# 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

# Manufacturing, Distribution and Marketing Department

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, nonaqueousphase 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 ground-water.

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 7 addresses approaches to the control, recovery, and remediation of petroleum hydrocarbon.

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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
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
ASTM <sup>1</sup>	
E1739	Standard Guide for Risk-Based Corrective
	Action Applied at Petroleum Release Sites
PS03	Guide for Site Characterization for

USEPA<sup>2</sup>

SW-846 Test Methods for Evaluating Solid Waste

Confirmed or Suspected Petroleum

#### 1.5.2 OTHER REFERENCES

Releases

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

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<sup>&</sup>lt;sup>1</sup>American Society for Testing and Materials, 100 Bar Harbor Drive, West Conshohocken, PA 19428.

<sup>&</sup>lt;sup>2</sup>U.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.

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

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 wellrounded 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 1. API PUBLICATION 1628

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

Table 1—Ranges of Porosity Values for Various Earth Materials

*Effective porosity* means the ratio of the volume of interconnected 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 coarsergrained 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.

hydraulic conductivity (k) =
groundwater flow rate
- (hydraulic gradient)(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 arrid 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

			Hydraulic Co	onductivity	
Rocks	Deposits	(ft/day)	(cm/s)	(m/s)	(gal/day/ft <sup>2</sup>
Fractured igneous and	Deposits	$(ft/day)$ $(ft/day)$ $= 10^{6}$ $= 10^{5}$ $= 10^{4}$ $= 10^{3}$ $= 10^{2}$ $= 10^{6}$ $= 1$ $= 10^{-1}$ $= 10^{-1}$	$(cm/s)$ $\begin{bmatrix} 10^{2} \\ -10 \\ -1 \\ -10^{-1} \\ -10^{-2} \\ -10^{-3} \\ -10^{-4} \\ -10^{-5} \end{bmatrix}$	$(m/s)$ $\begin{bmatrix} 1 \\ -10^{-1} \\ -10^{-2} \\ -10^{-3} \\ -10^{-4} \\ -10^{-5} \\ -10^{-6} \\ -10^{-7} \end{bmatrix}$	$(gal/day/ft^{2})$ $\begin{bmatrix} 10^{-6} \\ -10^{-5} \\ -10^{-4} \\ -10^{-3} \\ -10^{-2} \\ -10 \\ -1 \\ -10^{-1} \\ $
San Li	le Sanc Inweathered Git	- 10 <sup>-3</sup>	- 10 <sup>-6</sup> - 10 <sup>-7</sup>	- 10 <sup>-8</sup>	$-10^{-2}$
ſ	Infractured umorphic and neous rocks Dha U I	- 10-5	- 10 <sup>-8</sup>	- 10 <sup>-10</sup>	- 10 <sup>-4</sup>
		- 10 <sup>-6</sup>	- 10 <sup>-10</sup>	- 10 <sup>-12</sup>	-10-6

Notes: ft/day = feet per day; cm/s = centimeters per second; m/s = meters per second;  $gal/day/ft^2 = gallons per day per square foot$ . 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. Hydrogeologists commonly classify aquifers as *unconfined* (water table) or *confined* (artesian).

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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

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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 1, 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.

hydraulic gradient (1) = 
$$\frac{difference in hydraulic head}{distance along the flow path}$$

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. These

Not for Resale





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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:

a. Gasolines.

b. Middle distillates—diesel, kerosene, jet fuels, and lighter fuel oils.

c. Heavier fuel oils and lubricating oils.

d. Asphalts and tars.

e. Coke.

#### 2.4.1.2 Gasolines

Gasolines and finished oils are blends of petroleumderived 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



		Density (gm/ml)		v	iscosity (centipois	e)
Fluid	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 <sup>a</sup>	7.74		4.04 <sup>a</sup>
Fuel oil #4	0.914	0.904	0.898		47.20	22.70 <sup>a</sup>
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	$7.35 \times 10^{7}$		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.<sup>a</sup>Data 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).

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#### Table 4—Properties of Selected Hydrocarbon Compounds

Name	Henry's Law Constant (H) (atm mol fraction)	Empirical Formular	Molecular Weight	Water Solubility at 25°C (mg/L)	Vapor Pressure at 20°C (mm Hg)	Soil Sorption Constant K <sub>oc</sub> (L/kg)
n-Butane	52,600	C <sub>4</sub> H <sub>10</sub>	58.12	61.4 (1 atm)	1,560	490
Isobutane	NA	C <sub>4</sub> H <sub>10</sub>	58.12	48.9 (1 atm)	2,250	420
n-Pentane	69,990	$C_4H_{12}$	72.15	41.2	424	910
Isopentane	75,770	$C_4H_{12}$	72.15	48.5	575	880
1-Pentene	22,110	$C_5H_{10}$	70.14	148	531	460
n-Hexan	1.03 E5	C <sub>6</sub> H <sub>14</sub>	86.18	12.5	121	1,900
I-Hexene	22,890	$C_{6}H_{12}$	86.16	50	150	910
2-Methylhpentane	96,100	C6H14	86.18	14.2	172	1,500
Cyclohexane	10,890	C <sub>6</sub> H <sub>12</sub>	84.16	59.7	77.6	960
Benzene	305	$C_6H_6$	78.11	1,780	75.2	190
n-Heptane	1.15 E5	C7H16	100.20	2.68	53.6	4,300
2-methylhexane	1.90 E5	C7H16	100.23	2.54	51.9	3,200
Methylcyclohexane	23,775	C7H14	98.10	15	36.2	1,800
Toluene	370	C7H18	92.14	537	21.8	380
n-Octane	1.79 E5	C <sub>8</sub> H <sub>18</sub>	114.23	0.66	10.5	8,200
2, 4-Dimethylhexane	NA	C <sub>8</sub> H <sub>18</sub>	114.23	1.5	23.3	5,200
Ethylbenzene	485	$C_8H_{10}$	106.17	157	7.08	680
m-Xylene	142	$C_8H_{10}$	106.17	162	6.16	720
2, 2, 4-Trimethylhexane	NA	$C_9H_{20}$	0.8	11.3	11.3	8,700
1, 3, 5-Trimethylbenzene	NA	C9H12	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	C12H26	170.3	0.005	0.075	88,000
MTBE	30	(CH <sub>3</sub> ) <sub>3</sub> COCH <sub>3</sub>	88.15	43,000	245	41
Methanol	.061	CH <sub>3</sub> OH	32.04	1.16 × 10 <sup>4</sup>	92	NA
Ethanol	NA	CH <sub>3</sub> CH <sub>2</sub> OH	46.07	$1 \times 10^{4}$	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):

a. Immobile residual liquids in the unsaturated zone above the area of the capillary fringe.

b. Free mobile liquids which migrate from the source area downward to the water table and then within the capillary fringe.

c. 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):

a. In infiltrating water in the unsaturated zone.

b. In the residual films of groundwater covering the surfaces of solid minerals in the capillary fringe and LNAPL plume zones.

c. 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

		Conce (parts pe	Concentration (parts per million) <sup>a</sup>		
Compound	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.

<sup>a</sup>Concentrations 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

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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. Coarsegrained 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 fluctuations, 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 EPAapproved 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:

a. Infiltration of water through the unsaturated zone containing residual hydrocarbon.

b. Movement of infiltrating groundwater in contact with the free hydrocarbon plume.

c. Groundwater in direct contact with an LNAPL plume.

d. 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:

- a. Depth to the water table.
- b. Hydraulic conductivity of earth materials.
- c. Recharge rates.
- d. Fluctuations in the water table.
- e. Groundwater velocities.
- f. Groundwater temperature.
- g. Residual hydrocarbon concentrations.
- h. Effective solubility of specific hydrocarbon chemicals.
- i. Adsorption and retardation effects.
- j. Attenuation factors.

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

FLUID SATURATION HORIZONTAL MOBILITY OF GENERALIZED **CROSS SECTION HYDROCARBON PHASES** DISSOLVED LNAPL VAPOR =|||= Unsaturated zone with residual hydrocarbons and hydrocarbon vapor Tank Limit of immobile hydrocarbons Mobile Mobile (+) Immobile Hydrocarbon A capillary fringe Capillary zone with ₹ Ţ B LNAPL Mobile Immobile Mobile Immobile C (D) Zone of Limit of water table immobile fluctuation hydrocarbons LEGEND Water table fluctuation zone with residual hydrocarbons Ŧ LNAPL Surface  $\nabla$ Effective water table surface Sand grain Water LNAPL Air/Vapor Saturated zone with dissolved hydrocarbons (\*) During infiltration or due to unsaturated flow

Source: Modified from Lundy and Gogel, 1988.

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

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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	Gener	alized Water Flow				
Vapor phase		Infiltration at land surface				
LNAPL	ξ	Insturated flow				
Z Residual LNAPL phase	4	Unsaturated now				
Dissolved phase in vadose zone		Groundwater flow				
Dissolved phase in groundwater						
Uncontaminated groundwater						

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 <sup>3</sup> )	(L/m <sup>3</sup> )	(Mg/Kg) <sup>a</sup>	(gal/ft <sup>3</sup> )	(L/m <sup>3</sup> )	(Mg/Kg) <sup>a</sup>	(gal/ft <sup>3</sup> )	(L/m <sup>3</sup> )	(Mg/Kg) <sup>a</sup>
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:  $gal/ft^3 = gallons$  per cubic feet; L/m3 = liters per cubic meter; mg/kg = milligrams per kilogram. Source: Modified from de Pastrovich and others, 1979. <sup>a</sup>Estimate 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:

$$R = 1 + \frac{\rho_{bK_d}}{n}$$

Where:

 $\rho_{\rm b}$  = Bulk density of earth material.

l

n = Porosity.

 $K_{\rm d}$  = Distribution coefficient.

The value  $K_d$  is defined by:

$$K_{\rm d} = f_{\rm oc} \left( K_{\rm oc} \right)$$



**Static Water Table** 



**Falling Water Table** 



**Rising Water Table** 

#### Legend



LNAPL

Residual hydrocarbons (below water table)

Source: Modified from Schwille, 1984.

Figure 6—Spreading of Hydrocarbons as a Result of Water Table Fluctuations **API PUBLICATION 1628** 

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#### Where:

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

- $K_{\rm oc}$  = 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 solublehydrocarbon 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.





Varying hydraulic conductivity

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. **API PUBLICATION 1628** 



Figure 8—RBCA Flowchart

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## 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 threetiered 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-sitespecific risk-based screening-level (RBSL) concentrations for chemical(s) of concern. These are for a variety of potential 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 screeninglevel concentrations, then further tier evaluation to develop sitespecific 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:

a. Is the approach or are the assumptions used to derive the current tier's site-specific target levels appropriate for conditions at this site?

b. Will the site-specific target levels developed under the next higher tier be significantly different from the current tier?

c. Will site-specific target levels developed under the next higher tier significantly modify the remedial action activities? d. 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:

a. 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:

a. Vapor control and abatement (fire and explosive conditions).

b. LNAPL control and abatement.

c. Groundwater use evaluation.

d. 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:

a. Evacuate people out of the area of concern.

b. Take proper precautions to protect personnel exposed to the release.

c. Notify the local fire department so that trained personnel can evaluate the fire and potential for explosive conditions.d. Use trained and certified personnel to test for explosive vapor concentrations.



- 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.

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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. Offsite 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

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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:

a. The presence, nature, concentration, and extent of liquid-, dissolved-, and vapor-phase hydrocarbon.

b. Source areas, types of chemical(s) of concern, and hydrocarbon migration pathways.

c. Hydrogeologic properties controlling hydrocarbon movement.

d. Receptors that could be adversely impacted by hydrocarbon (such as buildings with basements, underground utility trenches, water wells, and surface waters). e. Data required to help select, design, implement, and monitor corrective actions.

f. 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:

a. 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 vaporphase 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

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

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

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

		Lower Detection Li	Estimated Time for		
Procedure	Measuring Device	Soil and Water	Soil Vapor	Collection and Analysis (in minutes)	
General headspace analysis <sup>b</sup>	FID/PID/coloremetric detector tube/GC	10s-100s ppm ppb	10s100s ppm ppb	10-20	
Polyethylene bag sampling system	FID/PID colorimetric detector tube/GC	l ppm 10s-100s ppb	I–100's ppm ppb	10–20 20	
Extraction-colorimetric procedure, Immunoassay	N/A	Soil: 1 ppm <sup>c</sup> Water: 0.1 ppm	N/A	Soil: 45–60 Water: 10–15	
Soil vapor	FID/PID/colorimetric detector tube/GC	N/A N/A	l 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.

<sup>a</sup>Determined by spiked field standards.

<sup>b</sup>General headspace analysis refers to dynamic and static headspace analysis.

<sup>c</sup>May 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:

a. 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.

b. 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:

a. 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 setups are now being used in some cases to provide laboratoryquality 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.

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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 smalldiameter (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. The

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. Handlin 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 unsui able soils (caving) Large stones, boulders, or be rock cannot be penetrated Recovery well installation ca not 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 b 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	416 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 whil 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 typical 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 so Large boulders or bedrock cannot be penetrated No soil samples can be obtain 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

### Table 9—Basic Well-Drilling Methods

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Normal Average Drill Maximum Time Normal Diameter Expense Disadvantages Depth per Boring Advantages Type Boring Cone penetrometer 1-3 in. 100 ft Fast Inexpensive Rapid assessment of soil and Limited to unconsolidated soil groundwater conditions Large boulders and bedrock Geophysical log of stratigraphy cannot be penetrated and permeability data Dug wells Unlimited 10-20 ft Fast Inexpensive Wide availability Caving can be a severe problem Very large diameter hole is Limited depth easily available Greater explosive hazard when excavating into hydrocarbons 4-36 in. Unlimited Fast Expensive Same as rotary Same as rotary Reverse rotary Good in loose, sandy soil (fluids) Core barrel samples Reverse air 4-50 in. Unlimited Fast Expensive Good for large diameter holes Dual-walled drilling pipe is Less drilling fluid is required required Increased drill pipe handling 100 ft Moderate Good in loose sand Jetting 3-12 in. Fast Water is required as a drilling fluid

### Table 9—Basic Well-Drilling Methods (Continued)

Note: in. = inches; ft = feet.

inside opening allows for the insertion of a smaller-diameter sampling tool or drive sampler, which can be driven into earth material not yet penetrated by the auger. These types of techniques generally allow for the collection of relatively undisturbed soil sample cores.

Accurate descriptions of the vertical profile of earth materials sampled should be entered in a field log by a qualified professional. At depths below 15 feet the surface auger cuttings will be a mix of materials from various layers being penetrated by the auger bit. Therefore, a sufficient number of undisturbed samples should be obtained to characterize the site. Undisturbed samples can be obtained from drive samplers (for example, split spoons).

The following are characteristics that should be noted when describing drill cuttings or soil cores:

a. Color.

b. Hardness, plasticity, competency.

c. Soil type and grain-size distribution.

d. Presence or absence of water (dry, moist, or wet).

e. Evidence of LNAPL or other chemical(s) of concern, visual evidence.

f. Standard penetration test results, where appropriate.

g. Other observations (for example, organic matter content).

Other characteristics may be important depending on project requirements.

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

The ability to collect in-situ groundwater and soil samples has made the cone penetrometer and other driven-probe samplers valuable tools for rapid, cost-effective sampling. Driven-probe samplers similar to the cone penetrometer have been designed to collect discrete, relatively undisturbed soil samples. Special sampling devices can be used with either cone penetrometer testing (CPT) or other driven probes. The driven-sampling tube can collect an undisturbed sample up to 3 feet in length and 1 to 3 inches in diameter. The samplers should be cleaned after each sample is collected to prevent cross-contamination with residual materials from previous soil samples. Some Geoprobe units have portable laboratories.

One of the most common uses of the cone penetrometer is stratigraphic logging of soils. The penetrometer differentiates changes in soil horizons or strata by sensing changes in soil density and friction. Newer CPTs also use pore pressure to differentiate soil types. Logs generated by CPT data are more detailed than most field logs generated by field classifications and grain size distribution analyses of soils. Subsurface investigations performed by CPT methods are more rapid and may be more cost-effective than investigations in which conventional drilling methods are used. Under favorable conditions, it is possible to conduct 300 to 700 vertical feet of soundings



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Table 10-Relative P

					Direct Rotary					 	Diract Drive	
	Cable	Direct Rotary	Direct Rotary	Direct Rotary (Down-the-Hole	(Drill-Through Casing	Reverse Rotary	Reverse Rotary	Hydraulic		Cone Cone	(Well	c
Type of Formation	Tool	(With Fluids)	(With Air)	Air Hammer)	Hammer)	(With Fluids)	(Dual Wall)	Percussion	Jetting	Penetrometer	Points)	Auger <sup>a</sup>
Dune sand	6	s	NR	NR	6	Sb	9	5	S	4	3	S
Loose sand and gravel	2	ŝ	NR	NR	9	Sb.	6	S	5	7	ę	S
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Loose boulders in alluvial	373 <b>-</b>	2-1	NR	NR	5	2-1	4	-	1	R	2-1	_
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Limestone	Ś	S	ŝ	. م	N	<b>t</b> (		<b>.</b> 4	aN	an	an	NR
Limestone with chert nodule	Ś	ę	ŝ	9	NR	<b>x</b>	÷,	<b>.</b> .				
Limestone with small cracks	S	£	5	6	NR	-	2	4	NK	NK	XN	
or fractures				1	:	-		-	ND	AN	NR	NR
Limestone, cavernous	Ś	3-1	7	S	NK	- 1	•	- 4		an	an	an
Dolomite	Ś	ŝ	Ś	9	NR	n '	n i	•••				ND
Basalts, thin layers in	S	£	ŝ	6	NR	5	ŝ	0	NK	NK	NN.	
sedimentary rocks		,		•	ę	ç	•	"	an	NR	NR	NR
Basaltsthick layers	ŝ	~	4	<b>n</b>	ZK	<b>n</b> .	+ •	- <b>ר</b>		an a	aN	an
Basalts-highly fractured	ę	I	ŝ	ŝ	NR	1	4	-	XN	NK		
(lost circulation zones)		,		·		ŗ	Ŧ	"	an	NR	NR	NR
Metamorphic rocks	ŝ	ę	4	<b>n</b> 1	NK	<b>n</b> (	• •	יי	AN	an	an	NR
Granite	ŝ	•	5	Ś	NK	ۍ	4	n				
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3 Ĕ MOIS TID = 7 Note: NR = not recommended; Rate of penetration: 1 = impossible; Source: Modified from Driscoll, 1986.

<sup>a</sup>Applies to hollow-stem auguer drilling. Performance characteristics will differ if solid-stem auguers are used.

b Assuming sufficient hydrostatic pressure is available to contain active sand (under high confining pressures).

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in one day. Costs are reduced because there are minimal drill cuttings and no fluids to be contained for disposal, and the small holes are easily grouted up if they do not collapse when the instruments are withdrawn. Lithologic descriptions produced by CPT should always be correlated against at least one soil boring at every site. The use of CPT as a screening tool is not a substitute for monitoring wells, but allows more effective placement of monitoring wells. Caution should be exercised to prevent penetrating low-permeability zones, thus allowing vertical migration of LNAPL. Holes must be grouted when data collection has been completed.

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

In poor to moderately consolidated soil or sediment, soil samples must be collected using percussion drive samplers. Rock coring must be used in consolidated materials. The depths to the water table and the presence of LNAPL should be documented in the drilling log. These horizons are usually evident from texture and soil color. The presence of LNAPL in the soil boring is evidence that a free hydrocarbon plume has been penetrated. Soils sampled below free hydrocarbon accumulations may not be representative due to the potential for cross-contamination

#### 5.3.1.2.3 Laboratory Analysis

Based on field screening, selected soil samples may be submitted for laboratory analysis. Depending on the type of soil analysis desired, stainless steel, brass, or acetate sleeves can be used.

It is important that the following techniques be observed in preparing soil samples for shipment:

a. Cap each sample container with inert material (aluminum foil or fluorocarbon resin).

b. Label each sample container with the date, depth interval, and location of each sample.

c. Store each sample container on ice (< 4°C).

d. Prepare the chain-of-custody form and ensure it accompanies the samples during shipping.

Soil samples may also be stored on ice for preservation for future analysis, if required, in accordance with appropriate holding time limits. Additional information on soil sample collection, handling, and preservation is provided in API Publication 1629.

Most of the accepted methods for analysis of soil are adapted from a series of EPA methods developed for either water or solid waste and published in SW-846. All of these methods require the removal or extraction of hydrocarbon from the soil matrix; thus, the primary problem involved in analyzing soils containing hydrocarbon fuels is the efficient removal of the hydrocarbon chemicals from the soils for analysis. Variables such as sample collection, handling, and storage can seriously affect loss of volatiles in laboratory analyses. Variations in results can also be attributed to the ways EPA methodologies have been adapted by different laboratories.

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

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

Several USEPA methods are commonly used to analyze for volatiles and semivolatiles. Soil samples are generally analyzed in the laboratory by GC or gas chromatograph/ mass spectrometer (GC/MS). Each of these methods has an associated target compound for which it was specifically developed and evaluated. A list of the methods commonly used to detect, identify, and quantify indicator parameters and specific petroleum hydrocarbon in soils is provided in API 1629.

### 5.3.1.2.4 Performance Considerations

Determining which type of analytical method to use depends on the type of hydrocarbon compounds in the soil

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samples. Analytical methods range from the generic TPH methods to the highly selective and sensitive GC/MS methods used to analyze specific chemicals (BTEX, for example).

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

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

These problems may be compounded by attempting to compare different fuel compositions. For example, gasoline and diesel fuels contain different classes of hydrocarbon chemicals. Therefore, gasoline in soil will consist of C<sub>6</sub> to C12 compounds, whereas diesel fuels in soil will consist of C10 to C25 compounds. No simple way exists for directly comparing soils containing gasoline with soils containing diesel fuels. Relating any potential environmental or health risks to concentrations of TPH is currently not practical. For these reasons, TPH has limited value as an indicator compound for clean-up criteria. Its widespread use as a soil clean-up criterion points to a lack of understanding of the proper use and limitations of the TPH method. When the regulatory objective is protection of groundwater quality, more specific chemicals (such as BTEX) should be used as indicator compounds.

Alternative techniques available for analysis of TPH are variations of existing EPA SW-846 and ASTM methodologies for petroleum hydrocarbon. Two common techniques are TPH-Gasoline or Gasoline Range Organics (GRO) and TPH-Diesel or Diesel Range Organics (DRO). GRO is a purge-and-trap GC-FID procedure used primarily for the measurement of petroleum hydrocarbon predominantly in the C<sub>6</sub> to C<sub>12</sub> range. DRO, developed for the measurement of diesel-range hydrocarbon (C<sub>10</sub> through C<sub>25</sub>), uses a solvent extraction followed by GC-FID. Several states have incorporated these or similar methods for analysis during

the assessment and remediation of petroleum hydrocarbonimpacted sites. Currently, there is no standard GC-FID method for the analysis of petroleum hydrocarbon products.

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

Another analytical issue of interest is recognizing appropriate detection limits for the methods in use. A critical concept in chemical analysis is the evaluation of the data generated in terms of its reliability (that is, with what degree of certainty does any given analytical value represent the true concentration of the analyte in the sample). This is particularly important when analyses are being conducted for complex matrices (such as for fuels in soil) in concentrations at or below the detection limits. For some compounds, this becomes a very real problem.

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

#### 5.3.1.2.5 Excavation

Although not commonly recommended as a site assessment technique, excavations can be made at some sites to allow visual inspection of, and access to, the shallow subsurface. Such excavations, which are normally limited to depths less than 15 feet, may be appropriate at sites with cohesive soil, and can provide additional information on the distribution of subsurface materials and structures that may be otherwise overlooked. For example, lateral continuities or discontinuities of various strata, animal burrows, soil fracturing, and root zones, all of which may be pathways for migration of LNAPL, can more easily be determined and described in excavations.

Following are some concerns which must be addressed when considering excavations:

a. Soil and groundwater handling and disposal may be necessary.

b. Business activities may be disrupted.

c. Subsurface utilities may be damaged.

d. Fugitive hydrocarbon vapor emissions may be generated. e. Safety concerns requiring shoring of sidewalls in accordance with Occupational Safety and Health Administration (OSHA) standards may be posed (Proper safety procedures and protocols must be followed in accordance with local, state, and federal regulations.)

f. Traffic and personnel control may be required.

### 5.3.1.3 Delineation of LNAPL

### 5.3.1.3.1 General

A LNAPL plume will develop if the hydrocarbon release exceeds the adsorptive capacity of sediments in the unsaturated zone. A plume will migrate by gravity downward until encountering groundwater or a relatively impermeable horizon. LNAPL can also accumulate and migrate preferentially in man-made pathways such as utility trenches. The presence of LNAPL in a subsurface structure is usually evidence that such hydrocarbon are, or were, present in adjoining earth materials. A test for determining if LNAPLs are currently present in earth materials surrounding a structure is to remove the liquids from inside the structure and observe whether the liquids return.

