

Guide for Assessing and Remediating Petroleum Hydrocarbons in Soils

API PUBLICATION 1629
FIRST EDITION, OCTOBER 1993



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



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Manufacturing, Distribution and Marketing Department

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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*.

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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.

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.

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)

1.5 Referenced Publications

A large body of reference material was assembled and used in developing this document. A list of relevant literature is presented in 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 ex-

tends 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 back-fill 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

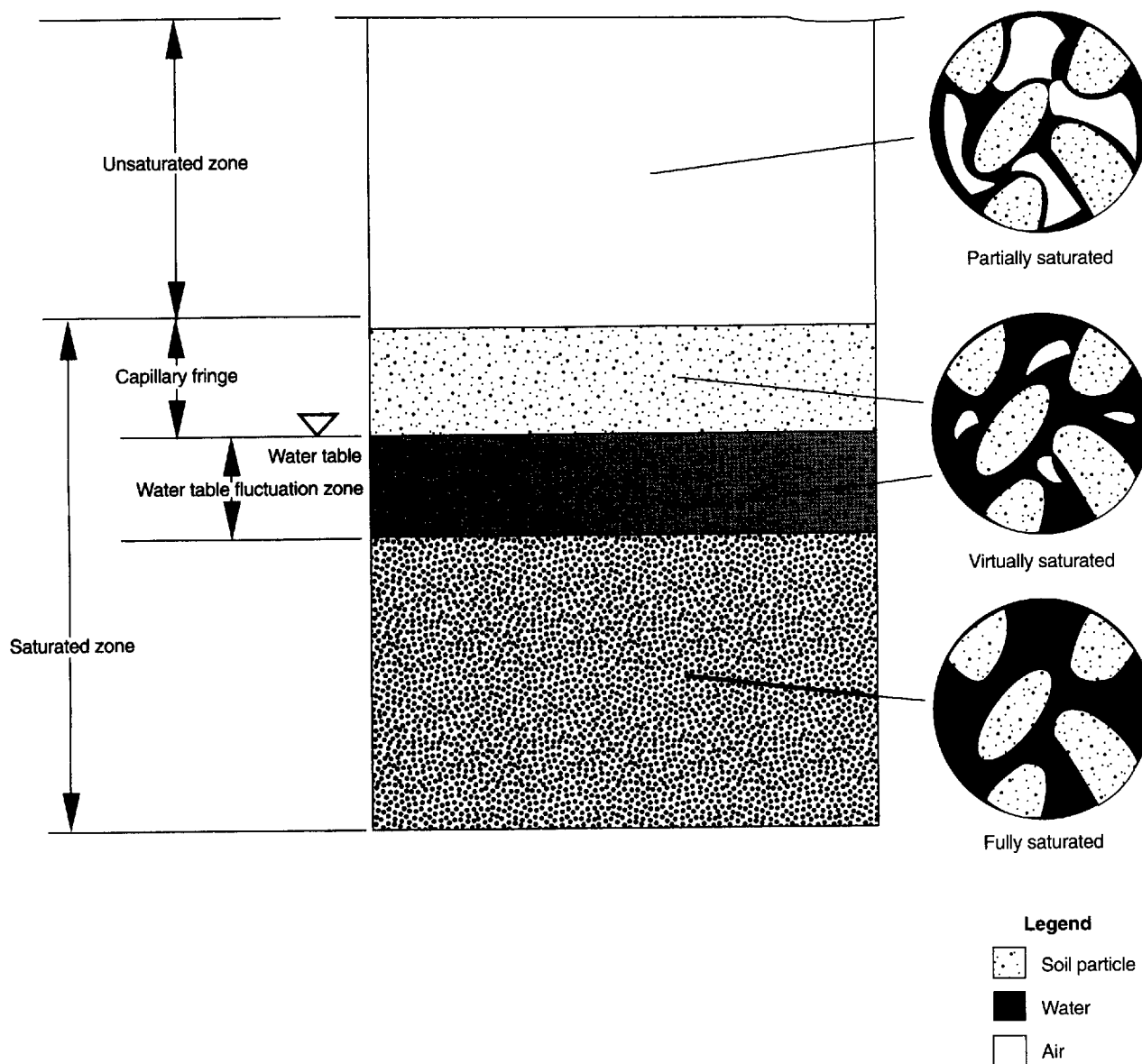
Porosity or *total porosity* is the ratio of the volume of void space in the soil to the total volume of soil material; it is expressed as a percentage. The following are typical total porosity values for different soils:

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.

