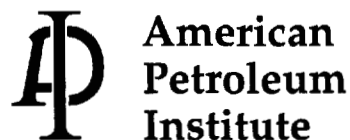


A Guide to the Assessment and Remediation of Underground Petroleum Releases

API PUBLICATION 1628
THIRD EDITION, JULY 1996





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A Guide to the Assessment and Remediation of Underground Petroleum Releases

SECTION 1—INTRODUCTION

1.1 Purpose and Scope

This publication provides a basic overview of proven technologies for the assessment and remediation of petroleum releases in soil and groundwater. This document does not address assessment and remediation of releases to surface-water environments, such as rivers, lakes, and oceans although releases to soil and groundwater may migrate to these receptors.

This document is intended as a guide for those who must deal with accidental releases arising from the production, transportation, refining, and marketing of liquid petroleum products or unrefined crude oil. This publication may also be a useful manual for environmental professionals, regulatory agencies, consultants, attorneys, fire marshals, and citizens. The use of technical terms has been avoided where possible. Technical terms used are defined when first mentioned in the text.

Since publication of the second edition of API Publication 1628 in 1989, new technologies and improvements in existing technologies for the assessment, characterization, and remediation of petroleum hydrocarbon releases have evolved. Examples include air sparging, passive bioremediation, and field screening and analytical techniques. Incorporation of risk and exposure assessment practices with the traditional components of corrective action, known as *Risk-Based Corrective Action* (RBCA), is gaining attention as a method to focus remedial measures and resources consistent with the level of risk posed by a site to human health and the environment. Moreover, ongoing research and field work in areas such as natural attenuation, optimization of liquid hydrocarbon and groundwater recovery, liquid hydrocarbon migration, and groundwater and vapor monitoring have resulted in effective and cost-efficient methods for assessing and remediating subsurface petroleum hydrocarbon releases. The development of new federal and state regulatory programs which require cleanup of petroleum releases has also contributed to the need for a supplemental publication. In conjunction with the revision of this document, API technical publications were prepared to provide additional detail on operation and maintenance considerations for remediation systems (1628E), optimization of hydrocarbon recovery (1628C), in-situ air sparging (1628D), risk-based decision making (1628B), and natural attenuation processes (1628A). These publications are available through API. Those seeking more information about specific topics are referred to Appendix A, a bibliography of technical papers, reports, and books.

1.2 Background and Organization

The objectives set forth in this third edition of Publication 1628 are three-fold: (a) to update the technical material and incorporate new proven technologies; (b) to provide more information on general design parameters and applicability of technologies given the additional level of experience with existing proven technologies, and (c) to integrate an overall theme that hydrocarbon releases can be handled through a RBCA approach which incorporates elements of site characterization, initial response, exposure assessment, and determination of risk-based target clean-up goals. A framework which incorporates these elements is provided in ASTM Standard E1739.

The terms *free hydrocarbon*, *free product*, *liquid hydrocarbon*, *phase-separated hydrocarbon* and *free liquid hydrocarbon* all denote lighter-than-water, nonaqueous-phase liquid (LNAPL) and are used in the literature to denote the separate phase resulting from a petroleum release. In this document, the term *LNAPL* will be used. The assessment and remediation of hydrocarbon releases can involve the application of several technologies to one or more of the following hydrocarbon phases:

- a. A liquid phase, LNAPL.
- b. A residual LNAPL.
- c. The dissolved phase hydrocarbon compounds in groundwater.
- d. The vapor phase.

The term *chemical(s) of concern* refers to specific hydrocarbon compounds that are constituents of the released material, and have been identified for evaluation in the site assessment and risk assessment process because of their potential to adversely affect human health or the environment. The term *contamination* denotes concentrations of chemical(s) of concern that are above the target levels appropriate for a site, based on risk to human health and the environment.

Section 2 details the characteristics of earth materials, subsurface water, and petroleum hydrocarbon. It explains the interplay of these phases as a release enters and migrates through subsurface materials. Section 3 discusses the RBCA framework. Section 4 details initial emergency response and initial abatement actions. Section 5 addresses methods used in assessment to determine the extent and potential for migration of the various phases. Section 6 reviews the principles of risk assessment. Section 7 addresses approaches to the control, recovery, and remediation of petroleum hydrocarbon.



The information in Sections 3 through 7 may be coordinated for a corrective action process that can be followed when a hydrocarbon release is suspected. Figure 1 illustrates this process as a flowchart. This process can ensure the efficient remediation of a hydrocarbon release while minimizing unnecessary actions and expenses.

1.3 Health and Safety

The first step in any site assessment involving a release of petroleum hydrocarbon is to determine if any immediate safety concerns exist. If an unsafe condition exists, the situation should be assessed and appropriate initial response implemented to protect health and safety. For example, a mixture of hydrocarbon vapor with oxygen can create concentrations which could explode and which may be ignitable by a spark from an electric switch or a flashlight that is not explosion proof. As an example, persons should never be allowed to smoke in the area where concentrations could create a suspected explosive environment.

Drinking-water wells located close to the petroleum release site are another example which needs consideration. A drinking water well believed to be in the path of a suspected release may require sampling to determine if petroleum hydrocarbon are present. The presence of regulated chemicals may necessitate water treatment, provision of alternative water supplies, or the discontinuation of well use.

1.4 Regulations and Codes

The major federal law governing hydrocarbon releases from underground storage tanks (USTs) is Subtitle I of the Resource Conservation and Recovery Act (RCRA). RCRA also contains corrective action provisions for other types of petroleum releases associated with waste handling areas. Many states have regulations governing releases from aboveground storage tanks (ASTs). Hydrocarbon releases to any streams, rivers, and lakes may further be regulated under the Clean Water Act and the Oil Pollution Act of 1990. Most states and many local governments have regulations which deal specifically with petroleum hydrocarbon releases.

The assessment and remediation of a hydrocarbon release requires interaction with local, state, and/or federal agencies. Depending on the particular jurisdiction, the amount of hydrocarbon released, results of assessment, remediation plans, and remediation progress usually must be reported, reviewed, and in some cases approved. Also, permits may be required to complete tasks such as excavating, drilling wells, pilot testing of remedial technologies, installing remediation systems, discharging water and vapor, and construction work. The responsible party must identify and meet applicable permit and reporting requirements.

1.5 References

Sections 1.5.1 and 1.5.2 contain references cited in the text. See Appendix A for an extensive bibliography of resources.

1.5.1 STANDARDS, RECOMMENDED PRACTICES, AND SIMILAR PUBLICATIONS

The following publications are cited in text (see also 1.5.2 for other types of references).

API

- RP 1615 *Installation of Underground Petroleum Storage Systems*
- RP 1621 *Recommended Practice for Bulk Liquid Stock Control at Retail Outlets*
- RP 1628A *Natural Attenuation Processes*
- RP 1628B *Risk-Based Decision Making*
- RP 1628C *Optimization of Hydrocarbon Recovery*
- RP 1628D *In-Situ Air Sparging*
- RP 1628E *Operation and Maintenance Considerations for Hydrocarbon Remediation Systems*
- Pub 1629 *Guide for Assessing and Remediating Petroleum Hydrocarbon in Soils*
- Pub 4509 *An Evaluation of Soil Gas and Geophysical Techniques for Detection of Hydrocarbon Sampling and Analysis of Gasoline Range Organics in Soil*
- Pub 4516 *Sampling and Analysis of Gasoline Range Organics in Soil*
- Pub 4552 *Treatment of Gasoline-Contaminated Groundwater Through Surface Application: A Prototype Field Study*

ASTM¹

- E1739 *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites*
- PS03 *Guide for Site Characterization for Confirmed or Suspected Petroleum Releases*

USEPA²

- SW-846 *Test Methods for Evaluating Solid Waste*

1.5.2 OTHER REFERENCES

The following references are cited in text (see also 1.5.1):

Oil Pollution Act, 40 *Code of Federal Regulations*, Part 112, available from the Government Printing Office, Washington, D.C., 20402.

¹American Society for Testing and Materials, 100 Bar Harbor Drive, West Conshohocken, PA 19428.

²U.S. Environmental Protection Agency, Government Printing Office, Washington, D.C. 20402.

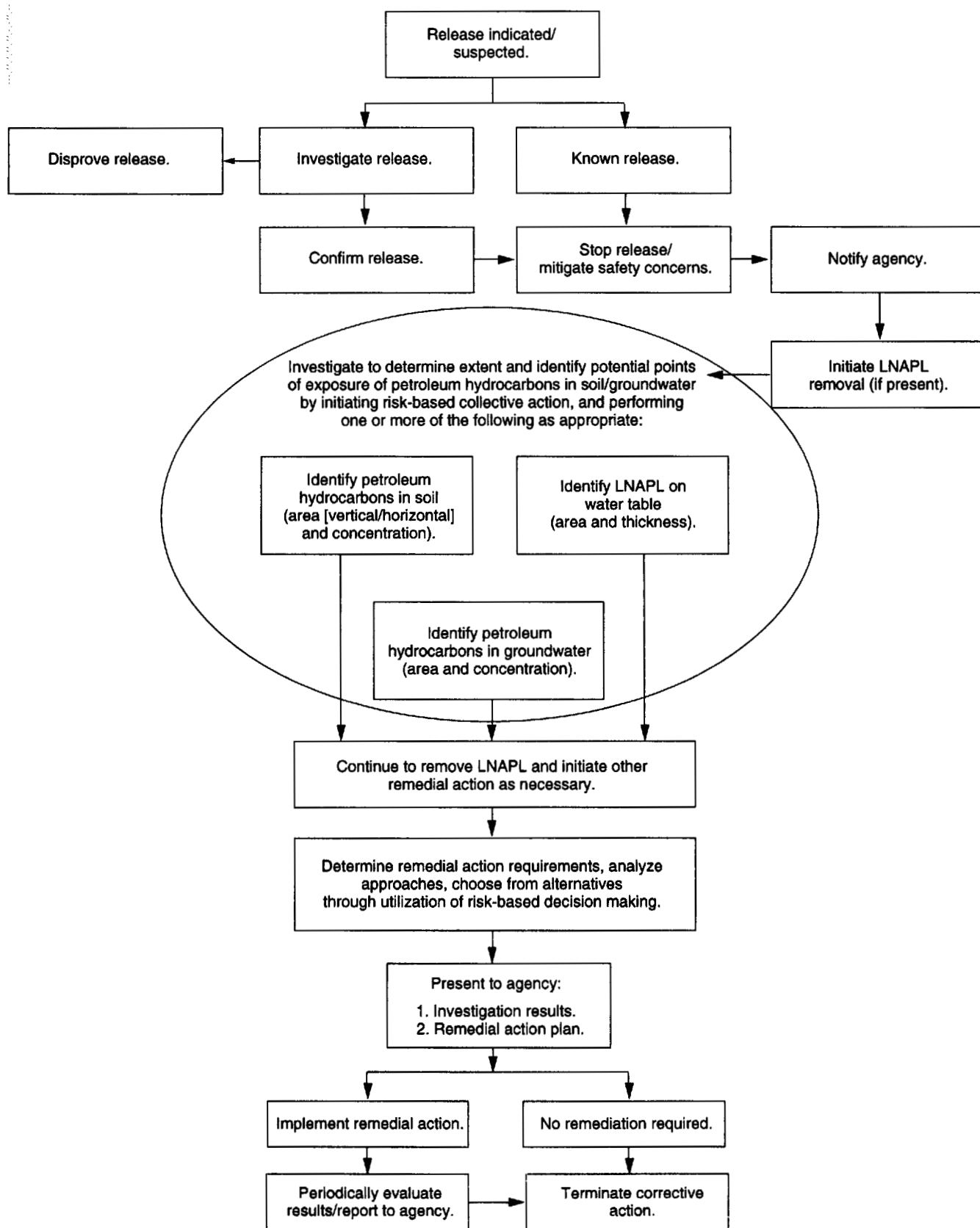


Figure 1—Corrective Action Process for Hydrocarbon Releases

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SECTION 2—FUNDAMENTAL TECHNICAL CONCEPTS

2.1 Overview

Some knowledge of basic concepts is necessary to implement an effective program to assess and remediate underground petroleum hydrocarbon releases. This section addresses the physical and chemical characteristics of earth materials and petroleum hydrocarbon, and details the principles of groundwater hydrology, which may affect the migration of groundwater and hydrocarbon phases, and distribution of hydrocarbon through the subsurface.

2.2 Characteristics of Earth Materials

The subsurface environment contains materials composed of inorganic minerals, organic materials (for example humus, peat), air, and water. The subsurface may also be the habitat of burrowing animals, plant roots, and microorganisms. In addition, man-made structures (such as basements, utility service lines) are commonly present. An understanding of the interactions between these materials and structures and the movement of petroleum hydrocarbon is necessary for effective assessment and remediation of hydrocarbon releases.

2.2.1 TYPES OF MATERIALS

2.2.1.1 General

Earth materials range from unconsolidated sediments (for example, sands, clay) to consolidated bedrock. Although the range of earth materials is very broad, those at any particular site are usually limited. Information on rock, sediment, and soil types present may be available from geologic reports and maps published by the U.S. Geological Survey (USGS) or state geological surveys, logs from local drillers, and county soil survey reports published by the U.S. Soil Conservation Service (SCS).

2.2.1.2 Unconsolidated Materials

Unconsolidated materials include loose, porous sediments, soils, and fill.