#### 5.3.1.3.2 Measuring LNAPL Thickness

A site assessment should include measurements of the thicknesses and rates of return of LNAPL in subsurface structures and wells. Figure 9 shows three methods for measuring LNAPL thickness in a well or other subsurface structures.

The first method requires lowering a measuring tape on which hydrocarbon- and water-sensitive pastes have been applied into the well. As the water and LNAPL contact the pastes, color changes in the paste occur that allow determination of the water/LNAPL and LNAPL/air interfaces. This method permits these interfaces to be determined to a high degree of accuracy (<sup>1</sup>/<sub>8</sub> inch), but is time-consuming when several wells must be measured. The chemical composition of the pastes must also be taken into consideration in areas that do not contain LNAPL, and dissolved chemicals are of concern. In these instances, the composition of the paste chosen and its dissolved chemicals should be known prior to use.

The second method, more commonly used, employs an electronic probe capable of sensing the electrical conductivities of the different fluids. Typically, different audible tones are emitted from the probe as the air/LNAPL and LNAPL/water interfaces are penetrated. This method also is accurate to within <sup>1</sup>/<sub>\*</sub> of an inch and is much quicker than using pastes. The third method uses a transparent bailer that is lowered into the well. A *bailer* refers to a cylindrical device with a check valve on the bottom and a hook for a cord on the top. The bailer must be long enough to ensure that its top will be above the air/LNAPL interface when the check valve is below the LNAPL/water interface. The hydrocarbon thickness measured in a bailer can be slightly greater than that actually present in the well. This is because a volume equivalent to the bailer wall thickness will displace the hydrocarbon. Some of these displaced hydrocarbon will enter the bailer, thus exaggerating the thickness of the LNAPL actually present. The bailer should be lowered slowly through the hydrocarbon layer to minimize this discrepancy.

In addition to hydrocarbon thickness, it is important to determine the elevations of the air/LNAPL and LNAPL/ water interfaces. The extent of the LNAPL plume and groundwater flow directions can be mapped from this type of information gathered from several wells or structures. Elevations can easily be determined by noting the depths at which the air/free hydrocarbon and free hydrocarbon/water interfaces were encountered below some measuring point marked on the well casing (such as the top of the structure or well casing) that has been surveyed to the nearest 0.01 foot relative to mean sea level or a local datum. The depths of the interfaces are subtracted from the surveyed elevation to determine fluid level elevations and LNAPL thickness. Refer to the following sections for further discussion.

Figure 10 generally illustrates that at static equilibrium the thickness of LNAPL floating in a well is usually greater than the thickness outside the well in the adjoining earth materials. However, as discussed in Section 2.5.2, the LNAPL does not distribute itself as a distinct layer floating on top of a capillary fringe or the water table.

The difference in thicknesses between that measured in a well and that in the earth materials can vary widely, depending on the specific gravity of the hydrocarbon and the hydraulic-conductivity and porosity of the earth materials. In fine-grained, low hydraulic conductivity soils such as clays, capillary pressure effects can be significant, and LNAPL thicknesses in wells can be several times actual thicknesses in earth materials. On the other hand, in coarsegrained materials such as coarse sands and gravels, the capillary pressure effect is minimized, and hydrocarbon thicknesses in the well and in the earth materials may be similar, with differences due primarily to specific gravity of the hydrocarbon. Subsurface structural controls can also affect hydrocarbon thicknesses in wells as can a fluctuating water table.

### 5.3.1.3.3 Using LNAPL Thickness Data

The measured hydrocarbon thickness should be adjusted to an equivalent water thickness to determine the total



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Figure 9—Methods for Measuring Accumulations of LNAPL in a Well

hydraulic head (water table elevation). However, this is generally done by multiplying the measured hydrocarbon thickness by the hydrocarbon density relative to water. The result is added to the elevation of the measured hydrocarbon/water interface to determine the equivalent groundwater elevation. Calculated water table elevations can be plotted and used to evaluate groundwater flow direction. Due to the dynamic processes of a rising and falling water table, this can be complex.

Exact measurements of LNAPL accumulations are also important in determining plume extent, apparent thickness, and optimum locations for remedial equipment. However, the area having the greatest thickness in wells is not always the optimum location for remedial equipment. As discussed in Section 5, factors such as groundwater flow directions and soil types also have to be considered, as does the thickness-exaggeration effect.

Procedures exist for gross estimation of LNAPL volumes in earth materials based on soil sampling, measurements in wells, and analyses of selected soil properties and include equations, baildown tests, and direct sampling and measurement. A listing of some of the various methods, references, and their level of complexity is presented in Table 11. No comparison of the accuracy of the various methods is given because the results of all of the methods are questionable. Used independently, the analytical equations are the most prone to misapplications. Values for equation parameters are difficult to determine in the field. Thus, results of volume calculations may be in error by several multiplication factors. For this reason, calculations of LNAPL volumes based on measured accumulations in wells is not recommended. However, these different methods used in conjunction with each other can provide a "qualitative" estimate of the free hydrocarbon present. The use of several of the equations, combined with bail-down tests performed in the field and observations from drilling or logging can provide a "relative" indication of the magnitude of free hydrocarbon present. This is most useful in evaluating well-planned remedial alternatives, and the recoverability of free hydrocarbon.

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Baildown tests can provide a "relative" indicator as to the recoverability of the free hydrocarbon present. Simply by plotting the rate of thickness accumulation (rate of inflow) in the well following bailing, a general indication of the mobility of the LNAPL can be obtained. A very slow rate of recovery of LNAPL levels (many hours or days) may indicate minimal thickness and/or that liquid recovery will be ineffective at a particular location. Again, these data should be evaluated in conjunction with the other hydrogeologic data at the site and by using some of the other procedures listed in Table 11.

### 5.3.1.3.4 Monitoring Well Screen Placement

Particular care must be taken to ensure that well screens are properly placed to detect LNAPL. This paragraph 36

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applies to monitoring wells, and requirements for wells installed for other applications are discussed in 7.4.3.3. Figure 11 illustrates that placement of the well screen too far above or below the water table can prevent the accumulation and detection of free hydrocarbon.

Wells for monitoring LNAPL accumulations should have screened intervals long enough to allow seasonal water table fluctuations to remain within the screened interval. Figure 12 shows that even with this design, extreme changes in the water table elevation can transfer all free liquids outside the well to residual liquids, thereby making detection of LNAPL impossible. For instance, a rising water table can cause the net loss of LNAPL to a residual state of saturation below the water table. Conversely, LNAPL accumulations in wells may increase with a falling water table.

### 5.3.1.3.5 LNAPL Sampling

LNAPL samples are commonly collected and analyzed to identify selected chemical and physical characteristics. This information can be useful in designing remediation schemes and occasionally can be used to fingerprint possible sources. Also, relative degrees of weathering can be

		Level	of Complexity to	o Apply	Ease of	of Parameter Esti	mation
Equations	How Derived	Low	Medium	High	Easy	Moderate	Difficult
van Dam (1967)	Theory			x			x
Zilliux & Muntzer (1975)	Theory/Lab. Model		x			x	
Concawe (1979)	Theory	х			x		
Blake & Hall (1984)	Imperical/Lab. Model	x				x	
Schiegg (1985)	Theory/Lab. Model	x				x	
	Theory/Imperical				x		x
Farr et al (1990)	Theory				x		х
		Bail-	down tests				
Gruszczenski (1987)	Imperical/Field tests	х				x	
Hughes et al (1988)	Imperical/Field tests	x				x	
		Direct s meas	ampling and surement				
	Continuous Core	x				x	
	Continuous Core	х				x	
Keech (1988)	Dielectric well logging		x				х

Table 11—Summary of Methods for Utilizing LNAPL Thickness Information

estimated from chemical analytical results; however, this information must be tempered with other considerations, such as the biological, physical, and chemical transformations to which the sample has been subjected between the times of leakage and collection. Estimates of how long the LNAPL have been in the subsurface based on weathering are subjective at best and should be used with caution.

A bailer is generally adequate for sampling LNAPL. The amount of sample needed will depend upon the number and types of tests to be conducted; however, one-half liter is usually adequate. Samples should be stored as directed by the laboratory and properly labeled and sealed. Sample bottles should be carefully packed in an adequate container (such as an ice chest) containing shock-absorbing materials to protect against breakage. Further, the U.S. Department of Transportation requires special precautions be taken when shipping flammable materials. As in other sample collection activities, pertinent data such as the date, location, and method of collection should be recorded. A properly documented chain-of-custody form must accompany the sample.

Table 12 lists several standardized physical and chemical tests used for analysis of LNAPL. Many of the physical tests are routinely completed at laboratories that provide such services for the petroleum industry. Most certified laboratories capable of analyzing waters and waste materials for organic substances can also perform similar chemical analyses on LNAPL.

Gas chromatographic techniques can be used to analyze LNAPL samples. A GC equipped with a capillary column rather than a standard hand-packed column can be used to achieve better separation of the compounds as they are eluted. LNAPL samples typically range from gasoline to lube oils, as shown on Figure 13.

Determining the hydrocarbon peak distribution in a LNAPL sample is accomplished by comparing the peaks on the chromatogram of the hydrocarbon sample to a "standard" chromatogram (that is, a chromatogram with known peaks). This peak identification method is typically used for benzene, toluene, and xylene peaks, as well as the  $C_8$  through  $C_{21}$ , pristane, and phytane peaks. Figure 14 presents an example of how peaks can be identified by comparing to a known standard. The identified peaks on the sample chromatogram demonstrate that this sample is composed of a gasoline product and a heavier distillate in the kerosene-diesel fuel range.

Many factors can affect a hydrocarbon sample from the time of the release to sample collection, handling, and analysis, including biological, physical, and chemical transformations. Changes in product characteristics can make the interpretation of resulting chromatograms speculative without further supporting information. GC data can be utilized 38

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Figure 11—Examples of Incorrect Installation of Well Screen (a) Above and (b) Below LNAPL Accumulation

most effectively in combination with other pertinent information including site-specific hydrogeological and geochemical data. Figure 15 illustrates a comparison of gas chromatograms for a non-degraded and degraded LNAPL sample. Note that the peak intensity for the lighter-end fraction of hydrocarbon compounds is reduced for the degraded LNAPL sample.

### 5.3.2 DELINEATION OF DISSOLVED PHASE

#### 5.3.2.1 General

As discussed in 2.4.2, some components of hydrocarbon (principally the aromatic hydrocarbon) are more soluble in water and sometimes contaminate fresh water aquifers used for public consumption. Thus, an essential part of most assessments is the delineation of chemical(s) of concern in the groundwater and unsaturated zone. This section discusses methods to sample and delineate dissolved-hydrocarbon plumes. Table 13 provides a list of standard USEPA tests used by laboratories to determine concentrations of dissolved-petroleum hydrocarbon in water.

Existing water-supply wells can provide valuable information on the local groundwater system. However, monitoring wells are usually necessary for the full assessment of site-specific problems caused by dissolved hydrocarbon. Monitoring wells are used for measuring water level elevations and obtaining representative groundwater samples. These wells are not typically designed to be effective for producing large quantities of fluids but on occasion can be converted to recovery wells. In addition to the use of monitoring wells, new methods for the collection of groundwater samples to delineate dissolved hydrocarbon include the use of the cone penetrometer and hydraulically or mechanically driven probe samplers (Section 5.3.1.2.2).

The number and location of monitoring wells required for an assessment are site specific. For instance, if the direction of flow (gradient) in a regional water table aquifer is unknown, a guideline is to assume that the water table has the same general shape as the land surface. At least three spatially distributed wells are necessary to verify the local hydraulic gradient, although additional wells may be helpful. At least one well is required upgradient of the suspected hydrocarbon source to provide background information. Additional upgradient wells may be useful, particularly if other possible upgradient sources are suspected. Monitoring wells constructed downgradient of the suspected source can be used to determine the extent of chemical(s) of concern. The use of the driven-probe samplers in shallow unconsolidated aquifers can (in some instances) allow for the collection of more site-specific information, in a reduced time frame, and for less cost than conventional monitoring wells. This can lead to more efficient monitoring well-plan-



Figure 12—Effect of Fluctuating Water Table on LNAPL Accumulation in a Well

ning. The use of these techniques should be evaluated based on the site-specific characteristics and data requirements. It is important to note that groundwater samples collected with driven probe samplers are "one-time" samples unless semi-permanent or permanent monitoring wells are installed. In order to monitor changes in groundwater concentrations with time, some number of permanent monitoring wells must be installed.

Dissolved hydrocarbon associated with petroleum releases tend to be detected in the upper portion of the saturated zone. This is because the released material has a specific gravity less than that of water. Thus, it should not be necessary to assess conditions in deeper confined aquifers unless there is a direct indication that migration of chemical(s) of concern has occurred or would occur. For example, nearby pumping wells completed deeper in the aquifer can create strong vertical flow gradients and induce downward contaminant migration. Such conditions can be assessed by installing monitoring wells screened at a deeper interval. Great care should be taken when installing wells deeper in the aquifer to prevent cross-contamination. When installing wells screened at a deeper interval, one should consider installing monitoring wells constructed with a surface casing sealed below the contaminated zone with an inner casing constructed with the monitoring-well screen below it. Also, seasonally saturated, perched groundwater zones may be present in the unsaturated zone at some sites. Shallow wells may be needed to monitor these zones for chemical(s) of concern in addition to wells constructed to monitor conditions in the true aquifer.

It is imperative that existing chemical(s) of concern not be allowed to migrate to deeper aquifers via wells or borings installed for assessment purposes. Special care and proper construction techniques must be used. Cluster wells installed within the same borehole are not advised given the high risk of aquifer cross-contamination. Double-cased wells are recommended in this situation.

An accurate log of earth materials and fluids found during drilling should be maintained. Auger rigs are best-suited for identifying the location of saturated materials. When drilling mud or water is used, as required with rotary or core drilling, knowledge of local hydrological conditions (for example, water table elevations) is important in estimating when to cease drilling. Local regulations that control the disposal of drill cuttings and drilling muds should be determined and followed.

#### 5.3.2.2 Monitoring Wells

A monitoring well may be one of two basic types shown on Figure 16. Both types of wells are required to be sealed from infiltrating surface waters with bentonite and a cement-bentonite grout between the well casing and the borehole wall.

The most common type of well is shown in Figure 16, View A, and is used in poorly to moderately consolidated and unconsolidated sediments, including soil or backfill. The design incorporates a well screen and surrounding filter pack to restrict movement of sediment into the well. Filter packs are typically designed based on screen opening size and lithology, and vary based on site-specific criteria.

The second type of well (see Figure 16, View B) is used in rock having fracture or solution porosity with little potential for producing sediment. The well employs open-hole construction below a surface casing. A screened well can

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### Table 12—Suggested ASTM Methods for Analysis of LNAPL

	Industrial		Middle		
Analysis	Aromatics	Gasolines	Distillates	Heavy Oils	Crude Oils
Gravity	D1298	D1298	D1298	D1298	D1298
·	D891	D1217	D1217	D1217	D1217
		D1298	D1298	D1298	D1298
Viscosity	D88	D88	D88	D88	D88
intrinsic	D4243	D4243	D4243	D4243	D4243
	D871	D871	D871	D871	D871
	D1795	D1795	D1795	D1795	D1795
kinematic				D2270	D2270
Boiling point	D850	D86	D86	D-2 <sup>a</sup>	D285
		D216	D1160	D196	D2892
Octane no.		D2886	D613	D850	
or acetone no. (diesel)		D909			
		D2700			
		D2699			
Hydrocarbon types	D4420	D4420	D3735	D3735	D4534
	D2600	D4534	E567	E567	D3735
	D4534	E567	D235		E567
Nitrogen		D4629	D4629	D4629	D4629
Sulfur		D4045	D4045	D4045	D3961
		D1552	D1552	D1552	D4045
		D2622	D2622	D2622	D1552
					D2622
Lead		D3237			
Alkylated lead		D1949			
Vanadium/nickel		D3605	D3605	D3605	D3605

Note: The numerical suffixes for all of the ASTM standards cited have been omitted to conserve space. <sup>a</sup>Proposed

also be employed in this type of installation. Note: screened intervals should be installed to prevent cross-contamination between the unconsolidated and bedrock zones.

A variation of the type of construction shown on Figure 16, View B, can be used to install wells to monitor deeper, unconsolidated aquifers below known contamination zones. In such instances, surface casing is first installed and cemented in place beneath the contaminated zone to prevent downward migration of chemical(s) of concern via the borehole. The well is then completed by deepening the hole and installing the well casing and screen within the surface casing. Because of its strength, it is common to use steel surface casing in such instances.

In low traffic areas, the well casing can extend 2 or 3 feet above grade and should have a locking cover. In high-traffic areas, the well should be flush-mounted as shown on Figure 17.

State and local health codes controlling well placement and construction should be followed and may preclude drainage into the subsurface from the flush-mounted protective casing. Also, the well should be locked and painted or otherwise permanently marked to allow identification as a monitoring well. Refer to API Recommended Practice 1615 for specific details. Monitoring well casings and screens can be composed of several materials. Table 14 lists commonly used materials and advantages and disadvantages of each. A good grade of polyvinyl chloride (PVC) casing and screen is acceptable in most petroleum-hydrocarbon assessments.

#### 5.3.2.3 Well Development

At drilling completion, drilling fluids and sediment that may have moved through the filter pack and screen during construction should be removed from each well. This process, termed well development, is accomplished by cyclic removal of water from the well with a pump or bailer. A device called a surge block, made of two circular blocks of wood and an intervening rubber gasket, can be used to enhance development. The surge block has a diameter slightly smaller than the well and is attached to a rod that allows the block to be moved up and down inside the well. Surge blocks should be used with caution in plastic wells to avoid well damage. This piston action of the surge block forces water and sediment to move back and forth through the screen and filter pack, allowing development of the well. Air-lift and diaphragm pumps are often used in development when sand production is expected which could damage centrifugal pumps.

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Figure 13—Approximate Boiling Ranges for Individual Petroleum Products

Development should continue until the well produces sediment-free water or until no further improvement is achievable. Proper management and recording of fluid discharges, water levels, clarity, and color are important to decide when to stop development. The total volume of water and hydrocarbon removed during development should be noted.

The water and LNAPL removed during development must be disposed of in compliance with local, state, and federal waste disposal regulations. In some cases, permission can often be obtained to discharge water to the municipal sanitary sewers.

Elevations of all monitoring wells and bodies of water (stream, and so forth) should be surveyed to the nearest 0.01 foot relative to mean sea level or an assumed datum to allow determination of groundwater flow patterns.

### 5.3.2.4 Groundwater Sampling

Groundwater sampling should be completed in accordance with standard practices acceptable to the governing regulatory agency. Relevant publications from these agencies are included in Appendix A. In addition, it is good practice to coordinate the sampling with a certified laboratory that can help select proper sample containers and chain-of-custody documentation. Proper quality assurance/ quality control of field and laboratory procedures should be followed during the sampling program. Such procedures are readily available from regulatory agencies.

Before sampling groundwater, water levels must be measured to evaluate groundwater flow direction. The well is then purged of sufficient water prior to obtaining a representative groundwater sample. Collection of water samples for dissolved constituent analysis from wells containing LNAPL is rarely possible without contaminating the sample. Therefore, such samples should not be collected. From wells capable of a sustained yield, measurements of pH, temperature, and specific conductance may be made as purging continues, until changes in values are within an acceptable range, usually within 10 percent in three consecutive measurements. When a well is not capable of producing a sustained yield, it should be purged completely and sampled when enough water has reentered the well to provide a sample. Under either condition, wells should be sampled soon and never more than 24 hours after purging. The mechanics of purging are discussed below.

Local hydrogeologic conditions and anticipated hydrocarbon concentrations must be considered when selecting sampling equipment. Sampling equipment must be capable of lifting the water from anticipated depths without altering water quality. Equipment must be decontaminated properly between wells to avoid cross-contamination. This applies also to other equipment that will contact the water, such as water-level measurement devices and bailers.

When sampling a well, remember to observe the following:



#### Standard

Figure 14—Product Sample Peak Identification

a. Select sampling devices made of relatively inert materials such as stainless steel, nonflexible PVC, or fluorocarbon resin. (See Table C-2 for a listing of advantages and disadvantages of various sampling equipment.)

b. Place plastic sheeting around the wellhead to prevent contact between soil or drill cuttings and any sampling materials (bailer rope, water level tape, tubing, and so forth).

c. Measure and record water level, LNAPL thickness if present, and well depths to the nearest 0.01 foot.

d. Purge the well by bailing or pumping. In wells capable of providing a sustained yield, this can be done by placing the pump intake a short distance beneath the water surface and pumping at a low enough rate to maintain pump submergence. In low-yielding wells, it will be necessary to follow the water level downward with the pump intake as the well is evacuated. Alternatively, a bailer can be used in lowyielding wells. Recent field studies have demonstrated that purging may not be necessary to obtain representative samples. e. Record pH, temperature, and specific conductance measurements if the well is capable of a sustained yield to determine when purging can cease. Discard the first few bails of water, and bail slowly while sampling.

f. Allow the fluid level to recover to within about 60 to 80 percent of the static level in low-yielding wells before sampling.

### 5.3.3 DELINEATION OF VAPOR PHASE

### 5.3.3.1 General

Vapor-phase hydrocarbon will generally occur in the earth materials within the unsaturated zone beneath a petroleum release site. Hydrocarbon vapor can migrate to the atmosphere or enter buildings or other structures and create potentially explosive conditions. This is particularly true in areas of more permeable soils or where the water table is close to the land surface.

Analysis of vapor-phase hydrocarbon, also called soil gas analysis, or soil vapor surveys (SVS), can be useful to define liquid and dissolved hydrocarbon plumes qualitatively. Often, such determinations help to define the optimum locations for monitoring wells. In addition, significant cost/time savings may be realized by using soil gas analysis techniques coupled with real time analyses (that is, field analyses) for delineating areas of chemical(s) of concern. As stated, soil gas analyses are most appropriate in areas with shallow water tables and porous earth materials. Soil gas surveys can be difficult to interpret in areas with a history of releases or several release sources, as differentiation between overlapping releases of different ages may not be possible. Additional site assessment activities may be necessary to define further the type and extent of chemical(s) of concern in such instances.

### 5.3.3.2 Sampling Techniques

Two techniques are used for soil gas sampling: passive collection and active collection. *Passive collection* is adsorption of soil gas onto activated carbon. Commonly employed passive collectors include Curie point wires and samplers for

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Figure 14—Product Sample Peak Identification (Continued)

industrial hygiene. Active collection involves pumping soil gas, for either direct field analysis or to a collector for subsequent on- or off-site analysis. Direct field analysis is commonly done by using a portable explosimeter, PID, or FID. Table 15 describes the characteristics of soil gas collection techniques.

These technologies each provide information on the relative concentrations of gases. However, results from different techniques are not equivalent to each other, and more than one method should not be used at a particular site. The principle uses of these sampling technologies are for identification of the source area(s) and plume delineation.

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

a. Driving, drilling or auguring a borehole, inserting an instrument probe, and taking a reading.

b. Driving a hollow-steel probe (typically less than 1 inch in diameter), (such as with a geoprobe) into the soil, collecting a sample with a gas-tight syringe, and injecting the sample into a field instrument for analysis.

c. Driving a hollow-steel probe into the soil and collecting the sample in a Tedlar (or the equivalent) bag for analysis with a portable field instrument.

d. Performing sampling directly from the soil vapor probe (in-line sampling) with a portable analytical field instrument, such as a PID, FID, or GC.

Soil air permeability tests and depth profiles may be performed as part of a soil vapor survey to assess the influence of permeability, stratigraphy, and moisture content on the soil vapor-sampling results and to assist in survey interpretations. Soil-vapor survey results provide qualitative information on the type and concentration of vapor-phase hydrocarbon, and the results should be interpreted by evaluating the level of hydrocarbon relative to those at other vapor-sampling points. Interpretation of soil vapor-sampling results should consider site characteristics such as highclay or organic matter content and moisture percentage.

Several ground-probe tools have been developed and are commercially available. All consist of a small-diameter steel tube and a removable drive point with ports for vapor entry (Figure 18). The probe is driven into the soil to the desired depth to collect a sample, retracted a short distance, and purged with a vacuum pump to permit sample collection. When analyses are required, gas samples should be stored on ice and analyzed using gas chromatography within 24 hours. In many instances, detailed analysis is not warranted, and field analytical screening methods (PID, for example) can be used.

Although not widely accepted, passive soil-vapor sampling and analysis uses a buried accumulator (shown on Figure 17) to collect a sample that represents the total mass of vapor accumulated over time. Compounds adsorbed to the accumulator are measured using mass spectrometry analysis in a laboratory.