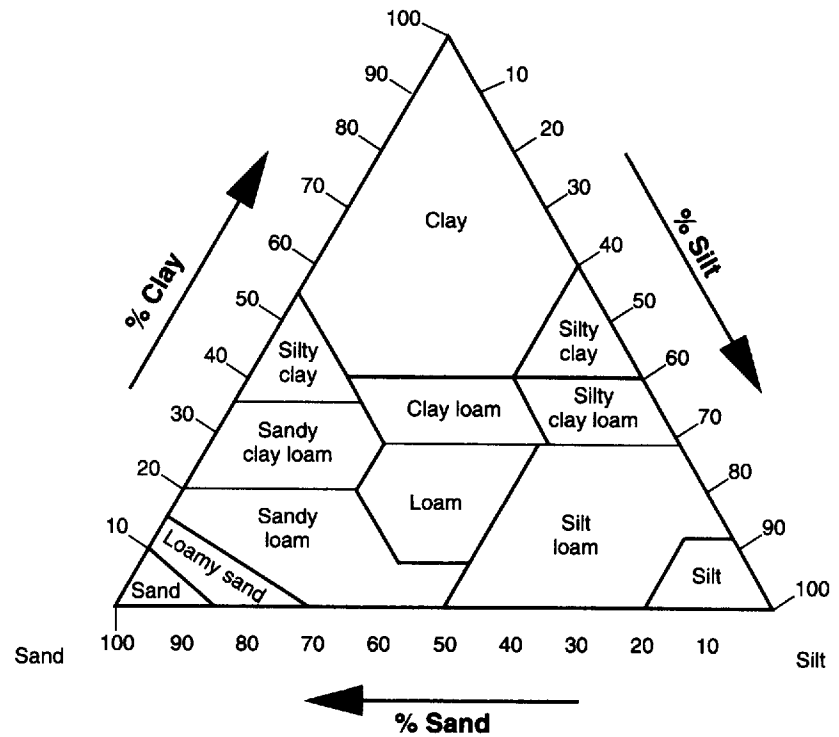
Porosity is also affected by the shape of the particles in the soil. Spherically shaped soil particles pack together more tightly and exhibit less porosity than particles of other shapes, such as plates or rods. Clay particles, for example, vary in shape and do not tend to pack closely together. Thus,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

