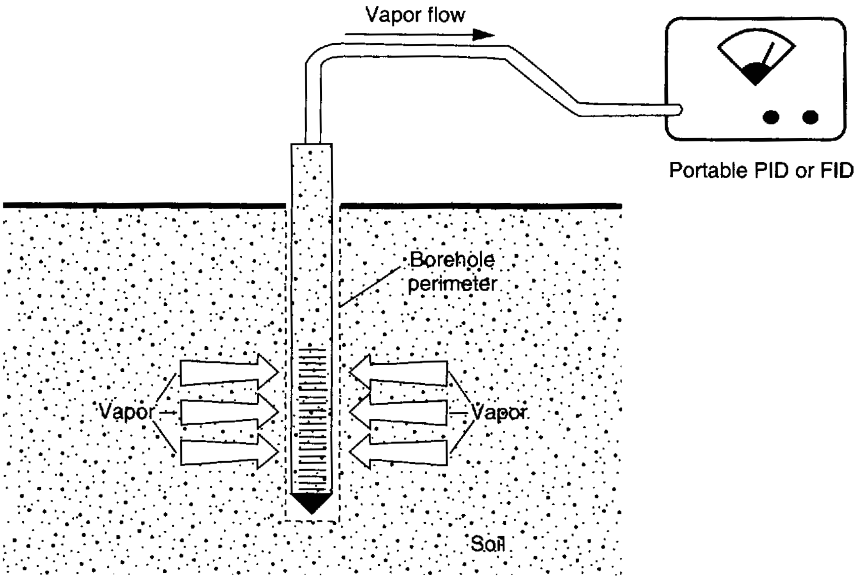
Alternative 2: Analyze soil vapor directly from bag with a portable FID or PID

Note: GC = gas chromatograph; PID = portable photoionization detector; FID = flame ionization detector.
Source: Modified from EPA, *Field Measurements: Dependable Data When You Need It* [13].

Figure 15—Collection of Soil Vapor in a Bag for Analysis by Portable GC, FID, or PID



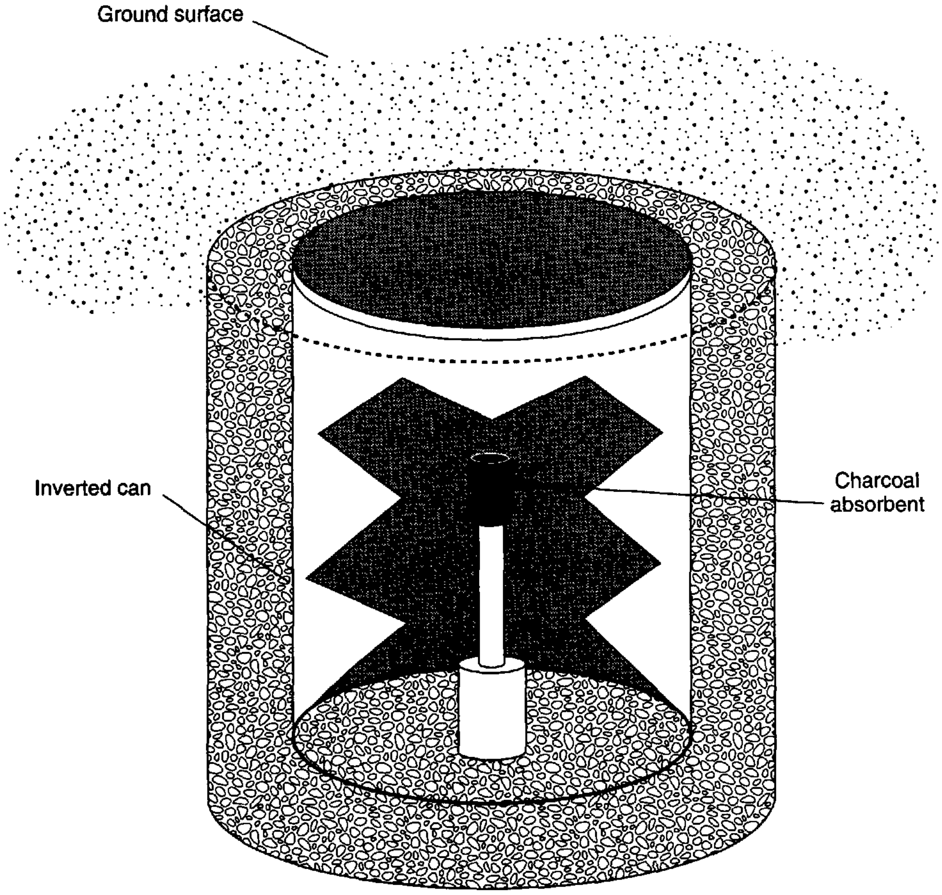
Alternative 1: Soil vapor collection and analysis using a GC



Alternative 2: Collection and analysis using FID or PID

Note: PID = portable photoionization detector; FID = flame ionization detector.
Source: Modified from EPA, *Field Measurements: Dependable Data When You Need It* [13].

Figure 16—Soil Vapor Collection and Analysis Directly From a Vapor Probe



Source: Modified from EPA, *Field Measurements: Dependable Data When You Need It* [13].

Figure 17—Buried Accumulator Device

tions are a function of the analytical detector's range of sensitivity.

The quality of data obtained with this procedure is considered good for soil analysis, and results are not significantly influenced by such soil matrix effects as high soil moisture or clay content. Performance data indicate that volatile hydrocarbon constituents in gasoline can be measured in soil at concentrations of less than 10 parts per million. Products with lower volatility, such as diesel fuel, yield less sensitive results (less than 200 parts per million) compared with gasoline.

5.3.1.4 Extraction-Colorimetric Procedure for Soil Analysis

The extraction-colorimetric procedure for soil analysis involves extracting aromatic compounds from soil, adding a reactant to the sample, and interpreting a color change in the sample extract, which indicates the type of contaminant and its concentration (the color indicates the type of compound, and the color intensity indicates the concentration). Training and experience are required to perform this analysis and to interpret the results. Waste chemicals from this analysis may be considered hazardous. Also, this analysis should be used with caution on soils since soil components other than contaminants may affect color change.

This procedure provides quantitative results for a variety of hydrocarbon constituents. It is especially effective for determining the presence of polynuclear aromatic hydrocarbons. Some investigators, however, have indicated that accuracy may be lower for the analysis of soils consisting of fine clays and silts [13].

5.3.2 FIELD ANALYTICAL INSTRUMENTS

A wide range of field analytical instruments is available for determining the presence of volatile petroleum hydrocarbons in soil. Some simply detect the presence or absence of unspecified groups of volatile chemicals, whereas other more sophisticated tools can identify and quantify specific constituents. The instruments presented in this publication are those commonly used to detect volatile organics; however, other instruments are available that will detect a broader spectrum of hydrocarbon constituents (see note).

Note: When using and relying on field equipment for decision making during assessments, be certain to (a) acknowledge the limitations of the instrument being used and (b) recognize the importance of proper usage and maintenance. Results can be misleading if the tools are misused or are not properly maintained and calibrated. Also, results generated by an instrument designed only to indicate whether or not volatile compounds are present cannot be interpreted to mean any more than just that.

The following subsections (5.3.2.1 through 5.3.2.4) briefly describe some of the different types of field analytical testing instruments, and Table 9 presents performance data on these instruments.

5.3.2.1 Colorimetric Detector Tubes

Colorimetric detector tubes, one of the simplest field analytical tools, are used to measure a specific vapor or gas in air. Each tube is basically a short length of glass tubing that contains a specific type of chemical packing. Air is drawn through the tube by breaking off the tube tip and connecting it to a hand pump. As an air sample containing hydrocarbons is pulled through the tube, it will react with the detector reagents to produce a color stain. Generally, the length and intensity of the stain are proportional to the concentration of the contaminant, which is a reading taken from the scale. The accuracy and detection range of a specific tube are stated in the manufacturer's literature. Although these tubes have some limitations in terms of accuracy and detection range, they have the advantages of being inexpensive and easy to transport, use, and interpret.

5.3.2.2 Photoionization Detector

Portable photoionization detectors (PIDs) are relatively easy to use in the field and particularly sensitive to aromatic hydrocarbon constituents. The PID ionizes the vapor sample to detect and measure the presence of organic vapors. An ultraviolet (UV) light in the instrument is used to ionize organic vapor molecules. An internal pump draws the air sample through the instrument probe and past the lamp. If the UV light can excite the air sample and cause it to ionize, a signal registers on the instrument meter or digital display. The strength of the signal is a relative measure of the concentration.

Some PIDs have interchangeable UV lamps that are sensitive to different ranges of compounds. All of the PID lamps have a specific sensitivity to BTEX. Different UV lamps can be used to detect different volatile constituents. The detection range for these instruments is about 0.2 to 2000 parts per million. Accuracy varies with the concentration level being measured, the type of constituents present in the sample, and the amount of moisture drawn into the instrument.

Because PIDs do not detect alkanes such as methane, they can be useful in detecting aromatic constituents released in areas where natural methane may exist (such as in septic fields, sewer lines, and bogs). Dry weather and temperatures above 50°F (10 °C) are the ideal conditions for conducting PID analyses. The responsiveness of PIDs decreases in moist conditions when the relative humidity of the sample or ambient air is high (above 90 percent).

5.3.2.3 Flame Ionization Detector

Flame ionization detectors (FIDs) are commonly used to measure the presence of organic gases and vapors. This instrument uses a hydrogen flame to ionize molecules of volatile organic constituents present in the vapor sample. The ionized molecules produce a current proportional to that of the sample. The FID will detect the presence of volatile vapors, including methane, that may yield high readings (false positives) in areas where methane levels are higher than normal (for example, wetlands, sewers, septic fields, and bogs). A direct-reading colorimetric detector tube specific to methane can be used in conjunction with an FID to evaluate methane concentrations. The FIDs are less sensitive than PIDs to environmental conditions such as relative humidity and temperature; however, winds, excess carbon dioxide, and depleted oxygen can extinguish the flame in the instrument. These instruments are also more sensitive than PIDs to alkanes such as hexane and butane, which make up a higher fraction of gasoline than do the aromatics.

5.3.2.4 Portable Gas Chromatograph

A portable gas chromatograph (GC) uses a separation column to isolate and analyze specific constituents in either a liquid or vapor phase in conjunction with a PID or an FID detection system. A portable GC consists of a sample injection system, a separation column, an output detector, and a detection system. A GC/FID system contains a combustible gas supply for the flame; a GC/PID system contains a UV lamp. Several different GCs with varying capabilities are currently offered on the market.

Vapor samples containing a mixture of compounds can be injected into the GC and carried through the sample column by an inert carrier gas. The vapors travel through the column at varying rates of speed and reach the detector at different times. Each component is separated by the time it gets to the detector. The lighter constituents elute or are extracted first, followed by those that are heavier and less volatile. This detection process is translated into a chart record (or chromatogram) showing the length of time from injection to maximum peak height. The peak height from the baseline to the top of the peak is proportional to the concentration of a constituent.

The portable GC is an extremely versatile and powerful tool for field use. Its performance, however, depends greatly

Table 9—Summary of Analytical Instrument Performance

Analytical Method/Device	Skill Level for Analysis	Calibration Frequency	Ease of[a] Maintenance	Operational Factors
Portable FID	Medium	1 to 3 times every day	Easy	Detects methane. Low oxygen levels cause flameout. Recommended ambient air temperature is >40°F (4°C). Requires battery recharge every 8 hours. Hydrogen gas is required. Flow rate below 1.2 liter/min. can yield inaccurate results. Complete destruction of sample does not allow further analysis. Detects the total concentration of many organic vapors and gases (alkanes and aromatics) within its ionization potential.
Portable PID	Medium	1 to 3 times every day	Very easy	Photoionization lamp requires periodic cleaning and changing. Moist atmospheric conditions (for example, rain) and high relative humidity (>90%) in the sample can "quench" the signal and result in low readings. Dust particles may absorb ultraviolet energy and cause erratic responses in PIDs that do not have filters. Responses may be affected by power lines, transformers, or radio wave transmitters. For concentrations >150 ppm TOV, the PID may provide nonlinear or erratic responses. Does not detect methane or other alkanes and thus eliminates anomalous methane contributions to total concentration readings.
Portable GC	High	Every 5 to 10 samples	Difficult	Ambient conditions can affect instrument performance if not calibrated under similar conditions. Specific constituents in mixtures can be difficult to resolve on a chromatogram. Separation of components with wide ranges of volatility can be difficult and time consuming. Injection and analysis of water sample require an additional extraction step using an organic solvent (methylene chloride). A qualified operator is required to assure accurate results. GCs are sensitive instruments that require frequent factory adjustments.
Colorimetric detector tubes	Low	Calibration by manufacturer	No maintenance	Tubes previously opened or past their expiration dates should not be used. High humidity can limit the sensitivity of a detector tube. Jagged edge of the stain sometimes makes it difficult to obtain accurate readings. Constituents that are similar may interfere with detection of the constituent of interest. Pump that draws a specific volume of sample into the tube should be checked for leaks. May generate hazardous waste as part of the extraction process. May not be appropriate for soil analyses.

Notes: FID = flame ionization detector; PID = photoionization detector; GC = gas chromatograph.

[a] On-site routine maintenance by the operator.

Source: Modified from EPA, *Test Methods for the Evaluation of Solid Waste* [14].

on the operator's capabilities; a substantial level of skill is required to operate and interpret the results.

5.4 Laboratory Analysis of Soils

Most state regulatory programs require laboratory analysis of soil samples as part of a site assessment and corrective action for soils containing petroleum hydrocarbons. Results of laboratory analyses can provide quantitative data for a range of indicator compounds in hydrocarbon fuels. The turnaround time for laboratory analyses (that is, the time it takes to receive results after a sample has been submitted for analysis) can take from 1 to 6 weeks depending on the premium paid for the analysis. In addition, an inherent variability exists among results from different laboratories because accepted analytical methods may have been modified to use different methods for containment extraction and analysis. Most of the accepted methods for analysis of soil are adapted from a series of EPA methods developed for either water or solid waste and published in SW-846, *Test Methods for Evaluating Solid Waste* [14]. All of these methods require the removal or extraction of hydrocarbons from the soil matrix; thus, the primary problem involved in analyzing soils containing hydrocarbon fuels is the efficient removal of the hydrocarbon constituents for analysis. Variables such as sample collection, handling, and storage can seriously affect loss of volatiles in laboratory analyses. Variations in results can also be attributed to the ways EPA methodologies have been adapted by different laboratories.

Most hydrocarbon fuels are composed of complex combinations of constituents that have different physical and chemical properties. As a result, the analytical methods must be broad in scope but capable of routinely and reliably detecting concentrations in the range of 1 to 10,000 parts per million. Some analytical methods are commonly used to measure a limited range of hydrocarbon constituents, although they are not designed to do this. As an example, EPA Method 418.1 is inappropriately named "Total Petroleum Hydrocarbons"; however, the results are often misinterpreted because they represent a wider range of all hydrocarbons present in soil.

5.4.1 METHODS OF IDENTIFYING CONTAMINANTS

Because of the physical and chemical complexity of petroleum products and the difficulties associated with analyzing them, the analytical process is often limited to identifying indicator compounds. *Indicator compounds* are usually defined as those that are considered the most toxic and most mobile in soil and groundwater. Many state regulatory guidelines or standards focus on BTEX because of their recognized toxicity and mobility. A second indicator compound commonly used is TPH, primarily because the test is a simple and inexpensive procedure. Although TPH may be useful in characterizing the general nature of petroleum hydrocarbons occurring at facilities, it has several shortcomings as an indicator of petroleum hydrocarbon concentrations in soils and, therefore, of the impact on groundwater or of health risks. These shortcomings are discussed further in 5.4.2.

Several EPA methods are commonly used to analyze for volatiles and semivolatiles. Soil samples are generally analyzed in the laboratory by GC or gas chromatograph/mass spectrometer (GC/MS). Each of these methods has an associated target compound for which it was specifically developed and evaluated. Table 10 lists the methods commonly used to detect, identify, and quantify indicator parameters and specific constituents in soils containing petroleum hydrocarbons.

For specific compounds that must be identified and removed from the soil matrix by volatilization or solubilization, the removal methods depend on the relative volatility of the target compounds. The methods are typically categorized as volatile or semivolatile. The volatile methods target key compounds such as BTEX that are routinely used for analysis of gasolines. Semivolatile methods are used for products like diesel fuel because they target key compounds such as naphthalene and phenanthrene.

The term *volatile* refers to those compounds that can be effectively recovered from soil by the purge-and-trap method (EPA Method 5030A [14]). In the purge-and-trap method, a portion of the soil is dispersed in methanol, polyethylene glycol, or tetraglyme to dissolve the volatile organic constituents. The resulting solution is then combined with reagent-free water in a purging chamber. The sample is purged at room temperature with an inert gas such as helium, and the volatile components are transferred from the aqueous phase to the vapor phase. The volatile compounds stripped from the sample are then trapped with a porous polymer adsorbent. The trapped compounds are desorbed directly into the inlet of a GC by rapidly heating the trap after the column carrier gas has been diverted to flow through it.

Nearly all of the methods for detecting specific hydrocarbon constituents or compounds in soil (BTEX, for example) use GC, and a packed-column technology is usually specified. Techniques in which GC columns are interfaced with mass spectrometers are emphasized. Mass spectrometers fragment the molecules separated by GC and produce a characteristic mass spectrum. These instruments are well known for their sensitivity and ability to detect specific organic compounds.

The PID is an alternate detector used with methods involving aromatic hydrocarbons. This detector has a relatively high selectivity for aromatics over aliphatic hydrocarbons. One series of methods also uses the FID detector, which gives nearly universal response to hydrocarbons and offers no selectivity. Identifying constituents by using GC/MS methods is based on chromatographic retention times and mass spectra, whereas identifying and measuring constituents by GC methods alone are based on chromatographic retention times only.

5.4.2 PERFORMANCE CONSIDERATIONS

Determining which type of analytical method to use depends on the type of hydrocarbon compounds in the soil samples. Analytical methods range from the generic TPH methods to the highly selective and sensitive GC methods used to analyze specific constituents (BTEX, for example).

The indicator parameter method mentioned earlier focuses on the common characteristics of several petroleum hydrocarbon constituents and is used as a screening method for identifying gross amounts present. Analysis of soil samples for indicator parameters such as TPH is quick and relatively inexpensive. These analyses involve extracting hydrocarbon residues from the soil by using an organic solvent or solvent mixture. The EPA methods for TPH specify the use of Freon™ as an extractant (CFC 113), which could pose environmental concerns.

Although the methods used to determine TPH (EPA Method 418.1 is the most commonly used [14]) are relatively inexpensive, their accuracy has not been fully documented for measuring petroleum-based fuel in soils. Such methods neither accurately measure the lighter fractions of gasoline (which include BTEX), nor identify any natural soil organics derived from biological activities. No performance data have been published on using these methods on soil (they were originally developed as an analysis method for water). Furthermore, because petroleum fuels are complex mixtures, it is difficult to establish standards for calibrating the results. Also, extraction efficiency (recovery) and detector response (detectability) of different hydrocarbon components will vary somewhat among different fuels and soil types.

These problems may be compounded by attempting to compare different fuel compositions. For example, gasoline and diesel fuels contain different classes of hydrocarbon constituents. Therefore, the TPH methods used for gasoline in soil will consist of C_6 to C_{12} compounds, whereas those used for diesel fuels in soil will consist of C_{10} to C_{25} compounds. No simple way exists for directly comparing soils containing gasoline with soils containing diesel fuels. Because of the inherent variability of the methods, relating any potential environmental or health risks to concentrations of TPH is currently impossible. For these reasons, TPH has limited value as an indicator compound for cleanup criteria. Its widespread use as a soil cleanup criterion points to a lack of understanding of the proper use and limitations of the TPH method. When the regulatory objective is protection of groundwater quality, more mobile constituents (such as BTEX) should be used as indicator compounds.

Perhaps the most frequently recognized problem with soil analysis is not the analytical work itself but the difficulties encountered in maintaining sample integrity (that is, preventing the loss of volatile compounds during the interval between initial field sampling and final analysis). One means of avoiding this situation is by using field preservation of the sample. API has developed a method using either methanol or methylene chloride as the preservative (see API Publication 4516 [15]). The method also contains detail on using appropriate reference standards for the analytical procedures, as well as approaches to quantifying contaminant concentrations.

Another analytical issue of interest is recognizing appropriate detection limits for the methods in use. A critical concept in chemical analysis is the evaluation of the data generated in terms of its reliability (that is, with what degree of certainty does any given analytical value represent the true concentration of the analyte in the sample). This is particularly important when analyses are being conducted for complex matrices (such as for fuels in soil) in concentrations at or below the detection limits. For some compounds, this becomes a very real problem. For example, no published method detection limits exist for benzene in soil; however, EPA's SW-846 suggests a method detection limit for Method 8020 of 2.0 micrograms per liter (2.0 parts per billion) but notes a practical quantitation limit (PQL) of between 2 and 250 micrograms per liter for soils with so-called low to high levels of contamination [14]. The terms low and high are not further defined in the publication.

Providing a precise, generic, limit for detecting organic compounds such as benzene in soil is impossible because the true detection limit depends on the nature of the specific interferences provided by the soil matrix and the other organic chemicals present. These interferences will vary among soil types (for example, sandy soils typically have fewer interferences than do silty or clayey soils) and among fuel types (such as weathered fuels). Although it is not always practical to identify these interferences and determine their effect on the detection limit, all individuals who must rely on these chemical analyses in their decision-making processes should have a thorough understanding of these concepts.