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Figure 15—Comparison of Nondegraded and Degraded Samples

Analytical Group	Constituent	Analytical Method <sup>a</sup>
Gasoline	1, 2-dichloroethane	EPA Method 8010
(motor gasoline, aviation	Benzene	EPA Method 8020
gasoline, and gasohol)	Toluene	EPA Method 8020
	Ethylbenzene	EPA Method 8020
	Total xylenes	All detectable compounds by EPA Method 8020
	Total volatile organic aromatics	
	1, 2-dibromoethane	EPA Method 8010 with EDC substituted (EDB) for Hall detector; 2-column confirmation
	Methyl-t-butyl ether	EPA Method 8020
	Total volatile organic aromatics	EPA Method 418.1
	-	EPA Method 8015 Modified (California)
Middle distillates	Napthalenes and other semivolatiles	EPA Method 8270
(kerosene, diesel fuel, jet fuel,	Benzene	EPA Method 8020
and light fuel oils)	Toluene	EPA Method 8020
-	Total xylenes	EPA Method 8270
	Ethylbenzene	EPA Method 8020
	n-propylbenzene	EPA Method 8020
	Total volatile organic aromatics	All detectable compounds by EPA Method 8020
	Volatile organic halocarbons	All detectable compounds by EPA Method 8010
	Polynuclear aromatic hydrocarbons (PAHs)	EPA Methods 8100, 8270, or 8310
	Total petroleum hydrocarbons	EPA Method 418.1
		EPA Method 8015 Modified (California)
Other or unknown	Priority pollutant metals	Typically atomic adsorption; particular method
Ranzana	Priority pollutent voletile organics	EPA Method 8240
Toluene	Priority pollutant extractable organics	FPA Method 8270
Total vylenes	Nonpriority pollutant organics (with GC/MS	FDA Methods 8240 and 8270
Fthylbenzene	neaks greater than 10 pph)	LIA MUNUS 0240 and 0270
Total petroleum hydrocarbons	Total netroleum hydrocarbons	FPA Method 418 I
tom periorean ny broom cons	Total ponoroun ny aroom cons	EPA Method 8015 Modified (California)

#### Table 13—List of Dissolved Hydrocarbons and Corresponding Methods of Analysis

Note: EDB = 1, 2-dibromoethane (ethylene dibromide); EDC = ethylene dichloride; GC/MS = gas chromatography/mass spectrometry; ppb = parts per billion; n = normal; t = tertiary.

<sup>a</sup>Alternative methods, such as the EPA 500 and 600 series, exist and can be used in lieu of the EPA 8000 series. These methods have other detection limits or varying quality assurance/quality control criteria or both.

Advantages of this technology are its simplicity, ruggedness, ease of installation, and relatively low cost. The disadvantages are longer sampling analysis periods, potential interference from high-background concentrations near the land surface, and lack of acceptance. Results are not reported as concentrations that can easily be compared with other data, which is a major limitation.

Buried-accumulator and ground-probe devices are difficult to install in hard soils and bedrock. Soil gas samples are difficult to collect from wet, clay soils because of limited vapor-phase migration.

### 5.3.4 IDENTIFICATION OF HYDROGEOLOGIC CONDITIONS

### 5.3.4.1 General

Groundwater systems underlying the site should be identified to determine groundwater flow directions and regional recharge and discharge areas. The impacts of man-made structures such as fill material around buildings or buried utility lines on the hydrogeology and hydrocarbon movement must be identified. These structures can have a considerable impact on the movement of chemical(s) of concern in the subsurface. The local geology should be understood in order to interpret its impact on the depth, quantity, and quality of groundwater. Understanding the impacts of local pumping or seasonal reversals on groundwater flow directions and the effects of a hydrocarbon release on the groundwater system is necessary. For example, the existence of perched water should be determined as well as the type of confining layer. This information may be available in the form of reports and maps prepared by state and federal geological surveys.

#### 5.3.4.2 Water Table Elevations

The water table is the major hydrogeologic feature requiring definition. It serves as the boundary to downward

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46 **API PUBLICATION 1628** 0.3' Maximum 0.3' Maximum Key padlock Key padlock Cap with venthole + Cap with venthole + 5 17777 VIIIAN + 2.5 Protective + 2.5 Protective casing casing Cement grout Cement grout Top of bedrock Coupling weathered zone Top of -2' Minimum firm bedrock Bentonite pellets or slurry seal 3.0' Minimum Centering 2' Minimum device Bottom of casing (if appropriate) Filter pack Well screen Water table Open rock hole fluctuation zone Cap or plug A. Well designed for B. Open-hole well design unconsolidated material for bedrock materials



migration of liquid-phase hydrocarbon and affects the distribution of the other phases. The elevation, fluctuation, and gradient of the water table must be known to determine directions and rates of water and hydrocarbon migration. This information can be derived from direct observations of static water levels in wells and other structures intersected by the water table. When using local supply-well drillers' logs for water table elevations, one should take care because many supply wells are installed in deeper, confined aquifers to avoid surface contamination.

If seasonal trends in groundwater flow patterns must be assessed, water levels in available wells should be documented for a period of one year (on a seasonal basis). Such data will allow an evaluation of the role of water table fluctuations in the distribution of liquid and dissolved hydrocarbon accumulations. Contour maps may be constructed to illustrate LNAPL distributions, areal changes in accumulations, and migration trends. Maps showing the distribution of dissolved hydrocarbon concentrations may also be constructed for several time periods. This type of presentation will also allow hydrocarbon concentration changes over time to be depicted graphically. The maps can be used to evaluate the effectiveness and progress of recovery programs as well.

### 5.3.4.3 Field Tests

Porosity values for various aquifer materials can usually be estimated using published values. However, site-specific values for hydraulic conductivity should be determined using accepted field test procedures because hydraulic conductivity varies in earth materials as noted in Table 1. This information can be supplemented with laboratory-derived hydraulic conductivity data from soil or rock cores, especially where vertical hydraulic conductivity is important. Field tests, if properly conducted, can be completed using monitoring wells and production wells. Reliable results require that the effect of LNAPL be considered. Such information is useful in determining the migration rates of chemical(s) of concern and in the optimum design of a recovery system. Refer to Appendix A for information sources on such field tests.

Several types of field tests are commonly used to determine aquifer hydraulic parameters. In an *aquifer pumping* 

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Figure 17-Typical Flush-Mounted Well and Vault

test, groundwater is pumped at a steady rate from a well, and resulting water level changes are measured over time in the pumped well and nearby observation wells. The rate of drawdown and recovery of water levels, once pumping has ceased, can be used to determine hydraulic parameters such as hydraulic conductivity. The aquifer pumping test provides an estimate of average conditions near the test and observation wells. Before conducting the pumping test, one frequently performs a step test to determine the sustained yield from a well. An aquifer pump test under recovery conditions can sometimes be used to estimate hydraulic conductivity. In this type of aquifer pump test, after pumping has ceased, measurements are made on the recovery well and nearby observation wells as the water table rebounds. Although not as accurate, this method should yield results that are comparable to the steady-rate pumping test. A recovery test can be used at a site with an existing recovery system to verify the estimates of hydraulic conductivity. An advantage of a recovery test for a site with an active recovery system is that the test begins immediately when the recovery system is shut down. The test, therefore, minimizes recovery system downtime in controlling hydrocarbon movement. However, once a recovery system is shut down, the capture zone is lost and may take some time to completely reestablish itself. A complete discussion of pumping test procedures and protocols is provided in *Groundwater and Wells* (Driscoll, 1986)

A second field test, termed a *slug test*, entails the instantaneous removal or addition of a known volume of water from or to a well, and measurement of water levels over time as they recover to the original pretest level. Such a test allows estimation of hydraulic parameters in the immediate area of the well tested.

### SECTION 6—RISK ASSESSMENT

### 6.1 Overview

This section discusses risk assessment principles used to implement a risk-based approach for evaluating potential threats to human health and the environment from the release of petroleum products. These principles are the basis for the risk-based corrective action (RBCA) process discussed in Section 3 of this publication.

Risk assessments are useful in identifying and managing potential human health risks or risks to ecological receptors

associated with impacted sites. Risk assessment is a process that quantifies (a) the potential risks to identified receptors associated with exposure to site-related chemicals or (b) the site-specific remediation target levels for impacted environmental media that are protective of human health and ecological receptors if exposure to the identified receptors occurs. Generally, a risk assessment is used to predict the potential adverse risks to human health and the environment associated with exposure to chemical(s) of concern at a site. 48

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#### Table 14—Advantages and Disadvantages of Different Well Casing and Screen Materials

Туре	Advantages	Disadvantages		
Rigid PVC (polyvinyl chloride)	Lightweight Excellent chemical resistance to weak alkalies, alcohols, aliphatic hydrocarbons, and oils Good chemical resistance to strong mineral acids, concentrated oxidizing acids, and strong alkalies Readily available Low-priced compared with stainless steel and	Weaker, less rigid, and more temperature sensitive than metallic materials Some constituents from groundwater may be adsorbed Poor chemical resistance to ketones and esters and other pure solvents		
	Teflon®			
Polypropylene •	Lightweight Excellent chemical resistance to mineral acids Good to excellent chemical resistance to alkalies, alcohols, ketones, and esters Fair chemical resistance to concentrated oxidizing acids, aliphatic hydrocarbons, and aromatic hydrocarbons	<ul> <li>Weaker, less rigid, and more temperature sensitive than metallic materials</li> <li>Reactive with constituents and may leach some constituents into groundwater</li> <li>Poor machinability (it cannot be slotted because it melts rather than cuts)</li> </ul>		
	Low-priced compared with stainless steel and Teflon®			
Teflon®	Lightweight High-impact strength Fair resistance to chemical attack; insoluble in all organics except a few exotic fluorinated solvents	Tensile strength and wear resistance are low compared with other engineering plastics Expensive relative to other plastics and stainless steel Adsorbs and desorbs hydrocarbons		
Kynar®	Greater strength and water resistance than Teflon® Resistant to most chemicals and solvents Lower priced than Teflon®	Not readily available Poor chemical resistance to ketones such as acetone		
Mild steel	Strong, rigid; temperature sensitivity is not a problem Readily available Low-priced relative to stainless steel and Teflon®	Heavier than plastics Reactive with constituents and may leach some constituents into groundwater Not as chemically resistant as stainless steel		
Stainless steel	High strength at a great range of temperatures Excellent resistance to corrosion and oxidation Readily available Little sorption/desorption of compounds	Heavier than plastics Corrosion and possible leaching of chromium in highly acidic waters Catalytic in some organic reactions Screens are higher priced than plastic screens Expensive		

Note: Source: Modified from Driscoll, 1986.

Using risk assessment methodology to determine if residual concentrations of chemicals of concern are protective of human health and the environment can be cost-effectively conducted using a tiered approach. This process is outlined in Section 3 of this publication.

### 6.2 Risk Assessment

The goal of a risk assessment is to evaluate the magnitude and probability of actual or potential harm by the threatened or actual release. The components that are required to achieve this goal are as follows:

a. Analyze all relevant environmental media (air, soil, water).

b. Evaluate relevant environmental fate and transport mechanisms.

c. Evaluate potential exposure pathways and extent of expected exposure.

d. Identify human and ecological populations at risk.

e. Identify the intrinsic toxicological properties of the

released materials or components of the released materials at or near the site.

f. Evaluate the extent of expected harm and the likelihood of such harm occurring (that is, characterize risk).

The risk assessment process can be reduced to three areas of investigation, which are described in the following:

- a. Exposure assessment.
- b. Toxicity assessment.
- c. Risk characterization.

### 6.2.1 SITE CHARACTERIZATION

Prior to conducting a risk assessment and during the site assessment, data are collected on the site and surrounding area. Typically, the nature and extent of chemical(s) of concern are delineated. Additional information on land use surrounding the site should be collected to help identify potential receptors in the next step of the risk assessment, exposure characterization.

	Passive '	Techniques			Active Techniques		
Characteristics	Industrial Hygiene	Curie Point Wire	Dynamic Trapping	FID	Explosimeter	PID	Standard Laboratory
Sample collection time		Weeks	Minutes	Minutes	Minutes	Minutes	Tens of minutes
Analysis time		Weeks <sup>a</sup>	Weeks <sup>a</sup>	Instantaneous	Instantaneous	Instantaneous	1-2 hours <sup>b</sup>
Detects total volatiles	Yes	Yes	Yes	Yes <sup>c</sup>	Yes	Yes	Yes
Detects individual compounds	Yes	Yes	Yes	Yes <sup>c</sup>	No	No	Yes
Lower detection limit				*	1,000 ppm	0.5 ррт	
Ease of use Comments	Easy	Easy	Easy	Moderate	Easy	Easy	Moderated

#### Table 15—Characteristics of Soil Gas Collection Techniques

Notes: FID = flame ionization detector; PID = photoionization detector; \* = 0.1 ppm benzene in the chromatographic mode, 1.0 ppm benzene in the survey mode; \*\* = FID should not be used in a potentially explosive environment; + = 20 to 30 percent accuracy; ppm = parts per million. Source: API Document 4509 aNormally weeks, shorter turnaround much more expensive.

<sup>b</sup>If a mobile laboratory is used. Standard laboratory turnaround if mobile laboratory not used.

"FID may be operated in either surveying or chromatographic mode which detects total volatiles or individual compounds, respectively.

<sup>d</sup>Need specialized equipment and a person to run the gas chromatograph if a mobile laboratory is used.

A second step within the site characterization is identification of the chemical(s) of concern. The chemical(s) of concern encountered in hydrocarbon releases typically include benzene, toluene, xylenes, and lead (for example, for a leaded-gasoline release). Benzene and toluene are mobile chemicals that readily partition into vapor- and dissolved-phase hydrocarbon. Lead occurs in free liquid and residual hydrocarbon sorbed to soil particles, and leaches into groundwater with the dissolved-phase hydrocarbon. Caution should be exercised in using lead as a chemical of concern, since it occurs naturally in soil material. The use of lead as a chemical of concern has decreased since the phaseout of leaded gasoline production.

#### 6.2.2 EXPOSURE ASSESSMENT

An exposure assessment is conducted to predict possible migration routes and to identify areas where a hydrocarbon release may have an impact on human health or the environment. In an exposure assessment, all available information must be integrated to determine the movement of all hydrocarbon phases toward potential receptors. A complete exposure pathway consists of a source, a transport mechanism, a point of exposure, and an exposure route. The pathways for liquid- and vapor-phase hydrocarbon in the subsurface environment are dictated by natural soil conditions and geologic barriers and conduits, as well as by man-made structures.

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

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

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

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

- a. Volume released.
- b. Adsorptive capacity of the soil.

c. Presence of perched groundwater and primary and secondary porosities in the earth materials.

 Relative permeability of the soil to dissolved- and vaporphase hydrocarbon and LNAPL.

e. Rates and directions of groundwater movement.

f. Processes such as dispersion. advection, and degradation that reduce concentrations and limit the area of the hydrocarbon-impacted zones.

The potential for soils containing residual LNAPL to act as a long-term source of hydrocarbon in groundwater should

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a. Buried accumulator device

b. Ground probe with vapor-collecting device



be considered. Computer models (both analytical and numerical, with varying levels of complexity and date requirements) are available to predict the impact of residual hydrocarbon in soil on groundwater concentrations. These models can be used with information collected during the site assessment to estimate the approximate concentration of hydrocarbon in groundwater at a given time and location. A monitoring-well network capable of delineating the hydrocarbon plume can be established to verify the model being used. The model then can be refined based on the monitoring data. These models can be very useful in (a) determining the need for corrective action, (b) establishing target levels and time frames, and (c) selecting and designing appropriate remedial actions based on the target levels.

### 6.2.3 TOXICITY ASSESSMENT

This section summarizes the methodology to be used in evaluating risk from exposure to the chemical(s) of concern. The general methodology for the classification of health effects and the development of health effects criteria is described in more detail in the API Publication 1628B.

For risk assessment purposes, USEPA guidance recommends that chemicals be separated into two categories of toxicity depending on whether they exhibit non-carcinogenic or carcinogenic effect. This distinction relates to the currently-held scientific opinion that the mechanisms of action for these categories differ. For carcinogens, any exposure is assumed to have a finite possibility of causing cancer (in other words, no threshold). Non-carcinogenic effects are assumed to occur if exposures are above a minimum dose, termed a *threshold*.

### 6.2.3.1 Health Effects Criteria for Potential Noncarcinogens

Reference doses (RfDs) and reference concentrations (RfCs) are generally used as health criteria for chemicals exhibiting non-carcinogenic effects. The RfD and RfC, expressed in units of mg/kg/day and mg/day, respectively, are estimates of the maximum human daily exposure level likely to be without an appreciable risk of deleterious effects during a lifetime. RfDs and RfCs are usually derived either from human studies involving workplace exposures or from animal studies and are adjusted using uncertainty factors. An attempt is made to consider sensitive subpopulations in deriving the RfD and RfC. The RfD and RfC provide a benchmark against which human intakes of chemicals estimated from exposures to contaminated environmental media may be compared.

### 6.2.3.2 Health Effects Criteria for Potential Carcinogens

Cancer slope factors are generally used as health criteria for potentially carcinogenic chemicals. They are derived from the results of chronic animal bioassays or human epidemiological studies and are expressed in units of (mg/kg/ day)<sup>-1</sup>. Animal bioassays are usually conducted at dose levels that are much higher than those resulting from human

exposure to environmental media. This procedure is followed to permit detection of possible adverse effects in the small test populations used in these studies. Since humans are generally exposed at lower doses, the animal data are adjusted using mathematical models. A linearized multistage model is typically fitted to data from animal studies to obtain a dose-response curve. The 95th percent upper confidence limit (UCL) on the slope of the dose-response curve is subjected to various adjustments, and an interspecies scaling factor is usually applied to derive a cancer slope factor for humans. Dose-response data derived from human epidemiological studies are fitted to dose-time-response curves on an ad hoc basis. In both types of analysis, health-conservative assumptions are applied. Then, the actual risks associated with exposure to potential carcinogens are not likely to exceed the risks estimated, but may be much lower.

### 6.2.3.3 Health Effects Criteria for Exposure to Lead

The USEPA has not established oral inhalation RfDs for lead (IRIS 1995), because measurement of blood lead provides a more accurate indication of potential health effects. A correlation can be made between exposure to lead and increases in blood lead levels and the health effects associated with these levels. Additionally, the available doseresponse data and results of animal studies do not adequately characterize the toxicity of lead, Dragun 1988.

Blood lead levels have been accepted as the best measure of the external dose of lead. Sensitive populations include preschool-age children, fetuses, and white males between 40 and 59 years of age. In both adults and children, a blood lead level of 10 micrograms per deciliter (mg/dL) has been associated with a level at which no adverse effects would be expected to occur.

Children have been considered to be the most sensitive receptors for lead exposure. The USEPA has developed a biokinetic/uptake model to calculate the blood lead level resulting from exposure to lead at a site and in background exposures such as air or drinking water. USEPA has developed a computer program of the biokinetic model called LEAD99. LEAD99 can be used to calculate a soil concentration which will not cause blood lead levels in children to exceed 10 mg/dL. A similar method can be used to evaluate exposure of adults to lead.

#### 6.2.4 RISK CHARACTERIZATION

This section summarizes the tools used to quantitatively evaluate risk. To quantitatively assess the potential risks to human health associated with the current and future use exposure scenarios considered in an assessment, the concentrations of chemicals in relevant environmental media (that is, exposure point concentrations) are used to calculate chronic daily intakes (CDIs) or doses. CDIs are the amount of a substance taken into the body per unit body weight per unit time, expressed in units of mg/kg/day. A CDI is averaged over a lifetime for carcinogens and over the exposure period for non-carcinogens.

For recognized and/or potential carcinogens, excess lifetime cancer risks are obtained by multiplying the CDI of the constituent under consideration by its cancer slope factor. A risk level of  $10^{-6}$ , representing the probability of one excess cancer case per one million exposed individuals, has been used by USEPA as a point of departure. USEPA considers potential excess lifetime cancer risks within the range of  $10^{-4}$ to  $10^{-6}$  to be acceptable and has recently stated, "Where the cumulative carcinogenic site risk to an individual based on reasonable maximum exposure for both current and future land use is less than  $10^{-4}$ , and the non-carcinogenic hazard quotient is less than 1, action generally is not warranted unless there are adverse environmental impacts" (USEPA 1991).

The likelihood of manifesting non-carcinogenic effects is not expressed as a probability as is the likelihood for carcinogenic risk. USEPA (1989) recommends evaluation of non-carcinogenic potential using a calculation of hazard quotients (HQs) and hazard indices (HIs). The HQ is a pathway-specific (for example, ingestion, inhalation) ratio of the calculated CDI for each constituent compared to the constituent-specific RfD. The HI is the sum of all the HQs for an individual pathway and from all pathways of exposure. If either the HI or HQ exceed a value of one, there "may be a concern for potential non-carcinogenic effects" (USEPA 1989). An HQ or HI less than one indicates a low potential of adverse health effects occurring for the evaluated exposure scenarios.

### 6.3 Development of Target Levels

Target levels are typically calculated to derive concentrations of chemical(s) of concern that are protective of potential human health exposures at release sites. Target levels are medium-specific (for example, soil) and element-specific (for example, lead) values calculated using assumptions based on potential current and/or future exposures. The assumptions developed in the exposure assessment are used to develop target levels. Target levels are basically a "back" calculation of a concentration (as in, soil) to which an individual could be exposed, yet no adverse health effects would occur.

Currently, there are no federal standards for acceptable levels of lead in soil. Typically, critical toxicity values established by USEPA (for example, cancer slope factors, RfDs) are used to calculate soil target levels. The blood lead approach described above would be used to calculate soil target levels for lead.

Regulatory agencies such as the USEPA typically have required a baseline risk assessment (an evaluation of current conditions) be performed prior to development of target levels. **API PUBLICATION 1628** 

If this were the case, target levels could be calculated only for those pathways which present a potential risk to human health. More recently, target levels have been derived early in the site investigation process to help focus the remedial investigation or to provide a basis for determining whether or not remedial action is required at a site (see Section 3).

# SECTION 7—SITE REMEDIATION

### 7.1 Overview

Site remediation involves the development and implementation of containment or clean up strategies. Containment strategies are intended to prevent further migration of mobile hydrocarbon phases by controlling hydrocarbon plume movement over a defined period within a specific area until concentrations are reduced to an acceptable level. The primary benefit of a containment strategy is that further migration is forestalled. Once the LNAPLs are recovered, the need for additional clean-up measures should be assessed, since residual hydrocarbon that come in contact with groundwater may act as a continuing source of dissolved hydrocarbon.

Site assessments, site characterization, exposure assessment, regulatory review, and development of clean-up objectives may be made in accordance with ASTM's RBCA Standard E1739 or other risk-based decision-making procedure acceptable to the applicable state and federal regulatory agencies. The RBCA flowchart is depicted in Figure 8. The choice of remedial strategy and the scope are governed by site conditions, possible methods of source control, the results of the exposure assessment economic considerations, and the potential impact on the affected areas as determined during the tiered assessments.

There are many proven remedial technologies, and no single approach can universally be applied with equal success at all sites. Two or more technologies are often required at a site and may be applied sequentially or in tandem. Available remedial technologies and the capabilities and limitations of each are discussed in this section.

The following four steps are typically followed in developing a remedial solution:

a. Establishing target levels: As discussed in Section 3, this involves identifying the areal extent and depths of hydrocarbon phases to be remediated and establishing the concentrations to which the phases will be reduced at key locations. The RBCA tiered process demonstrating protection of human health and the environment can be used to determine if active remediation is unwarranted at a site or, if remediation is warranted, to provide a method by which the degree of remediation is established.

b. Evaluating remedial alternatives and selecting the sitespecific recovery system: Remedial alternatives are identified based on knowledge of the site hydrogeology, the target levels, and the exposure assessment. The best alternative is selected on the basis of achieving the required level of risk reduction considering technical feasibility, target levels, and costs. The remedial design should recognize that as the remediation project progresses (time), the rate of removal (concentration) decreases. Therefore the remedial action plan should be prepared to efficiently address these changing concentrations over the "life-cycle" of the remediation project.

c. Preparing final designs and constructing the remedial system. d. Monitoring and maintaining the system and making adjustments as remediation proceeds.

### 7.2 Target Levels

In general, the removal of various hydrocarbon phases from earth materials and groundwater continues until concentrations decline to levels acceptable for the protection of health and the environment. The selection, design, and operation of a remedial system depends on the target levels determined. Target levels may be applied to in-situ remediation situations; to water, air, or soil being discharged or disposed of off-site; or to expected future uses of the site. These levels may be obtained from a RBCA Tier 1 look-up table or developed using site-specific data in Tier 2 or 3.

Site-specific factors affecting selection of target levels include the following:

a. Hydrogeologic conditions that affect the mobility of hydrocarbon phases.

b. The presence of receptors and potential threat to human health and the environment.

c. Potential for fire or explosive conditions.