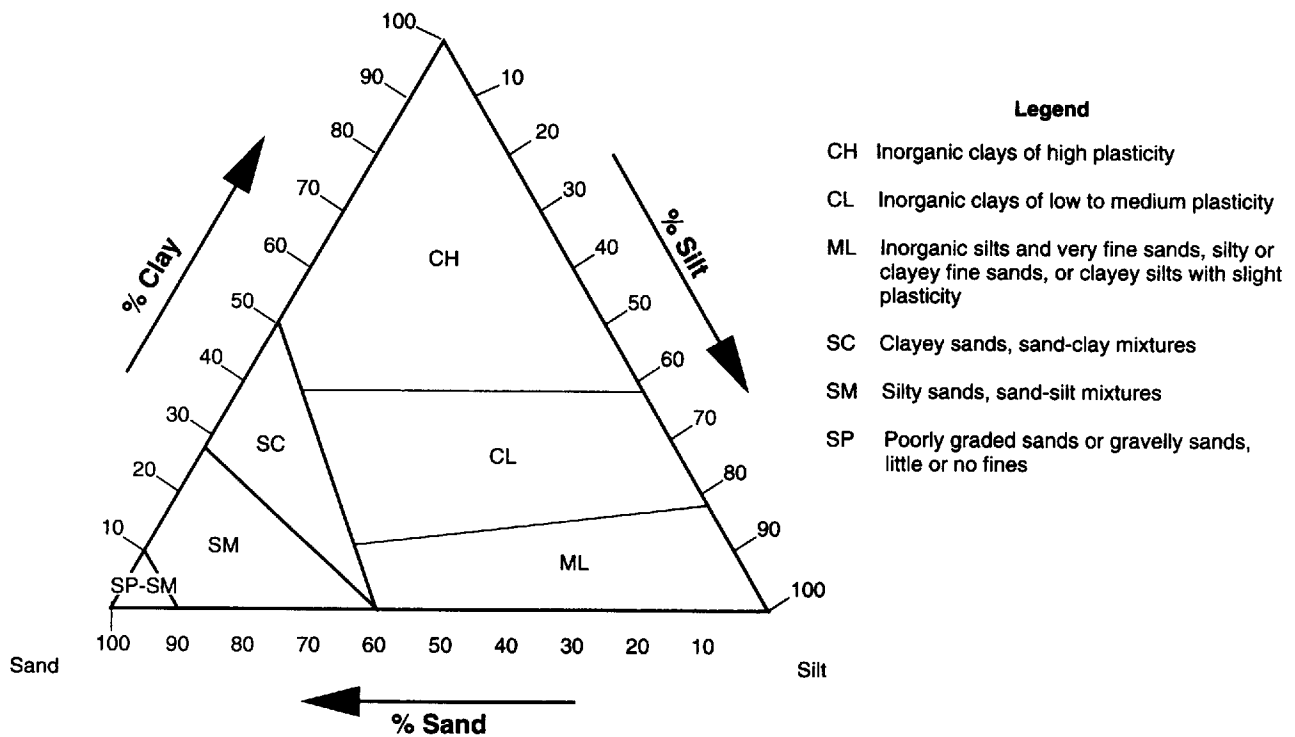


Source: Modified from API Publication 1628 [1].

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).

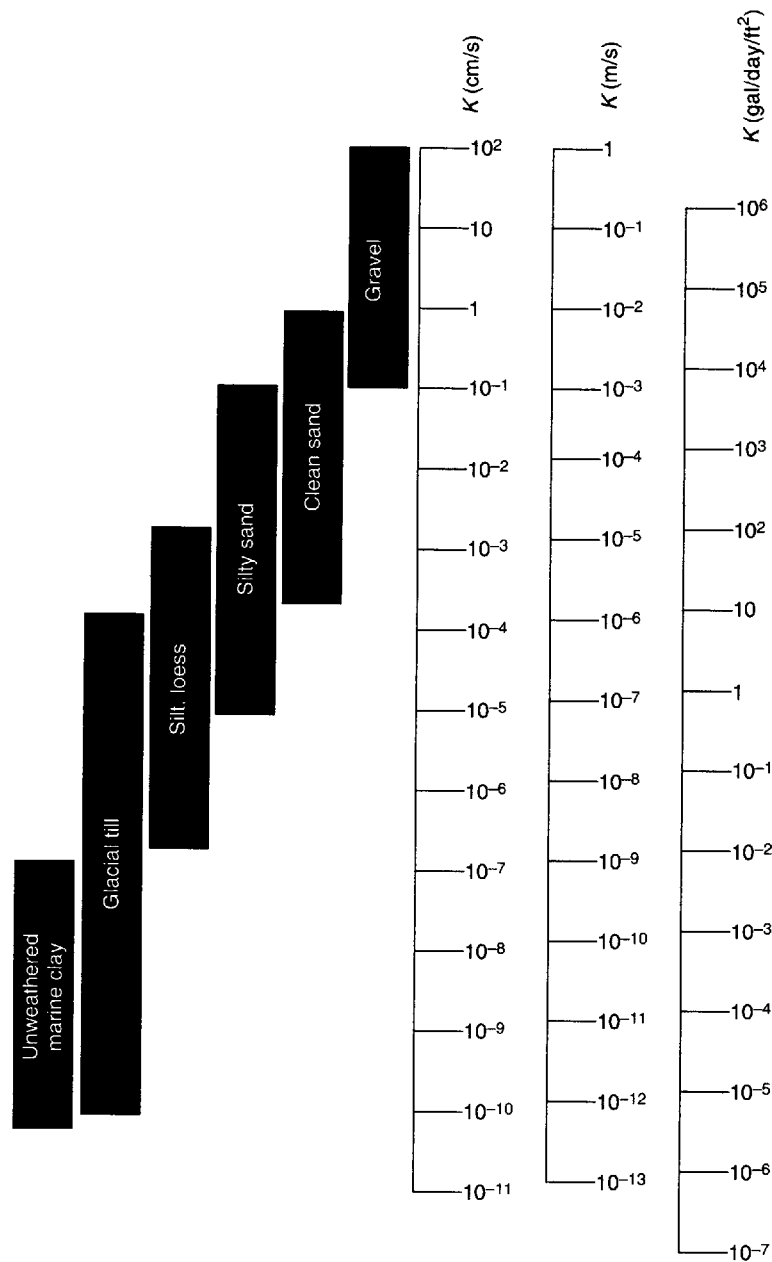
The composition of gasoline blends varies with different locations and seasons. Although the variations in the bulk blends are not large, the sulfur, oxygen compounds, trace metals, and volatile constituent contents (such as BTEX) vary significantly (14 to 20 percent by weight) [9]. Seventeen districts 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.