5.4.3 ANALYSIS OF HAZARDOUS WASTE CHARACTERISTICS

The Resource Conservation and Recovery Act (RCRA) hazardous waste characteristics promulgated by the EPA designate broad classes of wastes to be hazardous by their inherent nature. Because such wastes have been determined to be harmful to human health or the environment, the EPA has identified test methods and regulatory thresholds for determining specific characteristic properties. Thus, any solid waste that exceeds the regulatory threshold level for any characteristic property is considered a hazardous waste.

The analytical procedures used to determine if wastes should be characterized as hazardous under RCRA are listed in 40 *Code of Federal Regulations* Part 261 [16]. Sections

Table 10—Analytical Methods for Soil Samples

Parameter	Method[a]	Comment
Benzene, xylene, toluene, and ethylbenzene (aromatic volatile organics)	EPA 5030A EPA 8020A[b] EPA 8021A[b] EPA 8240A[b]	Purge-and-trap extraction method GC-PID, ignores MTBE. GC-ECD/PID in series. GC/MS (typically used for gasoline).
Polynuclear aromatic hydrocarbons (PAHs)	EPA 3550A EPA 8270A	Ultrasonic extraction method. GC/MS (typically used for used motor oil and unknown).
Total petroleum hydrocarbons	EPA 418.1[b,c] EPA 8015A[b]	Does not distinguish between naturally occurring oils and petroleum based oils. Does not measure lighter fractions, such as BTEX.
Napthalene	EPA 8100	
Benzene and 1, 2-dichloroethane (TCLP)	EPA 1311[d] EPA 8240A[b]	Zero headspace extraction. GC/MS analysis.
Lead (TCLP)	EPA 1311[d] EPA 6010 EPA 7421A EPA 7420A	TCLP leaching method. Inductively coupled plasma (ICP). Graphite furnace AA. Flame AA.
Ignitability/flash point	EPA 1010A EPA 1020A	Applies to liquids only but is used on soils.
Oil and grease	EPA 9071A	
Percent moisture	ASTM D2216	
pH	EPA 9045A	Soil pH method.
Organic matter concentration (total organic carbon)	EPA 9060A	High-molecular-weight oils.
Grain size analysis	ASTM D422	Sieve and hydrometer analysis.

---

[a] EPA, *Test Methods for Evaluating Solid Waste* [14].
[b] The method cannot distinguish between soil matrix interferences and the target compounds or constituents.
[c] EPA, *Methods for Chemical Analysis of Water and Wastes* [40].
[d] 40 *Code of Federal Regulations* Part 261, Appendix II [16].

261.21 through 261.24 detail the specific test methods used to characterize the material by ignitability, corrosivity, reactivity, and toxicity criteria.

A number of state and local regulatory agencies require testing of soils contaminated with petroleum hydrocarbons for specific hazardous characteristics. Because of the inherent characteristics of petroleum hydrocarbons, corrosivity and reactivity are not applicable to soils containing petroleum hydrocarbons; however, some attempts have been made to test solid wastes for ignitability as defined in RCRA. The ignitability tests used for liquid wastes clearly state that they are not appropriate for solid wastes, and the EPA is currently evaluating several procedures for their applicability to soils. The relevance of the characteristics of ignitability and toxicity to soils containing petroleum hydrocarbons is discussed in the subsections 5.4.3.1 and 5.4.3.2.

5.4.3.1 Characteristic of Ignitability

The characteristic of ignitability as defined in 40 *Code of Federal Regulations* 261.21 [16] has four provisions for determining whether or not a solid waste is legally a hazardous waste; however, only two of these provisions are relevant to soils containing petroleum hydrocarbons. (The other two provisions describe conditions under which solid wastes, such as compressed gases or oxidizers, are ignitable and,

Table 11—Maximum Concentration of Constituents for the Toxicity Characteristic

EPA HW No.[a]	Constituent	CAS No.[b]	Regulatory Level (milligrams/liter)
D018	Benzene	71-43-2	0.5
D028	1,2-Dichloroethane	107-06-2	0.5
D008	Lead	7439-92-1	5.0

---

[a] EPA hazardous waste number.
[b] Chemical Abstracts Service number.

therefore, considered hazardous; neither of these conditions pertain to soils that contain hydrocarbon fuels.) Thus, soils containing petroleum hydrocarbons may be classed as hazardous waste because of their ignitability if a representative sample of the soil has either of the following properties:

a. The soil contains a free liquid with a flash point of less than 60°C (140 °F). The free liquid is determined by the Paint Filter Liquid Test (PFLT) described in EPA's SW-846 [14]. Flash point is determined by one of the following: Method 1010, which consists of using a Pensky-Martens Closed Cup Tester in accordance with the test method specified in ASTM D-93 [17]; Method 1020, which consists of using a Setaflash Closed Cup Tester in accordance with the test method specified in ASTM D-3278 [18]; or an equivalent test method approved by the EPA administrator.

b. The soil is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture, or spontaneous chemical changes; and when ignited, it burns so vigorously and persistently that it creates a hazard.

5.4.3.2 Characteristic of Toxicity

Solid wastes have the potential for being classed as hazardous based on the characteristic of toxicity if the test extract from a representative sample of the waste contains any of a set of designated constituents in a concentration equal to or greater than the regulatory threshold level. Table 11 lists constituents of concern and their respective thresholds. For soils containing petroleum hydrocarbons, the two principal constituents of concern are benzene and lead.

The extract from a representative sample of the soil containing petroleum hydrocarbons must be obtained by using the Toxicity Characteristic Leaching Procedure (TCLP) (EPA Method 1311), which the EPA designed to determine the mobility or leachability of both organic and inorganic contaminants in liquid, solid, and multiphase wastes. Trained professionals must conduct the TCLP and the subsequent analysis of the extract in a laboratory. The technique for conducting the TCLP method is described in Appendix II of 40 *Code of Federal Regulations* 261 [16]. In brief, a TCLP and subsequent analysis for soil containing petroleum hydrocarbons involve separating liquids and solids, refining the solids, extracting with a zero headspace extraction device and a liquid reagent, separating the extract from the solids, and analyzing the liquid.

Petroleum-containing soil associated with UST cleanups is exempt from the toxicity characteristic test (see 5.4.3). Such soil is exempt from being classified as hazardous because of other hazardous characteristics, such as ignitability.

SECTION 6—CORRECTIVE-ACTION OPTIONS

6.1 Overview

For any given site, the selection of a corrective-action strategy should be governed by site-specific criteria, as well as federal, state, and local law. Parameters such as local hydrogeology, the distribution and character of released hydrocarbons, the potential threats to public health and the environment, and the time frame and budget available for remediation should be considered. Corrective action may also be performed on the groundwater in conjunction with soil remediation. The performance of the corrective action selected should be monitored regularly and reevaluated periodically to assure it is currently and effectively achieving the projected site cleanup goals. This reevaluation process will help to avoid continued use of a corrective-action technique after it is no longer beneficial.

The extent of cleanup required and selection of an appropriate remediation approach is determined by the results of the site and exposure assessments. The potential levels of exposure to humans and the environment are determined during the exposure assessment (see 4.3.4). If the assessment indicates that potential hazards exist at the site, a risk assessment may then be conducted to estimate the potential risk to human health and the environment and to determine the cleanup criteria and objectives. Risk assessments are discussed further in 6.2.1.

Depending on the condition of the site and possible short- or long-term health and environmental impacts, the broad remedial strategies of passive and active remediation may be considered. Descriptions and examples of these strategies are discussed in 6.1.1 and 6.1.2.

6.1.1 PASSIVE REMEDIATION

Passive remediation is appropriate when there is no significant risk to a sensitive receptor from exposure to the petroleum hydrocarbon release. This typically requires that the extent and concentrations of petroleum hydrocarbons in the soil are well defined and at a level that would not pose a threat to a receptor. Under these circumstances, corrective action can be left to proceed through natural mechanisms (biodegradation). Passive remediation is typically accompanied by periodic monitoring to verify the appropriateness of this strategy.

Example: Low concentrations of gasoline constituents are detected in the soils near a UST during a site assessment. The tank has tested tight, and the levels of contamination observed are believed to be due primarily to overfills that occurred before the installation of secondary containment around the tank fill ports. Groundwater is 40 feet (12 meters) below the base of soil contamination; groundwater flow velocities are low; and the nearest downgradient user of groundwater is approximately 0.5 miles (0.8 kilometers) away.

Based on the low concentrations, the absence of a continuing source, the low probability of groundwater impact, and the low risk of off-site migration and exposure if groundwater impact did occur, passive remediation would be appropriate. Groundwater quality downgradient of the tank field would be monitored quarterly or semiannually to verify the absence of hydrocarbon contamination.

6.1.2 ACTIVE REMEDIATION

Active remediation will be required when the risk posed by the released hydrocarbon fuels is unacceptable, and, therefore, a passive response should not be used. Active remediation may be either limited or extensive, although these words may not be defined in absolute terms because of the large number of remedial options and combinations of options possible for any given site.

6.1.2.1 Limited Action

When the risk associated with the release is too high to justify passive remediation but not high enough to warrant an extensive level of corrective action, an intermediate or limited response would be appropriate. This typically occurs when the extent and impact of hydrocarbons in the soil are very localized (limited to the immediate vicinity of the tank field) and the potential for groundwater impact or off-site migration is very low.

Example: Soils immediately around and below a leaking tank are found to contain moderate to high levels of gasoline constituents. Lower concentrations are also detected across a larger area centered around the tank field. Groundwater is present approximately 5 feet (1.5 meters) below the base of the higher concentration of hydrocarbon in the soil near the tank field. Groundwater flow velocity is low, but potential receptors are located within several hundred feet downgradient of the site.

Based on the higher concentrations of contaminants at this site and the increased potential for exposure to these concentrations, a passive response would not be appropriate. It may not be necessary, however, to actively address all of the soil impacted at the site in order to effectively mitigate the risk. Activities such as excavation or soil vapor extraction could be focused on the most highly impacted soils immediately surrounding the tank. The larger area of soils with relatively low levels of hydrocarbons might then be addressed with a passive approach. The leaking tank, of course, would either be removed, repaired, or closed in place depending on applicable state and local regulations and requirements.

6.1.2.2 Extensive Action

When exposure has already occurred or the potential for exposure is high, the corrective action implemented may be extensive. Extensive action implies that the level of planning, cost of implementation, and disruption to normal site activities will all be substantial.

Example: High levels of petroleum hydrocarbon constituents have been detected in soils across a large area that includes the tanks, the supply lines, and the dispensers. Soil contamination has apparently occurred due to leakage from several portions of the system. Groundwater is severely impacted, and the resulting groundwater plume has rendered several downgradient domestic supply wells unusable.

The high risk associated with such a scenario mandates extensive action to remediate the soils at the site (see note). This could include the large scale excavation of the most highly contaminated soils for on-site treatment and in situ remediation of other soils across the site using a bioventing approach.

Note: Groundwater remediation may also be required but is beyond the scope of this document. See API Publication 1628 [1] for further information.

6.2 Cleanup Objectives

6.2.1 OVERVIEW

Before a cleanup can proceed, the targets for the cleanup effort should be established. These targets will consist of acceptable levels of hydrocarbon constituents that may be allowed to remain within soils and groundwater after the conclusion of remediation. In determining these levels, consideration must be given both to what is necessary for the protection of the environment and public health as well as to technical and economic feasibility. The former will be based on the presence and nature of the exposure pathways as determined by the exposure assessment (see 4.3.4). Because of the nature of its exposure pathways, cleanup targets for groundwater are typically given more emphasis than those for soils. Soil cleanup targets typically reflect the potential for groundwater impact from the remaining or residual-phase hydrocarbons in the soil.

6.2.2 RISK-BASED CRITERIA FOR CLEANUP

Cleanup objectives must relate directly to the potential of the release to adversely affect the public and the environment. These objectives are subject to approval by one or more regulatory agencies, usually the state's regulatory agency for environmental protection or the state fire marshal. Most state regulatory agencies have standards for soil cleanup after petroleum hydrocarbon releases. Numerical cleanup standards such as these are typically based on worst-case generic or regional risk assessments or, in some cases, on analytical detection limits. Therefore, they may or may not be appropriate or attainable for individual sites. As an alternative to these broad cleanup guidelines, most states allow site-specific cleanup objectives to be developed through the use of risk assessments.

A risk assessment uses site-specific information, such as the extent and nature of contamination determined during the site assessment and the exposure pathways identified during the exposure assessment, to evaluate and quantify the potential impact. Because this potential, or risk, may be related to the concentrations of hydrocarbons in soils (among other factors), the reduction of these concentrations will reduce the risk. Thus, a risk assessment helps establish the degree of cleanup that will reduce the risk posed by the contamination to an acceptable level. The result is a set of site-specific risk-based cleanup criteria or objectives. It is important to recognize that, for a particular site, the cleanup objectives determined by a risk assessment may be either more or less stringent than the more general state requirements.

To assess the risk to health, the potential level of exposure is compared with chronic and acute toxicity data for the chemicals of concern. The potential effect of exposure is based on the following:

a. The type of receptor.
b. Fate and transport of hydrocarbon constituents.
c. The magnitude and duration of the exposure.
d. The expected effect of the hydrocarbon constituents on the receptor.

A number of specific approaches for calculating the risk are based on the factors listed in Items a–d. Regardless of which approach is used, it must be based on the known characteristics of the site and must be acceptable to the regulatory agency overseeing the cleanup.

In comparison to the complex and detailed risk assessments that are characteristic of cleanup operations under the Superfund program, risk assessments for hydrocarbon fuel releases are typically quite straightforward. Although gasoline is a complex mixture of hydrocarbons, most states are concerned primarily with the health effects of the following components that present significant risk: benzene, toluene, ethylbenzene, xylenes, and tetraethyl lead.

6.3 Soil Remediation Strategy

Several decision and action steps must be completed during the development and implementation of a corrective-action strategy at a release site. Although each site will have its own specific requirements, these steps may be structured as follows:

a. Step 1—Establish the cleanup objectives.
b. Step 2—Evaluate remedial options.
c. Step 3—Identify and select a remedial option.
d. Step 4—Implement and monitor the selected remedial option for a finite period.
e. Step 5—Terminate the selected remedial option when its effectiveness has ended.

A brief examination of each of these steps is presented below. Subsection 6.2 contains a more detailed discussion of the overall concepts involved in establishing cleanup objectives and selecting a remedial option (Steps 1 and 2). Because the concepts governing Step 4 actions are more specific to each remediation method, information on implementing and monitoring will be included in the discussion of each method in 6.3.

6.3.1 ESTABLISHING CLEANUP OBJECTIVES

Before a cleanup strategy is selected, it is critical to consider what the objectives of the remediation will be. The initial question is whether the risk present is sufficient to justify active remediation; if not, can a passive approach be used. If active remediation is required, how much of the site must be cleaned up, and what level of cleanup must ultimately be achieved. The answers to these questions will be based on the results of the site assessment (see Section 4) and the site-specific or general cleanup requirements of the government agency regulating the remediation. These objectives will include the following:

a. The hydrocarbon phases targeted for removal.
b. The appropriate cleanup targets for the site.
c. The general time and budgetary framework within which remediation should occur.

6.3.2 IDENTIFYING AND SELECTING REMEDIAL OPTIONS

6.3.2.1 Overview

The selected remedial options must be capable of achieving removal of the targeted hydrocarbon phases to the specified cleanup levels within the time frame set for remediation. They must also be technologically and economically feasible, given the nature of the site and its activities. Finally, they must be acceptable to all regulatory agencies overseeing the remediation. If these criteria cannot be met with existing technologies, the cleanup objectives may have to be revised.

6.3.2.2 Site-Specific Parameters Affecting Cleanup

Each site presents a particular set of constraints and problems that must be addressed when developing a corrective-action strategy. These constraints and problems often govern the selection of one or more corrective-action techniques. The parameters that most strongly influence the selection of a corrective-action technology, other than those relating directly to exposure pathways, include the following:

a. Site hydrogeology—the depth to water, distribution and character of high and low hydraulic-conductivity strata, presence of a water table or confined conditions, hydraulic gradient, and the rate and direction of groundwater movement.
b. Nature of the hydrocarbon fuel—the viscosity, volatility, solubility, age, and density of the released fuel.
c. Extent of subsurface hydrocarbons—the three-dimensional extent of soils and groundwater affected by the release; the distribution of concentrations within the boundaries of this area; the distribution of hydrocarbons among dissolved phase, vapor phase, and separate and residual liquid phases.
d. Nature of the site or facility—active or inactive; level of traffic; location and orientation of buildings, islands, and tanks; available utilities; and proximity to treatment or disposal center.

The relationship between the parameters listed in Items a–d and the applicability of a specific cleanup technique will vary depending on the technique considered. For this reason, site-specific factors affecting implementation and effectiveness will be addressed in the discussion of individual techniques in 6.3.

The conditions having the greatest effect on the selection of remedial options are those that affect the movement of hydrocarbons away from the point of release and their movement to a receptor or to a point of removal or treatment. Also important, however, are those parameters that will affect the installation and operation of the equipment required for remediation.

From a practical standpoint, it is important to note that not all of the information listed in Items a–d will be available for most sites. Even if a proper site assessment has been performed, the scope of investigation typical of most hydrocarbon release sites may not permit the detailed evaluation of complex hydrogeologic settings or the precise delineation of the extent and distribution of contamination. The investigator selecting cleanup objectives and strategies must therefore make intelligent assumptions based on an understanding of the typical migration behavior of released hydrocarbon fuels in various settings.

In many ways the effect of site-specific factors on the applicability of various cleanup alternatives seems to put the person selecting remediation strategies in a difficult position. Until these site-specific characteristics are known, it is difficult or impossible to select a remedial approach. It is often helpful, however, to be able to tailor an investigation to determine remediation-specific information, such as the nutrient content of soil for a bioremediation or the permeability of soil to air for a soil vapor extraction approach. In other words, many aspects of the investigation cannot be performed without selecting a remediation approach, but a remediation approach cannot be designated until the investigation has been performed. Additional investigations may be required in order to help determine the most effective remediation system.

The solution to this apparent contradiction is twofold. First, the assessment must be performed with an eye toward the possible remediation techniques that may be applicable. As information from the ongoing site assessment narrows the options for a cleanup approach, the investigation must be modified to provide more remediation-specific samples or data. This requires that the manager of the assessment have at least a general understanding of the types of remediations that may be applicable to any given site. Second, if the assessment is performed in two or more phases or stages, the initial phases could provide the information necessary to make a preliminary cleanup selection or selections. Later phases can then be tailored to support this preliminary choice.

6.3.3 IMPLEMENTING AND MONITORING THE REMEDIAL SYSTEM

This part of the corrective-action process includes design of the remediation system, installation and startup, normal operations and maintenance, and ongoing changes in the overall system to optimize its effectiveness.

For example, if soil vapor extraction (SVE) is selected as a remediation system, the design of the SVE system would then be conducted and tailored to the needs of the site. A soil air permeability test might be performed to assist with the system's design. After the design phase, the system components would be selected, acquired, and installed. The components would include extraction wells, piping, vacuum pumps, and vapor treatment. Following system startup, a period of system balancing and fine-tuning could occur during the early stages of operation.

The operation, maintenance, and monitoring of such a system could include a daily check of the basic system status, a more detailed monthly status check and maintenance visit, and the collection of extracted vapor samples for analysis as required. System effectiveness would be evaluated based on concentration reduction for specific hydrocarbons and concentration reduction in soil through evaluation of soil cones.

6.3.4 TERMINATING THE CORRECTIVE ACTION

Corrective actions are typically terminated either because the cleanup objectives have been achieved, or because the effectiveness of the remediation has decreased below the level that would justify its continued use. If the latter has occurred, it may be necessary to evaluate an alternative approach that can achieve the remediation objectives. If this is not possible, the cleanup objectives should be reevaluated in light of the performance of the corrective action. In some cases, continual remediation may be required in order to control migration of site contaminants.

6.4 Corrective-Action Technologies

Each corrective-action method is best suited for a particular set or range of conditions. Selecting the optimal technology for a given site must therefore be based on matching the capabilities and economies of the technology with the constraints posed by site-specific conditions.

Corrective-action techniques that can be used for fuel-impacted soils that are discussed in this publication are summarized in Table 12. As discussed in 6.1, these techniques can be subdivided into two basic types:

a. *Passive remediation*, which allows natural processes to remove released hydrocarbons and monitors the progress of this removal.
b. *Active remediation*, which attempts to actively remove the hydrocarbon impact from the soils, either in situ or aboveground, following excavation. Active remediation may be either limited or extensive.

Passive remediation is applicable in settings where the released hydrocarbons are limited in concentration and extent, and/or no significant risk has been identified associated with the release. Active measures must be taken where the risk posed is significant because of the extent of the release, the nature of the site, or both.

When active remediation is required, in situ techniques are typically favored because of the lower cost and minimal disruption of surface structures and processes. Although aboveground technologies involve significant disruption at a site and removal may present risk of fire, explosion, and air emissions, they do provide some advantages over in situ methods. First, by removing the soil and placing it within a reactor or treatment area, the impacted soils are typically isolated to a large degree from the environment. This decreases the potential for the spread of contamination into fresh soils and groundwater. In addition, the aboveground removal of hydrocarbons from soils is typically more rapid and complete than similar methods applied in situ. This is primarily due to the homogenization, permeability and porosity enhancement, and aeration that accompany the excavation process.