The requirements for disposal or discharge of materials from the site may be based on the following considerations:

- a. State regulations for waste disposal/treatment.
- b. Permits and control for wastewater discharges.
- c. Permits and control for air emissions.

The objectives governing the continued operation of an existing remediation system are typically determined based on one or more of the following conditions:

a. Potential for exposure as determined from the migration potential of the chemical(s) of concern and the exposure assessment.

b. Background levels of off-site or naturally occurring chemicals.

c. Concentrations of chemical(s) of concern approaching an asymptotic level (that is, continued remediation results in negligible concentration declines).



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d. Potential for attenuation through processes of natural biodegradation, volatilization, adsorption, and dispersion.

e. Resource management considerations such as the classification of the groundwater or aquifer based on local use and economics.

f. Statutory requirements.

g. Levels that constitute a nuisance (such as offensive odors).

h. Leaching potential of chemical(s) of concern from soil to groundwater.

#### Closure 7.3

The target levels established for the site determine when the remedial program can be terminated. Compliance monitoring and reporting are necessary to demonstrate that progress is being made, that modeling predictions and assumptions about the site are correct, and when target levels have been reached. Often, remediation may be halted where one or more of the following conditions are fulfilled:

a. Concentrations reach the target levels.

b. Concentrations approach an asymptotic level, and existing concentrations of chemical(s) of concern no longer pose a long-term threat to human health and the environment.

c. Regulatory agency approval is granted.

The remedial action plan depends on site-specific conditions and usually requires approval from the pertinent regulatory agency before implementation. A remedial action plan should consider the concepts of risk-based corrective action and of life-cycle design.

### 7.3.1 LIFE CYCLE OF A REMEDIATION PROJECT

Figure 19, Part A shows the normal life-cycle concentration of a remediation project. Often a remedial design is based only on concentrations found during the site assessment (early portion of the life-cycle curve). However, the concentration changes over the life of the project, and any design must address all of the concentrations encountered during the entire project.

Figure 19, Part A is a conceptual plot of concentration versus time. The plot shows that, as time increases, the concentrations decrease in a nonlinear relationship. As the project progresses over time, the rate of contaminant removal decreases. Figure 19, Part A shows the curve becoming almost parallel (asymptotic) to the horizontal axis over a period of time. There are several processes that may contribute to the flattening of this curve. These processes include physical processes (dilution, dispersion, filtration, and gas bubbles), chemical processes (complexation, acidbase reactions, redox reactions, precipitation-dissolution, and sorption-desorption), and chemical reactions (decay, respiration, degradation, and co-metabolism).

In the past, the methods used to determine what is "clean"

and when a remediation project could be terminated have been based on federal drinking-water standards, analytical detection limits, background concentrations, or some other regulatory or statutory requirement. The difficulty with this definition of "clean" is shown in Figure 19, Part B. As the site gets closer to "clean," the hydrocarbon concentration approaches an asymptote. While Figure 19, Part B represents a worst-case scenario in that the site never achieves the "clean-up" concentration, even in those cases where the site does reach "clean" the process can take many years.

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During the last years of the project, a remediation system is subject to diminishing returns. The remediation system continues to operate, but the reduction in concentration is significantly reduced.

Another level of the project life-cycle concept can be defined as active management. Active management is that period of time during the project when active remediation is occurring. Figure 19, Part C shows the life-cycle curve with the "clean" line and an active management line. The active management line represents the stage in the life cycle where active remediation (that is, pumping, venting, sparging, and the like) will no longer facilitate the clean up of the site. Active remediation could cease at this time. The period of time after active management ceases but before clean up objectives are achieved is a period of passive management where natural processes continue remediation. Monitoring would be the key project activity during this period.

#### 7.3.2 NATURAL ATTENUATION

Soluble plumes emanating from a hydrocarbon source area typically show that the concentrations of the hydrocarbon chemicals are decreased by several physical, chemical, and biological processes. Given sufficient flow distances and times, these processes can ultimately result in the complete attenuation of these dissolved hydrocarbon chemi-Natural attenuation processes are important to cals. consider when evaluating remedial responses and considering termination of active remediation.

The physicochemical processes, in general, decrease dissolved hydrocarbon concentrations by redistributing the hydrocarbon mass. However, by decreasing their concentrations and by redistributing mass, these processes can render the petroleum hydrocarbon chemicals more bioavailable and hasten their attenuation by biodegradation. Some of these physicochemical processes, such as adsorption and dispersion, are discussed in Section 7.6.5.4. A listing of references describing these and other physical and chemical processes are included in Appendix A. Note: More information can be found in API Publication 1628A.

The biological processes are chiefly responsible for the transformation of the dissolved hydrocarbon chemicals to simpler organic and inorganic compounds. These processes are almost entirely carried out by the microbiological, or microbial, populations inhabiting the subsurface. These





a. Life-cycle concentration during a remediation project.



b. Achieving "clean" during a remediation project.



c. Active management versus what is clean during a remediation project.

Figure 19—Life Cycle of a Remediation Project

microbial populations can mineralize the hydrocarbon chemicals, transforming them into carbon dioxide  $(CO_2)$ , water  $(H_2O)$ , and salts. This microbial transformation pro-

cess, known as biodegradation, is the major attenuation mechanism for petroleum hydrocarbon in the subsurface. A dynamic equilibrium will be reached with the release rate of hydrocarbon chemicals in the source area balanced by the biodegradation rates within the dissolved-phase plume with the rate of biodegradation determining the ultimate length of the plume. This equilibrium will result in a generally stabilized plume which will not continue to grow past a certain point. Those sites with long term (> 1–2 years) monitoring data, can usually use this data to evaluate plume stability.

Where long-term water quality data are lacking, biomodeling is an innovative extension of computer modeling methods (in other words, fate and transport modeling) and has been developed within recent years. Biomodeling is used as a design tool to ensure that the remedial system takes advantage of the biodegradation processes at the site so that the effort and resources used are appropriate. Biomodeling (for example, BioTrans, Bioplume II, and so on) goes beyond the capabilities of earlier flow and transport models to simulate the major processes that determine the distribution, rates, and extent of biodegradation of hydrocarbon. It is important to note that any model should be calibrated with site-specific data.

This method allows for fully interrelating the information on biodegradation processes with the other physical and chemical processes being monitored at the site. Furthermore, a biomodel allows the information collected both in the field and in the laboratory to be integrated, to determine the ultimate extent and magnitude of hydrocarbon at the site as well as off-site. These results are important when incorporated into a risk or fate assessment and can also be used to define appropriate clean-up objectives.

# 7.4 LNAPL Recovery Alternatives

LNAPL recovery systems can be grouped into two broad classes:

- a. Interceptor trenches and drains.
- b. Recovery wells.

### 7.4.1 TRENCHES AND DRAINS

Interceptor trenches and drains can be used to recover LNAPL that occur above a shallow water table or that are perched above zones of low hydraulic conductivity. A trench is usually excavated on the downgradient side of the LNAPL plume. The trench must be excavated several feet below the lowest seasonal fluctuation of the water table or to the geologic barrier on which the hydrocarbon are perched. Care must be taken not to penetrate the geologic barrier, for doing so would allow uncontrolled downward migration of LNAPL. The trench should be left open only when site access can be controlled, response time is limited, and safety considerations are met.

LNAPL will migrate into the trench under the influence of the natural groundwater gradient and can be collected by



pumping. LNAPL can be removed by several methods. If a skimming system is used to remove only LNAPL, an impermeable barrier can be placed on the downgradient side of the trench to prevent hydrocarbon movement yet allow water to pass. Skimming pumps must be capable of continuous operation with the ability to shut off automatically under high-water conditions. Otherwise hydrocarbon can accumulate in the trench and flow around the ends of the barrier.

Pumping groundwater from the trench provides hydrodynamic control by lowering water table elevations near the trench, thereby increasing the capture zone and inducing flow of LNAPL to the trench. The use of an impermeable barrier on the downgradient side of the trench can also increase the upgradient capture zone. In unconsolidated sediments, the rapid drawdown of the water table may cause loss of soil stability and slumping of trench walls. If soil stability, safety, or other considerations are such that the trench cannot be left open, it can be converted to a drain by backfilling with graded filter material (sand or gravel). Figure 20 details the design and operation of a typical drain. Sumps or wells installed at intervals along the drain can be pumped to collect the hydrocarbon. Perforated drain pipes can be installed in the bottoms of the backfilled trenches and connected to the sumps to improve the efficiency of the system.

Single-pump or two-pump systems can be installed in the sumps to remove groundwater and LNAPL. A hydrocarbon/water separator will need to be sized and installed with the pumping system if both hydrocarbon and water are pumped using a single pump. More details on the treatment of the produced groundwater are given in 7.5.3.

To reduce the cost of construction and soil disposal, the trench or drain should be kept as narrow as possible. The depth is usually limited to less than 15 to 20 feet, depending upon available excavating equipment and soil stability.

However, recent technological developments now allowing the installation of 10-inch wide drains to depths as great as 24 feet below grade are becoming more widely available. Newer trenching machines can now install the drainage pipe and gravel envelope in a continuous trenching operation. For large projects, special excavating equipment is available which can allow interceptor trenches to be installed at depths greater than 60 feet, by a slurry trench technique.

Trench and drain systems are applicable to a wide variety of hydrogeologic settings, and the only major limitations are the depth to which they can be installed and the availability of space for the installation. Some examples of hydrogeologic settings where trenches would be favorable for recovery include the following:



a. Heterogeneous earth materials in which fluid migration is through randomly occurring zones, such as discontinuous layers of sand.

b. Areas with high-water tables and relatively low hydraulic conductivity where interception of LNAPL in trenches or

horizontal wells are more practical alternatives than numerous closely spaced recovery wells.

c. Areas where the saturated thickness of the aquifer is minimal, making wells ineffective, such as zones along rivers which may be dry during parts of the year.

### 7.4.2 RECOVERY WELLS

### 7.4.2.1 General

The use of trenches or drains may not be economical due to factors such as excessive depths to the LNAPL plume, disposal concerns, and the existence of buried utilities. Recovery wells that offer flexibility in design, placement, and operation can be used in these instances.

Three basic types of recovery pump wells are used to recover LNAPL:

a. Skimming systems for hydrocarbon only.

b. Single pumps which collect both LNAPL and water.

c. Two-pump systems that pump LNAPL and water separately.

In addition to typical vertical recovery wells, horizontal well systems are being successfully used at hydrocarbon remediation sites. Horizontal well systems have characteristics of both trenches/drains and conventional recovery wells (Section 7.4.2.5).

Table 16 lists the advantages and disadvantages of each of these systems.

#### 7.4.2.2 Skimming Systems

Skimming pump systems are designed to remove LNAPL from the fluid surface in a well or sump with little or no water production. Skimming systems will not provide control of the dissolved plume. These systems generally operate at pumping rates of less than 5 gallons per minute (Table 17). Skimming systems are available in a variety of forms:

a. Pneumatic skimming systems with a top intake that allows skimming of fluids from the LNAPL/water interface, as shown on Figure 21.

b. Pneumatic skimming systems with a density-sensitive float valve that allows passing of water before the valve seats. c. Floating or depth-controlled skimming systems with conductivity sensors that activate the surface-mounted pump when LNAPL have accumulated to a sufficient thickness.

d. Filter skimming systems with a filter material that preferentially passes hydrocarbon, including absorbent skimming systems that remove hydrocarbon via a recirculating belt.

Because the total amount of fluid extracted by a skimming system from the aquifer is small, the depression in the water table, and the area of influence within which hydrocarbon are directed towards the well are also minimal.

Thus, skimming systems are normally used under the following conditions: 56









a. When water table depression is not critical for recovery.
b. Produced-fluid handling, treatment, and disposal capacities are limited, such as with many emergency response situations. In these situations, usually not much is known about the hydrogeology of the site, so skimming systems are used to avoid exacerbating the situation.

c. Periodic water table fluctuations may interfere with discharges from a stationary pump.

d. Settings where LNAPL are confined to the UST backfill in an area where the natural water table is below the bottom of the UST excavation.

#### Table 16—Advantages and Disadvantages of LNAPL Recovery Systems

Trenches and Drains	Skimming Pump Wells	Single Pump Wells	Horizontal Wells	Dual Pump Wells
		Advantages		
Simple operation and maintenance	Little or no water is produced	Simple to operate	Increased contact with LNAPL plume	Separation of the product and water within the well
Materials and equipment are available locally	Simple operation and maintenance	Inexpensive and reliable	More efficient use of limited space	Decreased soluble components in the produced water
Quick, cost-effective installations are possible if soil conditions are favorable	Inexpensive	Low operating and maintenance costs	Ability to locate in areas unavailable to vertical drilling techniques	Fully automated to maximize the rate of recovery
Complete plume interception		Create capture zones	Minimal impact on surface facilities	Create capture zones
		Disadvantages		
The entire width of the migrating plume must be bisected unless water is produced	Small area of influence	Need for aboveground LNAPL/water separation system	Availability of drilling equipment	Higher capital, operating, and maintenance costs
Depth limited by soil conditions, equipment, soil disposal considerations, and cost	Lack of hydraulic control, with continued migration of soluble plume	Tendency to emulsify the LNAPL and water	Cost	Initial start-up and adjustments require experienced personnel
Construction is difficult in congested areas		The dissolved components in the produced groundwater are increased	Limited performance data	Applicability to low transmissivity formations is questionable
Contaminated soil disposal			Large-foot print for installation	Larger volumes of production water require treatment and disposal

### 7.4.2.3 Single-Pump Systems

Single-pump systems produce both water and hydrocarbon. The pump can be surface mounted and operated by suction lift or submersible, depending on the depth to water (Figure 22). Since both water and LNAPL are produced by a single pump, these systems require separation of fluids. Single-pump systems may be arranged in a single- or a multiple-well configuration. In some instances, a series of wells can be connected together and pumped by a single surfacemounted suction-lift pump. Single-pump systems can be employed in situations where hydraulic conductivities are low to moderate and where flow rates for each well are less than 5 to higher than 20 gallons per minute (Table 17). Emulsification of LNAPL in produced water and increased dissolved hydrocarbon concentrations are the primary drawbacks associated with some single-pump systems (that is, especially electric, submersible pump systems). The tendency for emulsification can be reduced by the use of positive displacement pumps, or surface-mounted positive-displacement or peristaltic pumps when the depth to water is less than about 20 feet. If an existing industrial wastewater sewer system can effectively handle the produced water and LNAPL, combined fluids systems can be cost-effective at higher flow rates. However, cost-effectiveness decreases if an on-site treatment system must be constructed for separation and dissolved-phase treatment. For this reason, single-pump systems are normally limited to areas of low hydraulic conductivity where the volume of produced water is small. In addition, pumps that come in contact with hydrocarbon need to have ratings appropriate for working in hydrocarbon environments.

Vacuum-enhanced recovery is a technique that can be used to increase the performance of single-pump recovery systems. A vacuum is applied to a sealed single-pump well, or well system, to enhance the recovery rate and area of capture of LNAPL. The application of vacuum to a well or trench increases the driving force causing liquids to flow to well(s). Figure 23 illustrates two pumping options for use in conjunction with vacuum enhancement. The first option uses a suction pump to produce water and LNAPL while applying a vacuum to the well(s). The second option uses a submersible pump to remove the produced fluids and a separate vacuum pump.

Vacuum-enhanced systems are most effective in situations where conventional pumping and trench systems are inappropriate. These situations include the presence of deeper zones with small saturated thicknesses, low hydraulic conductivities, surface obstacles to trench installations, or perched hydrocarbon.

#### 7.4.2.4 Two-Pump Systems

Figure 24 illustrates a typical two-pump system. The system consists of a water depression pump installed with the

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		Fluid Production Rate Per Well	
Pump Type	Low (< 5 gpm)	Medium (5–20 gpm)	High (> 20 gpm)
Skimming			
down hole			
suction lift			
/acuum-enhanced			
shallow			
deep			
	,		
Pneumatic single pump			
submersible			_
suction lift			
lectric sincle pump			
submersible			
suction lift			
Suction int			
Two-pump systems			
submersible electric			
submersible pneumatic			
suction lift			

### Table 17—Operational Range for Common Pumping System

Note: gpm = gallons per minute.

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intake near the bottom of the well. Water is withdrawn at a controlled rate to create a cone-of-depression. A suspended hydrocarbon pump is placed above the water pump and adjusted so that the intake is at or slightly below the LNAPL/water interface. Automatic controls cycle both pumps on and off as hydrocarbon and water accumulate and are removed.

Numerous pumping options and control configurations are available. Two-pump systems use electric submersible pumps, pneumatic submersible pumps, or surface-mounted suction-lift pumps. These systems are normally used under the following circumstances:

a. When water table depression is necessary for recovery and achieving hydraulic control of the plume.

b. When hydraulic conductivities and saturated thicknesses are moderate to large.

c. When LNAPL/water separation facilities are limited or not desirable.

Pump separation should be maximized to minimize dissolved hydrocarbon concentrations. Vortex breakers between the pumps can also be used to minimize mixing of water and hydrocarbon.

Extreme care must be exercised during the initial start-up and adjustment of two-pump systems. Pumping rates and pump placement must be balanced so that the LNAPL/water interface is maintained at a constant level in the well. Stabilizing the fluid levels and maintaining good LNAPL/water separation can be difficult at low flow rates. Two-pump systems usually require larger diameter wells than single-pump systems and more technical skill for installation and maintenance.

### 7.4.2.5 Horizontal Well Systems

Over the last decade, horizontal drilling technology has been developed and applied in the petroleum industry for oil and gas production and in civil engineering projects for utility and pipeline installation.

Horizontal drilling and well completion technologies have been recently demonstrated to have application for hydrocarbon recovery and remediation projects. There appear to be numerous applications for this technology



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Figure 21—Pneumatic Skimming Pump

including remediation beneath buildings, storage tanks, refineries and plants, or any other circumstance where it is difficult to place vertical wells to perform sampling or remediation.

In other situations, where vertical wells now are used to extract groundwater for treatment, horizontal wells can offer significant advantages. By placing a long horizontal section through the contaminant plume, a single horizontal well can replace many vertical wells, while also reducing clean-up time and costs. Typically a horizontal well requires a large footprint to install. The installation may also be complicated by surface features and utilities. Soil vapor extraction (see also section 7.6) is another important application for horizontal wells. In addition, insitu remediation may benefit from horizontal drilling technology. For example, horizontal wells might be used to convey nutrients to enhance bioremediation processes.

# 7.4.3 SYSTEM DESIGN CONSIDERATIONS

#### 7.4.3.1 General

The selection of a proper recovery system depends on the hydrogeologic setting, the type of recovery program being



Figure 22—Single-Pump System

implemented, and the equipment and facilities available at the location. For example, what may be an acceptable and cost-effective alternative for an oil refinery, with available hydrocarbon separation and water-handling facilities, may not be acceptable at a retail service station where space and fluid-handling facilities are limited. The type of LNAPL and quality of the produced water will also have a major impact on the type of system selected. These factors have a significant influence on the operation and maintenance requirements of different systems. For additional information see API Publication 1628E.

### 7.4.3.2 Recovery System Placement and Hydraulic Influence

Based on the hydrogeologic properties of the site and the LNAPL properties, the following should be determined:

a. The capture zone of the recovery system.

b. The configuration of the system required to contain and remove the dissolved hydrocarbon LNAPL.

As illustrated in Figure 25, the *capture zone* refers to the zone of hydraulic influence within which LNAPL and groundwater will flow to the recovery point. It is obtained





Figure 23—Vacuum-Enhanced Single-Pump Options

62 **API PUBLICATION 1628** Water discharge Hydrocarbon storage Hydrocarbon pump Water pump controls controls Surface seal Casing Backfill/grout Bentonite seal 1111 LNAPL Hydrocarbon pump Hydrocarbon detection probe Well screen Hydrocarbon detection probe 00 Water pump 00,0,0,0 Filter pack

Note: Maximize pump separation.

Figure 24—Two-Pump System

by establishing a sustained cone of depression—created by pumping—in the water table. The groundwater-pumping rate and system location should create a capture zone that will encompass the LNAPL and dissolved-hydrocarbon plumes. The slope of the water table produced by pumping creates the gradient under which the LNAPL and dissolved hydrocarbon move toward the recovery point. The stagnation point is the point directly downgradient of the pumping well where the forces on the groundwater are balanced: the force of the natural gradient away from the well and the gradient created by the pumping well towards the well. Any groundwater or LNAPL beyond the stagnation point will not be pulled back to the recovery well. This calculated distance is important in designing recovery well networks to capture plumes.

Groundwater discharge from a recovery system should be controlled so that water withdrawal is minimized and










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Not for Resale

Stagnation point

**API PUBLICATION 1628** 

LNAPL withdrawal is maximized. Lower pumping rates cause reduced drawdown and limit the vertical section of the aquifer exposed to contact with LNAPL. This will also reduce the vertical extent of residual LNAPL. In many instances, several multiple wells pumping at lower individual rates will be more effective than a single well pumping at a high rate. Normally, recovery wells are best located near the downgradient part of the LNAPL plume to achieve total plume capture with the minimum number of wells and the lowest possible water withdrawal rates.

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Optimizing the location and pumping rates of recovery wells is critical for effective operation of the system. Several options, including modeling, are available for optimizing these operational parameters. A discussion of recovery optimization as it pertains to LNAPL recovery is presented in Section 7.4.4. Design and optimization procedures for dissolved-hydrocarbon recovery is discussed in Section 7.5.2. Note: For more information refer to API Publication 1628C.

# 7.4.3.3 Recovery Well Drilling and Design

Although monitoring wells are normally installed to obtain sediment-free representative water samples, recovery wells are built to maximize the production of groundwater and LNAPL.

Monitor-well drilling methods and their applicability to various types of geologic materials have been discussed previously in Section 5.3.1.2.2, and Tables 9 and 10 compare different methods used in the installation of monitoring wells. Drilling techniques for recovery well installation are similar. The primary factors to consider when selecting a drilling technique include the following:

a. Site-specific geologic and physical conditions (see Section 5.3.4).

b. Size and type of casing to be installed.

c. Availability and cost.

Recovery well efficiency is critical because inefficient wells can significantly increase recovery system costs. Improper well design can lead to poor pump performance, lower than expected fluid production rates, and higher energy consumption and maintenance costs. Moreover, if the pump cannot produce the required yield, additional recovery wells may be required, thereby increasing capital costs.

Data from a nearby soil boring or monitoring well can sometimes be used for designing screens and filter packs for recovery wells. The sizing of the screen and filter pack should be determined using water-well design procedures. The type and size of screen openings should be related to the hydraulic conductivity and grain sizes of adjoining earth materials as well as the filter pack. For example, continuous slot wire-wrapped screen can be used to maximize the open area but still preclude the movement of fine-grained material into the well by using an appropriate filter pack. Also, hydrocarbon provide a medium for bacterial growth which may eventually clog the screens. The more open area provided, the more space there is available in which to accomplish well development and/or maintenance. Iron bacteria can also rapidly clog well screens. Incrustation and corrosion of well screen materials may also be a problem in some groundwater environments. Compatibility of casing and screen materials with various chemicals is presented in Table 14. The groundwater should be tested to determine if iron bacteria, incrustation, or corrosion problems are likely. These factors should be considered in selecting the well casing and screen materials. A regular maintenance program may be required to ensure well efficiency.

The screen length should be placed to allow for the entry of LNAPL, considering seasonal groundwater fluctuations and expected pumping influence. If the screened interval is placed at an elevation below the water table elevation or drawdown is not sufficient to depress the water surface to within the screened interval, LNAPL will not enter the well.

The diameter of the recovery well casing and screen depends on the size of the pump, the type of aquifer materials and the method of well installation. Well diameters can vary from 2 inches to more than 36 inches to accommodate different pumping systems.

# 7.4.3.4 Pumping-System Design

The pumping equipment must be properly sized to match the production from the formation and to handle the expected loss in pressure in the discharge piping system. All system components must be compatible with the hydrocarbon being produced. Potential corrosion, incrustation, and biological fouling problems must be considered. Electrical and fire codes require the use of explosion-proof electrical and pumping systems in many areas. The use of equipment not specifically designed or modified for handling flammable liquids can endanger personnel and property. The following are the primary factors to consider when selecting pumping equipment:

- a. Pumping rate.
- b. Pumping lift.
- c. Compatibility of materials.
- d. Oil/water emulsification.
- e. Potentially explosive conditions operation.
- f. Operation and maintenance.
- g. Cost and availability.