Unconsolidated sediments refer to loose earth materials that result from erosion or weathering of bedrock. Examples include sands (beach sand and river deposits), silts, and clays. Unconsolidated sediments may have been transported significant distances by wind, water, ice, or gravity. They can range in size from microscopic particles to extremely large boulders.

Glacial till is dominantly unsorted and unstratified glacial drift, which is generally unconsolidated and deposited directly by and underneath a glacier without subsequent reworking by melt water and consisting of a heterogeneous mixture of clay, silt, sand, gravel and boulders.

Soils denote a form of unconsolidated sediments gener-

ally composed of very fine-grained mineral and organic material that have formed at the land surface from weathering and decomposition of underlying geologic materials and by decaying organic matter.

Fill is defined as any substance placed by humans that is used to backfill topographically low areas or previously excavated areas. Fill materials commonly consist of soils, sand, gravel, or rock. However, fill materials may also consist of demolition debris such as lumber, steel, concrete, and bricks.

2.2.1.3 Consolidated Bedrock

The term *consolidated bedrock* includes sedimentary rocks that have been hardened by natural cementation (shale, limestone, sandstone), igneous rocks that have crystallized from a molten state (granite, basalt), and metamorphic rocks that have recrystallized due to extreme temperature and pressure (slate, gneiss, marble).

2.2.2 FLUID-TRANSMITTING PROPERTIES

2.2.2.1 General

The two physical properties of earth materials that most affect fluid movement through sediments are porosity and permeability.

2.2.2.2 Porosity

Porosity, or *total porosity*, refers to the ratio of the volume of spaces between the earth material to the total volume of material. Porosity is expressed as a percentage and is dependent upon factors such as grain size and shape, the manner in which the earth materials are packed together, and sorting.

$$\text{Porosity}(n) = \frac{\text{Volume of pore space}}{\text{Volume of bulk solid}} \times 100$$

The porosity of unconsolidated sediments comprised of well-rounded particles of equal size will be greater than the porosity of sediments containing either angular or well-rounded particles of variable sizes. In the latter case, the smaller particles fill in the spaces between the larger particles. The wider the range of grain sizes, the lower the porosity.

Porosity is also affected by the shape and orientation of grains comprising the earth material. Spherically shaped grains pack together more tightly and have less porosity than particles of other shapes, such as plates or rods. Some clay particles, for example, have plate-like shapes and do not tend to pack closely together. Therefore, clays may have very high total porosities. The general ranges of porosity that can be expected for typical sediments are included in Table I.

Table 1—Ranges of Porosity Values for Various Earth Materials

Unconsolidated Sediments	$\mu(\%)$	Consolidated Rocks	$\mu(\%)$
Clay	45-55	Sandstone	5-30
Silt	35-50	Limestone/dolomite (original & secondary porosity)	1-20
Sand	25-40	Shale	0-10
Gravel	25-40	Fractured crystalline Rock	0-10
Sand & gravel mixes	10-35	Vesicular basalt	10-50
Glacial till	10-25	Dense, solid rock	<1

Effective porosity means the ratio of the volume of inter-connected spaces through which fluid can flow to the total volume of material. Although clays and some organic soils may have large total porosities, they generally have smaller intergranular voids, many of which are disconnected, and smaller effective porosities when compared to coarser-grained materials.

Fractures may develop in finer-grained clay soils and sediments as a result of the shrinkage or drying. Such development, through which fluids can migrate, is known as *secondary porosity*. Secondary porosity can also develop from animal burrows and root spreading. Fractures in bedrock are also another form of secondary porosity.

Although the effective porosity in bedrock is generally low, bedrock near the land surface is usually fractured by several processes, allowing development of secondary porosity through which fluids can migrate. Secondary porosity may also develop through dissolution of rock material by migrating groundwater, (such as caves which occur in limestone). Mammoth Cave, Kentucky, is an example of a cavern system which has developed by dissolution of limestone.

2.2.2.3 Permeability and Hydraulic Conductivity

The *permeability* of a geologic material denotes a measure of its ability to allow fluid flow. *Hydraulic conductivity* also denotes a measure of the ability of a geologic material to allow flow, but is dependent on the type of fluid passing through the material. For example, the hydraulic conductivity of water is greater for a given earth material than that of more viscous fluids such as crude oil or diesel fuel. Although both parameters are often used, the term *hydraulic conductivity* will be used throughout this publication.

$$\text{hydraulic conductivity (k)} = \frac{\text{groundwater flow rate}}{-(\text{hydraulic gradient})(\text{area through which groundwater flows})}$$

Table 2 shows that the range of hydraulic conductivities for various earth materials is very broad. This table pertains to soils in which water is the primary fluid. The hydraulic conductivities listed are not accurate when the fluids are LNAPL. Hydraulic conductivities for fractured materials cover a wide range and in some cases can be large. More discussion of hydraulic conductivity is provided in Section 5.

2.3 Characteristics of Subsurface Water

The voids of shallow earth materials are occupied by air and water. Figure 2 shows the distribution of air and water in two subsurface zones when neither the air nor water are moving.

2.3.1 SUBSURFACE AIR AND WATER DISTRIBUTION

Two subsurface zones define the major distribution of soil vapor and water in the subsurface: (a) the unsaturated zone and (b) the saturated zone. What is termed the *unsaturated zone* extends from land surface to the top of the capillary fringe and contains soil air and a small amount of water. The zone called the *saturated zone* is considered to extend downward from the top of the capillary fringe to the bottom of the ground-water flow system. Intergranular voids in the saturated zone are filled with water. The *capillary fringe*, so named because *capillary forces* (due to surface tension and molecular attraction) cause groundwater to move upward from the water table, is nearly saturated with water, and is considered to be the upper part of the saturated zone. The height of the capillary fringe can range from a fraction of an inch in coarse-grained sediments to as much as several feet in very fine-grained sediments, such as clays, and will typically vary as a function of soil type. The definition of a *water table* is the surface along which the water pressure in the voids is equal to local atmospheric pressure. In practice, the water table is equivalent to the level at which water stands in a shallow well, boring, or excavation.

2.3.2 GROUNDWATER MOVEMENT

The term *groundwater* means all water in the saturated zone. The source of most groundwater is precipitation. In arid climates, significant groundwater recharge can result from rivers and streams. Precipitation enters the groundwater system through earth materials by the process of infiltration (recharge areas), and moves slowly downgradient to an outlet such as a stream or pumping well (discharge area). The water table is a continuous surface that slopes from the recharge area to the discharge area. Shallow water tables generally follow the configuration of surface topography.

Table 2—Ranges of Values of Hydraulic Conductivity

Rocks	Unconsolidated Deposits	Hydraulic Conductivity			
		(ft/day)	(cm/s)	(m/s)	(gal/day/ft ²)
Karst limestone	Gravel	10 ⁶	10 ²	1	10 ⁻⁶
Permeable basalt		10 ⁵	10	10 ⁻¹	10 ⁻⁵
Fractured igneous and metamorphic rocks		10 ⁴	1	10 ⁻²	10 ⁻⁴
Limestone and dolomite		10 ³	10 ⁻¹	10 ⁻³	10 ⁻³
Sandstone		10 ²	10 ⁻²	10 ⁻⁴	10 ⁻²
Unfractured metamorphic and igneous rocks		10 ¹	10 ⁻³	10 ⁻⁵	10 ⁻¹
Shale		10 ⁻¹	10 ⁻⁴	10 ⁻⁶	10 ⁻¹
Unweathered marine clay		10 ⁻²	10 ⁻⁵	10 ⁻⁷	10 ⁻²
Glacial till		10 ⁻³	10 ⁻⁶	10 ⁻⁸	10 ⁻³
Silt, loess		10 ⁻⁴	10 ⁻⁷	10 ⁻⁹	10 ⁻⁴
Silty sand		10 ⁻⁵	10 ⁻⁸	10 ⁻¹⁰	10 ⁻⁵
Clean sand		10 ⁻⁶	10 ⁻⁹	10 ⁻¹¹	10 ⁻⁶
		10 ⁻⁷	10 ⁻¹⁰	10 ⁻¹²	10 ⁻⁷
			10 ⁻¹¹	10 ⁻¹³	

Notes: ft/day = feet per day; cm/s = centimeters per second; m/s = meters per second; gal/day/ft² = gallons per day per square foot. Source: Modified from Freeze and Cherry, 1979.

The elevation of the water table fluctuates with the amount of recharge naturally throughout the year. Depending on the area, this fluctuation can range from a fraction of a foot to several tens of feet. Figure 3 illustrates regional recharge and discharge areas conforming to a flow pattern affected by topography, local geology, climatic conditions, and groundwater usage.

An *aquifer* denotes a water-bearing permeable rock, sand, or gravel that can yield significant quantities of groundwater to wells and springs. The word *significant* is subjective, since the meaning depends on the quantity and quality of water that is needed for a particular purpose. For example, a fractured shale might be considered an aquifer if only small yields are necessary for stock watering. The same formation would not be considered an aquifer if the local demand for water is greater, such as for crop irrigation. Hydrogeolo-

gists commonly classify aquifers as *unconfined* (water table) or *confined* (artesian).

Those called *unconfined aquifers* are more frequently affected by hydrocarbon releases than confined aquifers. Recharge to unconfined aquifers usually occurs by downward seepage through the unsaturated zone, through horizontal groundwater inflow, or via upward flow from a deeper aquifer (Figure 3).

The ones called *confined aquifers* are formed when an aquifer is overlain by a geologic unit having relatively low hydraulic conductivity which retards movement of fluids (called the *confining layer*). Water in a confined aquifer is under pressure from being lower in elevation than the recharge area. Thus, water levels in a well completed in a confined aquifer will rise above the base of the confining layer. Recharge to confined aquifers can occur via soil water

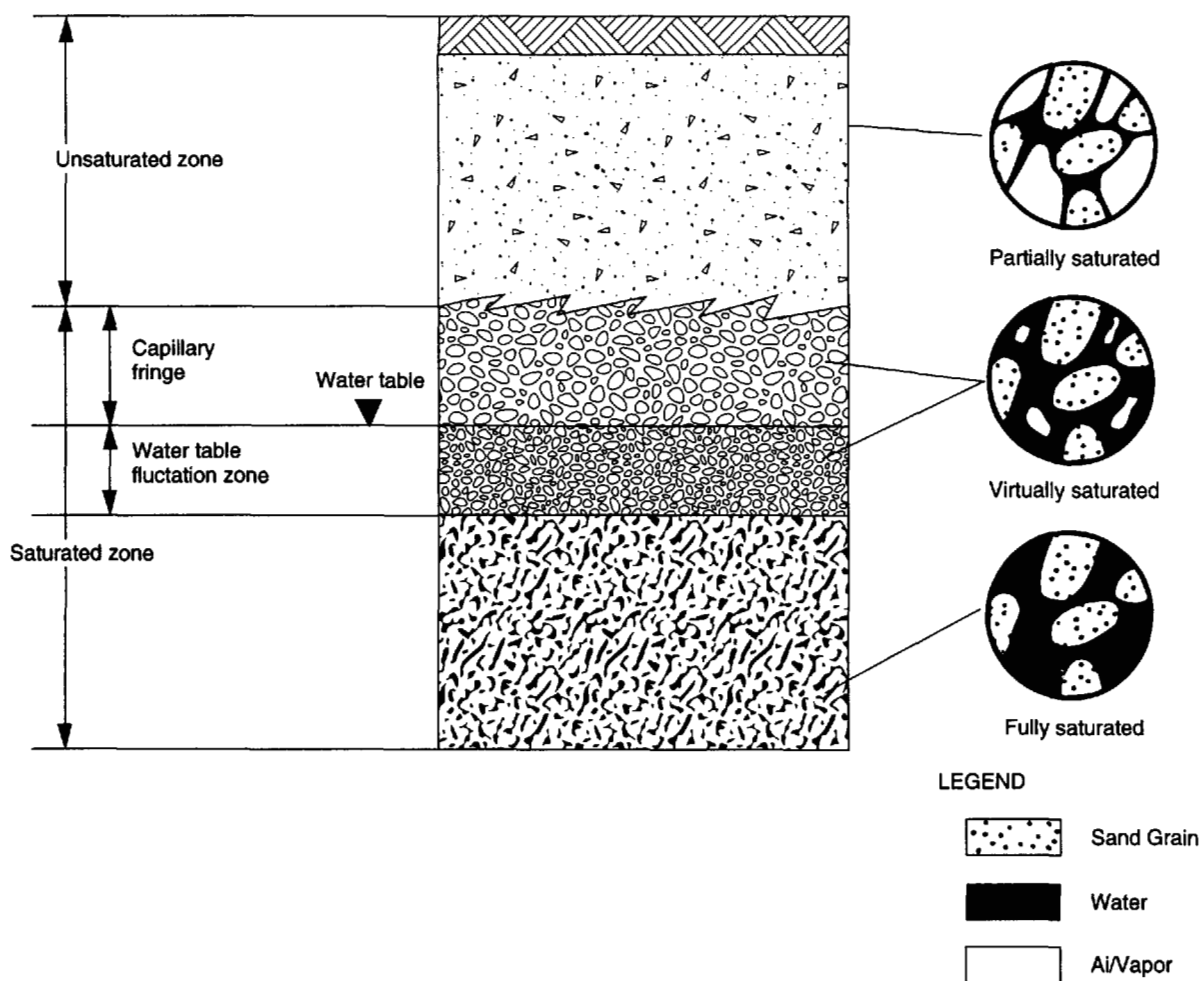


Figure 2—Distribution of Water and Air in the Subsurface

infiltration in recharge areas or by slow leakage through the confining layer.