Both active and passive remediation approaches described generally require the supplemental effort of site monitoring to track the performance of the corrective action. Monitoring typically consists of soil sampling or vapor probe analysis; however, it may also involve periodic groundwater sampling at selected wells if groundwater could be impacted.

Whether passive or active, any cleanup should commence with identifying the source or sources of the release (see Section 3). Otherwise, the probability of a rapid, effective cleanup is minimal.

6.4.1 PASSIVE REMEDIATION

Hydrocarbons tend to have a limited but varying persistence in natural systems. Naturally occurring microbes can metabolize many hydrocarbons that are present in less than toxic concentrations. Volatilization, hydrolysis, and oxidation also can modify or remove hydrocarbon components. Dilution associated with dispersion and diffusion may reduce hydrocarbon concentrations. In general, concentrations at sites that do not have continuing sources of hydrocarbon releases will gradually decrease over a time frame of years or decades.

Such a time frame is not typically regarded as acceptable when hydrocarbon concentrations are high before the contaminants degrade or when there is a high probability for public exposure or other environmental impact. When the absence of these conditions can be proven (or demonstrated using a model), passive remediation may be an acceptable option. Passive approaches can also be used at sites where other remedial approaches would be difficult to implement or minimally effective.

When appropriately applied, passive remediation has the following advantages:

a. It generates no waste streams.

(text continued on page 53)

Table 12—Summary of Corrective-Action Options for Hydrocarbons in Soil

Option	Cost	Advantages	Disadvantages
Passive remediation	Very low	Generates no waste streams. Eliminates risks of fire, explosion, and air emissions posed by removing and transporting hydrocarbon-containing soils. Substantially less costly.	Requires long time frame. May not be appropriate if potential receptors are nearby. Can only be used if acceptable to regulatory agency. Groundwater models to determine risk may not be accurate if not correlated to site conditions.
		IN SITU TECHNOLOGIES	
Bioremediation	Moderate to high	Achieves relatively low cleanup levels from toxic constituents. Can be used in areas not accessible for excavation. Eliminates risks of fire, explosion, and air emissions posed by removing and transporting hydrocarbon-containing soils.	May take years to achieve cleanup levels. Complete biodegradation of hydrocarbon mixtures may be difficult. Not effective in soils with low hydraulic conductivity. Groundwater recirculation is usually required. May mobilize contaminants into groundwater. Not effective for metals.
Soil flushing/ leachate recycling	High	Less expensive than aboveground technologies. Best for soils with high hydraulic conductivity ($>10^{-3}$cm/s) and shallow groundwater [<15 feet (<4.6 m)]. Eliminates risks of fire, explosion, and air emissions posed by removing and transporting hydrocarbon-containing soils.	Regulatory agencies reluctant to approve. Large volumes of leachate generated for treatment. Leachate treatment difficult. Not effective in soils with low hydraulic conductivity. Residually saturated hydrocarbons may not be easily removed. Requires hydraulic control.
Soil vapor extraction	Low to moderate	Removes volatile hydrocarbons from the unsaturated zone. Suited for soils of moderate hydraulic conductivity. Appropriate for gasoline. Used to enhance biodegradation.	Removes only volatile constituents. Less volatile constituents in diesel fuel and fuel oil not removed unless used in conjunction with bioventing. May not be effective in soils with low hydraulic conductivity. Eliminates risk of explosion, fire, and air emissions posed by removing and transporting hydrocarbon-containing soils.
Air sparging	Low to moderate	Can enhance and accelerate the effectiveness of soil vapor extraction and downgradient groundwater pumping for remediation. Increases oxygen in saturated soil, which can enhance biodegradation. Can reduce concentrations of volatile hydrocarbon. Relatively simple and low in cost.	Not effective in soils with low hydraulic conductivity or in soils with confining layers. Eliminates risk of explosion, fire, and air emissions posed by removing and transporting hydrocarbon-containing soils.

(table continued on page 52)

Table 12—Summary of Corrective-Action Options for Hydrocarbons in Soil (Continued)

Option	Cost	Advantages	Disadvantages
ABOVEGROUND TECHNOLOGIES			
Bioremediation			
Land treatment	Low	Relatively moderate to long treatment times. Simple, inexpensive, and effective.	Regulatory requirements may limit use. Large amount of space required.
Soil venting piles	Low to moderate	Short treatment times. Simple and effective. Treated soil may be used on site as backfill.	Regulatory requirements/ permitting may limit use.
Bioreactors	High	Short treatment times relative to other bioremediation processes. Can treat higher hydrocarbon concentration levels. Can uniformly treat most hydrocarbons to nondetectable levels in months. Treated soil may be used as backfill.	Side waste streams may need treatment. Regulatory requirements may limit use. Large amount of space required.
Asphalt and cement incorporation	Moderate	Short treatment times. Viable alternative to landfilling. Minimizes hazard liability.	May require specific analyses to be accepted for incorporation.
Thermal treatment			
Low-temperature Thermal desorption	Moderate to high	Very short treatment times. Minimizes hazard liability. Depending on soil type and treatment process, the soil may be reused for fill. Can treat soils with concentrations <10,000 parts per million TPH.	Highly contaminated soil may have to be mixed. High soil moisture content may influence effectiveness. States and localities require operational permits. Highly visible operation.
Incineration	High	Very short treatment times. Reduces volume of solids. Minimizes hazard liability. Achieves excellent final product quality. Can treat full range of concentrations. Can effectively treat other hydrocarbon contaminants unexpectedly found at the site.	Disposal requirements of ash depend on classification. If nonhazardous, ash may require mixing with soil for compaction. Disposal of ash that fails TCLP will require further treatment. High soil moisture will increase costs. States and localities require operational permits. May incur additional liability for ash disposal.

b. It eliminates the potential for human contact with impacted soils that exists during installation and operation of an active remedial system.
c. It is substantially less costly than other methods.

The main disadvantage is that a long time frame is usually required to reach the cleanup target levels along with the possibility that monitoring may be required until it is certain that no receptor is impacted. This corrective-action technique is not appropriate if potential receptors are nearby and contamination is likely to be mobile.

6.4.2 IN SITU TECHNOLOGIES

In situ treatment of soils may be selected for several reasons. Releases of petroleum hydrocarbons are often associated with structures that can interfere with soil excavation. Examples are aboveground structures, such as railroads, roadways, and buildings; and underground structures, such as pipelines and tanks. Also, the depth to which hydrocarbons have migrated within the soil may extend beyond the maximum depth of excavation. The interference to traffic or site activity posed by an excavation effort may be unacceptable given the uses of the site. The selection of either in situ treatment or aboveground corrective-action techniques will depend on factors that are specific to the technology selected and the site conditions.

In terms of configuration, in situ technologies typically access the impacted soils via a system of wells, trenches, or infiltration galleries. In situ technologies also include equipment such as blowers, controllers, or nutrient reservoirs, which are typically located within the boundaries of the site. At active sites, this equipment is usually compact so as to avoid significant interference with site traffic or processes. At inactive sites, size is less of a concern.

Various options are available for treating soils in place. In situ technologies to be discussed here include the following:

a. Bioremediation.
b. Soil vapor extraction, bioventing, and air sparging.
c. Soil flushing and leachate recycling.

These methods have gained varying degrees of acceptance because of the ease with which they can be implemented, their economy, and their general effectiveness.

6.4.2.1 Bioremediation

6.4.2.1.1 Description

Bioremediation is a treatment for petroleum-impacted soils that can be carried out in situ. (For a discussion of the bioremediation of excavated soil, see 6.4.3.3.) All soils have indigenous populations of various microorganisms, some of which are capable of degrading petroleum contaminants. Bioremediation involves adding oxygen and/or nutrients to a release area to enhance the natural microbe population.

In situ bioremediation of soils involves the enhancement of natural aerobic biodegradation by manipulating environmental conditions to optimize the degradation of hydrocarbons. This is accomplished by adding oxygen and essential nutrients to the release area. The lack of available oxygen and nutrients such as nitrogen and phosphorous can limit microbial growth and degradation of petroleum hydrocarbons. Figure 18 is a general schematic of in situ bioremediation. The most commonly used methods rely on the delivery of a source of oxygen (such as hydrogen peroxide) and nutrients (such as nitrogen and phosphorous) to the subsurface through an injection well or infiltration system to stimulate the aerobic (oxygen-requiring) degradation of petroleum contaminants by naturally occurring microbes. This treatment technology can also be used in conjunction with soil vapor extraction systems for increased oxygen in the subsurface by using a technique referred to as bioventing (see 6.4.2.4).

If ideal conditions are maintained, aerobic biodegradation produces carbon dioxide, water, and biomass (an increase in the population size of microbial organisms) from hydrocarbon fuel constituents. Given sufficient time and nutrients, naturally occurring microbes are usually adequate for in situ bioremediation of hydrocarbons within soils.

The specific advantages of in situ bioremediation include the following:

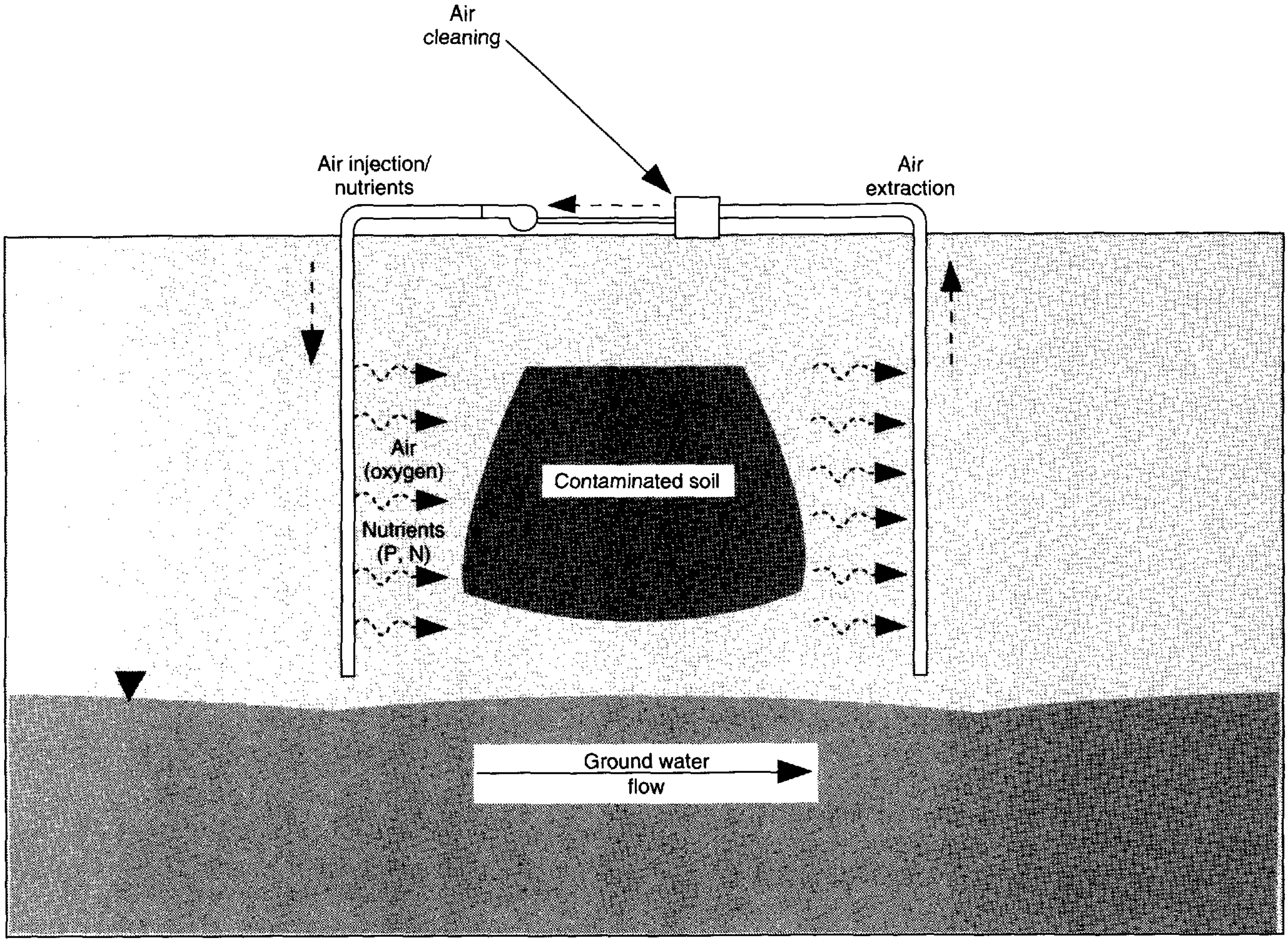
a. It can provide an effective corrective action at a moderate cost under appropriate conditions. The effectiveness of in situ bioremediation largely depends on the hydraulic conductivity of the soil and the availability of nutrients and oxygen.
b. It can be used in a corrective-action plan involving other technologies (for example, soil vapor extraction).
c. It can be used in areas not accessible or suitable for excavation with controllable disruption to surface activities, such as under roads and buildings and where there are concerns for soil and foundation stability.

The disadvantages or limitations of in situ bioremediation include the following:

a. It may take years to achieve appropriate cleanup levels, depending on site conditions such as permeability, soil moisture, and the type of hydrocarbons present. The time frame needs to be considered if selling a property.
b. Hydraulic conductivity or permeability can directly affect the effectiveness and time frame by limiting the circulation of nutrients and oxygen.

6.4.2.1.2 Feasibility and Design Considerations

The following parameters have the greatest impact on the success of any in situ bioremediation program: oxygen concentration, soil pH, soil temperature, available nutrients, soil moisture content, the type of petroleum hydrocarbons present, and the soil's hydraulic conductivity. Oxygen concen-



Note: P = phosphorous; N = nitrogen.
Source: Western States Petroleum Association, *On-Site Treatment of Hydrocarbon-Contaminated Soils* [25].

Figure 18—Schematic of In Situ Bioremediation of Vadose Zone Soils

tration is the most critical factor. Although degradation may still occur without oxygen (referred to as anaerobic biodegradation), a lack of oxygen will severely limit the rate of cleanup (for example, benzene does not appear to degrade readily under anaerobic conditions). Extremes of pH and temperature will limit the activity of microorganisms and degradation of the hydrocarbons. A pH range of 6.0–8.0 and a temperature range of 15°C to 35°C (59°F to 95°F) are recommended. The addition of critical nutrients (such as nitrogen and phosphorous) to the release area is always necessary if naturally occurring levels are insufficient to sustain microbial population growth. Maintaining a soil moisture content of 10 percent to 20 percent by weight is also recommended to ensure microbial viability and degradation of hydrocarbons. The amount of required moisture is optimized relative to the available pore space for oxygen circulation. Measurements of oxygen and carbon dioxide concentration, soil pH and nutrients, and microbial population counts are made to determine the degree of biodegradation occurring and the feasibility for degrading hydrocarbons. Hydraulic conductivity or permeability are also determined usually during on-site pilot tests to evaluate nutrient delivery systems. Oxygen and carbon dioxide concentrations can be used in conjunction with microbial population counts to monitor the progress of in situ bioremediation.

While petroleum fuels are generally considered biodegradable, microbes discriminate between the various constituents of petroleum products such as gasoline and preferentially degrade certain constituents. In general, aliphatic hydrocarbons are more readily biodegraded than lighter aromatic hydrocarbons.

The ultimate feasibility of in situ processes for bioremediation is largely determined by the hydraulic conductivity of the soils at the site. Even when all of the preceding factors are optimal, in situ bioremediation would be cost prohibitive if the low hydraulic conductivity of the soils on-site prevents the added nutrients from reaching the areas where the microbes and petroleum hydrocarbons exist.

6.4.2.2 Soil Flushing and Leachate Recycling

6.4.2.2.1 Description

Soil flushing refers to the in situ process in which water percolates or is injected into soils containing petroleum hydrocarbons. These soils are flushed with water, or water is allowed to infiltrate the soil to mobilize (via leaching or dissolution) the hydrocarbons into the groundwater. Water used by itself for flushing may be relatively ineffective. Nontoxic and/or biodegradable surfactants may be added to the water to improve the solubility and recovery of the hydrocarbons. However, surfactants may impact groundwater quality and may not be allowed in certain jurisdictions. Groundwater is collected downgradient of the flushing or infiltration site in strategically placed extraction wells. The recovered water is then treated to separate the hydrocarbons and surfactant. Special water treatment may be required. The treated water may then be reinjected to create a closed-loop system; or, if appropriate, it may be discharged to a sanitary or storm sewer system. This treatment technology can be used in conjunction with groundwater treatment systems. When surfactants are added, higher than normal hydrocarbon concentrations in groundwater will occur, requiring special water treatment.

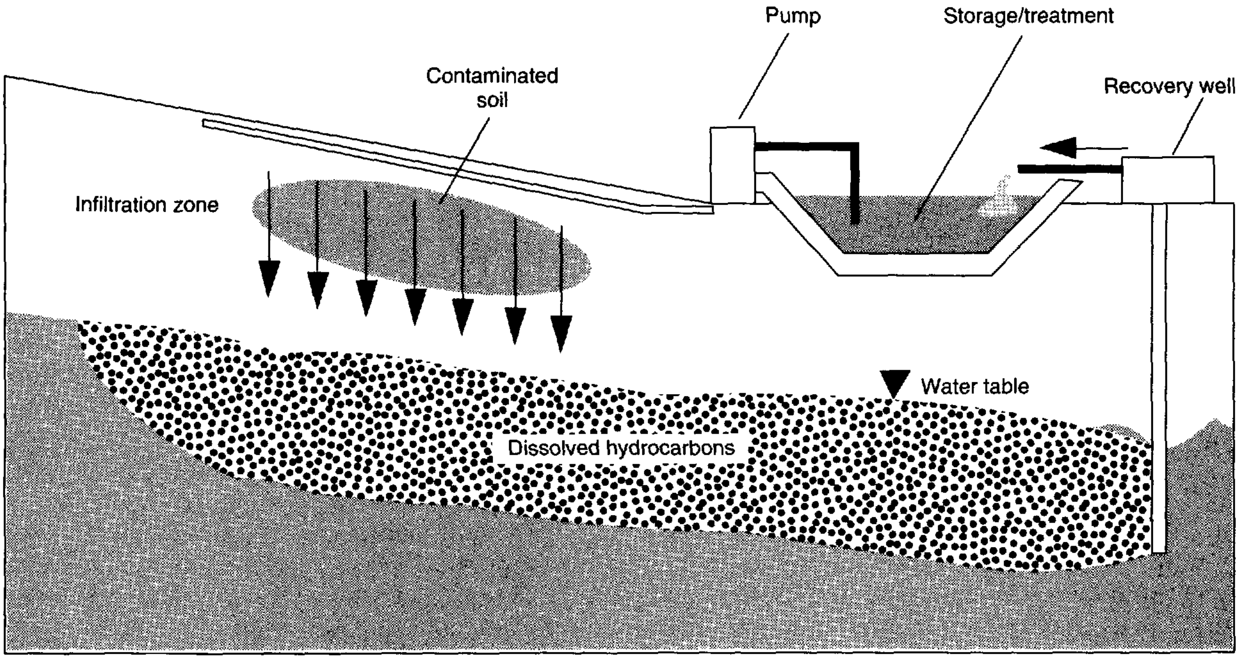
Modifications to the basic technology of soil flushing primarily involve differences in the delivery and recovery system. The two general choices of delivery methods are (a) forced delivery and recovery (injection wells), and (b) gravity delivery (for example, flooding, ponding, ditches, infiltration galleries, or infiltration beds). Figure 19 shows a flushing system that uses gravity delivery.

The specific advantages of soil flushing include the following:

a. It can effectively remove hydrocarbons in soils with high hydraulic conductivity and shallow depth to groundwater.
b. It can be lower in cost than excavation, transportation, and disposal.
c. It has the high potential of flushing zones of interest.

The disadvantages or limitations of soil flushing are as follows:

a. It can require large volumes of water or water and surfactant mixture to be effective; it is not effective in soils with low hydraulic conductivity; residual hydrocarbons may not be easily removed.
b. Separating the hydrocarbon and surfactant mixture from the water and proper disposal may increase costs.
c. Regulatory agencies are reluctant to approve the treatment because of its impact on groundwater quality.



Source: Modified from L. M. Preslo *et al.*, *Remedial Technologies for Leaking Underground Storage Tanks* [26].

Figure 19—Schematic of a Soil Flushing System

d. Residually saturated hydrocarbons may not be easily removed.
e. It must be performed in conjunction with groundwater recovery.
f. Some groundwater modeling may be necessary to adequately understand the groundwater system end design.
g. It can be higher in cost than other in situ technologies.

A primary concern among state regulators is the potential impact on groundwater. Groundwater modeling can be used in some cases to address this concern. State regulators should be contacted to verify whether or not soil flushing is acceptable prior to proceeding with this technique. Hydraulic control of groundwater normally will be required.