#### 7.4.3.5 Water-Handling Systems

Hydrocarbon remediation programs are complicated by the treatment and handling of produced waters. Depending on the recovery system employed, water volumes from less than a gallon per minute to thousands of gallons per minute must be handled in an environmentally safe manner. Procedures for treatment of the water are covered in 7.5.3. The following are some of the options available for managing the produced water. Consideration should also be given to a combination of these options:

a. Discharge to an existing water treatment system (that is, publicly owned treatment works (POTW)).

b. Permitted discharge to a surface water outfall [that is, national pollutant discharge elimination system [NPDES].

c. Treatment and recharge to the aquifer (that is, underground injection control [UIC] permit).

d. Treatment and reuse.

e. Evaporation.

Discharge of the produced water to a municipal sanitary sewer system can be an effective means of water handling. Other than an oil-water separator, no additional treatment will be necessary, and in many cases the hydrocarbon content of the water is low enough that municipal systems can effectively treat the water. However, a permit to discharge may be necessary, and requirements can vary among local municipal sewer districts. Guidance should be sought from the municipal treatment authority receiving the discharge. Standard safety precautions should be followed to prevent discharge of LNAPL.

If an existing treatment facility cannot accept the produced water, discharge of the water to a surface water system can be considered. The groundwater must be tested to assure that it meets the NPDES requirements following treatment, and a new permit must be obtained or any existing permit modified. However, the time required to obtain a permit as well as treatment costs may limit the use of this option.

Injection wells or infiltration galleries can be used to recharge produced water into the aquifer being remediated (or into deeper aquifers) if the hydraulic conductivity of the aquifer is sufficiently large to accommodate anticipated flow rates. When returning produced water to the aquifer, care should be taken to ensure the capture zone is maintained. Treatment of the produced water will normally be required prior to recharge either to improve injectivity rates or water quality. Water quality may produce conditions conducive for system fouling and should be monitored. The quality of the produced water, the method of recovery, and local environmental concerns will determine if treatment is required to improve quality for injection or if reinjection is feasible. Appropriate permits must be obtained as necessary. In many cases, a Class V UIC permit may be necessary.

Depending on the quality, produced water can be considered as a water source for industrial use. Examples of such use include cooling water for a power generating plant and makeup water for asphalt production.

### 7.4.4 RECOVERY OPTIMIZATION

Optimization of LNAPL recovery at a site is difficult due to the complexity of evaluating LNAPL flow in a watertable aquifer. This is essentially a three-phase (water/ LNAPL/air) flow problem for which it is difficult to develop simple solutions that will predict the recoverability of the LNAPL. Thus, the options for optimizing LNAPL recovery are limited to the simple and the complex. For further information, see API Publication 1628C.

In general, the same techniques presented in Section 7.5.2 concerning optimization of groundwater withdrawal systems are also applied to the optimization of LNAPL recovery systems. The same concepts apply in terms of developing capture zones and overlapping cones that will encompass the LNAPL plume. However, once the evaluation has been done to develop a system that will capture and contain the LNAPL, optimization of the liquid recovery process still remains to be accomplished. The established goals of the clean up will determine the approach to this optimization process, but, in most instances, the objective is to maximize the LNAPL recovery while minimizing the production of water and minimizing residuals in the formation. Minimizing residuals is extremely important as a significant percent of the LNAPL can be left in the formation. For this reason, it is also important to limit drawdown and reduce smearing of the LNAPL in the formation. The effect of hydrocarbon entrapment, residuals loss, and relative permeability combine to severely limit the recoverability of LNAPL. In general, reduced recovery efficiencies with greater residual hydrocarbon occur in less permeable sediments or in more heterogeneous formations. The approaches to system design optimization can be divided into several categories: (a) graphical solutions, (b) modified flow models, and (c) three-phase flow models.

#### 7.4.4.1 Graphical Solution Methods—Single Well

Movement of LNAPL is a very difficult process to model. Consequently, few analytical or simple calculations are available for design optimization of recovery of the free product. Nomographs have been developed that can be used as a tool to estimate the amount of LNAPL that can be recovered by a single pumping well. They use a two-layer oil and water model to simulate LNAPL recovery over a range of hydraulic parameters, oil thicknesses, and hydrocarbon properties. The rate and/or volume of hydrocarbon removal can be estimated based upon the following data:

- a. Hydraulic conductivity.
- b. Hydrocarbon viscosity and density (degree API).
- c. Hydrocarbon thickness.

Examples of these nomographs are shown on Figure 26 for K = 0.01 centimeters per second (cm/s), K = 0.001 cm/s, and K = 0.0001 cm/s.

These nomographs should be interpreted as approximations or general guidelines to be used to aid in evaluating what might be expected at a particular site. The variability between sites and other hydrogeologic complexities make these "rule of thumb" approximations only. 66 **API PUBLICATION 1628** K = 0.01 (cm/s)0.4 50000 API = 30 recovery rate API = 40 recovery rate 40000 API = 35 recovery rate LNAPL Recovery Rate (gpm) Approximate Recovery (bbl 0.3 API = 30 approximate recovery rate API = 40 approximate recovery rate 30000 API = 35 approximate recovery rate 0.2 20000 0.1 10000 Open symbols refer to left scale Solid symbols refer to right scale 0 0 2 8 10 12 0 6 LNAPL (ft) K = 0.001 (cm/s)0.2 20000 — API = 30 recovery rate API = 35 recovery rate API = 40 recovery rate -NAPL Recovery Rate (gpm) 0.15 API = 30 approximate recovery rate 15000 Approximate Recovery (bbt) API = 35 approximate recovery rate API = 40 approximate recovery rate 10000 0.1 0.05 5000 Open symbols refer to left scale Solid symbols refer to right scale 0 0 0 2 6 8 10 12 LNAPL

Source: Chiang et al., 1990.

Figure 26—Optimal LNAPL Recovery Rates and Total Recovery From a Single Pumping Well for an API 30, 35, and 40 Oil and a K-Value of 0.01 cm/s, 0.001 cm/s, and 0.0001 cm/s

#### 7.4.4.2 Flow Models—Modified

Another approach to design optimization for LNAPL recovery systems from a site-wide perspective is to use flow models to predict groundwater flow and containment. Tables 18, 19, and 20 list flow models that could be used for this groundwater modeling and their associated data requirements. Particle tracking is then applied to the model to obtain information on groundwater travel times to the extraction wells. These travel times for the groundwater particle tracks can then be modified for LNAPL migration

based on a calculated retardation factor (accounting for viscosity and relative permeability) for the migration of the LNAPL in accordance with the following approach.

The relative permeability of the formation to oil (in other words, LNAPL) can be calculated from the following:

$$K_{\rm o} = K[(\rho_{\rm o}/\rho_{\rm w})(\mu_{\rm w}/\mu_{\rm o}) k_{\rm ro}]$$

Where:

 $K_o = hydraulic conductivity to oil.$ 

K = saturated water conductivity.



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Source: Chiang et al., 1990

Figure 26—Optimal LNAPL Recovery Rates and Total Recovery From a Single Pumping Well for an API 30, 35, and 40 Oil and a K-Value of 0.01 cm/s, 0.001 cm/s, and 0.0001 cm/s (Continued)

- $\rho_0$  = density of oil.
- $\rho_w$  = density of water.
- $\mu_w$  = dynamic viscosity of water.
- $\mu_0$  = dynamic viscosity of oil.
- $k_{ro}$  = relative permeability to oil.

The value of  $[(\rho_0/\rho_w)(\mu_w/\mu_0) k_{ro}]$  will give the ratio or factor that can be used to adjust the water conductivity to that for oil. This same factor can then be applied to the migration times calculated for the water since there is a direct relationship between the K and the rate of migration.

Estimation of  $k_{ro}$  requires the evaluation of the relative saturation of the two fluids and determination of several characteristic constants that must be obtained experimentally or estimated from the literature. This factor can be applied to the water travel times to obtain travel times for the LNAPL to the wells. The well locations can then be adjusted in the model until travel times for the LNAPL, which meet the remedial goals for the site, are reached in the model. It is very important to remember that the analysis of relative permeability is a function of the oil saturation relative to that of water. As the hydrocarbon accumulations in the formation decline, so will the relative saturation of oil in the formation. Once the relative oil saturation drops to a critical value, the hydrocarbon will be immobile.

## 7.4.4.3 Three-Phase Flow Models

At the most complex sites, the use of three-phase flow models may be justified. These models can be used to simulate the migration of the water/LNAPL/air continuum, evaluate the LNAPL recovery effectiveness of various pumping scenarios, and optimize the flow system. However, these are very complex models and only skilled modeling practitioners should use these codes. These models also require a significant amount of experimental or field data, or these data must be estimated from the literature. Without adequate field data to support these complex models, the results of the modeling will be questionable.

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ARMOS is a two-dimensional finite-element model developed to model the movement of groundwater and separate-phase hydrocarbon. MOTRANS is a more complex model that can simulate the movement of air, water, and a separate-phase hydrocarbon, including the partitioning of the hydrocarbon in the dissolved and vapor phases. Both models require a significant degree of experience on the part of the modeler and also require significantly more site data than normally generated (see Tables 18, 19, and 20).

# 7.4.5 COMMON PROBLEMS

The common problems in the design, installation, and operation of LNAPL recovery systems have been discussed in 7.4.1 through 7.4.4, and are summarized as follows:

a. Hydrogeology is not adequately evaluated. The implementation of a remedial program without a thorough understanding of the hydrogeologic factors that control the 68

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# Table 18-Common Computer Models Used in Recovery Optimization

Note: "Basic (Screening) Models

1 = AIRFLOW; 2 = AQMAN; 3 = ARMOS; 4 = AIRTEST; 5 =  $^{a}$ AT123D; 6 = BIOPLUME II; 7 = BIOTRANS; 8 = CSUGAS; 9 =  $^{a}$ FLOWPATH; 10 = HSSM; 11 = HST3D; 12 =  $^{a}$ HYPERVENTILATE; 13 = MLAEM; 14 = MOC; 15 = MODFLOW; 16 = MODPATH; 17 = MOTRANS; 18 = MT3D; 19 = PATH3D; 20 = PLASM; 21 = PORFLOW; 22 =  $^{a}$ QUICKFLOW; 23 = RANDOM WALK 24 = RESSQ 21 = SWIFT II 25 = SLAEM 26 = SLAEM(S); 27 = SWIFT II; 28 =  $^{a}$ VENTING.

## Table 19—Data Requirements for Models Used in Recovery Optimization

	Data Requirements																		
Model Types	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Ground water flow models analytical numerical	•	•	•	•	•	•	•	•											
Dissolved transport models analytical numerical	•	•	•	•	•	•	•	•	•	•	•								
Multiphase flow models	•	٠	•	٠	٠	•	٠	٠	٠	•	•	٠	٠	•	٠	•			
Venting (air flow) models			٠			٠	٠					٠				٠	٠	٠	٠
Linear optimization	•	•	•	•	•		•	•											

Note: There is little difference in the categories of data required for the basic or screening models and the detailed models. The difference is in the level of detail. The detailed models usually require the spatial distribution of the hydrogeologic parameters and a heterogeneous site. The screening models usually assume constant or homogeneous site-wide hydrogeologic parameters.

1 = hydraulic conductivity; 2 = hydraulic gradient; 3 = aquifer thickness; 4 = recharge rate; 5 = storage coefficient; 6 = porosity; 7 = extent of LNAPL; 8 = extent of dissolved plume; 9 = dispersivity coefficient; 10 = retardation factor or  $K_d$ ; 11= half-life or decay coefficient; 12 = LNAPL density/vapor pressure; 13 = LNAPL viscosity; 14 = LNAPL saturation; 15 = relative permeability curves; 16 = intrinsic permeability; 17 = residuals distribution; 18 = subsurface pressure distribution; 19 = effluent vapor concentrations.

migration of hydrocarbon can result in ineffective systems and increased expense. Complex sites such as fracturedrock situations would fall in this category.

b. In the past, target levels were not adequately defined before designing the remediation system.

c. The remedial area or compliance point is not defined. Remedial measures are not necessarily employed over the entire extent of a plume. Depending upon regulatory requirements and results of the exposure assessment, some areas may not require active remediation.

d. Testing is inadequate (for example, dissolved iron levels, physical parameters of the aquifer, proper sizing of recovery

wells). Sample analyses during the investigative phase and pilot studies should be performed, if necessary.

e. Two-pump systems are used in high hydraulic conductivity areas. Two-pump systems are sometimes incorrectly employed in areas of low hydraulic conductivity. If water production rates are low (less than 3 gallons per minute), the use of two-pump systems should be evaluated critically.

f. The recovery system (biological or chemical) is fouled. Reduced efficiency of pumping wells through biological plugging or chemical incrustation is a common problem. Proper selection of well construction materials and pumping equipment, and the institution of an appropriate maintenance

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# Table 20—Summary Matrix of Groundwater Models

Model Name	Model Type	Developer	Availability	Applications	Output
AQMAN	Complex; 2-D; finitedifference	Lekoff & Groehick, USGS	USGS	Optimization for pump and treat systems	Optimum well locations/rates No graphics
ARMOS	Complex, 2-D, finite—element	Environmental Systems and Technology, Inc., (ES&T)	ES&T	Prediction of LNAPL cleanup time/volume/LNAPL thickness	Listing of head at each node LNAPL thickness at each node LNAPL recovery rates No graphics
AT123D	Basic, 3-D, semi- analytical	Yeh, Oak Ridge National Lab	International Ground Water Modeling Center	Simple analyses of dissolved compound migration under uniform gradient	Listing of concentration at each node No graphics
Bioplume II	Complex, 2-D, method of characteristics	Rifai et al, Rice University	Rice University	Dissolved compound migration with biodegradation	Listing of head at each node Listing of concentration at each node Dissolved hydrocarbon recovery rates No graphics
Bio Trans	Complex, 2D, finite—difference	Environmental Systems and Technology, Inc.	ES&T	Dissolved phase transport of organic compounds with natural or enhanced bioremediation	Post-processor produces contours of nodal values on site map
DREAM	Basic, 2-D, analytical	Bonn & Rounds	Lewis Publishers	Capture zone of pump and treat in 2D	Listing of head at each node Plots of streamlines
Flowpath	Basic, 2-D, finite—difference	Waterloo Hydrologic Software		Analysis of recovery system capture zones in 2D	Listing of head at each node Contour plots Plots of streamlines/particle paths
HSSM	Basic, 3-D, semi-analytical	Weaver, EPA and Charbeneau, University of Texas	RSKERL, EPA	Prediction of downgradient exposure concentrations from ground surface releases of LNAPL; <i>Windows</i> interface	Listing of lens size, constituents dissolution, and exposure concentra- tion Graphical output showing NAPL distribution in vadose zone, hydro- carbon lens size, constituents mass balance for lens, and exposure concentrations
HST3D	Complex, 3-D, finite—difference	Kipp USGS	USGS	Dissolved compound migration in 3D	Listing of head at each node Listing of concentration at each node Dissolved hydrocarbon recovery rates No graphics
MLAEM	Complex, 3-D analytic element method	Otto Strack University of Minnesota	Strack Consulting, Inc.	Dissolved phase particle tracking for capture zone analysis in a multi-aquifer system	Integrated graphical output for screen, DXF, or Postscript
MOC	Complex, 2-D, method of characteristics	Konikow and Bredehoeft USGS	USGS	Dissolved compounds migration in 2D	Listing of head at each node Listing of concentration at each node Dissolved hydrocarbon recovery rates No graphics
MODFLOW	Complex, 3-D, finite—difference	McDonald and Harboaugh USGS	USGS	Groundwater flow model that can be coupled with MODPATH or PATH3D to capture zone analysis of pump and treat systems in 3D	Listing of head at each node No graphics
MODPATH	Groundwater particle tracking	David Pollock USGS	USGS	3D particle tracking developed for use with MODFLOW	MODPATH-Pilot Displays groundwater streamlines
MOTRANS	Complex, 2-D, finite—element	Environmental Systems and Technologies	ES&T	LNAPL remediation/volatization	Listing of head at each node Listing of concentration at each node LNAPL recovery rates Dissolved hydrocarbonst recovery rates No graphics
MT3D	Complex, 3-D, hybrid method of characteristics	Chun Mino Zheng, University of Alabama	Papadopulos and Associates	Dissolved compounds migration (fate and transport) in 3D	Listing of concentration at each node Dissolved hydrocarbons recovery rates No graphics

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#### Table 20—Summary Matrix of Groundwater Models (Continued)

Model Name	Model Type	Developer	Availability	Applications	Output
PATH3D	Complex, 3D groundwater particle tracking	Chun Miao Zheng University of Alabama	Papadopulos and Associates	3D transients or steady-state particle tracking for use with MODFLOW	Post-processing utilities for plotting of pathlines
PLASM	Complex, 3-D, finite—difference	Prickett and Lonquist Illinois State Water Survey	T. Prickett	Capture zone of pump and treat in 2D	Listing of head at each node No graphics
Porflow	Complex, 3D, nodal point integration method	Akshai Runchal, ACRI	Analytical and Computational Research, Inc.	Multiphase fluid flow, heat and mass transport in fractured or porous media	Post-processor products contours of nodal values
QuickFlow	Basic, 2-D, analytical	Geraghty and Miller, Inc.	Geraghty and Miller, Inc.	Capture zone of pump and treat in 2D	Listing of head at each node Contour plots Plots of streamlines/particle paths
Random Walk	Complex, 3-D, random walk	Prickett <i>et al</i> Illinois State Water Survey	T. Prickett	Dissolved compound migration in 2D	Listing of concentration at each node Dissolved hydrocarbon recovery rates No graphics
RESSQ	Basic, 2-D, semi-analytical	Javandel et al	International Groundwater Modeling Center	Capture zone in 2D	Plots of streamlines/particle paths
SLAEM	Complex, 2D analytic element method	Otto Strack, University of Minnesota	Strack Consulting, Inc.	Dissolved phase particle tracking for capture zone analysis in a single aquifer	Integrated graphical output for screen,
SLAEM(S)	Complex, 2D analytic element method	Otto Strack, University of Minnesota	Strack Consulting, Inc.	Dissolved phase particle tracking for capture zone analysis in a single stratified aquifer	Integrated graphical output for screen, DXF, or Postscript
SWIFT II	Complex, 3-D, finite - difference	Reeves et al [33]	NTIS	Dissolved compound migration	Listing of head at each node Listing of concentration at each node Dissolved hydrocarbon recovery rates No graphics

program will minimize these problems. It is important to characterize the inorganic water quality prior to designing the system.

g. The operating and maintenance program is inadequate. Systems commonly fail from a lack of proper operating and maintenance procedures rather than improper design or construction. Operating and maintenance procedural manuals should be established for all recovery systems. If the system is to be operated by on-site personnel, a training program should be established following installation.

h. Overproduction exists. In many instances wells are pumped at maximum capacity to hasten recovery. This may result in increased residual hydrocarbon concentrations over a larger vertical portion of the aquifer and reduced total hydrocarbon recovery. The production rate should be designed to contain and recover the maximum amount of LNAPL without exacerbating the residual problem.

i. Well design and placement is poor. Inefficient wells can significantly increase the cost of remedial operations. Proper well development and optimal well placement will reduce overall system costs and improve effectiveness.

# 7.5 Dissolved Hydrocarbon Recovery Alternatives

### 7.5.1 GENERAL

Dissolved hydrocarbon recovery involves hydraulic control of the movement of groundwater containing dissolved petroleum hydrocarbon by pumping at locations and rates based on site hydrogeological conditions. This technology may be applied even if LNAPL are present in the subsurface.

Trenches, drains, and wells are suitable recovery systems for intercepting and containing dissolved hydrocarbon. The design and construction of these systems was as described in 7.4. In general, the design of containment and withdrawal systems is based on the concept of capturing the contaminant plume with as few extraction points as possible and at the lowest possible flow rate. Again, the goals of the remediation, such as limiting drawdown to maximize LNAPL recovery, may impact this basic scenario. Another important consideration is the potential need to treat and dispose of the extracted groundwater. These issues will be discussed in the following sections.

Air sparging is a recent technology that has been developed and applied to remediate both residual and dissolved hydrocarbon. Air sparging is an in situ method of stripping volatile compounds from the aqueous and soil phase into injected air as it rises through the saturated zones and into the unsaturated soils above. Additional detail on this methodology is provided in Section 7.6.2 and in API Publication 1628D.

Table 21 provides general ranges for the design and operational parameters of various approaches to the remediation of dissolved hydrocarbon.

# 7.5.2 DESIGN AND OPTIMIZATION

### 7.5.2.1 Basics of Containment and Recovery

As previously defined, a capture zone is the area within which LNAPL or groundwater will flow to an extraction point. In more technical terms, the capture zone is the zone of hydraulic influence within which liquids will flow to a recovery well (Figure 25). It is developed by establishing and maintaining a cone of depression (created by pumping) in the water table.

When a groundwater extraction system is being designed, the extraction-well locations and the pumping rates should create a capture zone that will encompass and prevent migration of the dissolved plume. In a system where the established goal is simply containment of a dissolved plume, then the design optimization of the system may involve the adjustment of the well locations and pumping rates to achieve capture at the lowest possible flow rate with the least number of wells. On a more complex level, the time frame to achieve capture and the degree of containment could also be considered. The optimization process can take several forms: from simply calculating the capture zone of a single well and then assuring that the wells have overlapping capture zones, to the use of complex groundwater flow and associated linear optimization models. The complexity of the design optimization process selected will depend on the desired accuracy and on the costs associated with the potential inaccuracies in the result. These approaches deal with the optimization of the design prior to installation. "Optimizing" the performance of the system can be accomplished only after the system is installed and operating. Once in operation, the actual performance of the system can be compared to the predicted design. If performance is observed to be outside of the design parameters, then modifications can be made to optimize system performance relative to the design.

If residual hydrocarbon are present, then pump and treat containment systems will not remediate a site due to the continued dissolution of chemical(s) of concern into the groundwater. Pump and treat systems must be coupled with other remedial techniques to address the residual concentrations of chemical(s) of concern and achieve the desired remedial goals. Thus, pump and treat systems have three common uses: a. Containment of dissolved plumes.

b. Enhancing separate-phase recovery through gradient control.

c. Dewatering to enhance the use of venting systems for volatization of residuals.

Containment implies either that (a) the area within the capture zone may not be remediated in a reasonable time frame, or (b) availability of locations to optimally place remedial systems does not exist at a site. Residual hydrocarbon may always remain in the soil pore spaces following recovery of the mobile separate-phase hydrocarbon. The amount of residual hydrocarbon is a function of (a) hydrocarbon type and properties, (b) soil type, and (c) distribution of LNAPL before pumping.

As noted, the approaches to optimizing the design of a containment system and selecting the number, location, and pumping rates of extraction systems vary with the level of effort expended and the complexity of the site. The methods for design can be divided into three categories: (a) those that use radius of influence calculations, (b) basic or screening models, or (c) detailed models. These methods and their data requirements are summarized in the following.

#### 7.5.2.2 Radius of Influence/Capture Zone Method

Radius of influence calculations using analytical solutions to determine well spacing for optimizing the containment of a groundwater plume are a very common approach. This method is normally accomplished using analytical techniques based on aquifer hydraulic properties estimated during pumping or slug tests of the aquifer at the site. At a minimum, slug tests, sieve analyses, and core samples should be taken to estimate the aquifer parameters required to use the radius of influence methods. The amount of field data that is collected and the effort used to develop these values (slug test versus multiple long-term aquifer tests) will be a function of the factors affecting site complexity. Some of the equations available for estimating these properties are presented in Table 22.

In this approach to design optimization, analytical equations are applied to the hydraulic properties calculated for the site to obtain an estimated radius of influence. The groundwater containment system is then designed based on this information, with the wells placed to assure that the capture zones overlap and encompass the plume. Previous comments regarding the stagnation point (see Section 7.4.3) are applicable here as well. Limiting assumptions must be made considering the analytical solution to be used. The questions that must be answered or assumptions made concerning the hydrogeology include the following:

- a. Confined or unconfined?
- b. Leaky or non-leaky?
- c. Artesian or non-artesian?
- d. Equilibrium or non-equilibrium?

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## Table 21—Design and Operational Parameter Ranges for Dissolved Hydrocarbon Recovery

Remediation	Tune	Hydrogeologic Conditions	Depth to Water	Pestrictions
	Турс		(1001)	
One-pump system	Submersible Suction-lift Vacuum enhanced	Low-highUnlimited Low-high Low	0–20 Unlimited	
Two-pump system		Moderate-high	Unlimited	
Trenches/drains	Linear interception	Low-high	0->50	Loosely consolidated formation; underground structures
Air sparging		Moderate-high	Unlimited	Stratified, nonuniform geology
Bioremediation	Enhanced	Moderate-high	Unlimited	Nonuniform geology

Note: cm/sec = centimeters per second; <sup>a</sup>Low =  $<10^{-4}$  cm/sec; Moderate =  $10^{-4}$  -  $10^{-3}$  cm/sec; High =  $>10^{-3}$  cm/sec.

e. Homogeneous or heterogeneous?