The elevation of the water level in a well, which is measured relative to a common datum (a surveyed benchmark), is equivalent to the total hydraulic head for the aquifer at that particular location. *Total hydraulic head* denotes what is usually expressed in terms of water-level elevation for both unconfined and confined aquifers. The *hydraulic gradient* I , refers by definition to the difference in hydraulic head ($h_2 - h_1$), divided by the distance, L , along the flowpath. Flow within an aquifer will occur from high head to low head. These concepts will define groundwater flow both horizontally and vertically.

$$\text{hydraulic gradient } (I) = \frac{\text{difference in hydraulic head}}{\text{distance along the flow path}}$$

Layers of sediments having relatively low hydraulic conductivities, such as clays, may occur as lenses (narrow discontinuous bands) above the regional water table. Sediments above these lenses that become saturated with

water are termed *perched-water-bearing zones* (Figure 3). Fluid (water and hydrocarbon) migration associated with these perched aquifers is discussed in 2.5.2.2. Perched water bearing zones are not usually laterally extensive.

2.4 Characteristics of Petroleum

Petroleum is a complex mixture of organic compounds called *hydrocarbon* and are mostly crude oil and its derivatives. Hydrocarbon consist of the elements hydrogen and carbon, with minor amounts of nitrogen, oxygen, sulfur, and other elements. Hydrocarbon fuels are formulated from refinery processing streams such as those called *distillation* and *cracking* that occur under industry specifications for physical properties and performance standards. Additives and blending agents are often added to hydrocarbon fuels to improve performance and stability. Refining processes such as distillation and cracking may also selectively produce pure compounds termed *petrochemicals*. This group includes compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX), and hexane and butane.

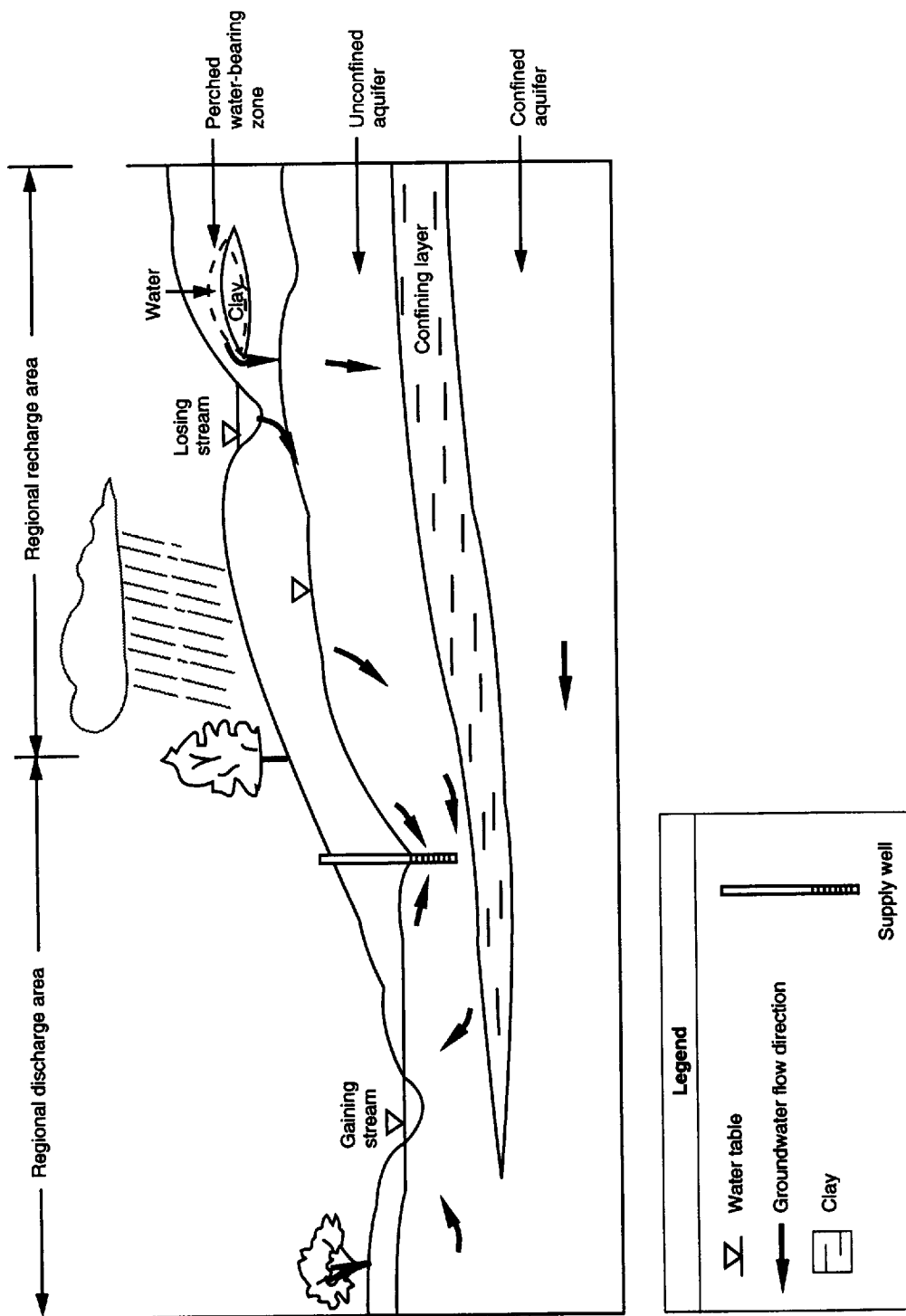


Figure 3—Circulation of Groundwater from Regional Recharge Area to Regional Discharge Area

materials are used as solvents, as raw materials in the chemical manufacturing industry, or for blending into fuel.

The movement of these compounds from the LNAPL phase to other phases and the migration potential of each phase in the subsurface is largely dependent on the physical and chemical properties of hydrocarbon compounds and their mixtures and on hydrogeologic conditions. A general knowledge of properties affecting migration is useful when performing a site assessment.

2.4.1 TYPES OF PETROLEUM

2.4.1.1 General

Crude oil is refined into petroleum products through several processes, (for example, fractional distillation, cracking). The resulting petroleum products can be mixtures of several hundred compounds which can be assigned to one of the following general groups:

- Gasolines.
- Middle distillates—diesel, kerosene, jet fuels, and lighter fuel oils.
- Heavier fuel oils and lubricating oils.
- Asphalts and tars.
- Coke.

2.4.1.2 Gasolines

Gasolines and finished oils are blends of petroleum-derived chemicals plus additives that improve fuel performance and engine longevity, assist in wear reduction, reduce the tendency of petroleum to cause unintended physical effects (such as foaming, oxidation) and color code the product. Most chemical compounds in gasoline are classed as either aliphatics or aromatics. *Aliphatic compounds* refer to organic compounds in which the carbon atoms exist as either straight or branched chains. Examples include ethane, propane, butane, pentane, hexane, and heptane. *Aromatic compounds* denotes those made up of carbon ring structures and include compounds such as BTEX. These compounds are somewhat more soluble, volatile, and mobile in the subsurface environment than the aliphatic compounds, and are useful indicators of hydrocarbon migration in the subsurface.

The BTEX compounds, either singularly or in various combinations, are present in many materials other than petroleum hydrocarbon. Thus, while the analysis for BTEX is recommended in all assessments involving petroleum hydrocarbon, the presence of one or two of the BTEX compounds without other evidence may not necessarily be an indicator of a petroleum hydrocarbon release.

Organic compounds that include oxygen atoms are called *oxygenates*. Oxygenates such as alcohols (for example, ethanol and methanol) and ethers (such as methyl-tertiary-butyl ether [MTBE]) are often used in gasolines as octane-boosters.

These compounds are more soluble than the aromatics, and are present in some gasolines in concentrations as high as 10 to 15 percent by volume. Ethylene dibromide (EDB) was present as a lead scavenger in some leaded gasolines (in the United States) and, along with lead, may be used as an indicator of a leaded gasoline release. Note that the presence of EDB in the subsurface can also be due to other sources, such as land application of agricultural chemicals, and should be used with caution as an indicator of petroleum hydrocarbon releases. The presence of lead as an indicator of hydrocarbon releases must also be used with caution. Native earth materials commonly contain inorganic lead. Because the inorganic lead fraction is part of the total lead chemical analysis, use of total lead concentrations as an indicator is not justified. Also, the use of lead and EDB as an indicator of a petroleum release is decreasing as the production of leaded gasoline is phased out.

2.4.1.3 Middle Distillates

The middle distillate group includes diesel, kerosene, jet fuel, and lighter fuel oils. Middle distillate products may contain as many as five hundred individual compounds; however, these compounds tend to be more dense, less volatile, less mobile, and less water soluble than gasoline-range materials. Diesel fuel is primarily composed of aliphatics. Fuel oils can be fractions of petroleum, residuals from refinery distillates, crude petroleum, or a mixture of these materials. Also, middle distillate materials usually contain low percentages of lighter-end aromatic compounds such as BTEX.

2.4.1.4 Heavier Fuel Oils and Lubricating Oils

Heavier fuel oils and lubricants are similar in composition and characteristics to the middle distillates and contain higher amounts of the heavier-end hydrocarbon compounds. These types of fuels and lubricants are relatively viscous and insoluble in groundwater and generally are relatively immobile in the subsurface.

2.4.2 PHYSICAL/CHEMICAL PROPERTIES OF PETROLEUM

A number of properties, including fluid density, dynamic viscosity, solubility, sorption, and vapor pressure can affect the mobility and partitioning of liquid-phase hydrocarbon in earth materials. *Fluid density* is defined as the mass per unit volume. Most liquid petroleum hydrocarbon have a density less than that of water [1 gram per milliliter (g/mL)]. *Viscosity* refers to a measure of the resistance of a fluid to flow. Table 3 presents typical density and viscosity data for selected LNAPL, oxygenates, and water. In general, as the density increases, the viscosity of a petroleum product increases, and the ability of the product to move through the

Table 3—Densities and Viscosities of Selected Fluids

Fluid	Density (gm/ml)			Viscosity (centipoise)		
	0°	15°C	25°C	0°	15°C	25°C
Water	1.00	0.998	0.996	1.79	1.14	0.89
Automotive gasoline	0.746	0.729		0.75	0.62	
Automotive diesel	0.838	0.827		3.90	2.70	
Kerosene	0.842	0.839	0.835	3.40	2.30	2.20
Jet fuel #5		0.844				
Fuel oil #2	0.874	0.866	0.840 ^a	7.74		4.04 ^a
Fuel oil #4	0.914	0.904	0.898		47.20	22.70 ^a
Fuel oil #5	0.932	0.923	0.917		215.00	122.00
Fuel oil #6 or Bunker C	0.986	0.974	0.964	7.35 × 10 ⁷		3180.00
Electrical lubricating oil	0.882	0.974		350.00	144.00	
Electrical lubricating oil, used	0.883	0.874		359.00	154.00	
Electrical insulating oil	0.892	0.882		37.80	18.80	
Electrical insulating oil, used	0.878	0.867	35.80	18.10		
Norman Wells crude	0.845	0.832	0.829	8.76	5.05	3.93
Avalon crude	0.846	0.839	0.834	575.00	11.40	25.60
Alberta crude	0.850	0.840	0.832	17.60	6.43	4.22
Transmountain Blend crude	0.865	0.855		650.00	10.50	
Bow River Blend crude	0.900	0.893	0.885	88.40	33.70	23.70
Prudhoe Bay crude	0.915	0.905	0.900	577.00	68.40	35.30
Atkinson crude	0.922	0.911	0.905	136.00	57.30	35.00
La Rosa crude	0.923	0.914	0.908	640.00	180.00	104.00

Note: gm/ml = grams per millimeter; °C = degrees Celsius.

^aData determined at 20°C.

subsurface decreases. The densities and viscosities of crude oil vary widely but are between the ranges shown for refined products. Densities and viscosities tend to decrease in most hydrocarbon with increasing temperature.

Solubility denotes the measure of ability of a hydrocarbon constituent to dissolve in water. The solubility of a hydrocarbon is generally dependent on the number of carbon atoms present in a compound (in general the solubility within a given class of hydrocarbons decreases as the number of carbon atoms increases). The influence of contact and mixing on dissolution in water is discussed in 2.5.2.3. Water solubility data for specific hydrocarbon chemicals are listed in Table 4. However these data can be misleading because the water solubility of a specific compound as part of a blend tends to be significantly less than the solubility of the compound alone in water.

As the relative concentration of a particular compound in a hydrocarbon blend increases, the solubility of the compound in water is also greater. These relationships are illustrated in Table 5. For comparison, the last column lists ranges of reported concentrations of solubility limits for pure compounds in water. Concentrations of compounds leached from a blend of compounds in gasoline can be as small as 1/100 of the concentration leached from the pure compound.

The tendency of a LNAPL constituent to transfer to the vapor phase is indicated by the *vapor pressure* of the com-

pound. The volatilization potential of gasoline is dependent on the vapor pressure of the chemicals; chemicals having higher vapor pressure have a greater tendency to volatilize. Table 4 lists vapor pressures for several petroleum hydrocarbon compounds. As with solubility, the volatilization potential of a compound will be dependent on the relative concentration of particular chemicals in a hydrocarbon blend. As illustrated, lower molecular-weight chemicals have greater vapor pressure and volatility than heavier molecular-weight chemicals. The tendency of a compound to move from the dissolved phase into the vapor phase is measured by the Henry's Law Constant (H) for the compound. Table 4 includes H values.