6.4.2.2.2 Feasibility and Design Considerations

Soil flushing has been used successfully to treat certain soluble hydrocarbon constituents, but its application may be limited by the physical nature of the soil and the type of hydrocarbons present in the soil. Because the method relies on the infiltration of an aqueous solution introduced through the soil to remove residual hydrocarbons, it is most feasible at sites where the following conditions exist:

a. Soils are relatively homogeneous, so that the solution permeates the targeted soils in a generally uniform manner.
b. Hydraulic conductivities of the soils are relatively high to permit the flushing solution to penetrate rapidly and pass through the targeted soils.
c. The hydrocarbon constituents will partition favorably into the flushing solution from a soil-sorbed condition; this will be a function of the particular hydrocarbon constituents, the soil type, and the specific aqueous solution used. (See Section 2 for a discussion of solubility and sorption capacity.)

Selection of a specific soil flushing system as a corrective-action option, therefore, depends on the following:

a. The extent and nature of the soil contamination.
b. Soil characteristics: type, porosity, permeability, hydraulic conductivity, stratigraphy, sorption potential, and mineralogy.
c. Surface drainage patterns and surface infiltration rates.
d. Groundwater elevations, flow directions, and aquifer directions.
e. The type of hydrocarbon constituents present.

The information in Items a–e can be used in designing the infiltration site configuration and determining the water injection and removal rate. Note that selection of soil flushing depends on acceptance by the appropriate regulatory agency. The method is somewhat controversial because many agencies are concerned about the intentional introduction of hydrocarbons into groundwater. Generally, this concern can be addressed with comprehensive groundwater modeling.

Gravity delivery systems for soil flushing depend strongly on site configuration, drainage, and groundwater parameters, whereas the forced delivery method is more flexible and can be used for a wider range of field conditions. Gravity methods are generally adequate in areas where (a) the hydrocarbon-impacted soils are located in the unsaturated zone, (b) the hydraulic conductivity of the soil is greater than 1×10^{-3} centimeters per second, and (c) the depth to the bottom of the zone is about 15 feet (4.6 meters). This technology can be selectively applied beneath utilities and pavement.

6.4.2.2.3 Control and Management of Side-Waste Streams

The application of in situ leaching or flushing has been limited, partially because of the reluctance of regulatory agencies to approve the use of processes that involve injecting or flushing additives into the groundwater. Typically, the large volumes of water-surfactant mixture required generate large volumes of hydrocarbon-surfactant-water leachate that must be treated. Also, some difficulties have been encountered in the treatment process with separating the water-surfactant mixture from the petroleum hydrocarbons. Without such separation, the water-surfactant mixture cannot be recycled back into the system.

6.4.2.3 Soil Vapor Extraction Systems

6.4.2.3.1 Description

Soil vapor extraction (SVE) is an in situ corrective-action technology typically used for removing a residual volatile hydrocarbon phase. The procedure involves mechanically withdrawing hydrocarbon vapors from soil pores via wells or trenches using a vacuum pump. The withdrawn air is discharged to the atmosphere either directly or after some form of vapor emissions treatment. SVE also can be used for excavated soils placed in a controlled system.

Volatile hydrocarbons within soils tend to partition to some extent into the soil vapor present in intergranular porosity or secondary permeability. The source of these vapor-phase hydrocarbons may be a liquid residual, an aqueous solution in soil moisture, or a sorbed phase on soil solids. Under natural conditions, the volatilization of these compounds ceases when equilibrium is achieved between the various hydrocarbon phases present.

By withdrawing soil vapor containing hydrocarbons and replacing it with hydrocarbon-free air from uncontaminated soils or the atmosphere, SVE disrupts the equilibrium condition. As a result of this disruption, compounds may continue to volatilize and subsequently be removed. The vapor initially withdrawn from the impacted soils is typically the most heavily laden with hydrocarbons and may be flammable. As the soil concentrations of high-vapor-pressure constituents and poorly sorbed constituents begin to decline, the vapor concentrations will tend to decrease asymptotically.

Figure 20 shows the configuration of a typical SVE system. The basic components of the system include a well or trench for withdrawing vapor, piping connecting the well or trench to the suction of the vacuum blower or pump, and some form of emissions control system. Vacuum pressures within the subsurface are measured by a vapor piezometer fitted with a magnehelic gauge or manometer port.

The most common application of SVE is for removing hydrocarbon dispersed throughout the soils of the unsaturated zone. The technology has been used to prevent the entry and accumulation of toxic and explosive vapors in building basements and sumps. It may be used in combination with groundwater extraction because the drawdown caused by water extraction tends to expose product residuals deposited as a result of water table drawdown. Finally, it may be used to enhance biodegradation (as described earlier in 6.4.2.1.1).

The specific advantages of SVE are as follows:

a. The ability to remove volatile organics, including the more toxic aromatics, at depths and below structures that would prohibit excavation.

b. The ability to remove hydrocarbons from the zone of water table fluctuation in conjunction with groundwater extraction.

c. The ability to perform remediation (in some cases) within soils of moderately low hydraulic conductivity, including those typically considered inappropriate for bioremediation and soil flushing.

The disadvantages or limitations of SVE include the following:

a. The expense and difficulty of complying with air emissions requirements when such requirements are relatively stringent.

b. The inability of the technique to readily address separate-phase hydrocarbons trapped as residuals within the saturated zone (for example, below the water table or capillary fringe). These trapped residual hydrocarbons can constitute a substantial fraction of the separate-phase hydrocarbons at many sites, particularly those with significant water table fluctuations.

c. SVE is much less applicable to semivolatile-rich hydrocarbon fuels, such as diesel fuels, than to volatile-rich fuels, such as gasoline. It may still be applied to remediations involving semivolatile-rich fuels, but the remedial process should then be geared toward bioventing.

6.4.2.3.2 Feasibility and Design Considerations

Soils with hydraulic conductivities as low as 10^{-5} centimeters per second are routinely treated by SVE. Soils with lower hydraulic conductivities may still be treatable, but they may require drying or using desiccation materials. For unsaturated zones less than 7 feet (2.1 meters) thick, relatively low wellhead vacuums [less than about 20 inches (508 millimeters) of water vacuum] must be used. In these cases, a vacuum rise in the water table can be countered by pumping. Higher vacuums will cause the water table to rise substantially in the vicinity of the extraction well or trench, which may inundate the well or trench and terminate airflow. In these settings, trenches are generally more appropriate than wells.

SVE may be applied at sites in which lower permeability soils are interbedded with those of higher permeability. For layers of lower permeability soils, such as clays and silts, which are only 2 to 3 feet (0.6 to 0.9 meters) thick, wells may be screened across the entire stratigraphic sequence of the targeted soil zone. Hydrocarbon vapors will typically diffuse vertically from the silt-clay layers into the interlayered sands or gravels, then travel laterally to the well or trench. The primary effect of the low permeability layers is the slowdown of the remediation process, since the rate of remediation is now rate limited by the diffusion of hydrocarbon vapors through low permeability soils. However, lower permeability soil sites should be evaluated with care.

For thicker clay-silt strata, it may be necessary to target separate strata with separate wells. This will permit the application of higher wellhead vacuums and the use of closer well spacings to the lower permeability strata.

Typically, the application of SVE is considered most appropriate for hydrocarbons with high vapor pressures and low solubilities in water because they tend to partition most readily into the vapor phase. Most of the constituents in gasoline fall into this category, as opposed to only a relatively small fraction of the constituents in diesel fuels, fuel oil, and jet fuels. As a result, SVE is more often applied to gasoline-release sites. Although the less volatile fractions of fuels other than gasoline are not readily extractable, SVE may still be applied to such fuel releases for the following reasons:

a. The more toxic aromatic constituents of fuels such as diesel and jet fuels are relatively volatile; therefore, SVE can reduce the overall toxicity of the release.

b. Constituents considered semivolatile have finite vapor pressures and will volatilize. The lower magnitude of their vapor pressures will prolong the time required for cleanup because the transfer into the vapor phase is relatively slow.

c. In some cases, the use of vapor extraction enhances aerobic biodegradation of petroleum hydrocarbons, including those with low levels of volatiles. This enhancement is possible when the oxygen content in the hydrocarbon-impacted soils has been depleted by microbial action, causing soil conditions to become anaerobic and slowing natural degradation processes. By drawing in oxygen-laden air from outside the spill area, vapor extraction can restore aerobic conditions and therefore enhance the rate of microbial metabolic action. An application of this phenomenon, called bioventing, is discussed in more detail in 6.4.2.4.

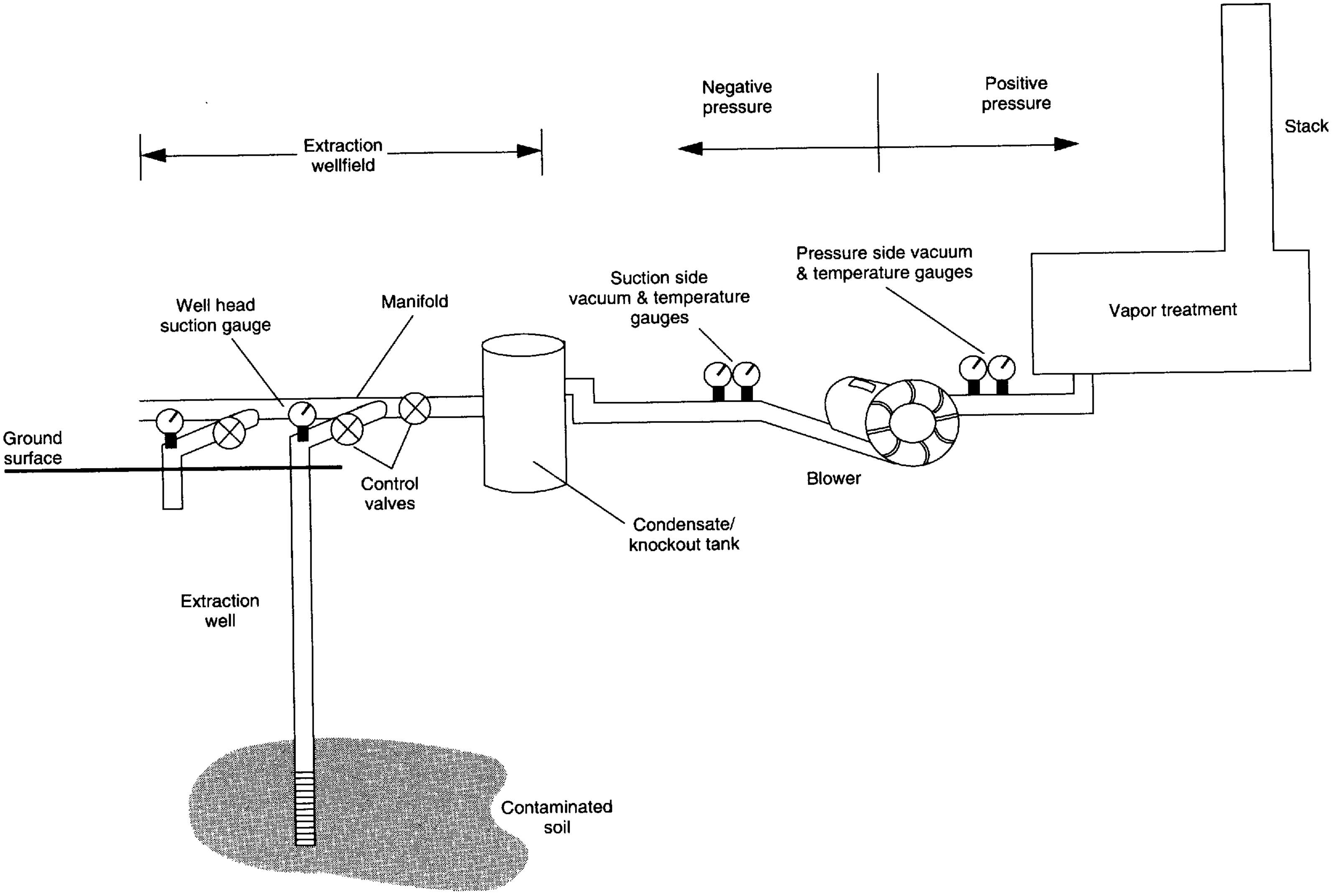


Figure 20—Conceptual Configuration for Soil Vapor Extraction System

The concentrations of hydrocarbons in extracted vapor tend to achieve maximum levels at or soon after the startup of the system and then decline steadily over a period of weeks and months. In sandy soils, concentrations may decline rapidly over a period of weeks. In clay-rich soils, in which diffusion and sorption effects are stronger, the decline may require months or even years. As the hydrocarbon concentrations decrease, the composition of the vapors should be evaluated along with residual hydrocarbons in soil cores. This evaluation will help determine when the system can be shut off.

Because hydrocarbon vapor concentrations serve as one of the best indicators of system performance, these parameters should be regularly monitored at both the system influent and effluent. Periodic intervals for such monitoring are often established. Specific site requirements may require more or less frequent monitoring. Operational parameters that should be measured regularly include the total well network and single well flow rates, the wellhead and blower suction pressures, and vacuum piezometer pressures. Regular monitoring results can be used to optimize the SVE system operation, which can keep the time and cost of cleanups to a minimum.

A summary of other major design parameters and factors driving design decisions specific to vapor extraction are provided in 6.4.2.3.2.1 through 6.4.2.3.2.4.

6.4.2.3.2.1 Well and Trench Construction

Vapor extraction wells may be either 2- or 4-inch (51- or 100-millimeter) diameter (or larger) and should be constructed using screen with the largest slot width possible. The filter pack in the unsaturated zone should be relatively coarse sand or fine gravel in order to maximize permeability. Fine sand filter packs, such as those used for monitoring wells, are not appropriate for vapor extraction wells, since no filtering function is required and maximum airflow is desired. There is no limitation on the possible depth of a vapor extraction well.

Vapor extraction trenches are typically constructed to maximum depths of approximately 12 feet (3.7 meters), although depths of 30 feet (9 meters) or more are possible with larger or specialized excavation equipment. Extraction trenches consist of an excavation that is as narrow as possible, in order to minimize the quantity of potentially contaminated soils removed. The excavation is backfilled with fine to coarse gravel and equipped with a horizontal perforated pipe. This pipe is equipped with a riser to permit its connection to the vacuum pump. When using trenches, it is important to confine the trenching-vacuum interval to the contaminated zone. Air flow in other zones will only limit system effectiveness.

Both wells and trenches require placing a low-permeability seal at the surface to prevent the short-circuiting of air downward through the trench or well annulus. It may also be advisable to seal the ground surface with pavement or a plastic membrane if the vertical permeability of the soils is anticipated to be relatively high, the site is unpaved, and the targeted soils are relatively shallow.

The trench depth, well depth, and/or screened interval will be controlled by the depth or depth interval of targeted soil contamination and by the distribution of contamination in targeted soils. For soils in which the horizontal permeability is much greater than the vertical permeability, including soils with substantial interbedding, soil vapor movement will be primarily horizontal, and the trench or screened interval of the well should match the depth or depth interval of soil contamination. However, for soils with vertical permeabilities that match or exceed horizontal values, the vertical component of vapor flow makes partially penetrating wells or trenches more effective. The trenches or screened intervals in wells in such soils would not necessarily have to coincide with the depth interval of the contamination.

6.4.2.3.2.2 Piping and Manifolds

Piping connecting the extraction wells or trenches into a single manifold or connecting the manifold into the vacuum pump suction may be placed either above grade or below grade. Above-grade piping is less expensive to install, repair, and maintain. It is not desirable for active facilities because it interferes with surface processes and is susceptible to damage and to freezing temperatures.

The design and construction of piping must take into account the condensation of moisture from the extracted soil vapor. If the piping is not properly sloped, this condensation will collect in any low points, eventually blocking the pipe. All piping should be sloped to a point of liquid collection, such as a sump, or at least to a point where the piping can be drained. Any changes in pipe level, such as a rise from below grade to the vacuum pump intake, are also susceptible to liquid collection. Each suction line connecting the well to the manifold should have a valve and pressure gauge assembly to help control flow to individual wells.

6.4.2.3.2.3 Vacuum Pumps

The vacuum pumps most commonly used for SVE are low-pressure, high-volume regenerative centrifugal and turbine types (see note). In selecting a vacuum pump for a site, the designer should be aware of the voltage, amperage, and phase requirements for both the pump selected and for the available power supply at the site. For example, at sites where three-phase power is not available, it may be possible to use two pumps with single-phase power requirements in parallel to achieve flow rates equivalent to those of a larger three-phase pump.

Note: As mentioned in 6.4.2.3.2, lower permeability soils may require the application of greater vacuums (more than approximately 120 inches of water vacuum). Rotary-lobe, liquid-seal, or sliding-vane type pumps are typically used. In general, the higher vacuum units require more maintenance and use greater power.

Recently, redesigned internal combustion engines have been used with great success. These engines can operate at flow rates ranging from 50 to 500 cubic feet per minute and treat exhaust through internal combustion and catalytic oxidation.

6.4.2.3.3 Design Methods

The specific responses to the design requirements detailed in the preceding subsections may be derived in one of three basic ways. If the system designer is familiar with the operations of SVE systems in similar settings, it may be possible to take an empirical approach to design. The designer selects well designs, well locations, and blower size based on experience with similar sites. Given the relatively wide range of conditions over which many blowers and vapor treatment systems can operate, this approach can be applied with minimal risk—but only if the designer has a base of experience with closely similar sites. The empirical approach is typically appropriate only for relatively simple sites of limited size. If appropriately applied by an experienced practitioner, however, it is probably the most effective way to design a system for such sites.

If the designer has no basis for an empirical design approach, more quantitative techniques may be used. One method utilizes soil hydraulic-conductivity data, either derived from geotechnical testing for air permeability or from aquifer testing, such as slug or pump testing. This data is entered into either a set of calculations or a numerical computer-driven model to ascertain design parameters, such as well placement, flow per well, vapor concentrations, and extraction time. A detailed analysis of this approach is provided in *A Practical Approach to the Design, Installation and Operation of Soil Venting Systems* by P. C. Johnson *et al.* [19].

The alternative is the performance of a pilot scale operation on a representative portion of the site. Such tests are typically performed using a single extraction well with several vapor piezometers at various radii from the test extraction well. The performance characteristics of that well (its capture zone, flow rate, wellhead pressure, and the hydrocarbon concentration in vapor) are measured during a test period of several hours to several days. The data acquired is then extrapolated to the remainder of the site to produce a full-scale system design. Analysis of soil air-permeability samples from across the site may be combined with pilot testing to evaluate how readily data from the test area may be extrapolated to the rest of the site.

6.4.2.3.4 Control of Side-Waste Streams

Vapor treatment requirements can easily double the cost of implementing and operating SVE systems, depending on the emissions rates and the state and local regulatory limitations on these emissions. Several options exist for removing or destroying hydrocarbons from airstreams. The following have been widely applied for hydrocarbon fuel remediation sites:

a. No treatment is appropriate when emissions rates are very low (below regulatory *de minimis* levels), which generally occurs when soil concentrations and/or airflow rates are low.
b. Activated carbon adsorption is appropriate when emission rates are very low but still exceed *de minimis* levels, which typically occurs under conditions similar to those for no treatment. The rate of carbon consumption generally makes this option undesirable for sites having high hydrocarbon concentrations.
c. Thermal treatment includes thermal incineration, catalytic incineration, and flaring (combustion external to any combustion chamber or vessel). It is appropriate when hydrocarbon concentrations exceed those at which carbon adsorption and "no treatment" options are feasible. It requires a fuel source (natural gas or propane) and usually requires substantial capital investment.
d. The internal combustion engine uses extracted soil vapor as a source of fuel and air. It is appropriate for low- to high-flow rates and a range of hydrocarbon concentrations. A supplemental fuel source (natural gas or propane) is typically required.

The selection of a particular emissions treatment method will be based on the following criteria:

a. Initial capital cost, or the cost to purchase and set up the equipment. This is typically moderate to high for thermal treatment and the internal combustion engine and low to moderate for activated carbon adsorption.
b. Operational cost, or the cost for maintenance and fuel or replacement material, such as change-out carbon. The operational cost depends primarily on the concentration and rate of hydrocarbon removal during extraction. If these are high, thermal and internal combustion methods will require almost no supplemental fuel and will be relatively inexpensive to operate. Carbon usage, in contrast, will be very rapid, and replacement carbon and change-out labor will result in very high operational costs. For low concentrations, the opposite is typically true.
c. Regulatory acceptance by local or state environmental, air pollution, or fire statutes or guidance that may limit the available options for a particular site. The fire marshal within a particular city, for example, should always be contacted for permission to implement a thermal treatment option at a gasoline retail location.

Another side-waste stream to consider is condensate. Air withdrawn from partially saturated soils is usually quite moist. If the airstream cools appreciably between the point of extraction (the well or trench) and the blower, it may drop below the dew point. An air-water separator, also referred to as a knock-out pot or condensate-collection tank, is often used on the blower to collect most of the resulting condensation. Usually, some condensation will also collect in the extraction piping. Because this air is in continual contact with hydrocarbon vapors, it may contain significant concentrations of dissolved hydrocarbons and require special handling and disposal procedures.

6.4.2.4 Bioventing

Bioventing is a permutation of SVE that is beginning to gain considerable attention. The basic approach is similar to that of vapor extraction but with a different basic intent. The intention of soil vapor extraction is to enhance the physical partitioning of hydrocarbon fuels into soil vapor so they can be removed from unsaturated soils. In contrast, the intention of bioventing is to enhance microbial degradation of the hydrocarbon fuels in unsaturated soils. This enhancement is produced by ventilating the soils to create and maintain conditions favorable for aerobic metabolism. Although some degree of biodegradation is often observed as a side effect of normal SVE operations, the process of bioventing must be regarded as distinct. The difference in intent leads to a modified approach to implementation and operation.