- f. Isotropic or anisotropic?
- g. Recharge effects?
- h. Boundary effects?
- i. Saturated thickness?
- j. Groundwater gradient?
- k. Partially penetrating wells?

Thus, the analytical solutions may be simple to use, but a good understanding of the hydrogeology is required for them to be applied correctly. Table 22 lists a few of the analytical solutions available.

Analytical approaches should be modified to include the additional consideration of the natural gradients at the site. The natural gradient will skew the capture zone for an individual well in the upgradient direction, making the capture zone elliptical in shape rather than circular. The effect of the site groundwater gradient on the capture zone and the resultant stagnation point are depicted on Figure 25. These modified analytical solutions give a much more realistic evaluation of the expected capture zone of an individual well, given the existing site conditions.

Another option to incorporating the effect of gradients is to do a flow net analysis and superimpose the calculated cones of depression from the analytical solutions onto a plot of the site gradients. This is a simple matter of addition and subtraction of the calculated drawdowns from the analytical solutions to the site gradient map.

Data requirements for these analytical approaches include hydraulic conductivity, transmissivity, storage coefficient, effective porosity, saturated thickness, and the existing hydraulic gradient across the plume. These requirements are summarized in Table 22. These analytical approaches are simple and efficient methods of evaluating capture zones but do not address the interference effects or the optimization of pumping rates for the entire system. All of these can result in an under- or over-designed system that is inefficient or costs more to operate than would be desirable.

# 7.5.2.3 Basic Flow Models or Screening Models

Screening models can be used to resolve one of the remaining optimization issues (well interference effects) and aid in the optimization of well location and pumping rates. The optimization of well location and pumping rates with these screening models is accomplished using iterations inside the model. Most screening models can be run with a minimum of effort, can provide a quick and effective way of evaluating various pumping scenarios at a particular site, and can significantly increase the confidence level of the proposed system. All models should be calibrated with actual site data.

Computer models are becoming more widely applied to groundwater remediation. A survey of groundwater modelers in the United States identified about 200 different models. Very few of the models are commonly used. Table 18 presents examples of models that can be used to simulate groundwater flow, dissolved-phase transport, multiphase (separate-phase) flow, air flow or venting, and linear optimization. Table 20 summarizes model type, developer, availability, applications, and output obtained from each. Examples of simple screening models include Quick-Flow<sup>TM</sup>, an analytical flow model, and FLOWPATH, which combines a numerical two-dimensional flow model with a particle-tracking model.

Each model type has its own data requirements. The amount of data increases with the complexity of the model. All models require a thorough understanding of the groundwater flow system, the model assumptions, and the chemical(s) of concern. Even though many of the models are in wide use, some of them have yet to be formally validated and should be used with caution. Data requirements by model type are presented in Table 19.

### 7.5.2.4 Detailed Flow Models

Detailed flow models are generally used on large sites with complex hydrogeology, where the risk of under-or over-designing the containment system outweighs the cost

Table 22-Examples of Analytical Solutions

Description	Equation	Terms	Reference
	Solutions	for Determining Hydraulic Parameters	
Unconfined equilibrium equations	$K = \frac{1055 \ Q \ \log r_2 / r_1}{(h_2^2 - h_1^2)}$	Where: $r_1 = \text{distance to the nearest observation well, in ft.}$ $r_2 = \text{distance to the farthest observation well, in ft.}$ $h_2 = \text{saturated thickness, in ft, at the farthest observation well.}$ $h_1 = \text{saturated thickness, in ft, at the nearest observation well.}$ Q = pumping rate in gpm.	(Driscoll, 1986)
Slug test solution Bower and Rice	$K = \frac{r_c^2 \ln (R_e / r_w)}{2 L_e} \frac{l}{t} \ln \frac{Y_o}{Y_t}$	<ul> <li>Where:</li> <li>R<sub>e</sub> = effective radial distance over which the head difference y is dissipated.</li> <li>r<sub>w</sub> = radial distance between well center and undisturbed aquifer (rc plus thickness of gravel envelope or developed zone outside casing).</li> <li>L<sub>e</sub> = height of perforated, screened, uncased, or otherwise open section of well.</li> <li>y<sub>0</sub> = y at time zero.</li> <li>y<sub>t</sub> = y at time t.</li> <li>t = time since y<sub>0</sub>.</li> </ul>	(Bouwer, 1978)
	Solution	s for Determining Radius of Influence	
Unconfined equilibrium equations	$Q = \frac{K(H^2 - h^2)}{1055 \log R/r}$	<ul> <li>Where:</li> <li>Q = well yield or pumping rate, in gpm.</li> <li>K = hydraulic conductivity of the water-bearing formation, in gpd/ft<sup>2</sup>.</li> <li>H = static head measured from bottom of aquifer, in ft.</li> <li>h = depth of water in the well while pumping, in ft.</li> <li>R = radius of the cone of depression, in ft.</li> <li>r = radius of the well, in ft.</li> </ul>	(Driscoll, 1986)
Modified nonequilibrium Cooper and Jacob	$S = 264 \frac{Q}{T} \log \frac{.3Tt}{r^2 S}$	<ul> <li>Where:</li> <li>s = drawdown, in ft, at any point in the vicinity of a well discharging at a constant rate.</li> <li>Q = pumping rate, in gpm.</li> <li>T = coefficient of transmissivity, in gpd/ft.</li> <li>t = time since pumping started, in days.</li> <li>S = coefficient of storage (dimensionless).</li> </ul>	(Driscoll, 1986)
Capture zone analysis	$r_{stag} = \frac{Q}{2\pi h K I}$	Where: $r_{stag}$ = distance from well to stagnation point, (ft). Q = pumping rate from the well, (ft 3/day). h = Saturated thickness of the aquifer, (ft). I = hydraulic gradient, and (ft/ft). K = hydraulic conductivity (ft/day).	(Keely & Tsang, 1983)

Note: ft = feet; gpm = gallons per minute; gpd = gallons per day.

of the modeling effort. These models can incorporate a linear optimization routine that will locate wells and adjust pumping rates automatically to arrive at the optimum well locations and pumping rates. This resolves the last optimization problem of balancing the number and location of wells with the goal of minimizing the water production, yet still achieving containment. However, it is very important that the user verify and understand the parameters going into the model, since all models are simplifications of reality and may not accurately reflect site conditions.

An example of a detailed numerical model is MOD-FLOW, the most commonly used numerical model in the U.S., according to a survey. Particle tracking can be performed using MODPATH, which interfaces with MOD-FLOW to define the capture zone around the pumping system. Tables 18, 19 and 20 provide a summary of these models, their uses, and output.

As discussed in the preceding, the amount of data required increases with model complexity. Most detailed flow models require detailed information on contaminant and hydrogeologic parameters and also require information on the horizontal and vertical variations of these parameters. Knowledge and confidence in the field data and hydrogeologic parameters are essential to the use of detailed models. If the data are limited or of questionable accuracy, then the use of a detailed model is not justified, since the level of

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effort would increase, but the model accuracy may not. The model results are only as good as the data entered. Data requirements for these detailed models are presented in Table 19.

# 7.5.3 GROUNDWATER TREATMENT ALTERNATIVES

### 7.5.3.1 General

The design and successful implementation of a groundwater treatment system requires the consideration of several factors such as the following:

a. Identification of specific target compounds to be removed from the groundwater.

b. Background levels of target compounds in the groundwater.
c. Expected or observed concentrations of these compounds in the untreated groundwater.

d. Clean-up target levels.

e. Identification of water quality parameters (organic and inorganic) that may inhibit the removal of target compounds or cause fouling or corrosion of the groundwater extraction and treatment system components.

f. Anticipated flow rate of the groundwater to be treated.

g. Site characteristics that may affect the practicality of using specific treatment methods.

Discussion of groundwater treatment technologies will focus on those which have been proven, or are likely, to be effective in the removal of the chemical(s) of concern identified in Section 2.4.

The selected treatment method should have the following characteristics:

a. The capability to reduce concentrations of chemical(s) of concern to acceptable levels.

- b. Reliability (proven-effectiveness).
- c. Cost-effectiveness.
- d. Compatibility with site conditions.
- e. Conformance with regulatory requirements.

The following are the most commonly used and proven methods for treating recovered groundwater:

- a. Air stripping.
- b. Activated carbon adsorption.
- c. Combined air stripping and carbon adsorption.
- d. Spray irrigation/evaporation.
- e. Biological treatment.

These technologies can be used individually or in combination. The capabilities and limitations of each of these technologies are described in Table 23. Other less common technologies include UV ozone/peroxide, which is a proven method to treat groundwater impacted with MTBE.

#### 7.5.3.2 Air Stripping

Air stripping is a relatively inexpensive, simple, and proven technique for the removal of BTEX and other volatile organics. This technology is based on the fact that volatile organics preferentially transfer from water to air. An air-stripping tower provides the mechanism for air and water contact. The more surface area exposed, the greater the opportunity for transfer of the organic compounds out of the water phase into the air phase. Properly designed towers can typically remove more than 99 percent of the dissolved BTEX hydrocarbon.

A typical air-stripping tower is illustrated in Figure 27. Produced water enters the top of the tower and flows down through the column packing. Air is forced upward through the column, allowing maximum air-water contact. The treated water leaves the bottom of the tower and is discharged or collected. Air exits the top of the tower along with the volatile organics that were stripped from the water. Depending on air pollution regulations and safety requirements, an air discharge permit and an acceptable plan for air treatment may be required.

The design and performance of an air-stripping system are affected by a variety of factors, including the following:

- a. Characteristics of packing material.
- b. Temperature of air and water.
- c. Air/water ratio.

d. The presence of inorganic substances in the water to be treated.

e. Characteristics of hydrocarbon compounds to be stripped (that is, Henry's Law).

- f. Target removal efficiency.
- g. System maintenance.

These factors must be considered in the stripping-tower design to ensure adequate treatment and minimize operational problems. The presence of inorganic chemicals in the water is an important consideration because groundwater commonly contains high concentrations of certain substances (iron and manganese, for example) that tend to precipitate from solution and clog the pores of the tower packing material over time. Water quality must be verified to maintain adequate removal of organic substances using this technology. In some instances, two stripping towers can be installed in series to meet treatment requirements, or the discharge water can be recirculated through the stripper.

Other air-stripping systems include, but are not limited to, low profile tray strippers, slat tray aerators, cascade aerators, and rotary strippers. These aeration technologies are generally not as efficient as packed columns for the removal of volatile organics from produced groundwater; however, site specific conditions (such as inorganic water quality, permitting/zoning considerations) can often dictate the specific type of aeration or stripping technology for groundwater treatment.

Table 23—Comparison of Treatment Alternatives for Removal of Dissolved Petroleum Hydrocarbons in Groundwater

Adsorption	Air Stripping	Carbon Adsorption	Spray Irrigation	<b>Biological Treatment</b>
		Capabilities		
Proven technology for removing aromatic compounds	Proven technology for removing aromatic compounds	Proven technology for removing aromatic compounds	Volatilization, biodegradation, and adsorption are used to remove dissolved organics	Proven technology for removing a wide range of organics
Flexible method that can be used with a variety of technologies	Low capital operating, and maintenance costs	Cost-effective because carbon is consumed only for for removing less volatile organics	Enhancement of in-situ biodegradation	Potential problems with air emissions are minimized
Readily available technology	Simple technology that is easy to operate	Readily available technology	Treated waters can be polished	Compounds not removable by other methods (t-butyl, alcohol, for example) may be removed
Tolerant of some fluctuations in concentrations and flow	Readily available techn- ology			
Potential problems with air emissions are minimized				
		Limitations		
Carbon costs can be high	Dissolved chemicals in groundwater, such as iron, may result in fouling of packing material	Higher capital costs because two-unit operations are required	A large area will be required for treatment	Higher capital, operating, and maintenance costs
Spent carbon must be re- generated or disposed of	Air emissions standards may require treatment of vapors	More complicated because two units must be operated and maintained	Available land must be suitable to handle anticipated hydraulic loading	Greater potential for malfunctions
Requires pretreatment for oil and grease removal where concentrations are greater than 10 ppm	Low temperature will result in poor removal efficiency			System requires more monitoring
Intolerant of high suspend- ed solids levels and may require filtering	Sensitive to fluctuations in hydraulic loading			Sensitive to hydraulic and organic loading

As an alternative to air-stripping towers or trays, air

Note: ppm = Parts per million; t = tertiary.

sparge tanks are sometimes employed. Tanks called *air* sparge tanks operate by forcing air through the water to be treated in a water storage vessel to effect stripping of the volatile organics. Sparge tanks are not as efficient as stripping towers and are normally used in low-flow conditions and where fouling of stripping-tower packing is severe. Pretreatment of inorganics may be required (for example, iron, calcium carbonate).

#### 7.5.3.3 Activated Carbon Adsorption

What is called *activated-carbon adsorption technology* is based on the principle that certain organic chemicals preferentially adsorb to organic carbon. Activated-carbon systems are capable of efficiently removing very low concentrations of dissolved organics from groundwater. Carbon adsorption is a proven technology for removal of BTEX compounds and other less soluble organic chemicals and is marginally effective in removing ethers (such as, MTBE) under lowflow conditions. Carbon adsorption is ineffective for removal of more polar oxygenated compounds such as alcohols (for example, tert-butyl alcohol TBA).

The most common application of carbon adsorption is passing groundwater under pressure through fixed beds of carbon. A dual-bed activated carbon treatment system with an upstream LNAPL/water separator is illustrated in Figure 28. The treatment units in the figure contain activated carbon beds that remove dissolved chemicals from the water. Breakthrough of the chemical(s) of concern occurs when the carbon has reached its adsorption capacity. When breakthrough occurs in the first bed, it is taken out of service and is replaced by the second bed. A new

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Figure 27—Typical Air-Stripping Tower

adsorption bed can then be added to replace the spentcarbon bed. Spent carbon can be disposed of properly or steam regenerated.

The following factors must be considered in the design of an activated carbon adsorption system:

a. Influent composition and concentrations.

b. Characteristics of the activated carbon (such as size and surface area).

c. Characteristics of hydrocarbon to be adsorbed (for example,  $K_{oc}$ )

- d. Solution characteristics (for example, pH, temperature, presence of competing chemicals, suspended solids).
- e. Volumetric flow rate and resulting contact time.
- f. Pressure losses.
- g. Inorganics and suspended solids.

The primary cost of operating an activated-carbon adsorption system is incurred in the replacement and disposal, or regeneration, of the spent carbon.

In summary, activated-carbon adsorption systems are normally employed when low concentrations of organics are involved and in the presence of low-to-moderate flow and loading rates to remove chemicals that cannot be volatilized by air stripping. The adsorption process can also be used to polish previously air-stripped water.

# 7.5.3.4 Combined Air Stripping and Carbon Adsorption

Combined use of air stripping and carbon adsorption is warranted under either or both of the following circumstances:

- a. When chemicals have a wide range of volatilities.
- b. When stringent treatment requirements exist.

Under these conditions this combination of technologies is more effective in removing organic chemicals from water than either system alone. Where vapor off-gas treatment is required, however, a careful analysis of treatment trains should be made, since stripping may no longer be cost-effective.

Air stripping selectively removes the most volatile components from the water and leaves residuals of less volatile compounds. Carbon adsorption will remove most of these less volatile chemicals from the stripped water. Carbon adsorption is also often used to polish water or remove chemical(s) of concern from the air emitted from the stripping tower.





**GAC treatment units** 

Hydrocarbon separator

API PUBLICATION 1628

The disadvantages of the combined system are an intersection of the limitations that each of the two technologies have when used alone. Some chemicals, such as TBA, are not efficiently removed by the combined technologies. Frequently, biological treatment must be used to remove such components. Capital costs are generally higher for a system that combines technologies due to interdependence of the two systems. However, the operating costs of a combined system are lower than the operating costs for a carbon system alone because much less carbon is used for polishing, and air stripping units are less costly to operate than carbon systems.

#### 7.5.3.5 Spray Irrigation/Evaporation

The removal of dissolved hydrocarbon by spray irrigation/evaporation combines natural processes of volatilization, biodegradation, and adsorption. Volatilization occurs primarily as the water containing dissolved hydrocarbon is sprayed through the nozzles. This process will remove much of the BTEX compounds, depending on the humidity and temperature of the ambient air. Evaporation from the land surface will also remove the more volatile compounds. Biodegradation and adsorption will reduce concentrations further as the water infiltrates the soils. Biodegradation is enhanced by the ready source of atmospheric oxygen, and adsorption is improved by the presence of humic material in the soil. Figure 29 illustrates a typical spray irrigation/evaporation system. Field pilot testing of an irrigation system by the University of Waterloo demonstrated 99.97 percent removal of BTEX from a synthetic feed, with nutrient addition (see API Publication 4552). Implementation of this treatment technology may be limited by several factors including site space constraints, air permitting issues, and other land application or water infiltration permitting issues.

#### 7.5.3.6 Biological Treatment

Biological treatment techniques used by municipal wastewater facilities can be scaled down and applied to removal of dissolved hydrocarbon from groundwater. The hydrocarbon can serve as a food source for certain aerobic microorganisms that convert the organic compounds into carbon dioxide, water, energy, and biological solids.

Biological treatment techniques include fixed film and suspended-growth biological processes. The most common fixed-film biological processes are rotating biological contactors (RBCs), trickling filters, and biotowers. In these methods, a thin growth of biological solids is maintained on artificial media and exposed to process water by an induced flow. Oxygen for the aerobic bacteria is supplied by direct contact with the atmosphere.

In activated sludge treatment, which is a suspendedgrowth process, a large population of microorganisms is maintained in a liquid environment. Oxygen is provided by vigorous aeration, which mixes the water and solids. The aeration tank discharges to a clarification chamber that separates the biological solids from the final effluent. A small portion of the settled sludge is returned to the reaction chamber to maintain the biological population, and the remainder of the sludge is compacted to remove moisture and sent to final disposal. This is perhaps the most common biological approach to groundwater remediation.

Advantages of biological treatment techniques over other processes include degradation of hydrocarbon to harmless by-products and applicability to a wide range of chemical(s) of concern.

Disadvantages of biological treatment include higher capital, operating, and maintenance costs. Also, biological systems are more complex than other treatment systems and may be more prone to problems such as equipment malfunction, vapor emissions, frequent maintenance, intensive control requirements, and so forth. Biological systems require more frequent sludge handling and disposal. If the system is not continually monitored and adjusted, the process can be upset, and in extreme cases the population of microorganisms can be lost. Shutting down and restarting the system can be time consuming because the microbes must slowly be acclimated to the quality of influent water. Thus, daily analytical testing and operational control are needed because of the variable nature of the biological process.

# 7.6 Residual Hydrocarbon Mitigation Alternatives

Conventional pumping systems that are useful for the containment and removal of liquid and dissolved hydrocarbon are usually not effective in removal of residual hydrocarbon trapped in earth materials. However, groundwater extraction may be used in conjunction with vapor extraction to improve the effectiveness of mass removal from the smear zone. Methods to remediate residual hydrocarbon are described in 7.6.1 through 7.6.5.

### 7.6.1 VENTING/VACUUM SYSTEMS

#### 7.6.1.1 Soil Venting

Soil venting, otherwise known as *in-situ volatilization* or soil vapor extraction, are terms applied to the technique of removing residual hydrocarbon from the affected soils through the use of air currents to volatilize the hydrocarbon. Air movement can be induced either by forced or passive venting. Forced venting involves the use of vacuum pumps or blowers to draw air through the soil; passive venting relies only on changes in barometric pressure and concentration gradients to remove vapors from the subsurface. Passive venting systems have vents open to the atmosphere and do not require an energy input to remove vapors. Winddriven turbines on vent stacks are a form of passive venting. Generally, forced-venting systems are more effective than

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Figure 29—Spray Irrigation System

passive venting systems, since venting effectiveness is a function of air flow through the zone of interest. An added benefit of these systems is that they are capable of preventing vapor migration into structures. Soil-venting systems can be coupled with any hydrocarbon recovery system to control vapors and volatilize residual hydrocarbon. For more detailed information refer to API Publication 1628D.

A forced-venting system consists of three basic components:

a. Subsurface vents (that is, extraction points, either horizontal or vertical).

b. Blower, fan, or vacuum pump to draw air through the soil.

c. Vapor-handling and treatment system.

The vents provide conduits to allow sufficient air flow to be induced throughout the area of contaminated soils to remediate them (Figure 30). These vents, which may be installed vertically or horizontally, may consist of slotted casing or well screen with or without a filter pack. Commonly, subsurface vents are used to extract vapors; however, vents may also be used for air injection purposes or to allow for the passive inlet of air to be drawn into the subsurface.

Vacuum pumps and blowers are used to induce subsurface air flow. Vacuum pumps or blowers (with explosionproof motors) commonly used include the following:

a. *Liquid ring pumps* can be used to apply vacuums of up to 29 inches of Hg. These pumps generally require a high level of maintenance to keep them running properly.

b. *Rotor lobe blowers* are similar to liquid ring pumps, but usually operate at lower vacuums and require periodic maintenance.

c. Rotary vane blowers can attain a maximum vacuum of 27 inches of Hg and, when equipped with carbon blades, require low maintenance (for nonexplosive environments). d. Regenerative blowers achieve high vapor-flow rates with low-to-moderate vacuums and require minimal maintenance. e. Centrifugal blowers achieve very high flow rates, but operate at very low vacuum (for nonexplosive environments).

Vapor/liquid separators are used to remove groundwater condensate from the vapor stream. Types of separators include knockout tanks or drums, condensers, and demisters.

Vapors produced from these systems can be treated in several ways, depending upon regulatory constraints, extracted vapor concentrations, and economics. Methods of vapor treatment include:

- a. Venting and dispersion to the atmosphere.
- b. Thermal oxidation.
- c. Catalytic conversion.
- d. Internal combustion engines.
- e. Carbon adsorption.
- f. Vapor-phase bioreactors.

Characteristics that affect the feasibility of venting/vacuum systems include extent and nature of the hydrocarbon's vapor pressure, Henry's law constant, aqueous solubility, diffusivity, partition coefficients, soil permeability and character. Chemical(s) of concern and soil conditions affecting feasibility of using venting/vacuum systems are provided in Table 24.

Venting/vacuum systems can be used effectively in a wide variety of situations. The rates of recovery and the applicability API PUBLICATION 1628



Condition	Favorable	Unfavorable
Chemical of Concern:		
dominant form	Vapor phase	Solid or strongly sorbed to soil
vapor pressure	>100 mm of mercury	<10 mm of mercury
water solubility	<100 mg/L	>1,000 mg/L
Henry's Law Constant	>0.01 (concentration-based) [convert to atm units]	<0.01 (concentration-based) [convert to atm units]
Soil:		
temperature	>20°C (usually will require external heating of soils)	<10°C (common in northern climates)
air conductivity	>10 <sup>-4</sup> cm/s	<10 <sup>-6</sup> cm/s
moisture content	<10% (by volume)	>10% (by volume)
composition	Homogeneous	Heterogeneous
surface area of soil matrix	$<0.1 \text{ m}^2/\text{g of soil}$	>1.0 $m^2/g$ of soil
depth to groundwater	>20 m	<1 m

Table 24—Conditions Affecting Feasibility of Use of Vacuum Extraction

Note: Source: Metcalf & Eddy, Inc., 1992. mm = millimeters; mg/L = milligrams per litre; m = metric; g = gram.

to a given site depend primarily on the properties of the formation and the volatility of the hydrocarbon. For example, in high hydraulic-conductivity materials, high-volume, lowvacuum blowers can be used to volatize residual hydrocarbon. In low hydraulic-conductivity materials, higher-suction vacuum pumps are required to induce air movement. The following factors must be considered to determine if soil venting/vacuum systems will be applicable to a given site:

a. Soil porosity, permeability, and contaminant distribution which influence the movement of vapors and the rate of air flow.

b. Soil water content, which affects hydraulic conductivity of the unsaturated zone to air flow and vapor movement.

c. Chemical and physical properties of the hydrocarbon.

Petroleum products are complex mixtures of hydrocarbon with wide ranges of volatile components. Venting is generally most applicable to the more volatile substances such as gasolines. Typically, the rates of recovery are initially high and decline rapidly as the more volatile components are removed. This is an important consideration in the selection of vapor-phase treatment systems.

Design considerations for a soil-venting/vacuum system typically include the following:

a. Vent spacing: The location based on projected influence for a given vent at a given air extraction rate must be determined either by field testing or by calculation and length of time to remediate.

b. Vent depth/interval: The area over which the vent is to be open to the zone of residual hydrocarbon will be determined both by the site hydrogeology including depth to water and permeability and the distribution of residual-phase hydrocarbon.

c. Blower sizing: The sizing and number of extraction/ injection pump(s) are based on site hydrogeology, vent spacing, and residual hydrocarbon concentrations. Airflow rates, pressure drops, and safety must also be considered. d. Vapor treatment.