Sorption refers to a measure of the bonding of a hydrocarbon constituent onto the surface of an earth material grain and depends on the particular compound and characteristic of the soil particle, itself. LNAPL chemicals that are present in groundwater aquifers will transfer into the dissolved phase in proportion to their organic carbon partition coefficients (K_{oc}). This will occur with chemicals that tend to strongly sorb to earth material grains migrating more slowly than chemicals which tend to sorb less strongly. Sorption will increase in direct proportion to the organic content of the earth material. Values of K_{oc} can vary more than two orders of magnitude, depending on the hydrocarbon constituent and the earth material characteristics (Table 4).

Table 4—Properties of Selected Hydrocarbon Compounds

Name	Henry's Law Constant (H) (atm mol fraction)	Empirical Formula	Molecular Weight	Water Solubility at 25°C (mg/L)	Vapor Pressure at 20°C (mm Hg)	Soil Sorption Constant K_{oc} (L/kg)
n-Butane	52,600	C ₄ H ₁₀	58.12	61.4 (1 atm)	1,560	490
Isobutane	NA	C ₄ H ₁₀	58.12	48.9 (1 atm)	2,250	420
n-Pentane	69,990	C ₅ H ₁₂	72.15	41.2	424	910
Isopentane	75,770	C ₅ H ₁₂	72.15	48.5	575	880
1-Pentene	22,110	C ₅ H ₁₀	70.14	148	531	460
n-Hexan	1.03 E5	C ₆ H ₁₄	86.18	12.5	121	1,900
1-Hexene	22,890	C ₆ H ₁₂	86.16	50	150	910
2-Methylpentane	96,100	C ₆ H ₁₄	86.18	14.2	172	1,500
Cyclohexane	10,890	C ₆ H ₁₂	84.16	59.7	77.6	960
Benzene	305	C ₆ H ₆	78.11	1,780	75.2	190
n-Heptane	1.15 E5	C ₇ H ₁₆	100.20	2.68	53.6	4,300
2-methylhexane	1.90 E5	C ₇ H ₁₆	100.23	2.54	51.9	3,200
Methylcyclohexane	23,775	C ₇ H ₁₄	98.10	15	36.2	1,800
Toluene	370	C ₇ H ₈	92.14	537	21.8	380
n-Octane	1.79 E5	C ₈ H ₁₈	114.23	0.66	10.5	8,200
2, 4-Dimethylhexane	NA	C ₈ H ₁₈	114.23	1.5	23.3	5,200
Ethylbenzene	485	C ₈ H ₁₀	106.17	157	7.08	680
m-Xylene	142	C ₈ H ₁₀	106.17	162	6.16	720
2, 2, 4-Trimethylhexane	NA	C ₉ H ₂₀	0.8	11.3	11.3	8,700
1, 3, 5-Trimethylbenzene	NA	C ₉ H ₁₂	120.20	72.6	1.73	940
2, 2, 5, 5-Tetramethylhexane	NA	C ₁₀ H ₂₂	142.29	0.13	6.47	14,000
1, 4-Diethylbenzene	NA	C ₁₀ H ₁₄	134.22	15	0.697	2,900
Dodecane	3.96 E5	C ₁₂ H ₂₆	170.3	0.005	0.075	88,000
MTBE	30	(CH ₃) ₃ COCH ₃	88.15	43,000	245	41
Methanol	.061	CH ₃ OH	32.04	1.16 × 10 ⁴	92	NA
Ethanol	NA	CH ₃ CH ₂ OH	46.07	1 × 10 ⁴	43.9	2.2

Note: Hg = mercury; atm = atmosphere; mg/L = milligrams per liter; mm/Hg = millimeters per mercury; L/kg = liters per kilogram; C = degrees Celsius; NA = Not available. Many values, including all K_{oc} values, are estimated by using empirically derived relationship.

Sources: API 1629, API 4497. Modified to include Henry's Law Constant from Florida DER Manual, Getting.

2.5 Subsurface Migration Process

Petroleum releases can occur on the land surface through poor product transfer activities or equipment failure; or petroleum may be released directly into the subsurface from pipelines and storage tanks. The various phases that hydrocarbon can assume when released to the subsurface are discussed in 2.5.1. The migration mechanics of the various phases are discussed in 2.5.2.

2.5.1 CHARACTERIZATION OF HYDROCARBON PHASES

Hydrocarbon can be present in the subsurface in solid, liquid, dissolved, and vapor phases, or in combinations of several phases. Solid phases include substances like asphalt and bitumen, which would remain solid and essentially immobile unless the temperature rises above their respective melting points or they are contacted by a substance which makes them more mobile. Such temperatures are rare in shallow groundwater regimes; thus, solid hydrocarbon phases will not be further discussed.

LNAPL can exist in the subsurface in the following forms (Figure 4):

- Immobile residual liquids in the unsaturated zone above the area of the capillary fringe.
- Free mobile liquids which migrate from the source area downward to the water table and then within the capillary fringe.
- Immobile residual liquids trapped in the saturated zone.

The particular phase and form is determined by the degree of hydrocarbon saturation in the earth material void spaces and by the amount of water and air present (Figure 4).

Dissolved phase hydrocarbon exist in the following subsurface areas (Figure 4):

- In infiltrating water in the unsaturated zone.
- In the residual films of groundwater covering the surfaces of solid minerals in the capillary fringe and LNAPL plume zones.
- In groundwater within the saturated zone.

Vapor in soil air can exist in two ways. Most vapor exists in void spaces in the unsaturated zone not occupied by water or LNAPL. Such vapors are considered mobile and travel at a rate which is a function of subsurface pressure gradients.

Table 5—Mixing Experiment Results for the Dissolved Phase of Three Grades of Gasoline Using USEPA Method 624

Compound	Concentration (parts per million) ^a			
	Regular Leaded	Regular Unleaded	Super Unleaded	Pure Compound
Benzene	30.50	28.10	67.00	1740-1860
Toluene	31.40	31.10	107.00	500-627
Ethylbenzene	4.04	2.42	7.40	131-208
1, 2-Dichloroethane	1.33	ND	ND	
Methyl-t-butyl ether (MTBE)	43.70	35.10	966.00	
Tertiary butyl alcohol (TBA)	22.30	15.90	933.00	
Di-isopropyl ether (DIPE)	ND	ND	ND	
M-xylene	13.90	10.90	11.50	134-196
O, P-xylene	6.05	4.84	5.66	157-213
1, 2-Dibromoethane (EDB)	0.576	ND	ND	

Note: ND = non-detectable.

^aConcentrations are rounded to three significant figures.

and diffusion from source areas. The second occurrence includes vapors that are residually trapped, notably in the space of water table fluctuation.

2.5.2 MIGRATION OF HYDROCARBON PHASES

2.5.2.1 General

To assess hydrocarbon releases properly, an understanding of the transport mechanisms of the various hydrocarbon phases is essential. The movement of liquid-, dissolved-, and vapor-phase hydrocarbon in the subsurface is discussed in 2.5.2.2 through 2.5.2.4.

2.5.2.2 LNAPL

The distribution of LNAPL in the subsurface is a complex process and depends on the amount of the release, the type of LNAPL, capillary pressure, and the pore size distribution of the earth material. Released LNAPL tends to move downward through the unsaturated zone in response to gravity and capillary forces until either a relatively impermeable zone or the water table is encountered. As these hydrocarbon migrate downward or laterally, a portion is left behind as residual. Some horizontal spreading will occur within this zone as vertical migration proceeds because of capillary forces between the LNAPL and solid granular surfaces and varying hydraulic conductivities of the earth materials. The presence of low hydraulic conductivity layers of earth material within the unsaturated zone also promotes spreading of LNAPL horizontally. Downward moving fluids (water or LNAPL) can accumulate, or perch, above these layers. These fluids will tend to migrate around laterally discontinuous perching layers, when present, and then continue downward migration toward the water table or until the liquid has all gone into a residual state (Figure 5, Part A).

As the LNAPL plume passes through the unsaturated zone, some LNAPL will remain behind in a residual state, having been trapped by capillary forces. A thin film of water will normally coat the solid surfaces of most minerals and rocks, thereby acting as a wetting fluid. LNAPL can also function as a wetting fluid by coating the water film and mineral grains as migration occurs through the unsaturated zone and capillary fringe toward the water table (Figure 5, Part B).

Residual saturation levels resulting from such wetting phenomena are generally higher in fine-grained soils than in coarse-grained soils. The finer grains have greater total surface area than coarser-grained materials and, thus, can adsorb more fluid. Approximate ranges of residual hydrocarbon concentrations in the unsaturated zone for different petroleum hydrocarbon and earth materials are presented in Table 6. LNAPL can also be present in the residual state due to strong capillary forces between the earth material grains. In either circumstance, the mobility of the LNAPL is significantly reduced, thus the term *residual*. The more soluble and volatile components of these residual phase hydrocarbon can subsequently transfer into water as dissolved chemicals or volatilize into the vapor phase, thereby acting as a potential source of release to groundwater and/or posing a safety concern to surface or subsurface structures.

Several variables, including the volume of the release, hydraulic conductivity of the earth material, depth to the water table, and adsorptive capacities of the subsurface materials will determine whether LNAPL will ultimately migrate downward to the area of the capillary fringe and the water table. Figure 5 Part A depicts the disposition of a LNAPL release that does not reach the water table. Figure 5 Part B shows the distribution of a liquid release that has migrated to the water table. A large hydrocarbon release that occurs rapidly will tend to exceed the capacity of the

earth material to adsorb the LNAPL. This type of release will tend to spread more laterally, impact a larger volume of earth material, and more readily migrate to the saturated zone.

As downward migration toward the capillary fringe and water table proceeds, the LNAPL will displace water and air at varying rates. LNAPL will be variably distributed in this area, along with air and water (Figure 4). The percentage of air present in void spaces will decrease in the area immediately above the water table, and this area will be occupied by LNAPL and water. The hydrocarbon plume will begin to migrate laterally downgradient in response to gravity and groundwater flow. The LNAPL is the lateral extension of the hydrocarbon release in the subsurface. The rate of downgradient movement can vary significantly, depending on factors such as the rate of groundwater flow, amount of loss, and the hydraulic conductivity of the aquifer.

The size of the LNAPL plume is also strongly affected by the release volume, release rate, porosity of the earth material, hydraulic conductivity, and the slope of the water table (hydraulic gradient). As mentioned earlier, the water table serves to limit downward migration of the free hydrocarbon plume. Soils consisting of fine-grained materials have large surface areas, in addition to lower permeability, that will tend to retain more of the liquids in a residual state, thereby limiting the extent of the free hydrocarbon plume. Coarse-grained materials, and materials containing fractures and other secondary porosity features have less surface area. LNAPL moving through these materials will generate fewer residual hydrocarbon. In addition, the water table gradient strongly affects plume geometry. Generally, the steeper the gradient, the narrower the plume and the more rapid the migration from the point of release.

The extent of the LNAPL plume is also impacted by rates at which hydrocarbon chemicals dissolve into water, volatilize into the vapor phase, and degrade by natural biological processes. All else being equal and assuming no further release, the degree of spreading of the LNAPL plume is limited by a combination of the preceding discussed processes.

Water table fluctuations will tend to spread hydrocarbon vertically, as illustrated on Figure 6. LNAPL at the capillary zone will move downward as the water table drops, leaving residual liquid in the expanded unsaturated zone above the new water table. A subsequent rise of the water table will cause the capillary zone and associated LNAPL to move upward. Residual hydrocarbon present in the new portion of the unsaturated zone can be partially remobilized, causing lateral spreading at a different elevation. Further, residual LNAPL can remain in the saturated zone below the raised water table. The more soluble compounds in the residual LNAPL can dissolve into groundwater, adding to the dissolved hydrocarbon plume. Also, water table fluctua-

tions, such as those described, can affect the amount of free hydrocarbon available for recovery and hydrocarbon thicknesses in monitoring wells. This phenomenon is further discussed in Section 5.3.1.3.2.

The release of LNAPL to the subsurface can reduce the amount of dissolved oxygen and change the pH of the groundwater. These changes, which are related to microbial activity, will locally alter the inorganic groundwater quality which may, in turn, cause scaling or corrosion problems during remedial activities. Depending upon the remedial action chosen, it may be necessary to test groundwater for specific conductance, pH, temperature, hardness, iron, manganese, and dissolved oxygen. Established USGS and EPA-approved testing methods should be used.

2.5.2.3 Dissolved Phase

Dissolved-phase hydrocarbon result from contact between water and LNAPL. Contact between groundwater and LNAPL can occur in several ways, including the following:

- Infiltration of water through the unsaturated zone containing residual hydrocarbon.
- Movement of infiltrating groundwater in contact with the free hydrocarbon plume.
- Groundwater in direct contact with an LNAPL plume.
- Flow of water past residual, undissolved hydrocarbon present below the water table.

As water moves through the unsaturated zone, the more soluble components of the residual LNAPL are more readily transported as dissolved-phase hydrocarbon. Likewise, transfer of hydrocarbon compounds into water that contacts the LNAPL plume in the vicinity of the capillary fringe can provide the mechanism for hydrocarbon to become dissolved in the groundwater. The dissolved chemicals in the water will move in the direction of groundwater flow and decrease in concentration as a result of physical/chemical processes as described in the following.