For bioventing, the primary objective is to maintain optimum aerobic conditions in the targeted mass of impacted soil. Because oxygen is typically the factor that limits the rate of biodegradation of hydrocarbon fuels in soils, maintaining aerobic conditions is required to promote the desired microbial activity at many sites. For some sites, it may also be necessary to add nutrients or supplemental moisture to achieve the maximum microbial degradation rate.

The difference in implementation and operation between SVE and bioventing remediations is that SVE reduces soil vapor to a level that is just sufficient to maintain oxygen at aerobic levels. This flow reduction minimizes moisture loss from the soils and reduces the mass of hydrocarbons withdrawn with the soil vapor. Because microbial action is favored by the presence of some soil moisture, minimizing soil drying favors microbial growth. The reduction in hydrocarbon mass withdrawal rates is also helpful, as it may eliminate or reduce the vapor emissions treatment requirements for a system.

An alternative approach would be to inject atmospheric air into the targeted soils rather than extract soil vapors. In addition to improving oxygen levels in soil vapor, this approach eliminates the need for any emissions treatment, because no vapor is extracted. It also may help disperse hydrocarbons through a larger soil volume, which may improve the effectiveness of biodegradation. This approach, however, should not be regarded as an easy solution to high vapor emissions treatment costs. It does have possible significant disadvantages, such as the potential for spreading hydrocarbons to previously unimpacted soils, possibly even beyond site boundaries. This method also may result in the discharge of hydrocarbon vapors upward through the ground surface in the treatment area. In areas predominantly covered with paving or concrete, this could result in concentrated discharge through any penetrations in that paving, such as utility lines or building foundations. As with any injection method, the appropriate regulatory agencies should be contacted for approval and possibly for permits before implementation.

For any bioventing remediation, the system operators should monitor oxygen and carbon dioxide concentrations closely, as well as hydrocarbon vapor levels. These gases should be monitored both within the extracted vapor stream and for in situ soil vapors. The latter would be sampled by using probes or vapor piezometers. Oxygen concentrations should be maintained above 5 percent volume in the soil vapor of the biovented soils. By monitoring these gas concentrations both before and periodically after initiating bioventing, the operators can note when both carbon dioxide and hydrocarbon concentrations decrease and oxygen concentrations increase, which indicates the possible termination of biodegradation. In addition, by temporarily halting vapor withdrawal and monitoring relative changes in oxygen and carbon dioxide concentrations, the operators may be able to estimate the rate of hydrocarbon destruction within the biovented soils.

6.4.2.5 Air Sparging/SVE Systems

Recently, an integrated approach to remediating hydrocarbon-impacted soils has been developed to enhance SVE and bioventing. Typically, SVE/bioventing systems are designed to address hydrocarbons in soil above the groundwater table in the unsaturated zone. In many cases, however, residual hydrocarbons are present in soils below the water table. These hydrocarbons become trapped below the water table as a result of seasonal groundwater table fluctuations, drawdown during pumping operations, and the presence of dense nonagueons-phase liquids that sink to the bottom of the water table. Contaminants in soils in the saturated zone appear to have been effectively removed by using SVE/bioventing systems in combination with air-sparging systems to strip and biodegrade residual and dissolved-phase hydrocarbons.

Air Sparging (also referred to as in situ aeration or stripping) systems involve injecting pressurized air into soils below the water table and extracting the resulting vapors via SVE wells located above the water table. Figure 21 shows an integrated air sparging/SVE system. As air is forced through the injection points, it moves outward and upward, displacing water from the soil pores and allowing the air to come in contact with residual and dissolved-phase hydrocarbons. Lateral movement of air can be significant if the horizontal permeability of the soil is greater than the vertical permeability. As the air moves through the saturated zone, volatile constituents in the soil or water partition into the vapor phase and travel upward (via buoyancy forces) to the unsaturated zone, where they are captured by SVE wells. The extracted hydrocarbon vapors are either treated or discharged to the atmosphere, depending on the level of contamination and local *regulatory requirements*. The injected air also provides oxygen to stimulate aerobic biodegradation of hydrocarbons by indigenous microbe populations.

Air sparging/SVE systems can be effectively used at sites where the following conditions are present:

a. The injected air can pass upward through the water table to the unsaturated zone. A site where groundwater is confined by a relatively impermeable clay layer above the water table would not be appropriate for air sparging/SVE/bioventing systems.
b. The soil in the saturated zone is sufficiently permeable to allow injected air to move to the unsaturated zone.
c. The volatile constituents must have low solubilities (such as BTEX). Highly soluble constituents will not partition into the air and therefore cannot be effectively volatilized; however, air sparging does enhance biodegradation of such constituents.

For effective operation, the air sparging/SVE system must be designed to ensure effective air distribution and capture. The quantity of air injected must be less than the quantity of air withdrawn, and the injected air must be within the SVE zone of influence to assure adequate capture of air and volatile hydrocarbons (that is, the vertical and horizontal spacing of the air injection and SVE wells must be adequate for proper air distribution and capture).

When air sparging/SVE systems are installed, the SVE system begins to extract volatile hydrocarbons whose concentrations in the exhaust air usually decrease sharply after startup and then begin to level off. Air sparging is started when the concentration of volatile hydrocarbons recovered by the SVE system has leveled off, and it is operated simultaneously with the SVE system. As the air removes volatile hydrocarbons from below the water table, the concentration of hydrocarbons in the exhaust will increase sharply and then decrease over time.

Bioventing has also been used successfully in conjunction with air sparging to aid biodegradation of hydrocarbon constituents in both the saturated and unsaturated zones. In general, as oxygen levels in the unsaturated zone and dissolved oxygen levels in the saturated zone increase from air sparging, laboratory and field evidence suggest that biodegradation is enhanced. Determining the relative contribution of biodegradation (compared with other processes) to hydrocarbon degradation is difficult.

6.4.3 ABOVEGROUND TECHNOLOGIES

6.4.3.1 Overview

Aboveground technologies involve the excavation of soils impacted by petroleum hydrocarbons and their subsequent treatment on- or off-site. Despite the positive aspects of in situ treatment, the removal of soils for treatment may be more appropriate in the following situations:

a. Sites where the hydrocarbon impact is highly localized in the shallow subsurface so that the bulk of the hydrocarbon mass can be readily removed via excavation.
b. Sites where the potential risk posed by the presence of the released hydrocarbon fuels is so high that removing them must be accomplished quickly.
c. Sites where subsurface conditions (such as hydraulic conductivity) impair the feasibility of in situ options.

This list of situations is not all-inclusive; it is intended simply to illustrate the importance of site-specific constraints on the selection of aboveground versus in situ techniques. Probably the most critical constraint is the nature of surficial and near-surficial structures (such as buried utilities) and activities, which can often prohibit excavation and thus narrow the options to in situ methods.

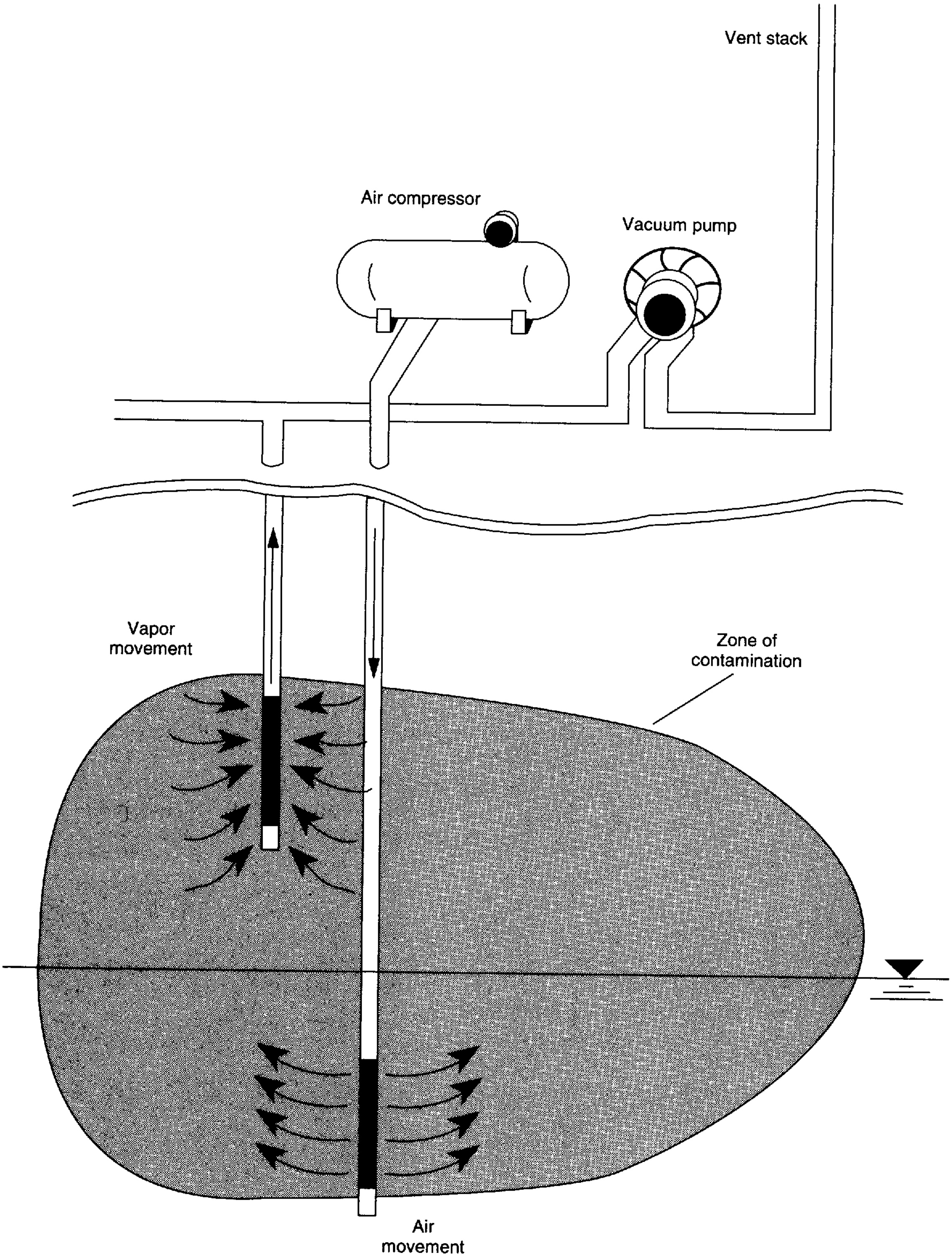
In the past, the corrective-action option for soil containing hydrocarbons was usually to excavate and remove the soil to an appropriate disposal site. More recently, this option has become less attractive. Available landfill space has diminished as many landfill sites have closed, and the expansion of others has become increasingly difficult. Also, federal land disposal restrictions are limiting off-site disposal options. Consequently, the cost of off-site disposal options has increased. The potential for long-term liability associated with off-site disposal options also must be considered. Because this corrective action merely transfers the soil containing the hydrocarbons from the point of origin to another location, liability for the material persists.

With the use of aboveground technologies, excavated soils impacted with hydrocarbons can be treated either to remove or to destroy the residual hydrocarbons. It is often beneficial to treat these soils on-site because on-site treatment eliminates transportation and handling costs and removes the liability posed by transporting contaminated materials off-site. Many aboveground technologies, however, require so much space they can only be implemented off-site or at inactive sites.

Over the years, several forms of treatment have been developed for removing hydrocarbon fuels from soils. Some of these, such as bioremediation and thermal treatment, actually attempt to destroy the hydrocarbons within the soil matrix. Others, such as asphalt batching and cement incorporation, simply reuse the soil matrix and fuel residue in an acceptable manner. The following treatments have been used successfully at several different sites and are therefore considered proven techniques:

a. Bioremediation (includes bioventing in soil piles).
b. Soil aeration (discussed in 6.4.3.3.1).
c. Solidification by incorporating asphalt and cement.
d. Thermal treatment.

Each of these technologies is described in 6.4.3.3 through 6.4.3.5 (with emphasis on applicability, design considerations, and waste stream treatment).



Source: Modified from Billings and Associates, Inc., *SVVS Remediation Technology* [41].

Figure 21—Schematic of an Air Sparging/Soil Vapor Extraction System

6.4.3.2 Management of Soil-Handling Operations

Excavating soil at a hydrocarbon-release site can be complicated greatly by the presence of surficial and near-surficial activities and structures. If proper consideration is not given to the limitations posed by these activities and structures, the result will probably be chaotic and could be dangerous.

6.4.3.2.1 Planning an Excavation Effort

Given the space requirements of even a modest excavation effort and the potential for underground utility and product-line damage, it is often judicious to halt commercial operations at active sites until the excavation is completed.

Several activities involved in soil excavation require advance planning. The more significant of these include the following:

a. Develop an adequate health and safety plan.
b. In some states, it may be necessary to obtain regulatory permits, permission, or oversight for the excavation. It is typically appropriate to notify local fire authorities, who may choose to be present.
c. Identify and locate underground utilities, such as water, electric, sewer, product supply, and other services at the facility. Include both municipal and large commercial activities, which can be located either by contacting all pertinent utilities or a single utility locating service. Either approach will require several days to 2 weeks of advance notice.
d. Arrange for adequate excavating equipment or an appropriate subcontractor to perform the excavation to the required depth. It may also be necessary to arrange for a means of penetrating any pavement or concrete surfaces in the excavation zone.
e. Arrange for storage or off-site transport of the excavated soil.
f. Arrange for sampling and analysis of the excavation base and walls to ensure the efficacy of the removal effort.
g. Arrange for air-quality monitoring (if required).
h. Arrange for equipment and supplies to maintain the stability of the excavation (shoring, for example).

6.4.3.2.2 Space Requirements

The space required for an excavation effort will probably far exceed the actual two-dimensional area of the excavation itself. In addition, the excavated soil must be at least temporarily stockpiled by the excavation. Depending on the volume and types of soil involved, this will require three to five times the area of the excavation itself. The digging equipment must have access to the digging area as well as sufficient room to maneuver in and out of position. Aboveground barriers to operation of the equipment, such as power lines or canopy covers, will pose difficulties just as substantial as those posed by buildings and pump islands. Finally, loading and transport equipment must have access to the soil piles generated by excavation.

6.4.3.2.3 Health and Safety Considerations

In addition to the normal hazards posed by heavy equipment, excavating fuel-impacted soil poses the following special health and safety problems:

a. Because these operations typically occur in populated, heavy traffic areas, the presence of a large population often must be considered in planning excavation activities.
b. The excavation, if successful, will unearth soils containing hydrocarbon fuels. If these fuels are inhaled, contacted, or ingested, they may pose a hazard to workers on the site. Odors or vapors also may reach the public downwind of the site. Hydrocarbon vapors may also be present in sufficient concentration to form explosive or flammable vapors.
c. The excavation has a likelihood of encountering and damaging undocumented product lines and/or utilities.
d. Excavation typically proceeds in close quarters where a slope failure could result in building damage or collapse.

Overall, the nature of the work is such that the potential for injury is great. Digging activities should be performed by those with experience in removing fuel-impacted soils and with sufficient training in safety procedures and in using protective equipment to perform the work safely. The excavation should be overseen by an experienced operations supervisor, and the atmosphere should be checked regularly with an organic vapor analyzer and explosimeter. The public must be completely excluded by barricades, fencing, or other means. A broad range of requirements covering soil excavation activities are defined by OSHA.

6.4.3.2.4 Handling Excavated Soils

The following are some of the more critical of the several issues relating to the storage, preparation for treatment, and sampling of soils generated by an excavation effort:

a. Stockpiling. Most states have specific procedural requirements for stockpiling fuel-impacted soils on-site. Typically, these procedures are aimed at preventing leaching of hydrocarbons out of the soil and across the ground surface or back into the subsurface. A commonly applied requirement is the placement of soil on a plastic membrane, surrounding the stockpile with a berm (such as bales covered with a liner membrane), and covering the soil with additional plastic. Measures to exclude the public and consideration of the uses of neighboring property (such as schools, residences, or vacant lots) are also necessary for most operations.
b. Piping. Many types of on-site treatment require the movement of air or liquids into and/or out of the excavated soil. If this can be accomplished by layering the soil with horizontal perforated piping, placing this piping during the initial exca-

vation and stockpiling process should be considered. This is generally the most efficient approach because it reduces the number of times the soil piles must be shifted.

c. Segregation based on material. Surficial materials such as concrete and asphalt should be segregated from the soil materials and handled separately.

d. Segregation based on hydrocarbon impact. If the soil can be segregated into highly impacted, slightly impacted, and unimpacted segments by some method of field screening, the mass of soil requiring treatment may be reduced. Field screening techniques for volatiles using field analytical instruments are often used for these purposes. An example of such a field measurement technique is dynamic headspace analysis, which uses photo- or flame-ionization detectors. For less volatile constituents, it may be cost-effective to use a portable gas chromatograph or mobile laboratory to make the necessary distinctions. After segregation, a less costly alternative treatment of the slightly impacted soil may be possible. The unimpacted soil may be replaced in the excavated area. It is very important, however, that the field screening method be approved by the pertinent regulatory agencies before its use.

e. Physical arrangement of the stockpiles. No single arrangement or configuration is most correct. As with other aspects of a corrective-action strategy, the physical arrangement of the soil stockpiles must be tailored to suit the site-specific operational constraints. If certain soil is to be transported offsite, for example, it should be accessible to loading and transport equipment without having to shift soil remaining on-site. Placement of soil to be treated in an on-site bioreactor should allow untreated soil to be moved to the reactor and treated soil to be moved away from the reactor with maximum efficiency. Thus, it is necessary to anticipate how later phases of the corrective action can affect the physical placement and movement of the soil stockpiles.

6.4.3.3 Bioremediation

6.4.3.3.1 Description

Aboveground bioremediation techniques can be applied to excavated soil containing petroleum hydrocarbons. The three general types of aboveground bioremediation are land treatment (derived from land farming), soil piles, and bioreactors/slurry reactors. These aboveground bioremediation techniques can be used for on-site treatment, depending on the size and use of the site.

Land treatment involves removing soil that contains hydrocarbons and spreading it on a surface that has been lined to prevent the migration of soluble constituents in runoff water. A RCRA permit may be required. This method relies primarily on naturally occurring microbes to degrade the hydrocarbons. The soil is periodically tilled to help promote degradation by aeration. In addition to aeration, nutrients (depending on the naturally occurring nutrients in the soil) and water may be added to stimulate degradation. Volatilization, chemical degradation, and photochemical degradation are supplementary processes associated with land treatment. Figure 22 presents a schematic of the land treatment process. This process frequently uses commercially available microbial cultures.

Soil piles consist of excavated soil placed in a pile constructed with conduits for aeration to enhance biodegradation (see Figure 23). Typically, the pile is constructed by first placing a plastic liner on the ground and then adding 1 to 2 feet (0.3 to 0.6 meters) of soil lifts at a time. Piping is placed between the lifts for passive or active aeration to promote microbial growth and to allow for volatilization. An additional piping network may be installed for aboveground SVE to extract volatile hydrocarbons. Nutrients also may be added in the form of fertilizer between lifts. Water may be added to maintain optimum moisture content, and microbial cultures may also be added to augment the indigenous microbial populations. The pile is covered with black plastic and surrounded by a berm to control rainfall runoff.

Both volatilization and biodegradation are enhanced in this approach. For passive systems, the black plastic absorbs heat and increases both the volatilization and biodegradation rates. The off-gas generated will be emitted through the piping system and into a treatment unit if necessary. Active systems also force air into the pile and remove soil vapor containing hydrocarbon vapors via SVE for further enhancement of the biodegradation.

Bioreactors/slurry reactors involve the treatment of soil or sludge containing petroleum hydrocarbons (see Figure 24). The soil is first made into an aqueous slurry. Oversized debris is separated from the soil, and the soil is mixed with water to obtain the appropriate slurry density. The slurry is mechanically agitated in a bioreactor vessel to keep the solids suspended and to maintain contact between microbes and petroleum hydrocarbons. The bioreactor is also used to control the appropriate environmental conditions. In addition, nutrients, oxygen, and acid or alkali for pH control may be added to maintain optimum conditions. Bacteria also may be added to initiate the biodegradation, or they may be added continuously to maintain the optimum biomass population. The residence time in the bioreactor varies, depending on the soil or sludge matrix, the physical and chemical nature of the petroleum hydrocarbon, and the susceptibility of the petroleum hydrocarbons to biodegradation. When treatment is complete, the slurry is dewatered. The residual water removed from the slurry may have to be treated further before its disposal. Figure 24 shows a generic slurry reactor.

The specific advantages of aboveground bioremediation techniques are as follows:

a. Land treatment is simple and low in cost relative to other corrective-action options.

b. Bioremediation in soil piles is simple and involves relatively short treatment times compared with other bioremediation processes.
c. Soil treated in soil piles or land treatment can be used on-site as backfill.
d. Bioreactors have short treatment times relative to other bioremediation processes and can uniformly treat most hydrocarbons to nondetectable levels in less than 2 months.
e. Bioreactors can treat higher hydrocarbon concentration levels than other bioremediation processes can.

The disadvantages and limitations of aboveground bioremediation techniques include the following:

a. A large amount of space is required for bioreactors but generally less than that required for land treatment. Soil piles require less space than land treatment.
b. Side-waste streams generated from bioreactors may require proper treatment and disposal.
c. Land treatment may require relatively moderate to long treatment times.