Common venting/vacuum design approaches fall into five broad categories: (a) intuition or empirical, (b) match existing equipment, (c) radius of influence analyses, (d) screening model analysis, and (e) detailed modeling analysis. A summary of these five approaches is provided in Table 25.

Venting/vacuum system monitoring is performed to evaluate actual system effectiveness compared with design criteria. In general, the overall objectives of a monitoring program are as follows:

a. Assess site conditions to determine remediation approach.

b. Evaluate the progress of in-situ treatment.

c. Determine site conditions following treatment.

Data collection requirements for a variety of data interpretation/analysis requirements using venting/vacuum monitoring and related data are provided in Table 26.

### 7.6.1.2 Bioventing

Bioventing is the exchange of soil gases to promote biodegradation of hydrocarbon in unsaturated-zone soils. The process provides atmospheric oxygen to establish or maintain aerobic conditions. The most effective method of degrading most hydrocarbon compounds is via aerobic processes so that maintaining adequate oxygen concentrations is a key process parameter in hydrocarbon biodegradation.

Bioprocess reactions occur in the thin film of moisture that surrounds soil particles. Also present in this moisture film are dissolved hydrocarbon, microorganisms, dissolved inorganic nutrients, and dissolved oxygen. As the bioprocess occurs, hydrocarbon are degraded, dissolved oxygen is consumed, nutrients are incorporated into the synthesis of new cell material, and carbon dioxide is produced as an end product of the reaction. Atmospheric oxygen present in the 82

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# Table 25—Soil Vapor Extraction-Based Processes Design Approaches

Approach	<b>Required Information</b>	Advantages	Disadvantages
"Intuition," or empirical approach based on past experience	1,2	Quick, easy, low skill level required	Unknown system performance, technology may not even be applicable
Match system design to existing equipment	1,2, inventory of existing equipment	Quick, easy, minimizes new capital expenditure, maximizes use of existing equipment	Unknown system performance, technology may not even be applicable
Radius of influence-based approach	1, 2, 4, 5 <sup>a</sup> , 6	Insures containment of hydrocarbon vapors	Unknown system performance, does not insure remediation in reasonable time frame
Based on screening-level model results	1, 2, 3 <sup>b</sup> , 4, 5, 6	Little effort required, design based on desired performance; cost of analyses not prohibitive	Requires higher level of expertise and ability to interpret data
Detailed modeling, numerical optimization	1, 2, 3, 4, 5, 6, 7, 8, 9, economic data	Design can be optimized and based on desired performance	Requires highest level of expertise and ability to interpret data; cost may be prohibitive

<sup>a</sup>Refers to activities defined on the later half of this table.

<sup>b</sup>Optional, not always used in this approach.

Activity	Description
	Preliminary Characterization Activities
1	Hydrocarbon assessment vertical/horizontal hydrocarbon characterization (type, boiling point distribution, identification of chemical(s) of concern)
2	Geologic/hydrogeologic assessment identification of soil strata permeability assessment (core tests, sieve analysis, and so on.) static water table determination (and seasonal fluctuations) subsurface conduits, piping, tanks, obstructions, and so forth
	Laboratory Characterization Activities
3	Laboratory soil column feasibility studies (optional)
	Field Pilot-Scale Activities
4	Airflow vs. applied pressure/vacuum test vacuum test for vapor extraction wells pressure test for air injection wells
5	Effluent vapor characterization vs. time total hydrocarbon concentrations chemical(s) of concern speciation hydrocarbon characteristics (boiling point distribution) $O_2$ and $CO_2$ analyses
6	Subsurface pressure distribution as function of depth and distance steady-state and transient measurements
7	Subsurface vapor concentrations distribution as function of depth and distance hydrocarbon concentrations and composition $O_2$ and $CO_2$ analyses
8	Groundwater elevation changes resulting from air extraction/injection
9	Groundwater Monitoring hydrocarbon levels dissolved oxygen
10	Tracer gas tests

# Table 26—Process Monitoring Options and Data Interpretation

Data Interpretation/Analysis Requirement	Data Collection Requirement	
Concentration vs. time Composition vs. time Flow rate vs. time Applied pressure/vacuum vs. time Mass removal rate (mass/time) vs. time Cumulative removed by volatilization (mass) Identify mass transfer limitations	1	
Aerobic biodegradation contribution to removal rate (mass/time) vs. time Aerobic biodegradation contribution to cumulative removed (mass)	1, 2, 6 <sup>a</sup>	
Total remediation costs (\$) vs. time Cost per mass of hydrocarbon removed (\$/kg-removed) vs. time	1, 2 <sup>b</sup> , 3	
Effect of environmental factors (qualitative)	l, 2 <sup>b</sup> , 4	
In-situ assessment of treatment with time (qualitative areal impact)	1, 2 <sup>b</sup> , 4 <sup>a</sup> , 5, 6b, 8 <sup>a</sup> , 9 <sup>c</sup>	
Define zone of vapor containment (qualitative areal impact)	1, 5 <sup>a</sup> , 7, 11 <sup>a</sup>	
Closure monitoring report	1, 2 <sup>b</sup> , 3 <sup>a</sup> , 4 <sup>a</sup> , 5, 7, 8, 9, 10, 11 <sup>a</sup>	
Areal impact of air sparging	1, 2, 4 <sup>a</sup> , 5 <sup>a</sup> , 6 <sup>a</sup> , 7, 8 <sup>a</sup> , 9, 10, 11 <sup>a</sup>	
Effect of water-table elevation changes	1, 2, 4, 5, 6, 7, 9, 10	
Injection/extraction flowrate optimization Flow field definition	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11	
Notes: Source: Johnson et al, 1992. <sup>a</sup> Optional, or as required. <sup>b</sup> Applicable for bioventing applications.		

"Relevant to air sparging.

Data Collection Requirement Key: 1 = Process monitoring data; extraction/injection flow rate(s) and vacuum(s)/pressure(s), extraction vapor concentration and composition. 2 = Respiratory gas  $(O_2, CO_2)$  monitoring of extracted vapor stream. 3 = Cost monitoring; capital, operation and maintenance, and utilities costs. 4 = Environmental monitoring; temperature, barometric pressure, precipitation. 5 = In-situ soil gas monitoring; vapor concentration and composition. 6 = In-situ soil gas monitoring; respiratory gases  $(CO_2 \text{ and } O_2)$ . 7 = Subsurface pressure distribution monitoring. 8 = Soil samples. 9 = Groundwater monitoring. 10 = Groundwater elevation monitoring. 11 = Tracer gas monitoring.

soil pores dissolves by diffusion into the thin moisture film where it is utilized in the reaction. This results in declining concentrations of oxygen in the soil pores. Concurrently, carbon dioxide is produced as a reaction end-product and eventually is released into the soil pores. The net effect is decreasing concentrations of oxygen and increasing concentrations of carbon dioxide in the soil pores. In order to keep the reaction process moving forward, oxygen must be replenished in the soil pores. Thus, periodic exchange of soil gases must occur.

In many ways, bioventing is very similar to soil vapor extraction in that soil gases are removed from the unsaturated-zone soils. The primary differences between soil vapor extraction and bioventing are that the frequency of soil pore volume exchanges is considerably lower for bioventing, and the emphasis is on the management of soil gas oxygen and carbon dioxide concentrations rather than the volatilization and removal of organic compounds. The design of extraction-well construction and locations, blower sizing, and offgas treatment processes are similar, though the design is generally for lower-airflow volumes and extraction-system operating vacuums.

This exchange of soil gases is the only active aspect of the bioventing process. For bioventing to be utilized as a remedial process, there should be active, indigenous microbial populations capable of degrading hydrocarbon, adequate nutrients to provide some degree of metabolic activity, sufficient soil permeability to permit airflow for soil gas exchange, and some degree of soil moisture in which the biological reactions can occur.

Several field tests should be performed to evaluate the potential and to develop specific design data for using bioventing as a remedial process, including the following:

a. Soil gas evaluation to determine the occurrence of biological processes evidenced by carbon dioxide (>1 percent above background) accumulation in soil pores.

b. Vacuum testing to determine the radius of influence and airflow rates relative to site-specific lithology and permeabilities. c. Oxygen depletion testing to evaluate site-specific degradation rates.

d. Off-gas analysis to determine any treatment requirements prior to discharge.

A number of researchers have been involved in developing field-test protocols for designing full-scale bioventing systems. The U. S. Air Force has been heavily involved in the development of application procedures for bioventing and has developed protocols for design and implementation of biovent-based remedial programs.

Bioventing systems can be operated on a continuous or intermittent basis depending on the following:

- a. Concentrations of hydrocarbon in the unsaturated zones.
- b. Apparent degradation rates.
- c. Oxygen uptake and carbon dioxide production rates.
- d. Off-gas treatment requirements for extracted soil vapors.

Active operations to exchange soil gases on a frequent basis is typically performed during the initial stages of soil remediation. After the major portion of hydrocarbon mass has been removed from the subsurface, the bioventing process may be operated on an intermittent basis as the oxygen demand decreases and carbon dioxide production also is reduced. Optimizing the frequency of soil-pore volume exchanges to maintain an optimum growth environment and, hence, the rate of biodegradation, will result in the most cost-effective remediation.

The application of data generated during bioventing remedial programs is subject to various interpretations. Many researchers use stoichiometric oxygen and carbon dioxide relationships to estimate biodegradation rates and, ultimately, time for completion of remedial programs. Data generated during bioventing programs, such as carbon dioxide production, oxygen consumption, and hydrocarbon removal rates, must be critically evaluated to estimate the completion time. These are useful tools to guide an estimate of remedial time frames, but they must be used with an understanding that accurately predicting completion may be difficult.

## 7.6.2 AIR SPARGING SYSTEMS

In-situ Air Sparging (IAS) is still in the development and evaluation stage. The processes and effectiveness of IAS are still not well understood.

In-situ air sparging is the injection of air into groundwater under controlled conditions of pressure and flow to remove residual volatile compounds. It is used for the removal of volatile hydrocarbon that are dissolved in groundwater, adsorbed to the surface of saturated zone soils, and trapped in soil pores of the saturated zone. Essentially, air sparging is an in-situ method of stripping volatile compounds from the aqueous phase into the injected air as it rises through the saturated zones and into the unsaturated soils above. The stripped volatile compounds can then be extracted from the unsaturated zone soils. This technology is commonly used in conjunction with venting/vacuum systems (described in Section 7.6.1) to provide control and removal of soil vapors containing stripped chemical(s) of concern from the subsurface environment.

In application, air is injected through sparge points that are completed as wells with screened intervals of 0.5 to 2.0 feet. The wells are installed and screened beneath the maximum depth of residual dissolved hydrocarbon. Air is injected at controlled rates and pressures, typically 2 to 10 cubic feet per minute (cfm) per sparge point, and at a pressure great enough to overcome the combined hydrostatic head of the aquifer (bubble pressure) and the friction losses through the piping, fitting, and screens. As the air is released from the bottom of the sparge point, it travels upward through the saturated zone as either fine bubbles or as larger bubbles in channels. Volatile hydrocarbon present in the saturated zone dissolve into the air bubbles and are carried upward to the unsaturated zones. The vapors can then be collected for discharge or treatment using a soil vapor extraction system.

Air-sparging systems design and configurations are usually developed on the basis of field pilot testing. This testing is performed to define the area of influence of a sparge point, the amount of air pressure required to produce flow through the saturated zone, the air flow rate to optimize removal of hydrocarbon, and other design information. Usually, an air-sparging test is conducted along with a field test of soil vapor extraction. The tests are conducted in series, and then the systems are operated together. Field design testing is performed by first establishing an air injection point. The depth of the injection point screen should be located beneath the deepest known depth of dissolved/residual hydrocarbon, while recognizing that air can be easily directed by subsurface heterogeneities. A series of monitoring probes are installed radially and at various distances around the injection point. The monitoring points should be screened only in the saturated zone. As air is injected into the sparge well, measurements of response to this air injection are made by measuring changes in water-level elevations, dissolved oxygen, and pressure at the monitoring points. These data are used to define the area of influence of the air-sparging wells. Air samples can be collected and analyzed to determine the effect of the sparging and the anticipated concentrations of recovered vapors.

The data generated during field testing will determine the number and spacing of wells, the operating air flow rates and pressure of the injected air, and the anticipated concentration of any soil vapors generated from the air-sparging process.

There are limitations to the use of the technology. Site specific limitations include difficulty in producing effective air flow in low hydraulic conductivity, saturated zone soils (generally less than 0.001 cm/sec), any confining or overburden layers of very low hydraulic conductivity that may



inhibit upward migration (and potentially cause lateral spreading) of stripped compounds, and thin unsaturated zone thickness (less than 3 to 5 feet). Hydrocarbon properties that may limit its application include those with low Henry's Law constants and low compound volatility. Even relatively small hydraulic conductivity differentials between adjacent soil layers may have a significant effect on bubble propagation.

Air sparging may be operated in either continuous or intermittent modes depending on site-specific conditions such as groundwater velocity, hydrocarbon concentrations, and Henry's Law constants for the chemical(s) of concern. Under conditions of low groundwater-flow velocities and highly strippable compounds, operation of sparging activities may be less frequent for shorter operating durations than for high groundwater-flow velocity conditions with less strippable compounds. Operating strategies should be devised to optimize operating periods for air sparging. This may significantly impact the cost of required off-gas treatment.

The air-sparging process also provides for the transfer of oxygen into groundwater, and indirectly into overlying unsaturated zones. This may be of significant benefit in remedial programs where natural biodegradation of compounds is occurring but is rate limited due to oxygen limitations. See API Publication 1628D for more detail.

# 7.6.3 EXCAVATION

# 7.6.3.1 General

Excavation of soils is normally performed when small quantities of soils containing hydrocarbon require treatment or disposal. Excavation is normally not an alternative unless in-situ remediation will not be effective. An example would be removal of soils when small releases or spills have occurred. These soils can be removed or treated on-site. Extensive soil excavation is often too costly and disruptive to normal operations to be considered. Other in-situ remedial alternatives should be carefully considered before excavating large volumes of soil.

Many types of equipment are available for excavation, loading, and removal of soils. Standard construction equipment is typically employed, but numerous factors such as safety, depth of contamination, and soil stability influence equipment selection and use.

Excavation of contaminated soil creates increased potential for exposure to site personnel, the public, and the environment. In confined spaces, air vapor concentrations should be monitored to ensure that safe levels are maintained. Field-testing procedures are available for determining hydrocarbon concentrations in the soils. These field tests can be used to define the extent of excavation required as it progresses.

Transportation of contaminated soil requires conventional earth-moving equipment. The major hauling cost factor is the distance to the disposal facility. Site-specific conditions, community and interstate relations, and regulatory measures affect disposal costs. In some states, the soils are considered a hazardous waste and must be handled, hauled, and disposed of accordingly.

#### 7.6.3.2 Landfilling Requirements

Landfill disposal of excavated soils has been a common remedial action. Levels of hydrocarbon allowable for landfilling under applicable regulations must be determined in developing a sound disposal strategy.

## 7.6.3.3 On-Site Treatment

The following methods of on-site treatment and soil replacement can be viable if approved by the regulatory agencies:

a. Land treatment (landfarming or biopiles): This is a process by which contaminated soils are removed and spread over an area to enhance naturally occurring processes such as biodegradation and volatilization. This technique is discussed in more detail in 7.6.5.3.

b. Aeration/enhanced volatilization: Soil aeration by mixing and exposure to air can reduce hydrocarbon concentrations to acceptable levels. This process may be as simple as overturning the soils with excavation equipment, tillers, or shakers to increase volatilization or enhancing vapor removal by forced or passive venting with an engineered venting system.

c. Soil washing.

d. Thermal treatment: Incineration and low-temperature stripping or thermal desorption of residual hydrocarbon are methods employed in some circumstances for the on-site treatment of soils. Treatment costs and local air quality regulations will be major factors controlling the use of these techniques.

e. Isolation/Containment: This is a process in which the impacted soils are isolated through the use of caps, slurry walls, grout curtains, or cut-off walls.

f. Chemical fixation: This is a process where chemicals are mixed with impacted soils, rendering them inert.

g. Soil slurry bioreactor: The soil slurry bioreactor process entails mixing soil and water in a fashion that suspends the soil in a column of water, in a manner similar to activated sludge in wastewater treatment.

#### 7.6.3.4 Asphalt Incorporation

Asphalt incorporation is a process whereby soils containing residual hydrocarbon are incorporated into hot asphalt mixes as a partial substitute for aggregates. During the heating of the mixture, the more volatile components are vaporized, and the remaining compounds are incorporated into the asphalt mixture.

# 7.6.4 SURFACTANTS

The use of surfactants to reduce surface tension and

increase the yield of hydrocarbon has been tested in several laboratory studies. At this time, surfactants are not a proven technology for application in most native earth materials. The surfactant must be compatible with the hydrocarbon of interest and soil matrix, and must be applied to the zone of interest. To be effective, the solution of water and surfactant must make good contact with the zones containing residual hydrocarbon. Full recovery of the surfactant from native earth materials can be a limitation because the surfactant may itself be considered a contaminant. Accordingly, the recovered water containing the surfactant and hydrocarbon would require further treatment. Use of this technology should be approved by applicable permitting agencies.

## 7.6.5 BIOREMEDIATION OF SOILS

#### 7.6.5.1 General

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*Bioremediation* refers to a set of technologies for enhancing the natural biodegradation of dissolved and other residual hydrocarbon phases in soils. There are three basic types of bioremediation techniques that can be used to treat soils containing residual hydrocarbon:

- a. Active in-situ bioremediation.
- b. Land treatment, landfarming, or biopiles.
- c. Passive remediation.

#### 7.6.5.2 Active In-Situ Bioremediation

Active in-situ bioremediation involves the enhancement of biodegradation by manipulating site-specific conditions to optimize degradation of target compounds. It involves adding oxygen and/or nutrients into the subsurface environment that makes contact with contaminated soils. The blend of chemicals and water is controlled along with temperature, pH, and other environmental conditions to optimize the rate of biodegradation by indigenous microbial populations.

Treatability studies (that is, plating tests) and respirometry tests are commonly performed to assess the presence of aerobic microbial populations. Plating tests are used to determine total heterotrophic populations, as well as microbial populations specifically capable of degrading gasoline or other petroleum products. Respirometry tests are typically performed to determine the respiration rate (in other words, the rate of oxygen consumption and carbon dioxide production) attainable by the soil microbial populations.

Figure 31 illustrates an in-situ bioremediation system consisting of a recovery well, a treatment system with mixing tank, and infiltration gallery. Groundwater withdrawal from the recovery well creates a capture zone to mitigate further migration of the dissolved hydrocarbon plume. The recovered groundwater is subsequently treated (see Section 7.5.3) and transferred to a mixing tank. In the mixing tank, nutrients such as phosphorus and nitrogen may be added along with oxygen or hydrogen peroxide. Seepage of the mixture from the infiltration gallery allows its re-entry into the contaminated soil and groundwater zone.

In-situ bioremediation has limitations. Successful biodegradation requires that nutrients and oxygen are made available to microorganisms in zones where chemical(s) of concern are present. As with surfactants, water movement is limited in zones of low hydraulic conductivity, and the microorganisms, nutrients, and oxygen may not have sufficient contact. Hence, biodegradation may only occur in limited regions. When materials of low hydraulic conductivity restrict the rate of extraction and injection of water, the rate of degradation will be slowed and may not be cost-effective. As concentrations of organics decline, microbial activity decreases, and eventually no further biodegradation will occur. Thus, the success of the process is limited by a specific set of subsurface conditions that must be met. Technologies for enhancing in-situ bioremediation of subsurface soils in regard to its applications and limitations are presented in Table 27.

#### 7.6.5.3 Land Treatment

Land treatment, or landfarming, involves tilling of soils to enhance biodegradation and volatilization of hydrocarbon. Landfarming can be used to treat soils in place, or soils that have been excavated. In-situ methods are generally applied to the upper 5 feet of earth materials. Soils containing hydrocarbon that are beneath this depth can be excavated and treated near the surface. Other land treatment alternatives effective in remediating contaminated soils are called *biopile* or *biocell* treatment processes. In general, these treatment processes involve the addition of oxygen and/or nutrients to soils to stimulate aerobic bacteria.

Most of the factors affecting system operation are readily controlled. Factors such as soil moisture, oxygen and nutrient availability, and hydrocarbon loading are directly manipulated by active or passive aeration processes. The application rates of soils, fertilizer, water, and oxygen are easily controlled. In addition, soil pH can be controlled with lime. Because land treatment involves mixing of the soils from different horizons, the required nutrients, oxygen, and microorganisms can be distributed so that treatment of all of the soils, including portions containing significant amounts of clay or silt, is possible.

Land treatment requires a large open area. Thus, it is generally not applicable to retail gasoline stations where space is usually limited. In addition, control of vapor emissions and control of stormwater should be considered.

### 7.6.5.4 Passive Remediation

Passive remediation allows natural processes to remove hydrocarbon from soils and groundwater. Activity undertaken includes an on-going monitoring program to evaluate the effectiveness of the remediation. Natural processes that are capable of reducing hydrocarbon concentrations include





Figure 31— In-Situ Biodegradation of Dissolved and Residual Hydrocarbons

the following:

a. Biodegradation: Microorganisms convert the hydrocarbon to carbon dioxide and water relatively quickly for benzene, toluene ethylbenzene and xylenes in the presence of oxygen and may also degrade these compounds, but more slowly, under anaerobic (oxygen-limited) conditions.

b. Volatilization: Volatile components will tend to vaporize and migrate to the atmosphere.

c. Adsorption: Hydrocarbon may adhere to the soil particles and become immobile. Only water-soluble components contacted by infiltrating water will become mobile. In general, heavier hydrocarbon have lower water solubilities and would tend to be retained in the soil.

d. Dispersion/dilution: The rate of flux of the soluble components may be nondetectable in the impacted groundwater or surface-water body. Simple dispersion and dilution of the chemicals may reduce levels to acceptable standards.

e. Photolysis: Sunlight can provide energy to transform hydrocarbon to other chemical compounds.

Usually, natural remediation occurs to some extent at most sites. For this reason, passive remediation should be evaluated at any site where the impact on the environment, migration, and health and safety considerations are appropriately considered. Many case studies involving passive remediation have been reported in the scientific literature. These cases are characterized by conditions favorable to passive remediation. The installation of monitoring wells completed at different depths has been used to clearly define the dissolved hydrocarbon plume in terms of size and movement. On some sites, the natural microbiological conditions

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#### Table 27—Management Strategies for Addressing Factors Limiting In-Situ Bioremediation of Subsurface Soils

Limiting Factor	Management Response	Delivery or Recovery Technique
Oxygen deliverability/redox	Add oxygen	Bioventing, hydraulic fracturing, cyclic pumping, radial drilling
Bioavailability limited due to LNAPL	Reduce LNAPL mass	Gravity or forced delivery; soil flushing, steam stripping, hydraulic fracturing
Bioavailability limited by sorption or slow mass transport through soil matrix	Reduce sorption, Increase mass transport	Soil flushing, steam stripping, hydraulic fracturing
Moisture	Add water or water saturated air	Gravity or forced delivery; bioventing, cyclic pumping
Toxicity	Remove chemicals	Soil vacuum extraction, soil flushing, steam stripping
pH	Adjust soil pH	Gravity or forced delivery
Temperature	Increase temperature	Radio frequency heating, steam stripping
Substrate addition	Add in water or air	Gravity or forced delivery; bioventing, hydraulic fracturing
Heterogeneity	Add or withdraw material in more restrictive layers	Cyclic pumping, hydraulic fracturing, radial drilling

Note: Source is Sims et al, 1993.

have been studied to demonstrate that either the dissolved plume in groundwater or the vapor plume in the unsaturated zone has reached a steady size and is not moving towards any potential receptors. Continued monitoring is used to demonstrate that hydrocarbon are being degraded.

Note: For more detailed information, refer to API Publication 1628A.

# 7.7 Operation and Maintenance

# 7.7.1 GENERAL

In addition to proper system design, operation and maintenance (O&M) is extremely critical in optimizing effective remediation system performance. Costs for O&M can vary significantly depending on the type of system and the operating environment. Since long-term O&M costs can be the most expensive item associated with a corrective action project, it is important to consider O&M requirements when selecting remediation technologies and to plan and execute routine O&M procedures.

Typically, O&M problems fall into one of three major categories: (a) inadequate routine monitoring/adjustment, (b) the physical environment within which the system is exposed, and (c) poor system design. Any of these factors can result in a significant increase in costs associated with O&M, which can often be prevented.

Routine O&M monitoring and system adjustment can provide for optimal operation of hydrocarbon remediation systems. Common problems associated with inadequate routine evaluations include the following:

- a. Loss of plume containment.
- b. Inefficient recovery of free product.
- c. Water discharge violations.
- d. Other permit violations.

- e. Excessive power usage and utility costs.
- f. Extended remediation time.