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Note: K = hydraulic conductivity; cm/s = centimeters per second; m/s = meters per second; gal/day/ft² = 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 ₃ OH	C ₂ H ₅ OH	(CH ₃) ₃ COCH	(CH ₃) ₃ COCH	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.

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

^bCalculated.

^cSAE Recommended Practice J312 [37].

^dAPI Technical Data Book—*Petroleum Refining* [36].

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

^fPetroleum Product Surveys, *Motor Gasoline* [27, 28].

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

^hPetroleum Product Surveys, *Diesel Fuel Oils* [31].

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

^jAPI Publication 723 [35].

^kP. V. Cline *et al.*, "Partitioning of Aromatic Constituents into Water from Gasoline and Other Complex Solvent Mixtures" [11].

^lShill, 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 oxy-

genates 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 re-

main 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)



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Table 3—Properties of Selected Hydrocarbon Constituents

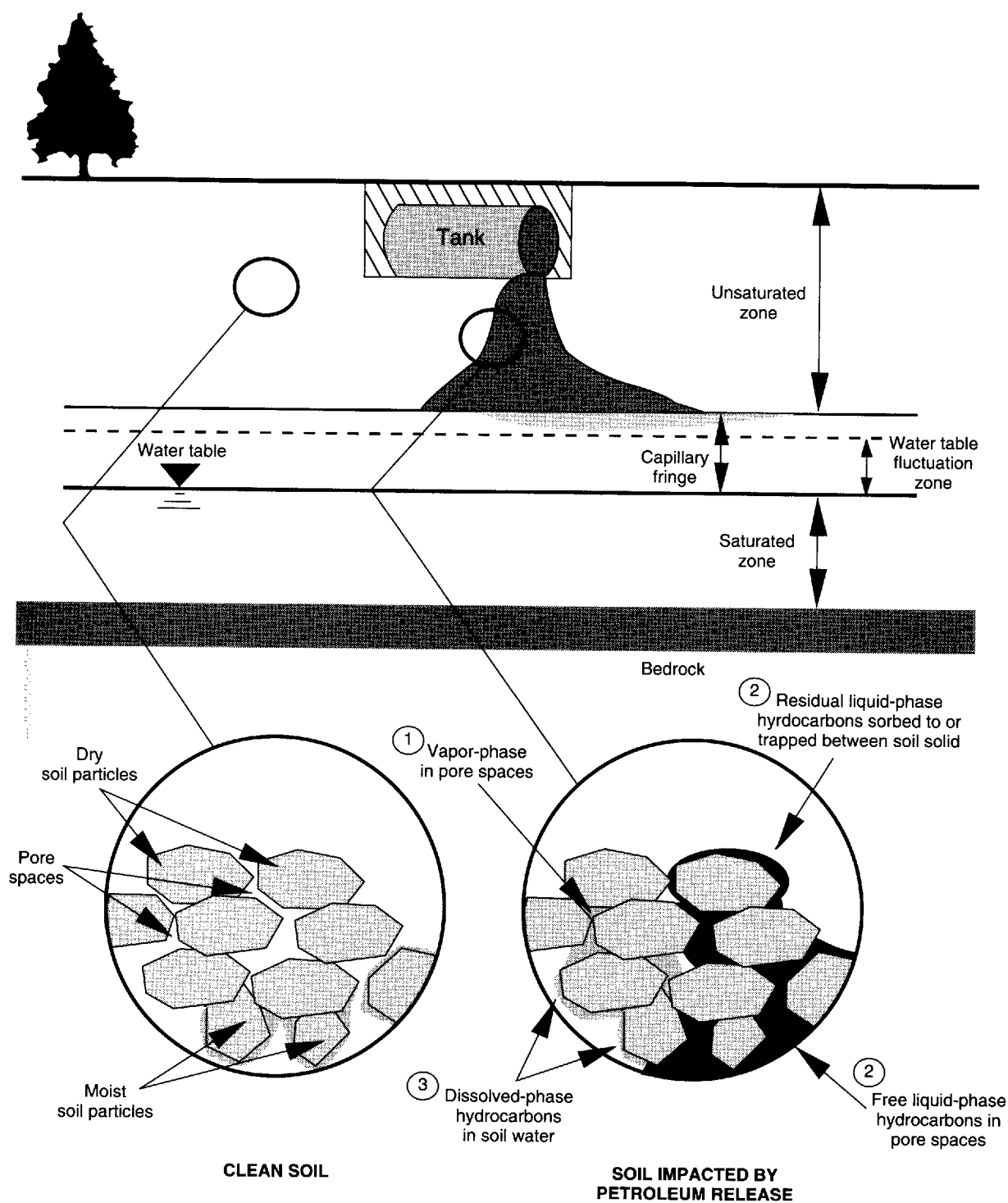
Name	Empirical Formula	Molecular Weight	Water Solubility at 25°C (milligrams/liter)	Vapor Pressure at 20°C (millimeters Hg)	Soil Sorption Constant K_{oc} (liters/kilogram)
n-Butane	C ₄ H ₁₀	58.12	61.4 (1 atm.)	1,560	490
Isobutane	C ₄ H ₁₀	58.12	48.9 (1 atm.)	2,250	420
n-Pentane	C ₅ H ₁₂	72.15	41.2	424	910
Isopentane	C ₅ H ₁₂	72.15	48.5	575	880
1-Pentene	C ₅ H ₁₀	70.14	148	531	460
n-Hexane	C ₆ H ₁₄	86.18	12.5	121	1,900
1-Hexene	C ₆ H ₁₂	86.16	50	150	910
2-Methylpentane	C ₆ H ₁₄	86.18	14.2	172	1,500
Cyclohexane	C ₆ H ₁₂	84.16	59.7	77.6	960
Benzene	C ₆ H ₆	78.11	1,780	75.2	190
n-Heptane	C ₇ H ₁₆	100.20	2.68	35.6	4,300
2-Methylhexane	C ₇ H ₁₆	100.23	2.54	51.9	3,200
Methylcyclohexane	C ₇ H ₁₄	98.19	15	36.2	1,800
Toluene	C ₇ H ₈	92.14	537	21.8	380
n-Octane	C ₈ H ₁₈	114.23	0.66	10.5	8,200
2, 4-Dimethylhexane	C ₈ H ₁₈	114.23	1.5	23.3	5,200
Ethylbenzene	C ₈ H ₁₀	106.17	157	7.08	680
m-Xylene	C ₈ H ₁₀	106.17	162	6.16	720
2, 2, 4-Trimethylhexane	C ₉ H ₂₀	0.8	11.3	11.3	8,700
1, 3, 5-Trimethylbenzene	C ₉ H 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 coefficients.