6.4.3.3.2 Feasibility and Design Considerations

A wide variety of site, soil, and environmental factors can influence the use of bioremediation techniques.

The following factors affect the use of land treatment:

a. Types of microbes in the soil.
b. Types of petroleum hydrocarbons present in the soil.
c. Soil type and moisture content (which in general can be optimized).
d. Temperature [15°C to 35°C (59°F to 95°F)].
e. Soil pH (6.0 to 8.0).
f. Nutrients (nitrogen and phosphorus).
g. Precipitation.
h. Amount of oxygen added through aeration.
i. Amount of soil to be treated.
j. Space constraints on the site.

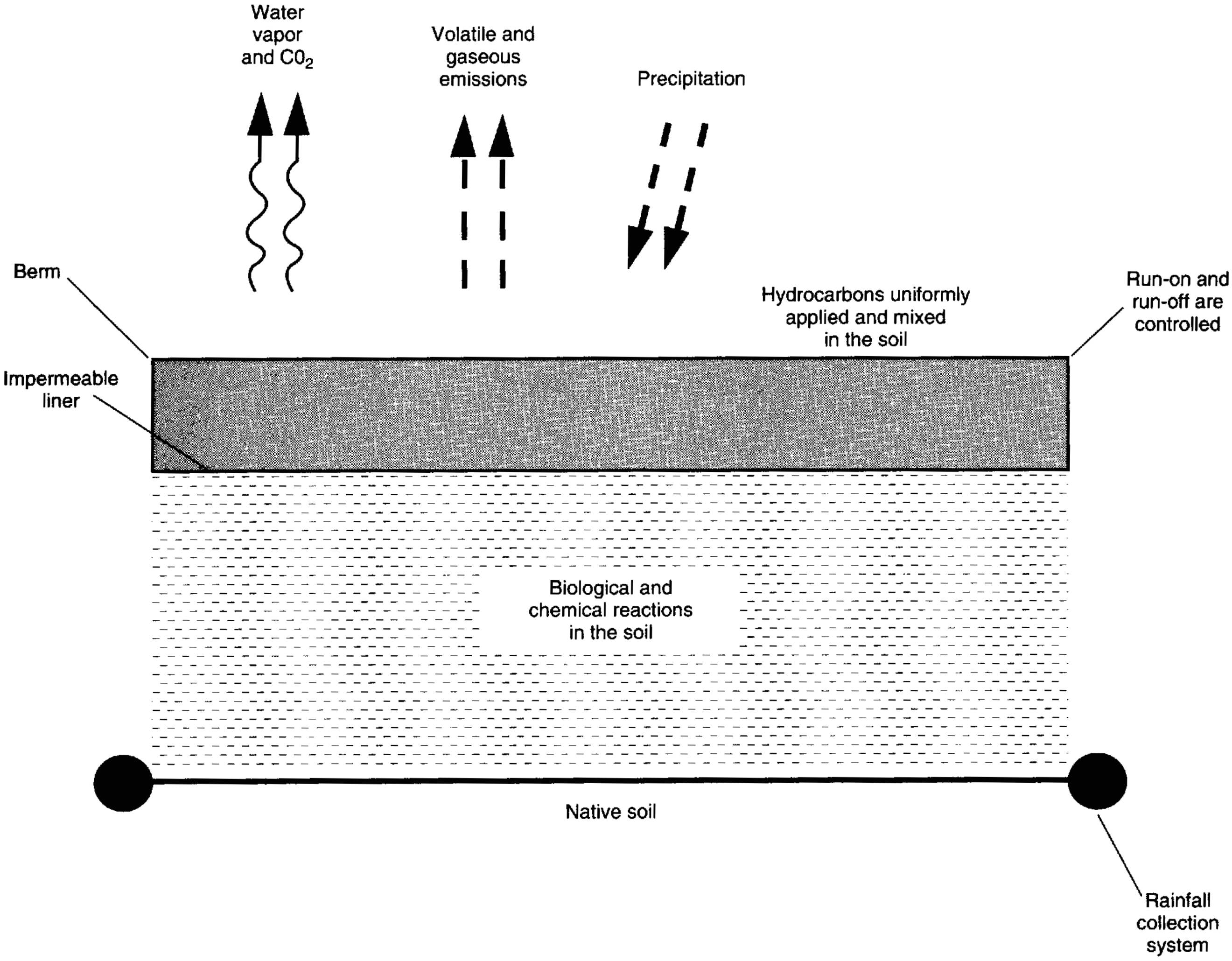


Figure 22—Schematic Cross Section of a Land Treatment System

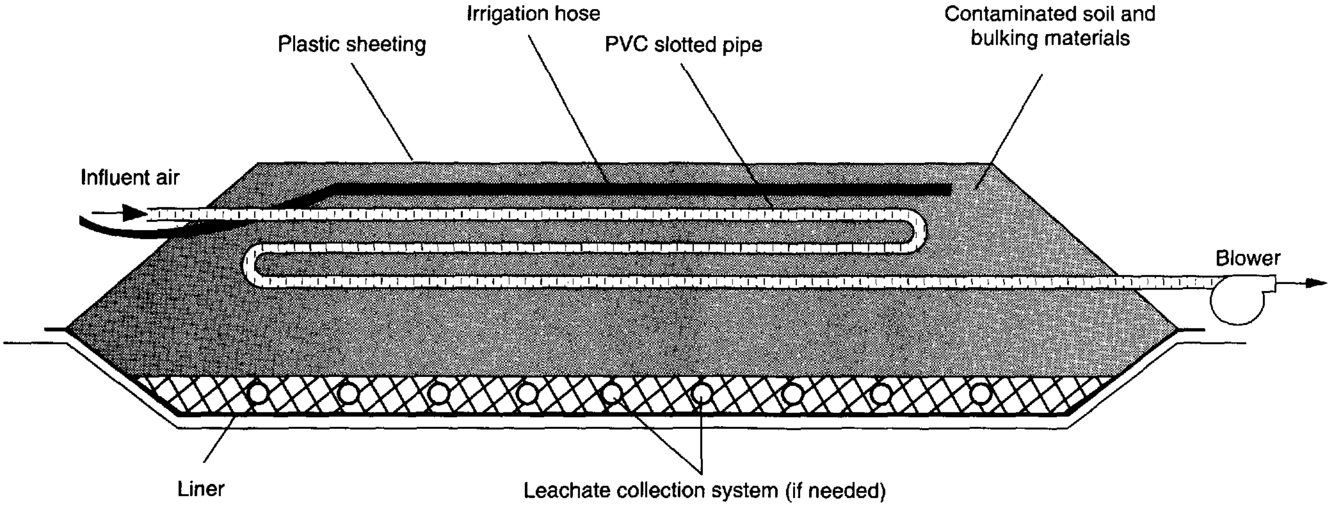


Figure 23—Schematic Cross Section of Bioremediation in Soil Piles

The design process for land treatment is similar to that for in situ biodegradation discussed in 6.4.2.1, except that the soil is excavated and removed to an aboveground location (either on-site or off-site). The soil is placed in lifts and periodically tilled and watered to add oxygen and moisture to enhance biodegradation. Soils that contain high levels of petroleum hydrocarbons are tilled or disked several times per week over a period up to several months to reduce the hydrocarbon load. After the initial tilling and the resulting decrease in the hydrocarbon load, the tilling is continued periodically until the hydrocarbon levels have been reduced sufficiently to meet the appropriate cleanup objectives. Nutrient addition is based on the carbon concentrations. Regulatory agencies in some areas will not permit land treatment if significant levels of volatile hydrocarbons are emitted from the soil lifts.

As a means of keeping soluble hydrocarbon constituents from migrating in runoff water, an impermeable liner and berms are placed to contain the soil being treated. A layer of fill material or sand is placed over the liner to prevent damage while tilling. Care should be taken during the tilling operation to prevent tearing the impermeable liner. A leachate collection system can be provided on the downgradient side of the treatment area where leachate can be removed, treated, or reapplied. The leachate collection system consists of a sump pump buried in gravel at the low end of the treatment area or drainage pipes leading from the soil treatment area to a lined containment area to remove leachate (infiltrated water and dissolved-phase hydrocarbons) from the soil being treated.

A wide variety of soil and environmental factors affect the use of soil piles and bioreactors. These factors include the following:

a. Soil type.
b. Type of hydrocarbons in the soil.
c. Ambient temperature.
d. Soil moisture content.
e. Available nutrients in the soil.
f. Oxygen level of the soil.
g. Soil pH.
h. Volume of soil.
i. Space constraints.
j. Time frame for remediation.

The microbial population present must be assessed to identify the indigenous culture and its ability to biodegrade the hydrocarbons present in the soil. The assessment of microbial population is conducted by laboratory analysis or bench-scale testing. Commercial microbes may be added initially to stimulate degradation, or they may be added continually to replace the indigenous culture.

Aboveground bioremediation of soil piles is relatively simple, and operating requirements are minimal. The treatment times are relatively short compared with those of other bioremediation processes. Most of the costs are associated with the soil excavation, handling, and transportation (if treated off-site). Soil treated in soil piles can be used on-site as backfill after treatment. In certain jurisdictions, air permits and treatment may be required for volatile hydrocarbons removed from the soil piles.

Treatment times in bioreactors/slurry reactors are relatively short for low volumes of soil containing petroleum hydrocarbons compared with times required by other bioremediation technologies. The volume of soil treated in a batch is limited by the size of the reactor. Higher hydrocarbon concentration levels can be treated by bioreactors rather than by

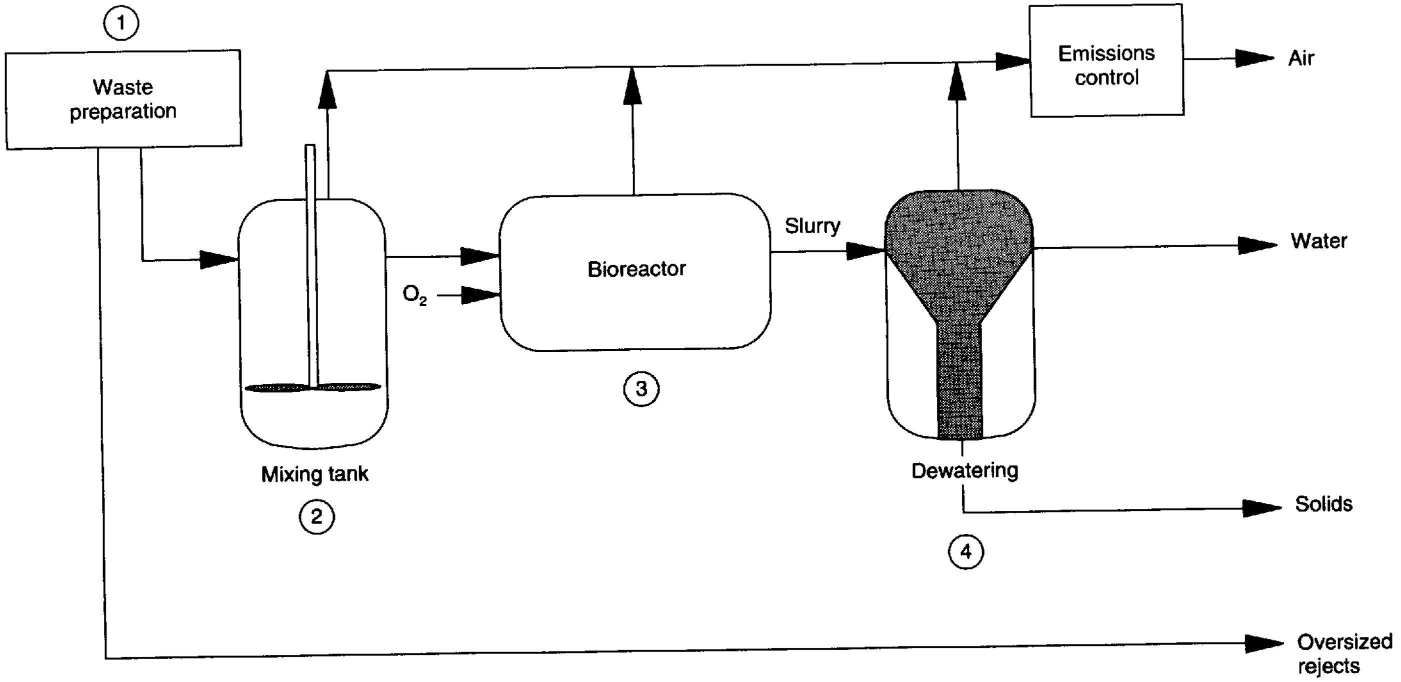


Figure 24—Schematic of the Soil Bioreactor Process

other bioremediation processes. These reactors can uniformly treat most petroleum hydrocarbons to nondetectable levels in 1 to 2 months. Bioreactors, however, also tend to be more expensive than other bioremediation options. In addition, associated air and residual-water permit requirements can delay implementation and increase the overall costs.

6.4.3.3.3 Control of Side-Waste Streams

Vapor emissions from soil piles are controlled by methods similar to those used for soil vapor extraction (SVE). The most commonly used system for treating vapor emissions from soil piles is activated carbon adsorption. Unlike vapor emission systems used for SVE, the treatment system for soil piles does not have to be used continually. Also, the hydrocarbon vapor concentrations generated from soil piles tend to be lower than those generated from SVE systems. Consequently, the amount of activated carbon required for carbon adsorption is minimized.

Side-waste streams generated from bioreactors/slurry reactors include residual water, sludge consisting of biomass, and hydrocarbon vapor emissions. The residual water may be treated with carbon adsorption or air stripping prior to discharging it, or it may be shipped off-site for treatment and disposal. The treatment process for residual water may have to comply with National Pollution Discharge Elimination System (NPDES) standards or local sanitary sewer and public owned treatment works (POTW) standards. The biomass sludge may undergo additional digestion or may be shipped off-site for treatment and disposal. Hydrocarbon vapors are recirculated in the reactors.

6.4.3.4 Asphalt and Cement Incorporation

6.4.3.4.1 Description

Asphalt incorporation involves mixing petroleum-laden soils into hot asphalt mixes as a partial substitute for stone aggregate; this mixture is then used for paving. The primary remediation mechanisms effected by incorporating soil into asphalt are volatilization and low-temperature thermal destruction or encapsulation of hydrocarbon constituents. The efficiency of these mechanisms for removing hydrocarbons is variable and depends on the asphalt-aggregate dryer temperature, residence time of the soil containing hydrocarbons in the dryer, and permit requirements. A secondary mechanism involves incorporating the heavier hydrocarbons into the asphalt/aggregate mix. The high temperatures in the dryer combined with the encapsulation of the soil in the asphalt mix can provide an adequate corrective-action measure. Figure 25 is a schematic diagram of a typical asphalt batch plant.

Some commercial cement kilns are also permitted to accept soils containing petroleum hydrocarbons for incorporation with raw aggregate material. Soils containing hydrocarbons that are high in silica are typically handled as part of the sand that is added to the cement for strength. This process is called *cement incorporation* and involves blending these soils with other raw materials (limestone, alumina, silica, and iron), grinding in mills, and placing the mixture in slurry tanks and then into a kiln. The petroleum organics are evaporated and thermally oxidized, and the heavy metals are entrained in the dry slurry and treated at a high temperature to form clinker (an intermediate cement product). The soil containing hydrocarbons can be "roasted" in a preheated unit similar to the asphalt aggregate dryer before being incorporated with the raw material. This practice reduces the volatile hydrocarbon content of the soil to within the process chemistry requirements.

The specific advantages of incorporating soil into asphalt or cement are as follows:

a. It requires relatively short treatment times and removes the material from the site.
b. It is cost-effective and a viable alternative to landfilling.
c. It eliminates any long-term liability.

The disadvantages and limitations of incorporating soil into asphalt or cement include the following:

a. Specific analyses of the petroleum-laden soil may be required before it is accepted by the asphalt or cement plant.
b. Contaminated soil handling at a treatment site is performed by contractors; however, the liability for the soil may remain for the site owner until the contaminants are below acceptable concentrations.
c. Transportation to the treatment site is an additional cost.

6.4.3.4.2 Feasibility and Design Considerations

When asphalt incorporation is being considered as a corrective-action measure for soil containing petroleum hydrocarbons, the following two factors should be evaluated: the availability of the process and the characteristics of the soil.

Only soil containing petroleum hydrocarbons that are considered to be nonhazardous can be incorporated into asphalt. The hazardous or nonhazardous designation varies among different states. For hydrocarbon-impacted soil that is nonhazardous, asphalt incorporation is an attractive alternative to other disposal options, such as landfilling.

The specific requirements of soil containing hydrocarbons for asphalt batching vary among different plants. The most suitable soil type is sandy; a wet heavy clay is unacceptable at nearly any plant; however, drier silty clay may be incorporated in small quantities. Analyses of composite samples typically required by most plants include TPH, TCLP, polychlorinated biphenyls (PCBs), and flash point.

The particle size and organic content of the soil also may have an effect on the quality of the asphalt mix. The strength and durability of asphalt mixes depend on the size, type, and

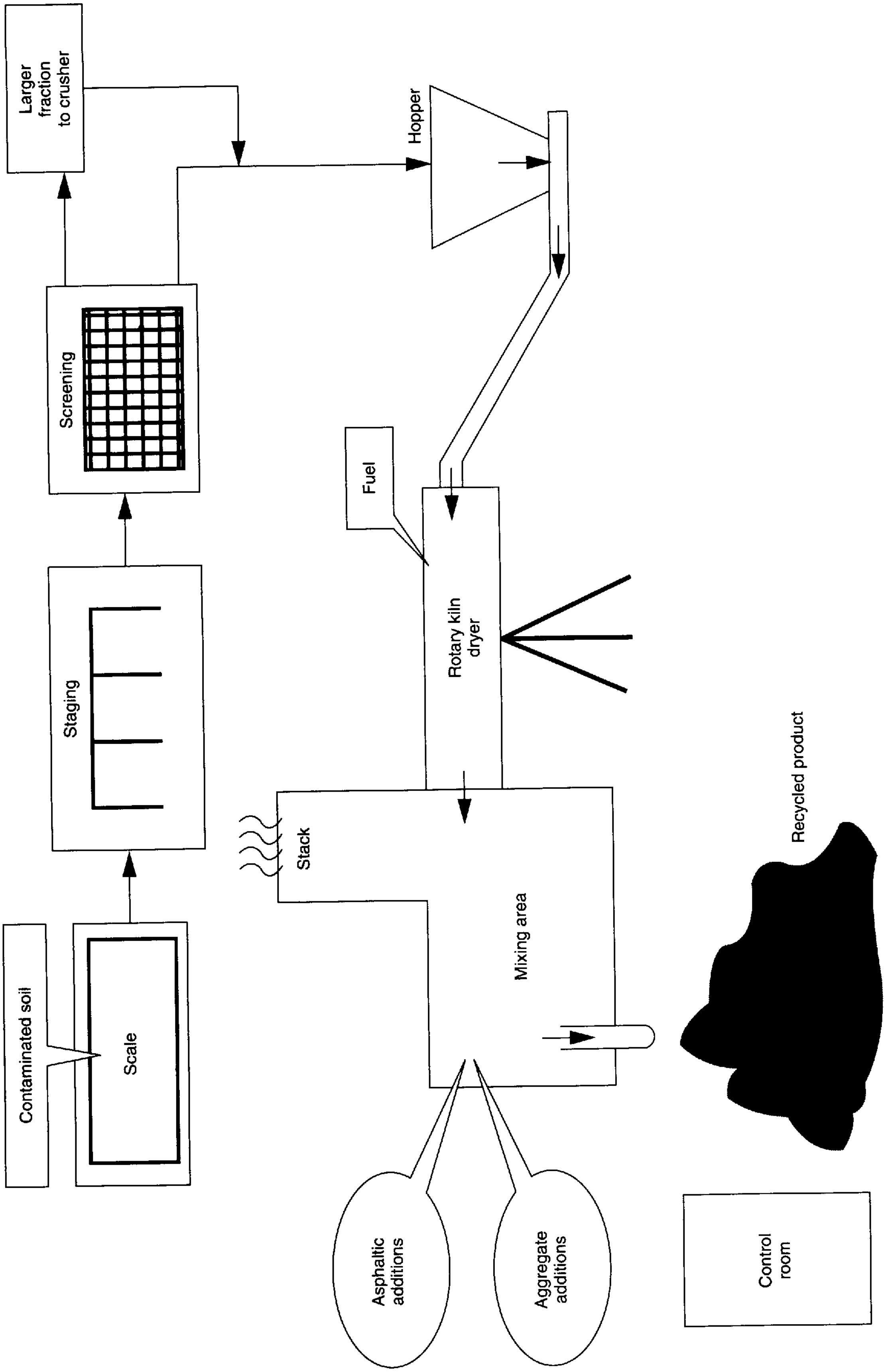


Figure 25—Schematic Diagram of the Asphalt Batching Process

amounts of aggregates used. In general, the amount of fine material is limited to between 2 percent and 10 percent of the mixture.

Cement incorporation involves mixing soil containing hydrocarbons with portland cement to form a monolithic, solid material. Cement incorporation can volatilize the light hydrocarbons and limit the mobility of higher molecular weight hydrocarbons by encapsulating them in a solid mass, unless the specific organic materials interfere with the hardening of the cement. The mobility of the higher molecular weight hydrocarbons is limited in this process, but they usually will not be completely stabilized or fixated because they do not react with the cement mixture. Some cement incorporation processes use nontoxic chemical additives to fixate organic compounds to the cement; this reduces the compounds' potential for leaching from the solidified waste.