The concentrations of dissolved hydrocarbon compounds in water and the rates of transfer to the groundwater depend on several factors including the following:

- Depth to the water table.
- Hydraulic conductivity of earth materials.
- Recharge rates.
- Fluctuations in the water table.
- Groundwater velocities.
- Groundwater temperature.
- Residual hydrocarbon concentrations.
- Effective solubility of specific hydrocarbon chemicals.
- Adsorption and retardation effects.
- Attenuation factors.

All of the preceding influence the degree of mixing between water and LNAPL. LNAPL gasoline compounds



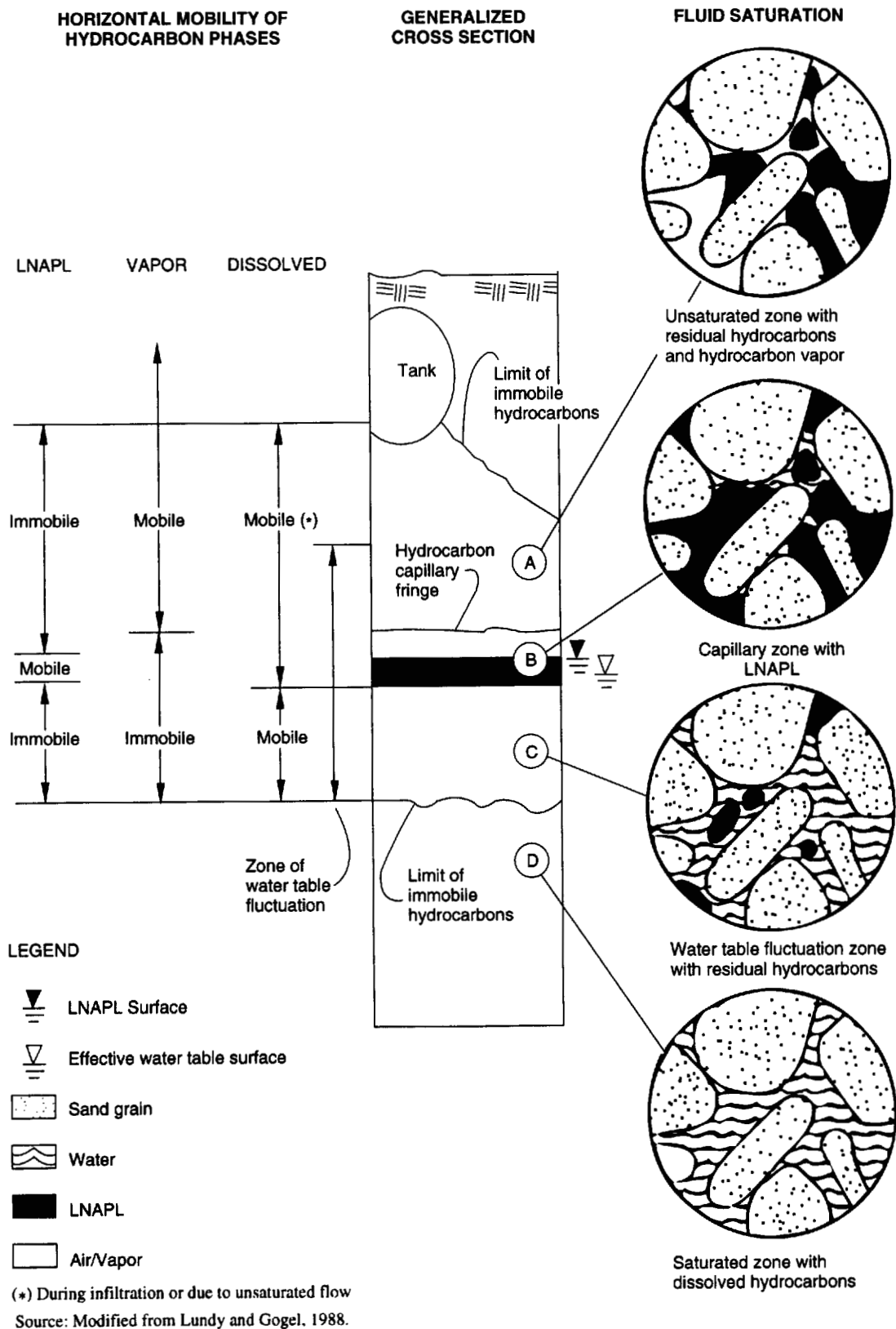
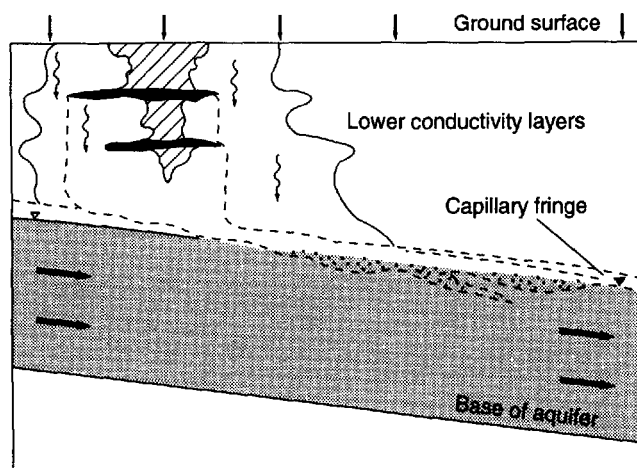
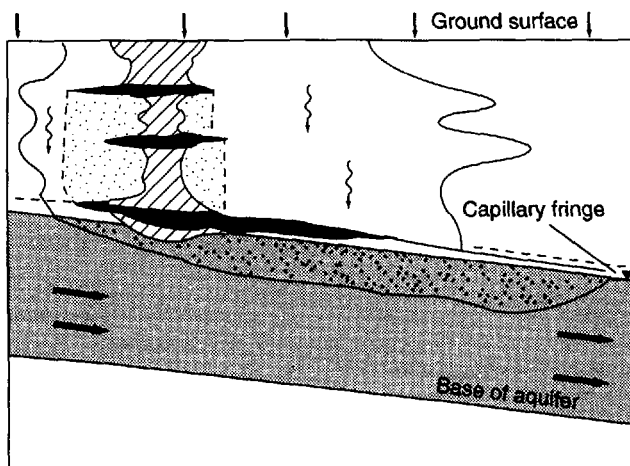


Figure 4—Vertical Distribution and Degrees of Mobility of Hydrocarbon Phases in Earth Materials



a. Release in which the LNAPL does not make direct contact with the regional groundwater zone.



b. Release characterized by LNAPL reaching the regional groundwater zone.

LEGEND

Hydrocarbon Phases

- Vapor phase
- LNAPL
- Residual LNAPL phase
- Dissolved phase in vadose zone
- Dissolved phase in groundwater
- Uncontaminated groundwater

Generalized Water Flow

- Infiltration at land surface
- Unsaturated flow
- Groundwater flow

Figure 5—Distribution of Hydrocarbon From a Small Release (a) and a Large Release (b)

such as oxygenates (ethanol, methanol, and MTBE), phenols, and aromatic compounds (BTEX), have relatively high solubilities (see Table 4) and tend to dissolve rather easily into water. Vapor-phase chemicals which typically consist of aliphatics and aromatic compounds can also dissolve into water (see 2.5.2.4).

The processes of advection and hydrodynamic dispersion are the primary factors controlling the movement of dissolved hydrocarbon in groundwater. *Advection* refers to the transportation of chemical constituents by groundwater movement and is, therefore, dependent on the hydraulic conductivity of the earth material. *Hydrodynamic dispersion*

Table 6—Ranges of Residual LNAPL Hydrocarbon Concentrations in the Unsaturated Zone

Earth Material	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	2200	0.07	10	4800
Coarse Sand	0.06	7.5	2800	0.1	15	6500	0.22	30	15000
Fine Sand/Silt	0.15	20.0	7500	0.3	40	17000	0.60	80	39000

Note: gal/ft³ = gallons per cubic feet; L/m³ = liters per cubic meter; mg/kg = milligrams per kilogram. Source: Modified from de Pastovich and others, 1979.

^aEstimate assumes an earth material bulk density of 1.85 gm/cm³ and liquid hydrocarbon densities of 0.7, 0.8, and 0.9 gm/cm³ for gasolines, middle distillates and fuel oils, respectively.

means the spread of a chemical constituent in directions other than would be expected due to groundwater movement only.

The effect of hydrodynamic dispersion is to reduce the hydrocarbon concentrations within the dissolved hydrocarbon plume. Hydrodynamic dispersion is caused by mechanical mixing of chemicals during advection and chemical diffusion. The primary dispersion mechanism called *mechanical mixing* is caused by the motion of groundwater as illustrated in Figure 7. This figure compares dispersion in two aquifers, one with relatively constant and the other varying hydraulic conductivity. The degree of dispersion in the former aquifer is much less than in the latter aquifer because groundwater velocities are more uniform in the aquifer, resulting in less mixing of the compounds. Field studies have demonstrated that dispersion is greatest in the direction of groundwater flow.

Dissolved hydrocarbon concentrations are also affected by physical/chemical processes such as adsorption of hydrocarbon chemicals onto earth material grains. The tendency to adsorb is different for each of the petroleum hydrocarbon chemicals and is represented in transport equations by the retardation factor. The *retardation factor* (R) refers to a function of bulk density of the earth material, porosity, and a distribution coefficient (K_d) which is related to what are called the soil *organic carbon content* (f_{oc}) and the *organic carbon partition coefficient* (K_{oc}). The equation which defines the process is:

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

Where:

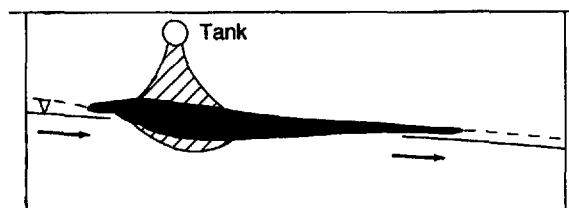
ρ_b = Bulk density of earth material.

n = Porosity.

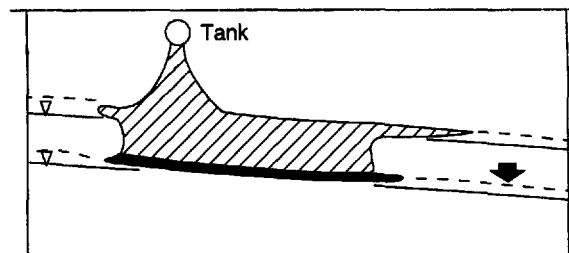
K_d = Distribution coefficient.

The value K_d is defined by:

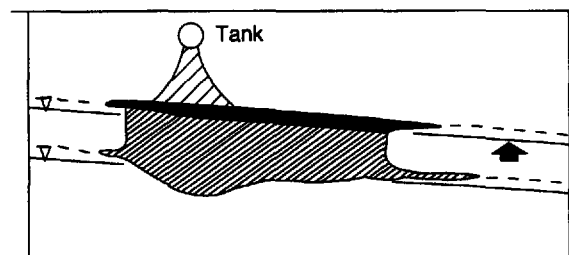
$$K_d = f_{oc} (K_{oc})$$



Static Water Table



Falling Water Table



Rising Water Table

Legend

- Residual LNAPL (above water table)
- LNAPL
- Residual hydrocarbons (below water table)

Source: Modified from Schwillie, 1984.

Figure 6—Spreading of Hydrocarbons as a Result of Water Table Fluctuations

Where:

f_{oc} = Organic carbon content of the earth materials.

K_{oc} = Organic carbon partition coefficient for the compound (function of K_{ow} , the octanol: water partition coefficient).

The theory which describes the roles of these phenomena is beyond the scope of this document. In general, however, finer-grained earth materials with greater clay content and, therefore, higher organic content retard the migration of hydrocarbon more than coarser-grained materials with lesser amounts of clay content. Refer to API Publication 1628A for more discussion on these issues.

Finally, natural biological processes affect the concentrations and migration potential of hydrocarbon chemicals dissolved in groundwater. These processes, collectively termed *biodegradation*, are the major attenuation mechanisms for petroleum hydrocarbon in the subsurface. In simple terms, biodegradation consists of naturally occurring subsurface bacteria altering the hydrocarbon chemicals into the harmless by-products carbon dioxide and water. This process, called *natural bioremediation*, serves to limit soluble-hydrocarbon plume migration in many cases.

2.5.2.4 Vapor Phase

Vapor-phase hydrocarbon originate in the unsaturated zone as mobile or residual LNAPL volatilize. Vapors can also form in the areas of LNAPL in the capillary zone, residual hydrocarbon in the unsaturated zone, and dissolved hydrocarbon downgradient from the release site. Vapor concentrations tend to be greater where the hydrocarbon consists of fresh, more volatile gasoline as opposed to diesel fuel. Gasolines contain more chemicals with higher vapor pressures and, consequently, greater volatility potential than diesel fuels.