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

Medium	Gasolines			Middle Distillates			Fuel Oils		
	(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/ft³ = gallons per cubic foot; l/m³ = liters per cubic meter; mg/kg = milligrams per kilogram.

^aEstimate assumes an earth material bulk density of 1.85 grams per cubic centimeter (gm/cm³) and liquid hydrocarbon densities of 0.7, 0.8, and 0.9 gm/cm³ 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].

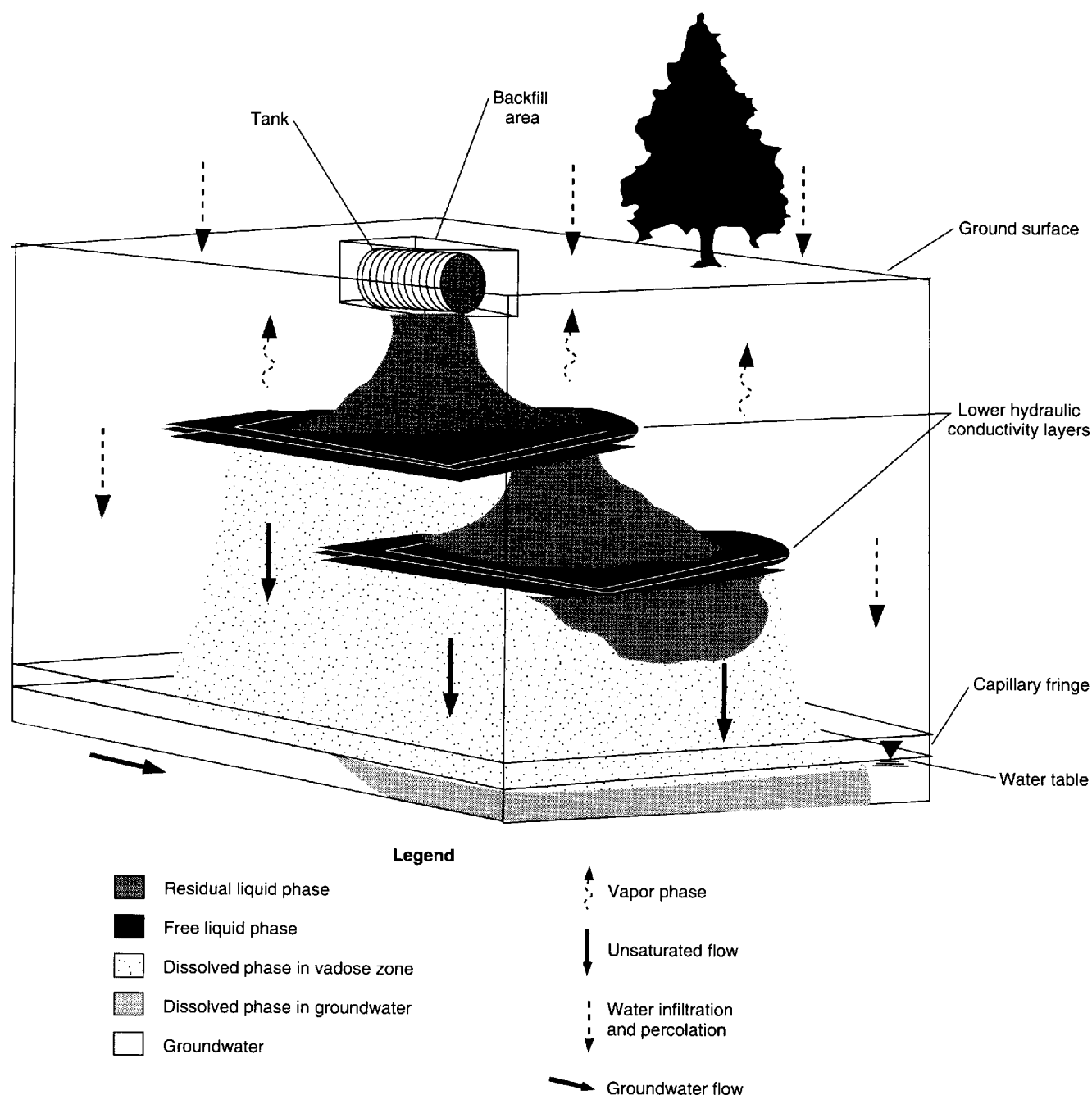


Figure 5—Schematic of Behavior of Hydrocarbon Phases in Soils

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

Constituent	Gasoline Composition Weight %			Aqueous-Phase Concentration, mg/l		
	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].



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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 hydrocar-

bons 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:

- Fire and/or explosion hazard, posed by petroleum hydrocarbon vapors that are concentrated in the explosive range.
- 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).
- 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:

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



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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 breathe 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:

- Take proper precautions to protect personnel exposed to the hazard.
- Notify the local fire department so that trained personnel can evaluate the fire and explosion hazards.
- Use trained personnel to test for explosive vapor concentrations.
- Use properly calibrated and maintained equipment with an explosion-proof rating.
- Prohibit smoking and eliminate all other sources of ignition (such as furnaces and hot water heaters).
- Ventilate the enclosure to reduce concentrations.
- 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 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.
- Visual evidence at the site (soil staining) or near the site (vapor in a basement, contaminated drinking water well) is found.
- Contamination is suspected during the replacement or upgrade of a UST system (this typically involves excavation of part or all of the UST system).
- 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:

- The presence, nature, concentration, and extent of liquid-, dissolved-, and vapor-phase hydrocarbons in soils.
- The source or sources of petroleum hydrocarbons and directions of migration.
- The effect of hydrogeologic conditions on the hydrocarbon phases.
- 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.)
- 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:

- 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).
- Interview site personnel to determine how liquid hydrocarbons are stored, transported, monitored, and removed from the site.
- Obtain available information on the location, type, and estimated quantity of petroleum product released and the duration of the release.
- 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.
- 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 off-site 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:

- To confirm the source and presence of petroleum hydrocarbons in soil.
- To define the nature and three-dimensional extent of hydrocarbon phases in soil.
- To understand the influence of hydrogeologic conditions on the fate and transport of hydrocarbons (see 4.3.3).
- 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:

- Reported or observed leakage.
- Large product inventory variance or discrepancies.
- Detection by release-detection systems.
- Problems with the piping system.
- 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 prac-