6.4.3.4.3 Control and Management of Side-Waste Streams

The greatest limitations for asphalt plants and cement kilns are associated with meeting the stringent regulatory air pollution control and permit requirements for the plants. State and local regulatory requirements vary among jurisdictions; consequently, the required air pollution control systems will vary. The asphalt and cement incorporation facilities must also have permits to accept petroleum-contaminated soil.

6.4.3.5 Thermal Treatment

Thermal treatment of hydrocarbon-impacted soils involves liberating organics (hydrocarbon constituents) from the solids into the gas phase followed by either condensation for recovery or thermal oxidation into combustion by-products. The primary factors influencing the applicability of thermal treatment to hydrocarbon-impacted soils or residues are the quantity and chemical characteristics of the constituents and the regulatory requirements, particularly the cleanup objectives. The key factors influencing the selection of the appropriate thermal treatment system include the operating temperature and the solids' residence time required to achieve cleanup objectives.

A number of different types of thermal treatment systems are currently being used to treat hydrocarbon-impacted soils and residues. Thermal treatment processes that use indirect heating transfer fluids, such as a screw-flight heat exchanger, are applicable only to soils or solids containing volatile and some semivolatile organic constituents. Thermal treatment processes that use indirect-heated or direct-fired thermal treatment equipment are applicable to soils, sludges, or solids containing both volatile and semivolatile organic constituents.

Thermal desorption as defined in this document is limited to any number of aboveground processes using either direct or indirect heat exchange to vaporize organic constituents from soil or sludge. Air, combustion gas, or inert gas is used as the transfer medium for the vaporized constituents. Thermal desorption systems are physical separation processes and are not specifically designed to provide organic decomposition. Thermal desorption is not incineration, since the decomposition of organic constituents is not the desired result, although some decomposition may occur.

Incineration is also any process that uses heat to indirectly or directly transfer heat to the soil. However, sufficient oxygen is required so that the organics are oxidized and converted to combustion by-products, primarily carbon dioxide and water. The level of contaminants and the specific cleanup levels for the site will influence the applicability of the thermal technology used at the site.

For solids contaminated with organics having low volatility or where very low residual contaminant concentrations must be achieved, high treatment temperatures are required. Low-temperature thermal desorption (LTTD) systems that operate at 200°F to 500°F (93°C to 260°C), such as screw-flight heat exchangers, may not be capable of meeting the treatment criteria for semivolatile hydrocarbon constituents. Thermal treatment processes that can provide higher temperatures of 400°F to 1000°F (204°C to 538°C)] are indirect-heated rotary tube and infrared systems and direct-fired rotary kiln and fluid bed incinerators.

6.4.3.5.1 Thermal Desorption

6.4.3.5.1.1 Description

A thermal desorption system consists of a screw-flight heat exchanger in which the soil and sludge are mixed and heated (indirectly) to drive off (desorb) moisture and organics in an oxygen deficient atmosphere. A variety of other thermal systems can be operated at low temperatures. These systems are limited to solids contaminated with volatile organic constituents at low to moderate concentrations. An indirect-heated system generates smaller off-gas volume than a direct-fired system.

Screw-flight heat exchanger designs have been used primarily to process soil and sludge contaminated with volatile organics such as solvents and gasoline. The exchanger consists of a screw conveyor, which is designed to circulate heat transfer fluids inside the screw shaft, and flights to indirectly heat the solids. These heat exchangers usually use an organic-based heat transfer fluid that can heat solids up to 500°F (260°C), but inorganic nitrate-salt-based heat transfer fluids can be used to achieve even higher temperatures of 600°F to 1000°F (316°C to 538°C). This type of system is compact in size due to the relatively small volume of off-gas generated and the small size of the gas cleaning system.

The specific advantages of thermal desorption systems include the following:

a. Treatment time is relatively short (15 to 60 minutes).
b. The system is compact and can be used for soil treatment on-site.
c. On-site use minimizes soil handling by eliminating transportation off-site.
d. Treated soil may be used as backfill.

The disadvantages and limitations of thermal desorption systems include the following:

a. Preprocessing of the soils to reduce particle size may be significant.
b. The heat transfer fluid must be environmentally and toxicologically acceptable should it leak.
c. Appropriate safeguards for fires must be incorporated into the design when organic-based heat transfer fluids are used.
d. The systems may not be capable of meeting low treatment criteria for low-volatility organics.

6.4.3.5.1.2 Feasibility and Design Considerations

Laboratory analyses of the soils are conducted to determine the efficacy of treating contaminated soil via thermal desorption. The analyses are used to determine the concentration and type of petroleum hydrocarbons, the physical characteristics of the soil, and the applicability of thermal desorption. The following physical characteristics may affect the design and performance of on-site thermal desorption:

a. Moisture content of the soil.
b. Particle size distribution in the soil.
c. Permeability of the soil.
d. Soil type.
e. Contaminant type, concentration, and distribution.
f. Soil compressibility.
g. Existence of metals, chlorinated compounds, and other contaminants.

Three factors that have an impact on the design of the solids-handling system of the thermal desorption system are particle size distribution, moisture content, and soil type. The soil particle size should be 0.5 to 1 inch (13 to 25.4 millimeters) in diameter for full-scale treatment units to minimize operating costs. Mechanical screens may be used to remove coarser soil particles that may reduce the overall effectiveness of treatment. Energy and residence time requirements for treatment are affected by moisture content, particle size distribution, permeability, and soil types. Contaminant concentration may also affect energy and residence time requirements, off-gas organic concentration, and ultimate soil disposition.

6.4.3.5.1.3 Management of Side-Waste Streams

Side-waste streams generated from thermal desorption systems include off-gases and residues from emission control (such as, activated carbon, condensate, and particulate filters). Depending on regulatory requirements, the off-gas treatment may be costly and constrained by strict emissions limits. Disposal of residues may involve analytical testing and proper disposal. Some operators have chosen to add an afterburner to the thermal desorption system to complete thermal destruction of the contaminants. Other possible alternatives for handling recovered organics include reclamation off-site or use of supplemental fuels.

The treated soil may require testing and regulatory approval before it can be used on-site as backfill. Specific testing required for treated soil may include nutrient levels, ability to retain moisture, compressibility, compaction, and ability to sustain plant and bacterial life.

6.4.3.5.2 Incineration

6.4.3.5.2.1 Description

Incineration systems can be either indirect-heated (rotary tube) or direct-fired (rotary kiln and fluid bed) systems. These systems are applicable to soils containing both volatile and semivolatile organics and can achieve low residual organic concentrations in the treated soil.

Indirect-heated systems are rotary tube designs that have been used primarily to process soils and sludges lightly contaminated with organic constituents. They consist of a nonrotating outer tube with a concentric inner tube that rotates and conveys the solids from the feed end to the discharge end (see Figure 26). In between the inner and outer tubes are multiple burners that transfer heat through the inner tube to the solids. Because they are indirectly heated, these systems are compact in size due to the small volume of offgas generated and the small size of the gas cleaning system. In addition, they can also process solids up to 2 inches (51 millimeters) in size. Because the inner and outer tubes are isolated (sealed) from each other, these systems can be designed to recover organics contained in the waste feeds. These indirect-heated systems can heat solids up to 1,000°F (538°C).

Rotary kiln incinerators are commonly used in *direct-fired systems* to treat hydrocarbon-impacted soil. These incinerators consist of a primary (combustion) chamber, in which the soil and solids are mixed and heated to drive off moisture and organics, and a secondary combustion chamber that oxidizes the volatilized contaminants from the primary combustion chamber (see Figure 27). Pyrolysis or oxidation of nonvolatile organics can also take place in the primary chamber; this may be important in meeting treatment criteria for residual organics. The most predominant type of system used for large-scale on-site treatment of organic contaminated soils has been rotary kiln incinerators.

Fluidized bed designs have been used on a limited basis to incinerate low-Btu content soils with small particle sizes. They maintain stable combustion of contaminated soils that have a broad water content range because the fluidized bed media provides a significant heat sink and temperature buffer. Fluidized and circulating bed designs have been used to incinerate sludges and soils (see Figure 28). Both systems rely on an inert bed (usually sand, but soil can be used as the bed material) as the heat transfer body. Pressurized air is forced into a vertical chamber where the air is used to fluidize the sand. Air passage through the bed promotes rapid and relatively uniform mixing and intimate air contact with the contaminated soil. Heat is transferred from the bed to the contaminated soil; and as a result, efficient combustion occurs at lower operating temperatures than in rotary kilns with excess air levels.

The specific advantages of incinerators are as follows:

a. Treatment time is relatively short (15 to 60 minutes).
b. They are capable of meeting low treatment criteria for low-volatility organics.
c. On-site use minimizes soil handling by eliminating transportation off-site.
d. Treated soil may be used as backfill.

The disadvantages and limitations of incinerators include the following:

a. Hazardous waste regulations may apply when treating RCRA wastes if organics are not recovered and recycled.
b. Potential fusion and slagging of low-melting-point eutectic mixtures result from the thermal treatment of diverse materials.
c. Treatment costs can be high.

6.4.3.5.2.2 Feasibility and Design Considerations

Prior to implementing on-site incineration, a trial burn may be necessary to demonstrate the suitability of this approach for a particular soil type. The feasibility and proper design of an on-site incineration system may be affected by:

a. Moisture content of the soil.
b. Particle size distribution in the soil.
c. Permeability of the soil.
d. Soil type.
e. Contaminant type, concentration, and distribution.
f. Existence of metals, chlorinated compounds, and other contaminants.
g. Ash fusion temperature of the soil.
h. Ash content of the end product.

The moisture content of the soil is inversely proportional to the operating efficiency. Soils generally possess low-Btu values, which result in high energy costs. High moisture content in the soil will further escalate energy costs for incineration. Therefore, soil with excessive moisture content should be pretreated before being incinerated. This soil can be treated by air-drying or by putting an additive (such as lime) into the soil.

A decision as to whether incineration should be conducted on-site or off-site depends on several factors, including the volume of contaminated soil, cost, utility availability, and pollution control equipment and regulatory permit requirements. This process also has substantial operation, maintenance, and monitoring requirements.

6.4.3.5.3 Management of Side-Waste Streams

Secondary wastes generated from high-temperature desorption systems will vary depending on the gas cleaning system used. Wastes will be either fly ash, if a dry or dry/wet system is used, or a wastewater purge stream, if wet pollution control equipment is used. These secondary wastes will contain carryover (such as fine soil particles) as well as alkali and metal salts, if present in the soil. The partitioning of metals in the thermal unit and in the gas cleaning system will be one factor in determining the final disposition of secondary wastes.

The water purge from a wet pollution control system may require treatment before discharge, depending on the discharge option. Treatment of purge water, particularly to remove suspended solids or heavy metals, will result in wastewater sludges that will require disposal.

(text continued on page 77)

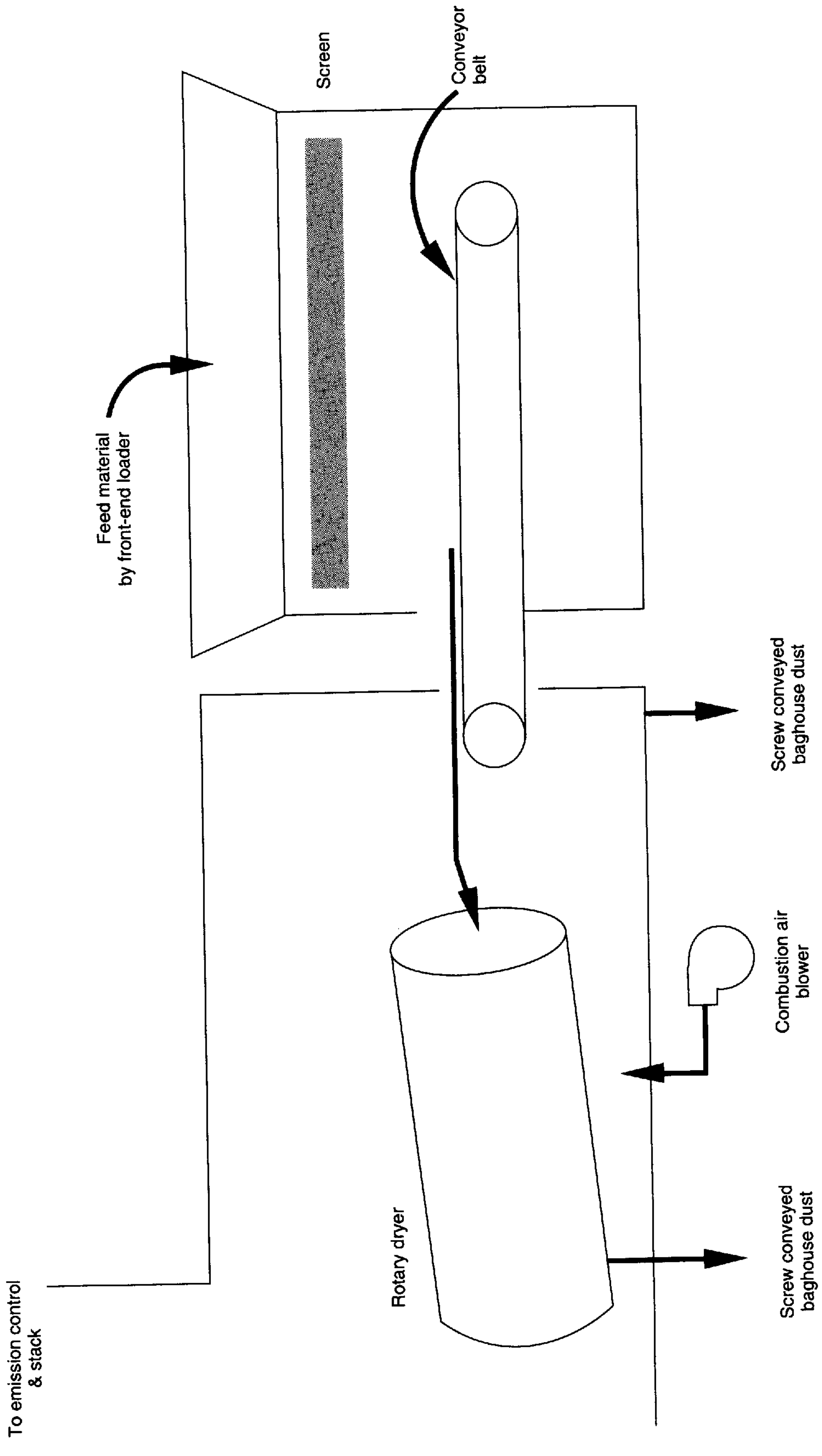


Figure 26—Schematic of a Rotary Tube System

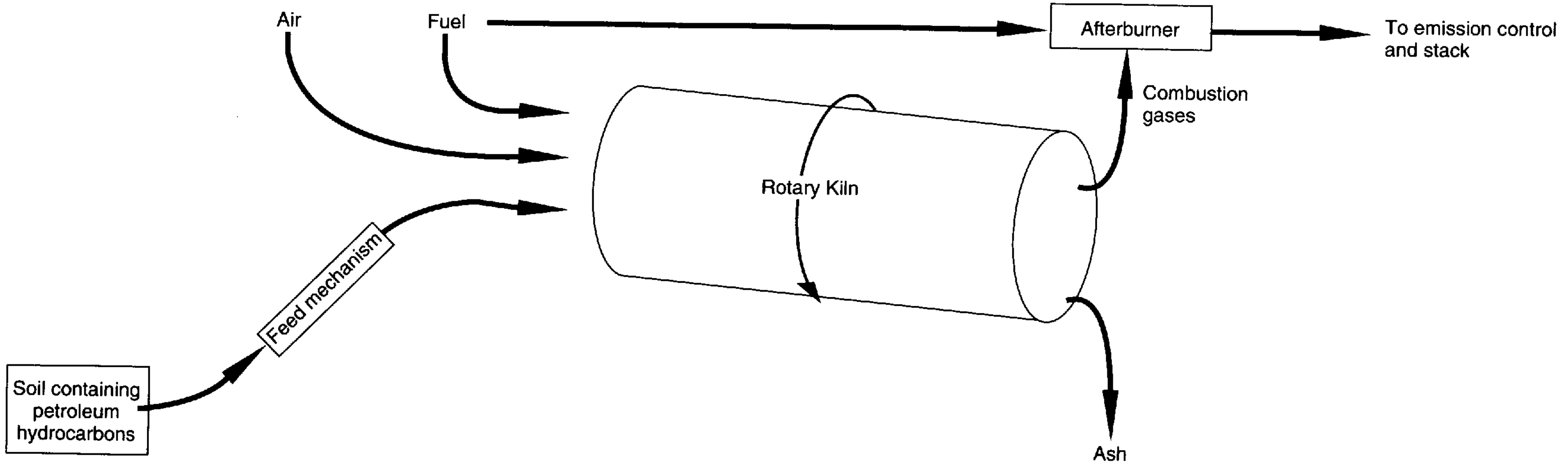


Figure 27—Schematic of a Rotary Kiln Incinerator

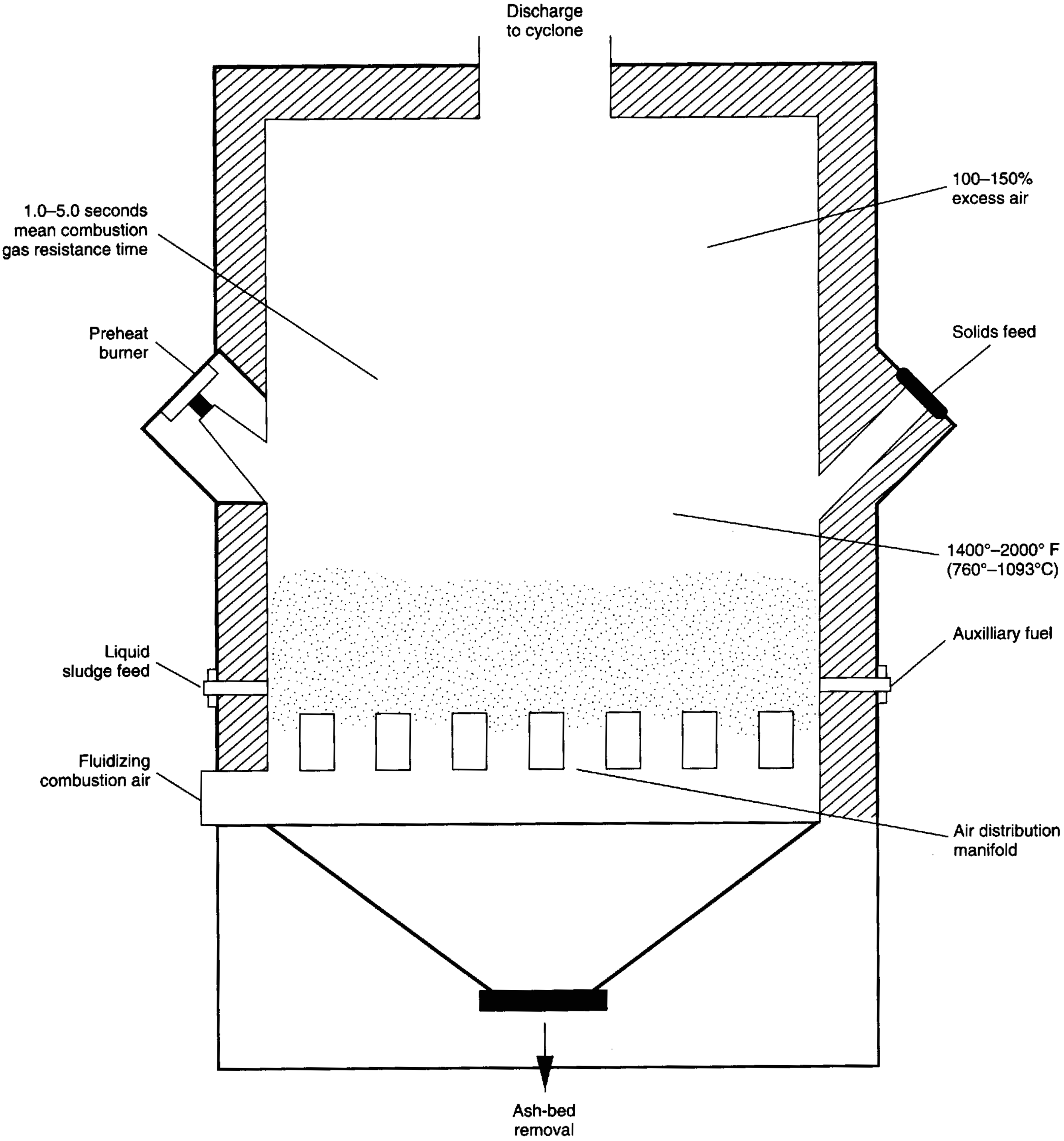


Figure 28—Schematic of a Fluid-Bed System

SECTION 7—REFERENCES

7.1 Referenced Publications

The following references are cited in this publication. Unless otherwise noted, the most recent editions should be consulted.