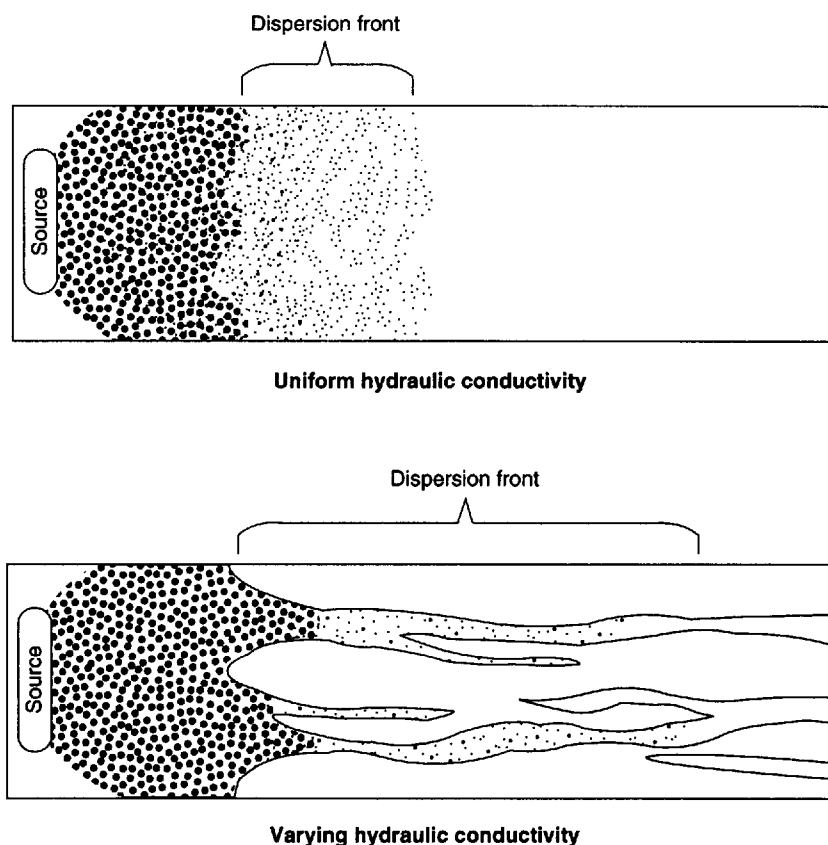
The migration of vapor in the subsurface is controlled

by many physical/chemical properties, including the following:

- a. Chemical and physical properties of released material:
 1. Effective vapor pressure.
 2. Effective solubility.
 3. Concentration.
 4. Density.
 5. Viscosity.
- b. Hydrogeologic properties:
 1. Hydraulic conductivity.
 2. Depth to groundwater.
 3. Flow direction of groundwater.
 4. Groundwater temperature.
 5. Porosity.
 6. Water content of soils.
- c. Miscellaneous:
 1. Barometric pressure.
 2. Rainfall duration and intensity.
 3. Man-made structures.

A portion of the vapor phase hydrocarbon can adhere to earth materials, with greater potential for adsorption occurring on earth material grains that are low in moisture content. Vapors can also emanate from the liquid and dissolved hydrocarbon plume as they migrate in a downgradient direction. Since the mechanisms that can affect vapor transport vary, detailed discussion of the physical mechanisms of vapor transport is not possible here.

It is important to note that vapors tend to follow more conductive pathways and migrate from areas of greater to lesser pressure. Since hydrocarbon vapor is more dense than air, it can accumulate in buildings, sewers, underground telephone vaults, and other structures and may potentially cause explosive conditions.



Source: Modified from Freeze and Cherry, 1979.

Figure 7—Effects of Hydraulic Conductivity on Mechanical Dispersion of Dissolved Compounds

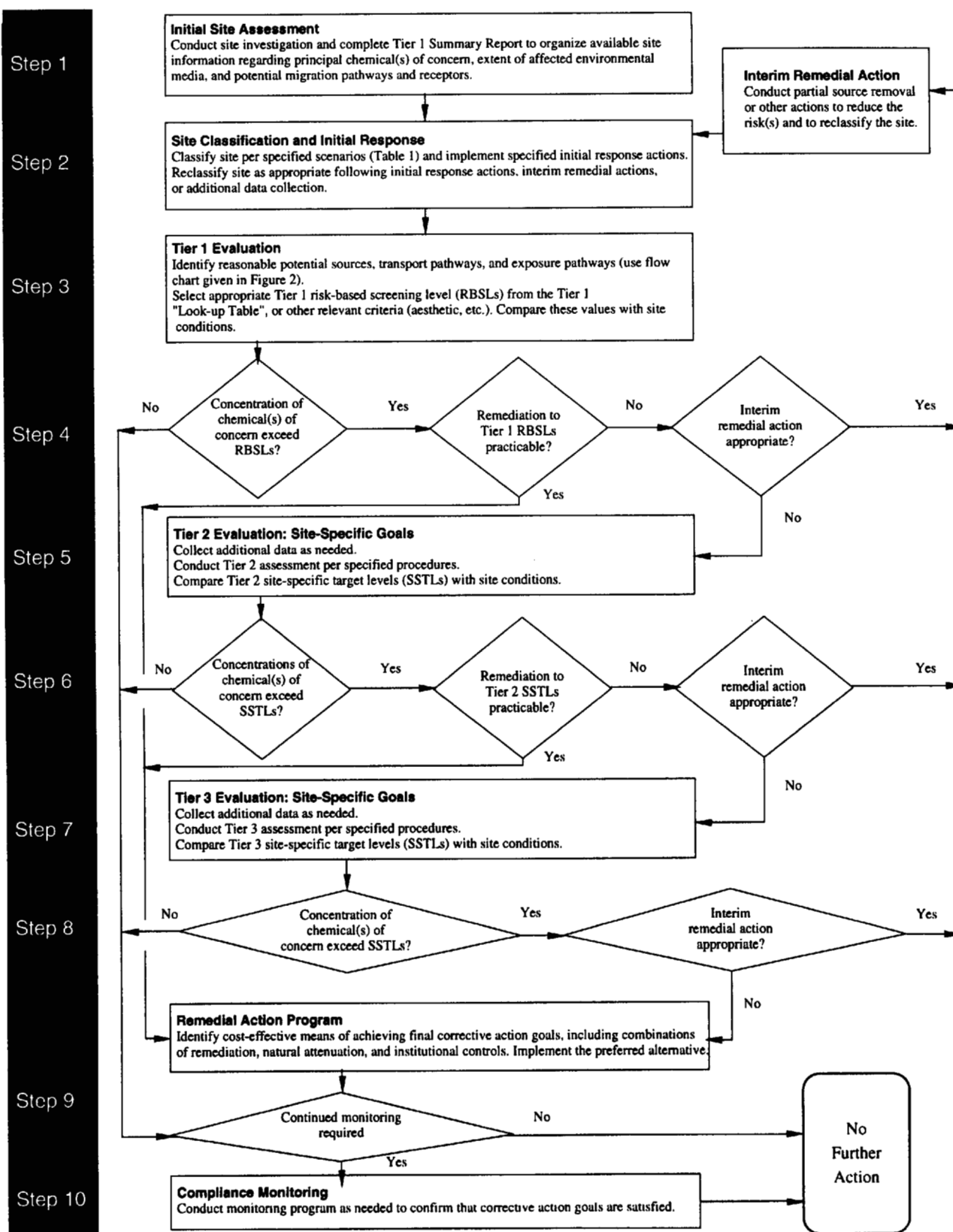
SECTION 3—RISK-BASED CORRECTIVE ACTION

3.1 Overview

Risk-Based Corrective Action (RBCA) is an approach that incorporates risk and exposure assessment practices with the traditional components of corrective action described in this publication (that is, emergency response, initial abatement, site assessment, remedial action) to focus remedial measures and resources consistent with the level of risk posed by a site to human health and the environment and to facilitate timely closure of hydrocarbon-impacted sites. The RBCA approach combines the information gathered during a site assessment with data on the health effects of the chemicals identified on site to evaluate a particular site for remedial actions. Chemical(s) and pathways of concern are identified and site-specific target levels are determined. Since, by definition, risk is dependent on both exposure and toxicity, there is no risk without an exposure. By applying the risk assessment principles, the likelihood that adverse health or environmental effects will occur as a result of exposure to chemical(s) of concern can be determined.

The RBCA process (Figure 8) is described in an ASTM consensus standard released as ASTM Standard E1739. The ASTM RBCA standard provides a framework to make decisions related to the urgency of response, site-specific target levels, and remedial measures based on protection of human health and the environment. Use of the RBCA process yields a technically defensible, protective, and cost-effective approach to address petroleum release sites.

A risk-based approach considering protection of human health and the environment should be used for all sites. Considerable resource/cost savings may be realized utilizing this approach, while still being protective of human health and the environment. Regulators in many states and the USEPA are looking to risk-based options. Before using a risk-based approach, the regulatory climate should be assessed and the process discussed with the lead regulatory agency, to establish applicability and goals for a risk-based approach to corrective action.



(Source: ASTM E1739)

Figure 8—RBCA Flowchart

3.2 Initial Site Assessment and Site Classification

The RBCA process begins with an initial site assessment and site classification. Initial data requirements should be focused from a risk perspective to characterize the land use (for example, residential, commercial, industrial) and resource use (for example, groundwater used as a drinking water supply) of the site and adjacent properties; and to identify chemical(s) of concern, source areas, potential exposure pathways, and receptors and identify concentrations of chemical(s) of concern at the source area and point(s) of exposure. This information can be collected from historical records, site inspection, and limited site assessment activities.

Using the initial data collection, the site can be classified based on the level of potential threats to human health and the environment; and initial response actions can be taken as appropriate. Site classification is designed to focus resources on those sites posing the greatest threat to human health and the environment. Responses may range from emergency response and initial abatement actions for those sites posing an immediate threat, to monitoring programs for sites having little potential for current or future impacts. Each classification defines responses that are appropriate for that classification.

3.3 Tiered Evaluation

The RBCA tiered-evaluation process begins with the first tier and moves to higher tiers as warranted. Moving through the tiers requires more focused site assessment activities and the development of more site-specific data. The three-tiered risk-based decision-making process reduces the data collection and evaluation burden at many sites. Sites with minor releases may be addressed through a health-protective screening approach in Tier 1. The majority of petroleum hydrocarbon sites probably can be addressed through a quantitative approach involving the assumption of realistic current and future site use and health-protective and ecologically protective, site-specific exposure parameters, as described by a Tier 2 evaluation. For those sites where multiple human or ecological exposure pathways exist, a more detailed and comprehensive evaluation may be warranted, and these sites would fall into Tier 3. Because site assessment and risk assessment processes increase in complexity with each tier level, costs, data requirements, and level of sophistication required also increase.

3.3.1 TIER 1 EVALUATION

Tier 1 involves the comparison of site-specific concentrations of chemical(s) of concern to a Tier 1 look-up table. The Tier 1 look-up table contains conservative, non-site-specific risk-based screening-level (RBSL) concentrations for chemical(s) of concern. These are for a variety of poten-

tial exposure scenarios (for example, residential, industrial) and exposure pathways (such as groundwater ingestion, dermal contact) to environmental media such as groundwater, soil, and vapors. Typically, these values are derived based on protection of human health and the environment, but may also consider aesthetic criteria. RBSLs are applied consistently to all sites. They are compared to site-specific concentrations of chemical(s) of concern for the site. If the concentrations of chemical(s) of concern are below the screening-level concentrations, then no further action is appropriate. If the concentrations are above the screening-level concentrations, then further tier evaluation to develop site-specific target levels may be appropriate. Remedial action using Tier 1 screening levels as target levels may also be considered.

3.3.2 FURTHER TIERED EVALUATION

If further tiered evaluation is appropriate, provisions are available under Tiers 2 and 3 to develop site-specific target levels (SSTLs). An important factor in any RBCA analysis is the protection of human health and the environment. In each case, the site-specific target levels will be health protective to the same overall level [for example, a target risk of 1 in 100,000 (10^{-5})]. The difference in higher tiers will be the use of site-specific data and chemical fate and transport analysis to replace the conservative assumptions and analysis. The decision to move to a higher tier is based on the following:

- Is the approach or are the assumptions used to derive the current tier's site-specific target levels appropriate for conditions at this site?
- Will the site-specific target levels developed under the next higher tier be significantly different from the current tier?
- Will site-specific target levels developed under the next higher tier significantly modify the remedial action activities?
- Will the cost of remedial action to current tier target levels likely be greater than further tier evaluation and subsequent remedial action?

3.3.2.1 Tier 2 Evaluation

Tier 2 uses more site-specific data than the first tier. This level of effort will apply to the majority of UST sites. This is a more site-specific assessment and typically involves "reasonable use" exposure assumptions and consideration of actual beneficial uses of resources. Tier 2 provides a tool for determining point(s) of compliance. Additional site assessment data may need to be collected as part of this evaluation. Site-specific target levels can be developed under a Tier 2 evaluation using any one or combination of the following:

- Use the methods and equations for development of the Tier 1 screening levels, but replace the default assumptions with site-specific parameters.

b. Apply the Tier 1 screening levels at point(s) of exposure, then back-calculate acceptable concentrations at the source area(s) based on estimated (for example, using predictive models), measured, or monitored attenuation.

c. Develop statistical representation of the source area(s) concentrations of chemical(s) of concern and compare the representative concentrations to the screening levels or site-specific target levels.

3.3.2.2 Tier 3 Evaluation

Tier 3 involves the highest level of effort and may include the use of site-specific numerical models, probabilistic analyses such as those involving Monte Carlo, or sophisticated analytical tools. Tier 3 may utilize tools such as API's Decision Support System for Exposure and Risk Assessment that provide analyses to support site-specific decisions. This tier may be best suited for sites where multiple pathway analysis is required (for example, exposure of

receptors could occur during work activities, recreational activities, trespassing, or a detailed analysis of ecological exposures). Tier 3 will typically require significant additional site-specific data for the use of complex numerical models and probabilistic analyses.