tices 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 tech-

niques 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

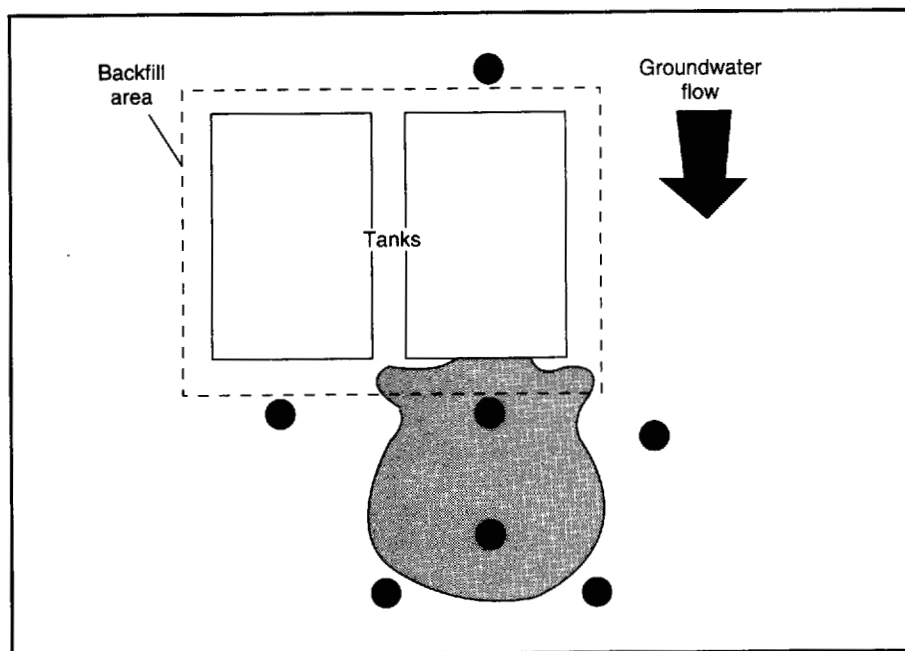
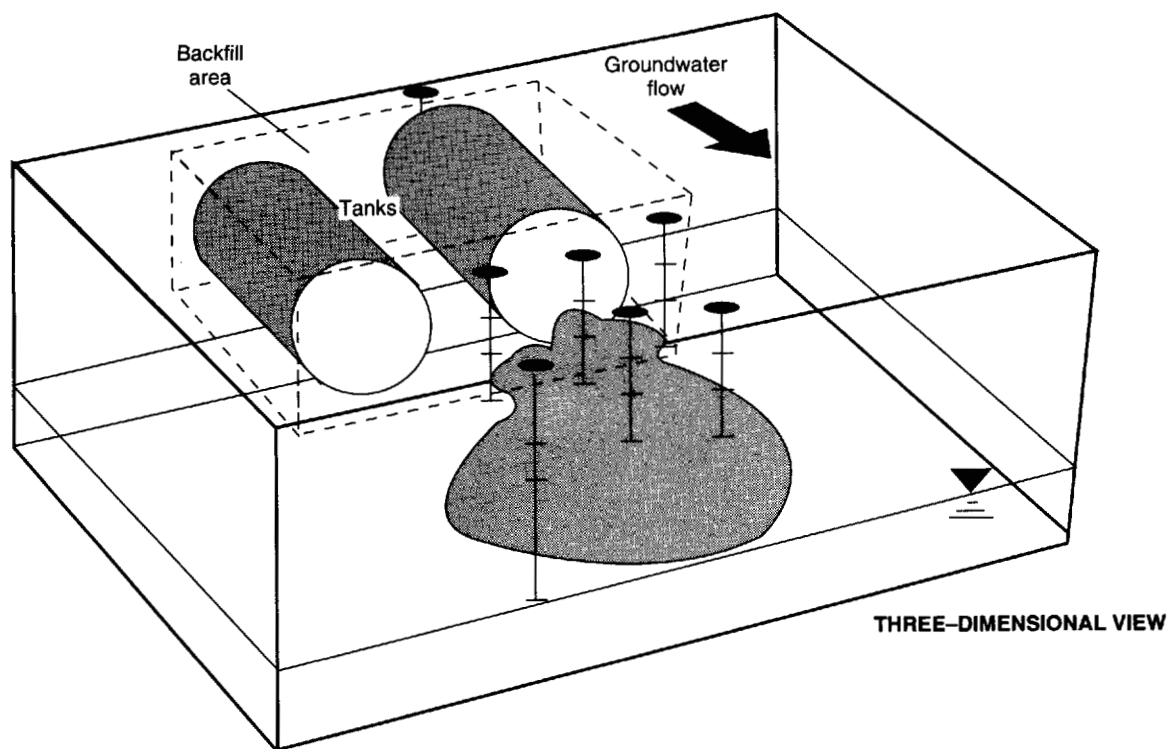
The initial phase of a site assessment is conducted to confirm a hydrocarbon release and to identify the source. A more extensive assessment is conducted to define the extent of vapor- and liquid-phase hydrocarbons in the soil. The sampling and analysis approach used to determine the lateral and vertical 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-

**Legend**

- Borehole location
- + Sampling depth and location
- Liquid hydrocarbon phase

PLAN VIEW

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

Figure 6—A Simplified Schematic of Selected Sampling Locations