1. API Publication 1628, *A Guide to the Assessment and Remediation of Underground Petroleum Releases*, American Petroleum Institute, Washington, DC.
2. *Guide to Chemical Hazards* (Publication No. 85-114), National Institute for Occupational Safety and Health, U.S. Department of Health and Human Services, Washington, DC.
3. 29 *Code of Federal Regulations* Part 1910, Occupational Safety and Health Administration, U.S. Department of Labor, Government Printing Office, Washington, DC.
4. *Threshold Limit Values and Biological Exposure Indices*, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio.
5. 29 *Code of Federal Regulations* Part 1910.1200, Occupational Safety and Health Administration, U.S. Department of Labor, Government Printing Office, Washington, DC.
6. 29 *Code of Federal Regulations* Part 1910.120, Occupational Safety and Health Administration, U.S. Department of Labor, Government Printing Office, Washington, DC.
7. *Underground Leakage of Flammable and Combustible Liquids* (NFPA 329) National Fire Protection Association, Quincy, MA.
8. 40 *Code of Federal Regulations* Part 280, U.S. Environmental Protection Agency, Government Printing Office, Washington, DC.
9. ABB Environmental Services, Inc., *Compilation of Data on the Composition, Physical Characteristics and Water Solubility of Fuel Products*, prepared for Massachusetts Department of Environmental Protection, Wakefield, MA, December 1990.
10. W. Lyman, "Environmental Partitioning of Gasoline in Soil/Groundwater Compartments," *Seminar Summary: Motor Fuel and Organic Chemicals Released in an Underground Environment*, Hazardous Waste Environmental Research Laboratory, U.S. Environmental Protection Agency, Edison, NJ, February 1988.
11. Adapted with permission from *Environmental Science and Technology*, May 1991, Volume 25, pp. 914–920. Copyright 1991 American Chemical Society.
12. API Recommended Practice 1621, *Bulk Liquid Stock Control at Retail Outlets*, American Petroleum Institute, Washington, DC.
13. *Field Measurements: Dependable Data When You Need It* (EPA-530/UST-90-003), U.S. Environmental Protection Agency, Washington, DC, 1990.
14. *Test Methods for Evaluating Solid Waste—Volume 1A:Laboratory Manual, Physical/Chemical Methods* (EPA SW-846), Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC.
15. API Publication 4516, *Sampling and Analysis of Gasoline Range Organics in Soil*, American Petroleum Institute, Washington, DC.
16. 40 *Code of Federal Regulations* Part 261, Appendix II, U.S. Environmental Protection Agency, Government Printing Office, Washington, DC.
17. ASTM D-93, *Test Methods for Flash Point by Pensky-Martens Closed Tester*, American Society for Testing and Materials, Philadelphia, PA.
18. ASTM D-3278, *Test Methods for Flash Point of Liquids by Setaflash-Closed-Cup Apparatus*, American Society for Testing and Materials, Philadelphia, PA.
19. P. C. Johnson *et al.*, "A Practical Approach to the Design, Installation and Operation of Soil Venting Systems," *Groundwater Monitoring Review*, Spring 1990, Volume 10, Number 2.
20. J. Dragun, *The Soil Chemistry of Hazardous Materials*, Hazardous Materials Control Research Institute, Silver Spring, MD, 1988.
21. R. A. Freeze and J. A. Cherry, *Groundwater*, Prentice-Hall, Inc., Englewood Cliffs, NJ, 1979.
22. *A Compendium of Superfund Field Operation Methods* (EPA-540/P-87/001), Office of Emergency and Remedial Response, U.S. Environmental Protection Agency, Washington, DC.
23. B. Manchon, "Workshop: Introduction to Cone Penetrometer Testing and Groundwater Samplers," presented at Fifth National Outdoor Action Conference on Aquifer Restoration, Groundwater Monitoring, and Geophysical Methods, National Ground Water Association, Dublin, OH, May 1991.
24. Geoprobe Systems, Sales Brochure, Salina, KS, 1990.
25. Environmental Solutions, Inc., *On-Site Treatment of Hydrocarbon-Contaminated Soils*, prepared for the Western States Petroleum Association, Glendale, CA, 1990.
26. L. M. Preslo *et al.*, *Remedial Technologies for Leaking Underground Storage Tanks*, prepared for the Electric Power Research Institute and Edison Electric Institute, Lewis Publishers, Inc., Chelsea, MI, 1988.
27. Petroleum Product Surveys, *Motor Gasoline*, Summer 1986, Number NIPER-148 pps, 87/1, National Institute for Petroleum and Energy Research, Bartlesville, OK.
28. Petroleum Product Surveys, *Motor Gasoline*, Winter 1986/1987, Number NIPER-150 pps, 87/3, National Institute for Petroleum and Energy Research, Bartlesville, OK.
29. API Publication 4261, *Alcohol and Ethers*, American Petroleum Institute, Washington, DC.
30. *Handbook of Chemistry and Physics*, 62nd edition, The Chemical Rubber Company Press, Inc., Boca Raton, FL, 1981.
31. Petroleum Product Surveys, *Diesel Fuel Oils*, October

1987, National Institute for Petroleum and Energy Research, Bartlesville, OK.

32. ARCO Chemical Company, *Determination of Co-Extraction Effects of Oxygenated Fuels Including MTBE*, report submitted to the Office of Toxic Substances, U.S. Environmental Protection Agency, July 1, 1987.

33. "Status of Alcohol Fuels Utilization Technology for Highway Transportation: A 1981 Perspective," *Spark-Ignition Engine*, May 1982, Volume 1 (DOE/CE/56051-7), Department of Energy, Washington, DC.

34. *Data Compilation Tables of Properties of Pure Compounds*, Design Institute for Physical Property Data, American Institute of Chemical Engineers, New York, 1984.

35. API Monograph Series, Publication 723, *tert-Butyl methyl ether*, American Petroleum Institute, Washington, DC.

36. API *Technical Data Book—Petroleum Refining*, Volume 1, Chapter 1, American Petroleum Institute, Washington, DC.

37. SAE Recommended Practice J312, *Automotive Gasolines*, 1988 SAE Handbook, Volume 3, Society of Automotive Engineers, Warrendale, PA, May 1986.

38. W. Shill *et al.*, "The Water Solubility of Crude Oils and Petroleum Products," *Oil and Chemical Pollution*, 1990, Volume 7, pp. 47–84.

39. J. W. Mercer and R. W. Cohen, "A Review of Immiscible Fluids in the Subsurface: Properties, Models, Characterization, and Remediation," *Journal of Contaminant Hydrology*, 1990, Volume 6, El Sevier Science Publishers, B.V., Amsterdam.

40. *Methods for Chemical Analysis of Water and Wastes* (EPA-600/4-79-020), Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH, 1979.

41. Billings and Associates, Inc., *SVVS Remediation Technology*, Albuquerque, NM, 1990.

7.2 Suggested Further Reading

The following publications are suggested materials for further information on assessing and remediating petroleum hydrocarbons in soils. Unless otherwise noted, consult the latest editions.

7.2.1 BACKGROUND

7.2.1.1 Basic Geology and Hydrology

H. O. Butman and N. C. Brady, *The Nature and Properties of Soils*, Macmillan Publishing Co., New York, 1972.

7.2.1.2 Physical and Chemical Behavior of Hydrocarbons and By-Products

API Publication 4415, *Literature Survey: Unassisted Natural Mechanisms to Reduce Concentrations of Soluble Gasoline Components*, American Petroleum Institute, Washington, DC.

API Publication 4528, *Petroleum Release Decision Framework—User's Manual*, American Petroleum Institute, Washington, DC.

B. Bauman, *Research Needs: Motor Fuel Contaminated Soils*, American Petroleum Institute, Washington, DC, 1991, pp. 1–12.

B. Bauman, *Soils Contaminated by Motor Fuels: Research Activities and Perspectives of the American Petroleum Institute*, American Petroleum Institute, Washington, DC, 1987, pp. 1–17.

S. L. Houston, D. K. Kreamer, and R. Marwig, "A Batch-Type Testing Method for Determination of Adsorption of Gaseous Compounds on Partially Saturated Soils," *Geotechnical Testing Journal*, GTJODJ, March 1989, Volume 12, Number 1, pp. 3–10.

Interim Report, Fate and Transport of Substances Leaking from Underground Storage Tanks, Volume 1—Technical Report, Office of Underground Storage Tanks, U.S. Environmental Protection Agency, Washington, DC, January 1986, pp. 1-1-8-12.

P. D. Kuhlmeier, "Movement of Gasoline Components Through Unsaturated Heterogeneous Soils," *Industrial Waste Treatment*, IT Corporation, Knoxville, TN, undated, pp. 350–371.

M. P. Maskarinec *et al.*, "Stability of Volatile Organic Compounds in Environmental Water Samples During Transport and Storage," *Environmental Science and Technology*, 1990, Volume 24, Number 11, pp. 1665–1670.

E. M. Shelton *et al.*, *Trends in Motor Gasolines: 1942-1981* (DOE/BETC/RI-82/4), Department of Energy, Washington, DC, 1982.

Short-Term Fate and Persistence of Motor Fuels in Soils, Radian Corporation, Austin, TX, July 11, 1988.

G. Thomas *et al.*, *Environmental Fate and Attenuation of Gasoline Components in the Subsurface*, Rice University, Houston, TX, 1988.

7.2.1.3 General

R. A. Conway and R. D. Ross, *Handbook of Industrial Waste Disposal*, Van Nostrand Reinhold Company, New York, 1980.

J. J. Hills, *A State's Perspective of the Problems Associated With Petroleum-Contaminated Soils*, Division of Environmental Health, Orange County, CA, undated.

Midwest Research Institute, *Survey of State Programs Pertaining to Contaminated Soils*, Office of Underground Storage Tanks, U.S. Environmental Protection Agency, Washington, DC, March 22, 1988, pp. 1–27.

7.2.2 ASSESSMENT OF HYDROCARBONS

API Publication 4394, *Detection of Hydrocarbons in Groundwater by Analysis of Shallow Soil Gas/Vapor*, American Petroleum Institute, Washington, DC.

API Publication 4449, *Manual of Sampling and Analytical Methods for Petroleum Hydrocarbons in Groundwater and Soil*, American Petroleum Institute, Washington, DC.

J. Fitzgerald, *On-Site Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure*, Department of Environmental Quality Engineering, Commonwealth of Massachusetts, Woburn, MA, undated.

T. Holbrook, "Combining Two Field Methods of Soil Gas Analysis to Define the Horizontal and Vertical Extent of Soil Contamination," *Proceedings—Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration,* 1988, Volume II, Water Well Journal Publishing Company, Dublin, OH, pp. 91–104.

T. Holbrook, *Investigating Subsurface Fuel Releases Using Ambient Temperature Headspace Analysis*, ERT, Inc., Fort Collins, CO, undated.

IT Corporation, "Sampling and Analytical Methods for Determining Petroleum Hydrocarbons in Groundwater and Soil," *Proceedings—API Workshop*, Denver, CO, November 1984.

P. C. Johnson, M. B. Hartz, and D. L. Beyers, "Estimates for Hydrocarbon Vapor Emissions Resulting from Service Station Remediations and Buried Gasoline-Contaminated Soils," *Petroleum Contaminated Soils*, 1990, Volume 3, Lewis Publications, Inc., Chelsea, MI.

Midwest Research Institute, *Site Sampling and Field Measurements Handbook for Underground Storage Tank Releases* (Draft Report), Office of Underground Storage Tanks, U.S. Environmental Protection Agency, Washington, DC, September 1987.

Midwest Research Institute, *Determining If Soils Contaminated With Petroleum Products Are Hazardous Wastes,* Draft Report, U.S. Environmental Protection Agency, Washington, DC, April 1988, pp. 1–19.

T. L. Potter, *Analysis of Petroleum-Contaminated Soil and Water: An Overview*, University of Massachusetts, Amherst, MA, undated.

G. A. Robbins *et al.*, "Soil-Gas Surveying for Subsurface Gasoline Contamination Using Total Organic Vapor Detection Instruments, Part 1: Theory and Experimentation," *Groundwater Monitoring Review*, 1990, Volume 10, Number 3, pp. 122–131.

G. A. Robbins *et al.*, "Soil-Gas Surveying for Subsurface Gasoline Contamination Using Total Organic Vapor Detection Instruments, Part II: Field and Experimentation," *Groundwater Monitoring Review*, 1990, Volume 10, Number 4, pp. 110–117.

G. A. Robbins, *Use of Headspace Sampling Techniques in the Field to Quantify Levels of Gasoline Contamination in Soil and Groundwater*, University of Connecticut, Storrs, CT, undated, pp. 307–315.

G. A. Robbins *et al.*, "A Field Screening Method for Gasoline Contamination Using a Polyethylene Bag Sampling System," *Groundwater Monitoring Review*, 1989, Volume 4, Number 4, pp. 87–97.

S. K. Stokman, *Estimates of Concentrations of Soluble Petroleum Hydrocarbons Migrating Into Groundwater From Contaminated Soil Sources*, New Jersey Department of Environmental Protection and Energy, Division of Hazardous Site Mitigation, Trenton, NJ, undated.

7.2.3 VENTING

"Air Sparging Improves Effectiveness of Soil Vapor Extraction Systems," *The Hazardous Waste Consultant*, March/April 1991, Volume 9, Number 2, McCoy & Associates, Inc., Lakewood, CO, pp. 1.1–1.4.

API Publication 4410, *Subsurface Venting of Hydrocarbons from an Underground Aquifer*, American Petroleum Institute, Washington, DC.

API Publication 4429, *Examination of Venting for Removal of Gasoline Vapors from Contaminated Soil*, American Petroleum Institute, Washington, DC.

G. V. Batchelder *et al.*, *Soil Ventilation for the Removal of Absorbed Liquid Hydrocarbons in the Subsurface*, Groundwater Technology, Inc., Norwood, MA, undated, pp. 672–688.

P. C. Johnson, "Practical Screening Models for Soil Venting Systems," *Proceedings—Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Restoration*, Water Well Journal Publishing Company, Dublin, OH, 1988.

R. L. Johnson, "Soil Venting for Remediation of Subsurface Gasoline Releases: Implications of Subsurface Gasoline Transport on the Effectiveness of Soil Vacuum Extraction," presented at Petroleum Hydrocarbons and Organic Chemicals in Groundwater, NWWA/API Conference, Houston, TX, November 1989, National Ground Water Association, Dublin, OH.

Phase I-Case History Review, Field Evaluation of Above-Ground Venting of Gasoline-Contaminated Soils, Roy F. Weston, Inc., West Chester, PA, May 1988, pp. 1-1–7-1.

7.2.4 BIOREMEDIATION

API Publication 4448, *Field Study of Enhanced Subsurface Biodegradation of Hydrocarbons Using Hydrogen Peroxide as an Oxygen Source*, American Petroleum Institute, Washington, DC.

R. Bartha, "Biotechnology of Petroleum Pollutant Biodegradation," *Microbial Ecology*, 1986, Volume 12, Springer-Verlag, New York, pp. 155–172.

P. G. Berwick, "Physical and Chemical Conditions for Microbial Oil Degradation," *Biotechnology and Bioengineering*, Volume XXVI, 1984.

Bioremediation of Contaminated Surface Soils (EPA-600/9-89/073), U.S. Environmental Protection Agency, R. S. Kerr ERl, Ada, OK, 1989.

P. L. Brookner *et al.*, "A Cost-Effective Alternative for Diesel-Contaminated Soil Disposal: Biological Degradation Using Land Farming Techniques," *Proceedings—Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*, 1988, Volume II, Water Well Journal Publishing Company, Dublin, OH, pp. 613–624.

D. T. Gibson, *Microbial Degradation of Organic Compounds,* Microbiology Series, Volume 13, Marcel-Dekker, New York, 1984.

R. E. Hinchee *et al*, "Enhanced Bioreclamation, Soil Venting and Groundwater Extraction: A Cost-Effectiveness and Feasibility Comparison," undated, pp. 147–164.

V. W. Jamison *et al.*, "Biodegradation of High-Octane Gasoline," *Proceedings of the Third International Biodegradation Symposium*, edited by Sharpley and Kaplan, Applied Science Publishers, London, 1976.

D. H. Kampbell, *Removal of Volatile Aliphatic Hydrocarbons in a Soil Bioreactor*, U.S. Environmental Protection Agency, Washington, DC, October 1986.

P. D. Kuhlmeier and G. L. Sunderland, *Biotransformation of Petroleum Hydrocarbons in Deep Unsaturated Sediments*, Geraghty & Miller, Inc., Oak Ridge, TN, and O.H. Materials, Inc., Findlay, OH, undated, pp. 445–462.

J. Oudot, "Rates of Microbial Degradation of Petroleum Components as Determined by Computerized Capillary Gas Chromatography and Computerized Mass Spectrometry," *Marine Environmental Research 13*, Applied Science Publishers, London, 1984.

H. Song *et al.*, "Bioremediation Potential of Terrestrial Fuel Spills," *Applied and Environmental Microbiology*, 1990, Volume 56, Number 3.

7.2.5 TREATMENT

R. Ayen and C. Swanstrom, "Development of a Transportable Thermal Separation Process," *Environmental Progress*, August 1991.

Camp, Dresser & McKee, Inc., *Cleanup of Releases From Petroleum USTs: Selected Technologies*, prepared for U.S. Environmental Protection Agency, Washington, DC, April 1988.

Camp, Dresser & McKee, Inc., *Selecting Soil Treatment Technologies*, prepared for U.S. Environmental Protection Agency, Washington, DC, September 30, 1988.

P. Daley, "Clean Up Sites with On-Site Process Plants," *Environmental Science and Technology*, August 1989, Volume 23, Number 8, pp. 912–916.

D. C. Downey *et al.*, "Combined Biological and Physical Treatment of a Jet Fuel-Contaminated Aquifer," *Proceedings—Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*, 1988, Volume II, Water Well Journal Publishing Company, Dublin, OH, pp. 627–644.

Environmental Solutions, Inc., *On-site Treatment, Hydrocarbon Contaminated Soils*, prepared for Western State Petroleum Association, Irvine, CA.

H. Freeman, *Innovative Thermal Processes for Treating Hazardous Wastes*, Technomic Publishing Co., Lancaster, PA, 1986.

D. Hazaga *et al.*, *Thermal Treatment of Solvent Contaminated Soils*, U.S. Environmental Protection Agency, Atlanta, GA, undated, pp. 404–406.

ICF, Inc., *Petroleum UST Corrective Action Case Studies, A Look at the Real Work and Franchiser Opportunities for UST Corrective Action*, U.S. Environmental Protection Agency, Washington, DC, September 6, 1988.

IT Corp., *Selected Treatment Technologies for the Remediation of Oil and Gas Spill Sites,* prepared for Conoco, Inc., Cincinnati, Ohio, 1991.

M. Min, R. Barbour, and J. Hwang, "Treating Land Ban Waste," *Pollution Engineering*, August, 1991, Volume 23, Number 8, pp. 64–70.

J. Newton, "Remediation of Petroleum Contaminated Soils," *Pollution Engineering*, December 1990, p. 46–52.

PEI Associates, Inc., *Hazardous Waste Incineration Handbook,* prepared for U.S. Environmental Protection Agency, Center of Environmental Research Information, Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, September 1987.

PEI Associates, Inc., *Underground Storage Tank Corrective Action Technologies* (EPA/62516-87-0151), prepared for U.S. Environmental Protection Agency, Cincinnati, OH, January 1987.

R. Scholz and J. Milanowski, *Mobile System for Extracting Spilled Hazardous Materials From Excavated Soils* (EPA-600/2-83-100), prepared by Rexnord, Inc. for Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH, 1983.

Thermal Treatment Process for Fuel-Contaminated Soil, Staff Report, Toxic Substances Control Program, Alternative Technology Division, California Department of Health Services, March 1990.

VOC Testing, Inc., Emission Test Report, Rotary Kiln Asphalt Aggregate Dryer Used to Decontaminate Soil at South Coast Asphalt Products Company, Inc., Carlsbad and San Bernardino, CA, June 1986, pp. 1-1-5-1.

7.2.6 PROTECTION

C. E. Bell, P. T. Kostecki, and E. J. Calabrese, "State of Research and Regulatory Approach of State Agencies for Cleanup of Petroleum Contaminated Soils," presented at The First Annual Real Estate Assessment Conference, November 30–December 1, 1988, Environmental Health Science Program, University of Massachusetts, Amherst, MA.

California State Water Resources Control Board, California Underground Storage Tank Regulations and Related Health and Safety Code Sections, Division 20, Chapter 6.7, Sections 25280–25299.6, August 1985.

City of Los Angeles, California, "Underground Tanks," Fire Code, Division 31, Sections 57.31.01–57.31.05 and 57.31.30–57.31.54, 1987.

City of Los Angeles, California, "Abandonment of Underground Tanks," Fire Department Requirement, F.P.B. Requirement No. 41, September 10, 1987.

R. A. Ogle, "Disposal of Hydrocarbon Contaminated Soil," *Proceedings—Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration*, Water Well Journal Publishing Company, Dublin, OH, November 1986, pp. 459–469.

Policy Regarding Fuel-Contaminated Soil and Ground, Department of Health Services, County of San Diego, San Diego, CA, March 20, 1987.

State of California, Leaking Underground Fuel Tank (LUFT) Field Manual, Leaking Underground Fuel Tank Force, State Water Resources Control Board, Department of Health Services, Sacramento, CA, 1990.

Order No. 804-16290

1-1400—10/93—2.5M (9C)

American Petroleum Institute
1220 L Street, Northwest
Washington, D.C. 20005