3.4 Remedial Action and Monitoring

In the RBCA process, remedial action is determined to be appropriate, based on the comparison of representative concentrations to the target levels determined under the tier evaluation. Remedial actions may include a combination of aggressive and passive measures including engineering and institutional controls. Monitoring should be conducted following or during a remedial action to demonstrate that target levels are met and continue to be met and to verify the assumptions and predictions used in Tier 2 and Tier 3.

Note that more information can be found in Publication 1628B.

SECTION 4—EMERGENCY RESPONSE AND INITIAL ABATEMENT

4.1 Overview

The presence of hydrocarbon in structures, excavations, or other sensitive receptors may require the immediate control of liquid and vapor phases. Emergency response to, and initial abatement of a hydrocarbon release is intended to minimize potential risks to life, property, and the environment and also to minimize long-term costs and liabilities.

Emergency response commonly involves one or more of the following actions:

- Vapor control and abatement (fire and explosive conditions).
- LNAPL control and abatement.
- Groundwater use evaluation.
- Soil excavation.

Safety must be paramount in any emergency response situation.

Initial abatement may simply be containment of the release or preventing impacts to potential receptors (Note: site investigation is not "abatement"). Initial abatement of a known or suspected release includes notification of the affected parties, owner, or party responsible for the product storage or delivery system, if known. In some states notification of state and local regulatory agencies is required when a release is suspected. Refer to the appropriate state or local requirements to determine if reporting is required.

4.2 Vapor Control

Most liquid petroleum products are flammable or combustible, and many are volatile. The combination of these characteristics makes explosive vapor a potential concern.

Vapor can accumulate to explosive concentrations in a confined, poorly-ventilated area. Precautions must, therefore, be implemented to prevent fire and explosion.

The volatilities of petroleum products vary considerably. Gasoline, for example, is quite volatile and vaporizes readily at ambient temperatures and pressures. The volatility of gasoline, coupled with its low flash point, require that precautions be undertaken to prevent fire and/or explosion. On the other hand, heating oils have higher flash points and do not vaporize as readily at ambient conditions and, consequently, are not likely to generate explosive vapor concentrations.

The threat of a fire and/or explosion is a particular problem when vapor from a released petroleum product becomes trapped and accumulates in confined areas such as the basements of homes, sewer lines, septic tanks, tunnels, and underground utility vaults. Frequently, the backfill surrounding tanks, utility conduit trenches, and sewers provides a vapor migration route into such confined structures.

Vapors may initially be detected in a structure by their characteristic odor or through the use of vapor monitoring devices (a combustible gas detector, for example). When an explosion threat is present, the following actions should be taken:

- Evacuate people out of the area of concern.
- Take proper precautions to protect personnel exposed to the release.
- Notify the local fire department so that trained personnel can evaluate the fire and potential for explosive conditions.
- Use trained and certified personnel to test for explosive vapor concentrations.



Documents

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- e. Use equipment with explosion-proof ratings.
- f. Prohibit smoking, and eliminate all other sources of ignition.
- g. Ventilate the enclosure to reduce concentrations.
- h. Locate the vapor source and eliminate it, if possible.

Ventilating vapor from an enclosed space reduces its concentration to below explosive limits. This requires the movement of air through the enclosed space in order to displace the vapor. Ventilation must be continued for as long as vapor remains in, or has the potential to enter, the enclosed space. Ventilation of the structure should be begun before the source of the vapor is addressed, since it may not be safe for anyone to enter the structure otherwise.

The method used to ventilate an enclosed space will depend upon the type of structure and the source of the vapor. If the structure is aboveground, it may be sufficient to open windows and doors and allow natural airflow to dilute the vapors. An explosion-proof exhaust fan or a water hose discharging outward with the nozzle set in the spray position may be placed in a window to enhance natural ventilation. If the structure is entirely underground, ventilation using fans or blowers will likely be necessary. It is important to use explosion-proof equipment to avoid igniting the vapor.

In a potentially explosive environment, care should be taken to remove and avoid all potential sources of ignition. The National Fire Protection Association (NFPA) recommends that explosive conditions not be remediated by using fans to force air into a structure, as it is sometimes possible to provide enough oxygen for explosive levels to be reached. Instead, explosion-proof fans should be used to exhaust air and vapor. Only passive fresh-air inlets should be used. Ventilation by opening doors and windows may be sufficient to reduce the concentration of vapor to a safe level, after which positive pressurization of the structure by forced venting can prevent or inhibit vapor reentry. Subsurface soil-venting systems may initially be used to control the entry of vapor into structures and may be used later in site remediation. Soil venting is discussed in 7.6.1

4.3 LNAPL Control

The greater the interval between a hydrocarbon release and the start of remedial efforts, the greater the potential for hydrocarbon migration. Therefore, prompt installation of an appropriate LNAPL recovery system can limit the spread of LNAPL and reduce long-term efforts and costs to remove and control other hydrocarbon phases.

Emergency response contractors who normally have the materials, manpower, expertise, and proper certified training to respond quickly to different emergency scenarios can be used to install a temporary recovery system. Larger emergencies may require several emergency response contractors with skilled tradesmen and a variety of equipment and services. (Note: All personnel must have current and appropriate levels of emergency response training.)

Backhoes can be used to install temporary trenches, drains, or sumps to intercept and begin recovery of LNAPL at shallow depths. Local well drillers, preferably experienced at installing environmental monitoring wells, and possessing appropriate health and safety training, can install wells for investigation and recovery of LNAPL as long as completion techniques presented in Section 5.3.1.2.2 are followed. Many UST excavations have monitoring wells located in them that may be used to recover LNAPL.

Single-pump or skimming systems are normally used for emergency recovery operations, as these are readily obtainable and can be installed quickly. Positive-displacement, suction-lift pumps can rapidly be deployed to recover hydrocarbon from shallow sumps or wells. Pumping equipment should meet pertinent safety requirements. Compatibility of the hydrocarbon with the transfer equipment (pumps and hoses) and storage equipment (tanks and drums) must be assured. Vacuum trucks may be used as a means of quick response to remove and transport hydrocarbon from trenches, sumps, wells, or utility vaults.

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

4.4 Groundwater Use Evaluation

A quick inventory of water wells, surface water bodies, and other potential receptors near the site is necessary to identify potential points of dissolved hydrocarbon discharge. Water from these sources can be sampled and analyzed on-site with portable equipment, or in off-site laboratories, to determine if dissolved hydrocarbon are present. If the water is contaminated, continuous treatment may be necessary, depending on the concentrations of chemical(s) of concern and water use. Alternatively, a well can be taken out of service and replaced by a different water supply. Note that the slow movement of groundwater usually allows time to assess the extent of chemical(s) of concern before implementing groundwater recovery.

Other environmental receptors may include buildings with basements, underground utility trenches, and other man-made structures. A further discussion of potential environmental receptors is included in Section 6.2.2

4.5 Soil Excavation

Excavation of contaminated soil is sometimes a suitable method for removal of the hydrocarbon source and quick remediation of small releases. The decision to excavate depends on the volume of the hydrocarbon released, the depth and area of LNAPL penetration, and the ease with which soils can be removed, properly treated, and returned to the excavation or disposed of off-site.

The release volume, if possible to approximate, and general soil type can be used with data presented in Table 6 to make a conservative estimate of the volume of soil contaminated at residual saturation levels. Excavation may be a reasonable option if the depth of penetration is within the operating limits of a backhoe and if the removal volume is small enough so that normal site operations will not be greatly disrupted.

Soil excavation is often used as an initial remedial measure during an equipment removal, such as a UST removal. If a pre-removal evaluation has been performed for soil and groundwater conditions, a decision to remove a limited source with the USTs can be made. Soil excavation should be evaluated in the overall context of the site, since groundwater remediation must be addressed separately from the soil removal. Soil excavation is generally appropriate for small sources above the water table. Below the groundwater table, soil excavation may be of limited value. In addition, the evaluation of soil excavation as an initial response action depends on the quantity of data available. There is often

uncertainty in the estimated volume of soil to be removed because of the nature of movement of hydrocarbons in the unsaturated zone, making underestimations of volumes likely.

Petroleum-contaminated soil may be flammable or combustible and can be a source of potentially explosive vapor. Care must be taken, both during and following excavation, that vapor or liquid from the soil is not allowed to accumulate in a confined area and pose a fire or potentially explosive condition. Sparks from the excavation process have the potential for igniting a fire/explosion. If the soil is to be stored on-site after excavation, it should be covered or stored in a covered and bermed or otherwise contained area so that leached petroleum product cannot be released into surrounding soil, surface water, or groundwater. Off-site transport and disposal of contaminated soil must be in accordance with local, state, and federal regulations. Various treatment and disposal options for excavated soil containing petroleum hydrocarbon are presented in 7.6.3.

SECTION 5—SITE ASSESSMENTS

5.1 Overview

A site assessment is initiated when petroleum hydrocarbon are known or suspected to be present in the environment. This section presents some general guidelines and approaches for performing site-specific assessments. All sites have unique site problems that can generally be defined and handled by methods described in this section. The overall objective of a site assessment is to evaluate potential sources, potential receptors (for example, streams, basements), and potential migration pathways. The extent of site assessment should be consistent with the data necessary to make corrective action decisions. The information is used with exposure and toxicity information to help determine which chemical(s) of concern require remediation and to what level.

Many states have developed guidelines for performing site assessments. Guidance is also available through several publications, including the American Society for Testing and Materials (ASTM).

Information from a site assessment should be used to determine the following:

- The presence, nature, concentration, and extent of liquid-, dissolved-, and vapor-phase hydrocarbon.
- Source areas, types of chemical(s) of concern, and hydrocarbon migration pathways.
- Hydrogeologic properties controlling hydrocarbon movement.
- Receptors that could be adversely impacted by hydrocarbon (such as buildings with basements, underground utility trenches, water wells, and surface waters).

- Data required to help select, design, implement, and monitor corrective actions.
- Land use (past, present, and future).

Site assessments typically involve three general activities: gathering background information, planning and 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 additional data collection, to determine site-specific target levels, and to identify potential remedial action measures to achieve the target levels. A discussion of the RBCA approach is presented in Section 3.

This section presents some general guidelines and approaches for assessing the presence, source, and extent of subsurface hydrocarbon at sites where a release has occurred.

5.2 Gathering Background Information

The objective of gathering background information is to assess potential conditions and sensitive receptors in the area of the release from readily available records, reports, and interviews and to identify any relevant site characteristics that may affect the corrective action process. The following are suggested information-gathering tasks:

- Review site-related engineering drawings (for example, foundation soil borings; as-built diagrams of storage systems; and number, size, and location of past and present source areas).

- b. Obtain and review available maps, aerial photographs, and geologic and hydrologic information for the area. Sources of the latter data include the U.S. Geological Survey (USGS), state geological surveys, and the U.S. Soil Conservation Service (SCS).
- c. Interview site personnel to determine how LNAPL are stored, transported, monitored, and removed from the site.
- d. Obtain available information on the location, type, and estimated quantity of petroleum product released and the duration of the release, if known.
- e. Investigate the history of previous land ownership and land use, both on and near the site, and identify other possible sources of the hydrocarbon release or previous releases.
- f. Determine the locations and depths of all underground utilities, including product lines, 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).
- g. 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.
- h. Identify the waste materials generated on-site, especially those containing hydrocarbon, and determine how these are to be handled.
- i. Incorporate federal, state, and local agency requirements.

Information gathered through these activities will be used to help identify possible release sources, hydrocarbon types, migration pathways, potential receptors, and complete exposure pathways. Additionally, some of these items may require field verification. This information is critical for developing an appropriate scope of work for subsurface investigation, and for deciding whether or not active remediation is warranted.

5.3 Site Characterization

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

- a. To define the nature, extent, and source(s) of the liquid-, dissolved-, and vapor-phase hydrocarbon.
- b. To understand the influence of site-specific hydrogeologic conditions on the fate and transport of the released hydrocarbon.
- c. To provide the data required for selecting and designing appropriate corrective action options.

Prior to installing monitoring wells, screening-level assessments can be used to minimize subsequent field work. For example, use of soil vapor surveys may be useful in

determining the general area of impact. Also, technology available through specialized equipment such as geoprobes and cone penetrometry and the like, allows the cost-effective gathering of soil and groundwater data that can be used to better plan additional work. All of the screening methods have advantages and limitations based on soil types and depths to be investigated.

Proven investigative technologies and methods applicable to various hydrocarbon phases are listed in Table 7. There will be some overlap when applying these technologies. For example, monitoring well installation techniques can combine soil, vapor, and groundwater sampling activities. Pumping and bailing of monitoring wells installed during an assessment can be used for initial recovery of hydrocarbon that have accumulated in the subsurface. These wells may later be used to measure fluid elevations to estimate local groundwater flow directions.

Planned field activities should be structured from results of the background information and screening-level assessment. The locations and depths of borings and monitoring wells can be decided from a general knowledge of the source area or release, the local geology, soil types, hydraulic conductivity, depths to groundwater, inferred groundwater flow directions, and desired sampling depths. Current groundwater usage should be taken into account. For example, nearby shallow pumping wells can alter the local water table elevations and gradients.

Great care must be used in determining the depth to which borings and monitoring wells will be completed. The borings must not intersect multiple water bearing zones or penetrate potential confining units if the upper saturated unit has not been adequately defined and sealed-off.

5.3.1 DELINEATION OF LNAPL

5.3.1.1 General

The delineation of the LNAPL phase involves assessing the distribution of residual and LNAPL and possibly vapor-phase hydrocarbon. Delineation methodologies applicable for LNAPL are discussed in the following subsections. Delineation of dissolved-phase hydrocarbon is discussed in 5.3.2, and delineation of vapor phase hydrocarbon is discussed in 5.3.3.

5.3.1.2 Delineation Methodologies

5.3.1.2.1 Field Screening and Analytical Techniques

Properly performed field measurement techniques provide results more rapidly than laboratory analyses for making decisions on-site. 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. Several other technologies not as widely utilized are also

Table 7—Proven Investigative, Sampling, and Analytical Technologies Applicable to Various Hydrocarbon Phases

Hydrocarbon Phase/Zones	Investigative Technologies	Sampling Technologies	Analytical Technologies
Liquids	Soil borings	Drive sampling	Lab—SE, IR, GC, GC/MS
Unsaturated zones and capillary fringe	Geoprobe, Cone penetrometer	Shelby tube	
LNAPL plume	Monitoring wells	Split spoon	
	Existing subsurface structures	Bailer	Lab—GC, GC/MS
	Geoprobe, Cone penetrometer	Pump	
Dissolved	Monitor wells	Bailer	Lab—GC, GC/MS
Saturated zone	Existing supply wells	Pump	Field—GC, colorimetric
	Geoprobe, Cone penetrometer		
Vapor	Soil borings and excavations	Ground probe	Lab—GC, GC/MS
Unsaturated zone	Vapor wells	Buried accumulator	Field—FID, PID, IR, GC
	Existing subsurface structures		O2/1el meter
	Geoprobe, cone penetrometer		
Residual and Adsorbed	Soil borings	Drive sampling	Lab—A/D, GC
All zones	Geoprobe, Cone penetrometer	Coring	

Note: SE = Soxhlet extraction; IR = infrared spectrophotometry; GC = gas chromatography; GC/MS = gas chromatography/mass spectrometry; FID = flame ionization detector; PID = photoionization detector; A/D = adsorption/desorption experiments.

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	
General headspace analysis ^b	FID/PID/colorimetric detector tube/GC	10s–100s ppm ppb	10s–100s ppm ppb	10–20
Polyethylene bag sampling system	FID/PID colorimetric detector tube/GC	1 ppm 10s–100s ppb	1–100's ppm ppb	10–20 20
Extraction-colorimetric procedure, Immunoassay	N/A	Soil: 1 ppm ^c Water: 0.1 ppm	N/A	Soil: 45–60 Water: 10–15
Soil vapor	FID/PID/colorimetric detector tube/GC	N/A N/A	1 ppm 1–100s 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.

^aDetermined by spiked field standards.

^bGeneral headspace analysis refers to dynamic and static headspace analysis.

^cMay have limited applicability due to natural interferences.

presented in this section (see also ASTM PS03). Field screening methods are commonly used to identify the presence of volatile organic compounds in soil samples using field headspace techniques with portable instruments. Some of the advantages of field measurement procedures and instruments include the following:

- Reliable qualitative and semiquantitative data become available at the site and can be used to make quicker decisions regarding the need for further assessment and ongoing remediation.
- The lower cost of field measurements allows more sam-

pling points to be installed in a faster time frame, which results in more data when appropriate.

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:

- Depending on the procedure or instrument used, the results are semiquantitative or qualitative. (Note that portable gas chromatographs (GCs) can provide quantitative results.)



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- b. Some techniques that are less sensitive to nonvolatile chemicals (such as headspace methods), are not well suited for weathered products.
- c. Some techniques do not discriminate between naturally occurring organic materials and petroleum hydrocarbon.
- d. As with any analysis, field techniques are subject to procedural errors that can affect the reliability of the results unless proper quality assurance/quality control (QA/QC) protocols are followed.
- e. Generally, most agency actions are based on laboratory data. Field measurement results are most often used as a screening-level evaluation.

Although information collected by field measurement procedures may save time and money and enable quicker decision-making, many state and local agencies require laboratory analysis of soil and/or groundwater samples to verify field information, to quantify BTEX and total petroleum hydrocarbon (TPH) levels, or to test for less volatile products (for example, diesel fuel). Actual field laboratory set-ups are now being used in some cases to provide laboratory-quality data for individual compound analyses.

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.

Soil samples may be screened for hydrocarbon concentrations in the field using portable, direct-reading instruments which detect volatile organic compounds in headspace samples. Table C-1 (see Appendix C) provides additional information about these and similar instruments. The following instruments are commonly used to screen soil samples for the analysis of headspace vapors:

- a. Flame ionization detector (FID) with optional gas chromatograph.
- b. Ultraviolet photoionization detector (PID).
- c. Infrared spectrophotometer.

These instruments are capable of detecting total concentrations of many organic chemicals. Specific compound identifications are also possible, depending on the instruments used. Manufacturers' literature must be consulted for calibrating procedures and instrument limitations. For example, the instrument response may change with composition of the gases, the humidity, and the amount of oxygen or carbon dioxide in the vapor being sampled. Results are relative only to the calibration standard used. Field analytical results tend to be less complete and generally less accurate than laboratory results.

Field 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 (Table C-1). Temperature,

high soil moisture, and high levels of organics and clay in the soil can limit the amount of volatile hydrocarbon that will volatilize into the container headspace. Concentrations of volatile chemicals are lower in soils containing weathered petroleum hydrocarbon (hydrocarbon that have been in contact with the environment), compared with soils containing fresh releases, because the volatile chemicals decrease in varying degrees over time. Importantly, these field headspace analyses provide qualitative results that can be used as a general indicator (screening tool) of the presence of hydrocarbon.

Dynamic headspace analysis of soil by using a polyethylene freezer bag system involves collecting a soil sample, placing it in an airtight freezer bag, 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 (Table C-1). Measured concentrations are a function of the analytical detector's range of sensitivity.

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

Field analyses provide an indication of the relative amounts of volatile residual LNAPL present in the sample. However, while screening methods generally do not differentiate between individual compounds, field screening is very useful to help determine which samples should be sent for laboratory analysis, to determine order-of-magnitude estimates on concentrations, to delineate source areas, and to plan additional sampling activities.

Several screening methods have recently been developed and include the following:

- a. Ultra-violet derivative spectroscopy: this method uses heat to drive off the volatiles from the soils and ultraviolet spectroscopy to determine BTEX concentrations. The process takes about 10 minutes per sample, and hydrocarbon can be detected in the 1 to >100 ppm range.
- b. Solvent extraction: General solvent extraction kits are available for field determination of residual hydrocarbon in soils. These methods require that hydrocarbon be extracted from the soils using a solvent (for example, methanol); results are obtained from color changes. The speed of these analyses are highly dependent on the proficiency of the technician doing the tests. Hydrocarbon in soils can be detected in the 1 ppm to >100 ppm range.
- c. Immunoassays: Immunoassay technology uses a substance which reacts with BTEX, forming a colored material that can be detected. Total hydrocarbon in soils can be detected in the 1-75 ppm range.



d. Ultraviolet (UV) fluorescence: Most hydrocarbon fluoresce; that is, they emit a "burst of light" when exposed to a UV light source. Thus, exposure of soil samples to UV light can be used as a screening tool to detect the presence of LNAPL. Pores filled with hydrocarbon will fluoresce, and those filled with water or air will not. The intensity of fluorescence can be used as a relative indicator of the degree of hydrocarbon present.

All four of these direct field-screening methods are not widely used. However, each may have applications to a particular site-screening requirement and should be considered.

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

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

This technique typically involves the insertion of a small-diameter (less than 1 inch 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 photoionization detector (PID), flame ionization detector (FID), or portable gas chromatograph (GC). Depending on source depth and soil permeability, soil gas surveys may not always be effective.

Soil vapor sample locations are often determined based on a knowledge of potential site conditions. When little site information is available, a grid system can be used for selecting sample locations. However, enough information about potential source areas should be available for most petroleum facilities to implement a site-specific sampling plan. 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 vertical soil vapor sampling is generally used only to define the lateral extent of hydrocarbon, some investigators conduct it at selected sample points. This sampling is typically performed at sites where hydrocarbon are suspected of being present in the upper soil material or at sites where impermeable clay layers are present that would restrict hydrocarbon migration vertically. Soil vapor samples are collected beneath the suspected source area(s) or below the clay layer to determine whether or not the chemical(s) of concern have migrated vertically. If sampling below source area(s) is performed, great care must be taken in order to avoid spreading hydrocarbon vertically with the sampling tools.

Soil vapor measurements cannot be used to quantify the amount of petroleum hydrocarbon in soil or groundwater, but can be utilized in a relative manner to assist in determining their presence or absence. The results of soil vapor

measurements provide qualitative information on hydrocarbon concentrations in soil vapor (they are not directly comparable to soil concentrations), and these results should be interpreted relative to other soil vapor sampling points. An SVS is also useful in determining future sampling locations (for example, placement of monitoring wells).

5.3.1.2.2 Soil and Groundwater Sampling

Soil borings and monitoring wells are the primary means of assessing the extent of the chemical(s) of concern from any hydrocarbon phase. Direct push techniques are also utilized to assess the extent of the chemical(s) of concern.

CAUTION: A potential for small flash-type fires exists at or near soil borings that have penetrated LNAPL locations, and proper precautions should consequently be taken to avoid having ignition sources, such as smoking or welding operations, near the soil borings. The locations of product lines and underground utilities (gas, water, electrical, and sewerage) should be determined before commencing any boring or drilling activity. Drilling locations should be probed or dug by hand to a depth of at least 5 feet before beginning mechanical drilling operations to ensure subsurface utilities are not damaged.

A wide range of equipment is available for drilling, soil sampling, and installing monitoring wells. Methods for drilling soil borings and installing monitoring wells are listed in Table 9. The selection of a particular drilling technique is governed by (a) the type of material being drilled through, (b) anticipated drilling depths, (c) soil and rock sampling needs and capabilities, (d) equipment availability, and (e) cost.

Relative performance criteria for different drilling techniques are summarized in Table 10. Local drilling contractors and consultants can provide more specific information and recommendations on the capabilities and use of particular techniques. A qualified professional should supervise drilling operations. Such a professional will have the following capabilities:

- a. A knowledge of drilling operations.
- b. Conversant with drilling specifications.
- c. The means to ensure that proper installation techniques are followed and cross-contamination by drilling equipment is avoided.
- d. All certification and licenses required by the enforcing state agency.

Where conditions permit, a hollow-stem auger is commonly used for soil sampling and monitoring well installation. The helical hollow-stem auger, which consists of flights or ridges that carry soil upward when the auger is driven into the ground, are manufactured in 5-foot lengths; with outside diameters ranging from about 7 to 18 inches and inside diameters ranging from 2.5 to 12 inches.

Table 9—Basic Well-Drilling Methods

Drill Type	Normal Diameter Boring	Maximum Depth	Average Time per Boring	Normal Expense	Advantages	Disadvantages
Direct Rotary (fluids) Direct Rotary (air)	4–20 in.	Unlimited	Fast	Expensive	Good for deep holes Usable in soils and rock Wide availability Caving is controllable Core barrel soil samples can be obtained	Drilling fluid is required Potential bore hole damage from drilling fluid. Handling of drilling fluids
Solid stem auger	4–8 in.	100–150 ft	Fast under suitable soil conditions	Inexpensive to moderate	Wide availability High mobility Dry soil samples are obtainable while drilling	Casing cannot be set in unsuitable soils (caving) Large stones, boulders, or bedrock cannot be penetrated Recovery well installation cannot be accomplished Undifferentiated soil samples cannot easily be obtained
Hollow stem auger	4–12 in.	100–150 ft	Fast under suitable soil conditions	Inexpensive to moderate	Good for sandy soil Casing can be set through hollow stem High mobility Dry soil samples and split spoon samples can be obtained Caving is controllable	Casing diameter is normally limited to 4–6 inches Boulders or bedrock cannot be penetrated without special equipment Potential heaving
Kelley auger	8–48 in.	100 ft	Fast	Moderate to expensive	Large diameter recovery wells can be installed Holes can be drilled with minimum soil wall disturbance or contamination Good disturbed-soil samples can be obtained	Large equipment is required Availability in rural areas is limited Casing may be required while drilling Wet sandy soils cannot be negotiated effectively
Bucket auger	12–72 in.	90 ft	Fast	Moderate to expensive	Good disturbed-soil samples can be obtained Large diameter recovery wells can be installed Good in sandy soils	Drilling fluid is typically required Very large operating area normally required
Cable tool	4–16 in.	Unlimited	Slow	Inexpensive to moderate	Wide availability Usable in soil or rock	Method is slower than other approaches Hole is often crooked Casing may be required while drilling
Air hammer	4–12 in.	Unlimited	Fast	Expensive	Fast penetration in consolidate rock core barrel samples	Inefficient in unconsolidated soil Geologic logs are not typically detailed Control of dust/air release Excessive water inflow will limit use
Direct drive (well point)	2–24 in.	60 ft	Slow to moderate	Inexpensive	Wide availability Excellent portability	Limited to unconsolidated soil Large boulders or bedrock cannot be penetrated No soil samples can be obtained Generally inefficient method to install a recovery well
Geoprobe	1–3 in.	30–100 ft	Fast	Inexpensive	Moderate availability Rapidly assess soil and groundwater conditions	Consolidated materials, or boulders, etc., cannot be penetrated

Note: in. = inches; ft = feet.