In many cases, the physical environment in which the remediation equipment and systems are exposed can cause major O&M problems. When these conditions are persistent, O&M requirements become more difficult and complex, and associated costs escalate accordingly. Examples of the more common problems associated with the physical environment include the following:

- a. Temperature/weather extremes.
- b. Inorganic scaling.
- c. Iron bacteria and other biofouling.

O&M considerations should be incorporated during system design in order to select the most appropriate system for meeting the site-specific conditions. Examples of design issues that can affect O&M include the following:

a. Withdrawal and/or treatment approach not suited to the site.

- b. Incorrect pump sizing.
- c. Equipment not compatible.
- d. Poor well design.

Considering the preceding discussion, proper planning of O&M considerations during conceptual and detailed system design is critical for optimizing system performance and cost-effectiveness. The key to successful planning for system O&M lies with developing basic guidelines and consistency. During design, the following basic guidelines should be considered and incorporated into an organized O&M plan:

- a. O&M requirements and potential problems.
- b. O&M data collection checklist.

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c. O&M frequency.

d. Plan for routine data evaluation.

e. O&M data evaluation with design criteria.

f. System operation modification based on the preceding comparison.

# 7.7.2 ROUTINE OPERATION AND MAINTENANCE REQUIREMENTS

An O&M plan should be prepared prior to implementing a remediation system. An O&M plan should be in sufficient detail to be used as a guide in the operation and routine maintenance of the system by personnel who have little prior knowledge of the system or its operation.

At a minimum, O&M plans should include the following: (a) a general process description, where the separate subsystems of the remedial system are described; (b) an operations section, which includes safety issues, system start-up procedures, system optimization procedures, system operational indicators, and an O&M checklist for data collection; (c) a maintenance section, which outlines routine and scheduled maintenance procedures and sampling requirements, and includes tables to aid in troubleshooting system malfunctions; and (d) an updated procedures section, in which changes in O&M procedures will be documented. Equipment manufacturers' manuals and bulletins, system sampling procedures, operator logs, and pertinent engineering drawings should also be included in the plan.

Table 28 provides guidance on routine O&M data collection for different aspects of hydrocarbon recovery systems. Routine O&M data should be evaluated and compared with initial design data to determine if the system is operating properly.

## 7.7.3 REHABILITATION/PROBLEM TROUBLE-SHOOTING

Several factors cause O&M problems for hydrocarbon remediation systems and lead to the need for rehabilitation to restore operating efficiency. The more common O&M problems are associated with the following factors:

a. Poor design (leading to inefficient operation and frequent maintenance).

- b. Inorganic scaling.
- c. Iron bacteria/biofouling.
- d. Cold weather.

Any of these factors can result in inefficient operation and costly maintenance of either recovery or treatment systems. This section discusses the problems, troubleshooting, and solutions to the O&M problems associated with these factors.

#### 7.7.3.1 Poor Design

O&M problems are frequently the result of the decisions, methods, and systems selected during design. These design

errors can lead to inappropriate or inadequate systems for site-specific conditions and may require frequent adjustments and maintenance to ensure satisfactory operation. Numerous examples of this type of problem exist; a few common problems, troubleshooting methods, and potential solutions are discussed in the following paragraphs.

**7.7.3.1.1** Poor well design: Some well design factors may lead to premature O&M problems (such as improper gravel pack sizing or screen size). Many times poor well design is identified through routine monitoring of well efficiency and specific capacity testing. Potential solutions may include more frequent well redevelopment and/or well replacement.

**7.7.3.1.2** Equipment not compatible: It is important to ensure that equipment used for hydrocarbon recovery and treatment systems be compatible with the hydrocarbon it will recover and treat. Equipment not compatible with the specific hydrocarbon may deteriorate rapidly or operate inefficiently. This problem might be recognized during efficiency monitoring or routine checks of equipment condition. Equipment replacement will probably be required.

**7.7.3.1.3** Incorrect pump sizing: Incorrect pump sizing can lead to inefficient flow rates and increased power costs. Testing pump efficiency and comparing actual operating data with manufacturers' recommended performance information can identify this problem. Adjusting operating conditions to appropriate ranges or equipment replacement may be potential solutions.

**7.7.3.1.4** Inappropriate treatment system: If a treatment system is being used that is not appropriate for site-specific conditions, then increased O&M may be the result. One example would be a site that uses carbon adsorption where carbon replacement costs far exceed O&M requirements for other applicable alternative treatment methods. Although routine efficiency monitoring and evaluation will likely identify this problem soon after system start-up, this type of problem could be avoided by adequate technical consideration during design. Since treatment requirements are likely to change with time, appropriate measures should be evaluated during design to ensure cost-effective treatment throughout the life of the project.

# 7.7.3.2 Inorganic Scaling

Inorganic scaling or fouling of recovery wells, equipment, and/or treatment systems can lead to plugging and reduced efficiency. Scaling occurs when chemical changes cause certain inorganics to precipitate and build up on recovery/treatment system surfaces. Primary sources of inorganic fouling include iron, manganese, and hardness (particularly, calcium and magnesium).

Under reducing conditions, caused by the depletion of dissolved oxygen due to the natural degradation of hydro-

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### Table 28—O&M Data Collection Requirements for Hydrocarbon Remediation Projects

LNAPL Recovery Systems	Groundwater Recovery Systems	Soil Vapor Extraction Systems	Groundwater and Air Treatment Systems
Cumulative LNAPL recovered	Actual and corrected groundwater table elevations for each recovery and monitoring well	Vapor flow rates	LNAPL/water separation efficiency
LNAPL and groundwater recovery rates	Water quality from selected wells	Vacuum readings	Influent concentrations
LNAPL thicknesses at individual observation wells	Pumping rates for individual wells	Vapor concentrations	Effluent concentration
Corrected groundwater table elevation for each observation well	System pumping rate	Vapor composition	Flow rates
Pump settings relative to LNAPL elevation	Power usage	Temperature of soil and ambient air	Line pressures
General equipment condition and power usage	General equipment condition	Water-table elevation	Percent downtime
Pump/well efficiency data	Pump/well efficiency data	Meteorological data	Equipment condition
Line pressures	Line pressure LNAPL information		Power usage

carbon, inorganics (such as iron and manganese) will remain in solution. During pumping and/or aboveground treatment, these inorganics are exposed to oxygen, which can cause precipitation and scaling problems. Hardness is usually precipitated due to a shift in pH towards alkaline conditions. The most common reason for this type of pH shift is the stripping of carbon dioxide due to air stripping or hydraulic turbulence.

Troubleshooting requires monitoring and evaluation of system efficiencies, equipment condition, and routine waterquality checks for suspected inorganics. Concentration ranges with corresponding levels of effort for O&M are presented in Table 29.

Common solutions include filter changes (diffused air strippers), chemical treatment (wells and treatment systems), well redevelopment, and pH control.

#### 7.7.3.3 Iron Bacteria/Biofouling

Iron bacteria and other biofouling can be a difficult O&M problem. Natural microorganisms exist in the subsurface and can also be introduced into the wells during drilling operations. If these microorganisms adapt to, and begin to use hydrocarbon as a food source, they can multiply very rapidly. These microorganisms can build upon well materials, pumps, and treatment components and can cause severe plugging problems. This biomass will also accumulate on the gravel pack of wells and in the adjacent formation, causing reduced well yields. This results in a loss of well and treatment system efficiency and can lead to equipment deterioration.

Biofouling can be recognized by the presence of slime on pumps, probes, and other downhole equipment. Left unchecked, severe plugging may result. If not treated early, biofouling can ultimately lead to well and equipment replacement.

There are no easy solutions to O&M problems caused by biofouling. The best approach is to perform routine maintenance at the first sign of growth. At sites where biofouling is suspected, a test probe can be suspended in the well and checked routinely for the presence of slime. Once detected, the well can be treated with an acceptable biocide. Chlorine solutions or acids (for example, hydrochloric acid) can be used; however, these solutions may have undesirable reactions with the hydrocarbon present. Nontoxic biocides that may be more appropriate for this problem are available. After treatment is applied, the well may require redevelopment. Similar techniques can be used for treatment systems with this problem. Some form of continuous treatment may be required to control more serious biofouling problems.

# 7.7.3.4 Cold Weather

Cold weather can present many O&M problems. Primary impacts due to cold weather include the following:

- a. Freezing of groundwater in pipes, sumps, and reactors.
- b. Freezing of moisture in air lines.
- c. Reduction in treatment system efficiency.

A number of measures can be taken to prevent these coldweather problems. These measures should consider worstcase ambient conditions:

a. If water will be standing for a period in which it can freeze, that portion of the system should be located in a heated enclosure; this is a general rule for prevention of



#### Table 29 — Operational Consideration for Inorganic Scaling

Source of Fouling	Maintenance Requirement			
Iron (Fe), Magnesium (Mg)				
Concentration				
0–5 ppm	Maintenance as required			
5–10 ppm	Routine maintenance			
10–20 ppm	Constant maintenance			
>20 ppm	Pretreatment can be considered depending on the flow rate			
Maintenance:				
Diffused air strippers	Changing of filters			
Packed tower air strippers	Acid washing of packing or replacement of packing; required system shutdown			
Hardness				
Concentration				
0–150 ppm	Maintenance as required			
150300 ppm	Routine/constant maintenance			
>300 ppm	pH control			
Maintenance:	Required system shutdown and removal of scaling with muriatic acid.			
pH Control:	Requires continuous addition of hydrochloric acid (HCl) to maintain the pH of the influent in 4.0-5.0 range			

Note: ppm = parts per million.

cold-weather problems.

b. The water pipes and air lines should be heat taped and/or insulated.

c. The water pipes should be slightly sloped to enable the water to properly drain in case of a system shutdown.

d. In some situations, the treatment unit can be heated with immersion heaters or heat tape.

# 7.7.4 SYSTEM O&M COMPARISONS

The most appropriate time to consider implications of long-term O&M costs is during system design. Past experience with various remediation systems is valuable in designing a cost-effective system for a given site.

Numerous systems and combinations of systems are being utilized for hydrocarbon remediation. A comparison of common O&M requirements for various recovery and treatment systems is presented in Tables 30 and 23, respectively.

No one system is appropriate for every site. Several technical and economic factors, including O&M requirements, need to be evaluated during design to select the most effective system. In addition, site-specific conditions might dictate the use of a more O&M intensive system. O&M requirements should not be the only design factor evaluated.

# 7.8 Additional Considerations

# 7.8.1 COUPLING OF SYSTEMS



In each of the preceding sections, the basic approaches to remediation were discussed separately. In many instances, by using several technologies, site remedial goals and closure can be achieved more rapidly. For instance, LNAPL recovery systems can reduce/recover mobile hydrocarbon, and towards the end of this process, SVE can be implemented to further enhance remediation of the LNAPL. In terms of optimization of combined systems, there are no standard techniques available that take into account dissolved-, liquid-, and vapor-phase remedial evaluation simultaneously. Optimization of these systems is usually evaluated separately, and then areas where savings on duplication can be realized are incorporated into the system design. For instance, an existing groundwater control well could also be used as a vapor-extraction location. Coupling of systems can be a very effective technique to reduce remedial time frames, and it should be an approach that is evaluated during the design or later evaluation phases of a project.

# 7.8.2 COST CONSIDERATIONS IN OPTIMIZATION AND STANDARDIZATION

One of the key factors to evaluating the optimum solution is the evaluation of the overall cost of the solution. To adequately evaluate and compare various remedial scenarios on a cost basis, the long-term O&M costs associated with the system over its operational life must also be taken into account with the initial capital costs of the system. Another consideration is that a less expensive approach could be currently taken with the knowledge that an additional expenditure would be required in the future, or a larger sum could be currently spent to correct the problem. The question is "Which is better from an economic perspective?" "Present value" analyses can be used to answer these types of questions. The basic concept in the use of present value is to bring the expenditure of future dollars into today's dollars (in other words, the equivalence of any future amount to any present amount).

### 7.8.2.1 Example 1: Present Worth of a Future Amount

An example of a present-worth analysis is to evaluate two remedial alternatives in which one calls for a larger expenditure at a future date. \$150,000 can be spent now on a remedial

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# Table 30—LNAPL Recovery and Control Systems and Equipment

Systems	Relative Capital Costs	Relative Operating Costs	Relative Maintenance Costs	Potential for Product Removal	Advantages	Disadvantages
Skimming Systems Floating large saucer type small float type	L L	L L	M M	L–M L–M	No water pumped, skims very thin layers, moves up and down with GW	Limited radius of influence; clogging of screen, generally limited to shallow (<25 ft) applications
Floating inlet bailer/passive pneumatic pump	L L	L L	L L	L L	No water pumped, skims very thin layers, low cost	Limited radius of influence, manually adjusted, clogging; low removal rate (different for bailers and oneumatic pumps)
Absorbent absorbent bailer belt skimmer	L L	L L	L L	L L		
Single Pump Systems Diaphram pump	L	М	L-M	L-M	Low cost, low maintenance surface mounted pumps, easy to maintain low flows	Pumps water and LNAPL, requires o/w separator, shallow (<20 ft)
Centrifugal pump	L–M	М	М	L–M	Low cost and maintenance	Level sensor and o/w separator required (<25 ft), emulsification
Submersible pump	М	M–H	М	L-M	No depth limitation, ease of installation, removes water and LNAPL	Flow >5 GPM, o/w separator water treatment, emulsification
Pneumatic top filling product only	M M	M M	M M	M–H M–H	Can operate over wide range of low rates, can pump from deep, low K aquifers	Requires air compressor system and water treatment
Dual Pump Systems GWP and LNAPLP with separate levels and LNAPL	M-H	M–H	Н	Н	Cone of depression induces migration of LNAPL to well, high-potential LNAPL removal rates, pump GW and LNAPL, potential large radius of influence High initial cost, high maintena recovery well often become clogged and inefficient, wor best in clean sands and grav cycling the GWP on and off with level sensor not recommended approach	High initial cost, high maintenance, recovery well often becomes clogged and inefficient, works
GWP running steady with LNAPLP and LNAPLP	M-H	M-H	М	н		cycling the GWP on and off with level sensor not
GWP running steady with floating LNAPL skimming pump	M–H	M-H	М	н		recommended approach
Direct Removal Open excavations or trenches	_	L	_	М	Good initial remedial action using vacuum truck, absorbent pads, and so on	Not practical for removing LNAPL away from excavation area
Routine skimming or bailing of wells	—	L		L	Inexpensive, works on small localized LNAPL layers	Very limited radius of influence and removal rate
Vacuum Enhanced Pumping Drop tube suction lift In-well pump augmented by vacuum on well	M H	н н	L L	VH VH	Works well with low to medium permeability soils, large radius of influence; increases water and product flow by 3 to 10 times; can significantly reduce site remediation time	Requires high vacuum pump or blower, usually requires thermal air treatment system and water treatment

Note: Source: USEPA, 1993. GW = groundwater; GWP = groundwater pump; LNAPLP = LNAPL Pump; K = hydraulic conductivity; GPM = gallons per minute; L = low; M = medium; H = high; VH = very high; o/w = oil/water; ft = feet.

Approximate cost ranges based on a unit single well system including water handling and treatment:

Approximate cost in	inges based on a unit single wen sy
Capital Costs:	L - \$3,000-10,000
	M - \$10,000-25,000
	H - >\$25,000
Operating Costs:	L - \$500-1,000/mo
	M - \$1,000-3,000/mo
	H - >\$3,000/mo
Maintenance Costs:	L - <10% of Capital Cost/YR
	M - 10 to 25% of Capital Cost/YR

H - >25% of Capital Cost/YR

system that will remediate a given site, or \$10,000 can be spent now to satisfy initial regulatory requirements deferring installation of a more expensive remedial system costing \$200,000 in five years. Which option is less costly, assuming interest at 6 percent compounded annually?

Option A:

\$150,000

Present Worth (Option A) = \$150,000 Option B:

\$10,000

\$200,000

0

*Present Worth* (Option B) =  $10,000 + 200,000 (P/F_{i,n})$ 

Where:

- i = interest rate.
- n = number of years.
- P = present worth.
- F = future value.

The present worth (P) of a future value (F)  $(P/F_{i,n})$  is calculated as follows:

$$P = F \left[ \frac{1}{(1+i)^n} \right]$$
$$P = F (.747)$$
$$P = 200,000 (.747)$$
$$P = 149,451$$

*Present Worth* (Option A) = \$10,000 + \$149,451 = \$159,451

Based solely on the capital expenditures, Option A would be less expensive.

# 7.8.2.2 Example 2: Present Worth of Annual O&M Costs

Another common example is the comparison of the capital cost of equipment and the associated O&M costs. A company has the option of purchasing a \$10,000 piece of equipment now and maintaining it at a cost of \$6,000 per year or paying \$30,000 for a lower maintenance piece of equipment and maintaining it at a cost of \$1,000 per year. If at the end of five years, the salvage value is zero and the interest expense is 6 percent compounded annually, which is less expensive?

Option A:



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This requires a uniform series present-worth analysis. The present worth (P) of an annual cost (investment) (A) is calculated as follows  $(P/A_{i,n})$ :

Option A:

$$P = A \left(\frac{(1+i)^{n}-1}{i(1+i)^{n}}\right)$$

$$P = 6,000 \left(\frac{(1+.06)^{5}-1}{06\ 1+.06^{5}}\right)$$

$$P = 6,000 \left(\frac{.33}{.08}\right)$$

$$P = 6,000 \left(4.212\right) = \$25,272$$

$$Total Cost = \$10,000 + 25,272 = 35,272$$

**Option B**:

$$P = A \left(\frac{(1+i)^{n}-1}{i(1+i)^{n}}\right)$$

$$P = 1,000 (4.212) = 4,212$$

$$Total Cost = $30,000 + 4, 212 = 34, 21$$

Economically, Option B is the better choice since it has the smallest equivalent present cost.

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These are very simple examples of how economic analysis can be used to aid in evaluating remedial options. This is a very important consideration that is often overlooked in evaluating scenarios, although there are many other management criteria that must be considered in addition to these economic considerations.

Standardization of system design and installation has the potential to significantly reduce the costs of hydrocarbon remediation projects. Standardization involves the use of pre-engineered systems configured to meet site-specific conditions. Cost control advantages of standardization include the following:

a. Pre-engineering reduces design and fabrication time.

b. The complete system arrives on-site after factory testing. c. Installation requirements are minimal, and extended

operation and maintenance costs are reduced.

d. The ability to configure system for site-specific applications due to change-out capability.

e. The site may be reused as is or reconfigured for other sites.

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# APPENDIX A—BIBLIOGRAPHY

# A.1 Background

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# APPENDIX B—INVESTIGATION OF SUSPECTED RELEASES

# **B.1** Reasons to Suspect a Release

A release should be suspected when one or more of the following indicators exist:

a. Abnormal results from an inventory reconciliation, such as a discrepancy of 0.5 percent or more of throughput for each product during monthly inventory reconciliation or a significant gain of water within the storage tanks (see API Recommended Practice 1621).

b. For pressurized piping systems, activation of the line leak detector and/or loss of pressurization.

c. For suction piping systems, any indication of air in the line, such as a loss of suction-pump prime, hesitation, or erratic delivery of product at the dispenser. Other indications of air in a suction line include the pump running but not pumping liquid, the pump rapidly accelerating when turned on and then slowing down as liquid begins to flow, and erratic liquid flow, indicating a mix of air and liquid.

d. The presence of LNAPL in groundwater monitoring wells or evidence of LNAPL (liquid or vapor) in basements, water wells, sewers, ducts, waterways, backfill, soil, or other locations.

e. A system's failure of a tank tightness test or a hydrostatic test of piping.

f. The triggering of release detection devices, such as an interstice monitor for double-wall equipment.

### B.2 Appropriate Responses to Inventory Variance

If a loss is suspected because inventory reconciliation shows an apparent variance of 0.5 percent or more of the monthly throughput, but the existence of a release is not confirmed by any other leak detection device, the steps listed below should be taken:

a. All readily accessible below-grade physical facilities, such as fill boxes, sewers, sumps, pump pits, and areas below dispensers should be cautiously and carefully inspected for evidence of a release.

b. Inventory control records should be carefully reviewed to ensure that the discrepancy has not been caused by a recordkeeping error. If no error in the records is apparent, an independent calculation of apparent loss should be made by a qualified person, starting from the point where the records do not indicate a variance of 0.5 percent or more of monthly throughput, as described in API Recommended Practice 1621. c. If these steps described in a. and b. fail to confirm the release, but the recalculation of inventory records still indicates an abnormal loss or gain, the dispensers associated with the tank system being investigated should be calibrated in accordance with API Recommended Practice 1621.

d. Concurrent with the execution of the steps described in a. through c., employee operational procedures should be reviewed to assure that company policies for receipt and confirmation of product deliveries and security of stored product are being followed.

e. If the steps described in a. through d. do not account for the inventory variance and if the piping system can be tested without excavation, the piping system between the tank and the dispensers should be subjected to a hydrostatic test.

f. If the inventory control results remain unexplained after the execution of the step described in d., a tank tightness test should be conducted.

g. If the tank tightness test does not explain the release, daily inventory control should be continued, and the release detection systems monitored as applicable.

h. If the tank tightness test does indicate a release, the top portion of the storage tank should be exposed; all fittings, including bungs and manholes, should be tightened; and the vent lines should be isolated. The tank should then be retested. If the tank fails the retest, the existence of a release should be regarded as confirmed.

# **B.3** Piping Issues

If a release is suspected from the piping, the steps listed in a. through c. of the following should be taken. Such concerns include a piping release detection device indicating a release in the immediate vicinity of the piping; for suction piping, erratic product flow from the dispenser; or the system's failure of a hydrostatic test of piping.

a. The check valve, line release detector, or other detection device should be inspected. If any doubt exists that the check valve is seating tightly or that the release detector is functioning properly, the necessary repairs or replacements should be made.

b. If the circumstances described in step a. persist, the existence of a release is likely, and a hydrostatic test of piping should be conducted.

c. If the hydrostatic test of piping does not confirm a release, a 30-day inventory reconciliation should be conducted. If this reconciliation indicates a release by the criteria set forth in the previously discussed section on inventory variance (see B.2.1), the steps listed in a. through h. of that section, should be taken. If the 30-day reconciliation does not indicate a release, inventory control reconciliations should continue, and action should be taken as necessary.

# **B.4 LNAPL**

If a release is suspected as a result of the presence of LNAPL in monitoring wells or elsewhere, or if LNAPL are

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found during an investigation triggered by another release indicator, the steps listed in the following a. through c. should be taken.

a. It should be determined whether the LNAPL can be attributed to any overfill or prior release that has since been corrected or to another off-site tank system. If such a source cannot be confirmed, the investigation should proceed. If the source is confirmed, corrective action should be taken (see Section 4).

b. All readily accessible below-grade physical facilities, such as fill boxes, sewers, sumps, pump pits, and areas below dispensers should be cautiously and carefully inspected for evidence of a release.

c. The inventory control records should be carefully reviewed. If they indicate an abnormal loss or gain, the following steps described in d. through i. should be taken; if they do not, the following steps described in e. through i. should be taken.

d. If inventory records indicate an abnormal loss or gain, the dispensers associated with the particular tank system should be calibrated in accordance with API Recommended Practice 1621.

e. If the piping system can be tested without excavation, the piping system between the tank and the dispensers should be subjected to a pipe tightness test.

f. If no release from the piping system is found by the hydrostatic test of piping, a tank tightness test should be conducted.

g. If the tank tightness test does not indicate that a release is present, daily inventory control should be continued, and the release detection systems should be monitored as applicable.

h. If the tank tightness test does indicate a release, the top portion of the tank should be exposed; all fittings, including bungs and manholes, should be tightened; and the vent lines should be isolated. The tank should then be retested. If the tank fails the retest, the existence of a release should be regarded as confirmed.

i. If the tank tightness test or retest does not indicate a release, the tank should be regarded as tight; however, a site assessment and other response actions should proceed as necessary. This process may provide more information about the source of the LNAPL.

### B.5 Unsatisfactory Results From an Automatic Tank-Gauging System Test (ATGS)

If an ATGS operating in a release detection mode indicates that a release may be present, then the following steps listed in a. through d. should be taken.

a. The function of the ATGS should be checked, and another release detection test should be conducted.

b. Inventory control records should be examined for evidence of a release, as described in API Recommended Practice 1621.

c. All readily accessible below-grade physical facilities, such as fill boxes, sewers, sumps, pump pits, and areas below dispensers should be cautiously and carefully inspected for evidence of a release.

d. A tank tightness test should be conducted, and the steps described in g. and h. of Section B.2.1 should be taken.

### B.6 Unsatisfactory Results From a Tank Tightness Test

If a tank tightness test indicates a release, the top portion of the tank should be exposed; all fittings, including bungs and manholes, should be tightened; and the vent lines should be isolated. The tank should then be retested. If the tank fails the retest, the existence of a release should be regarded as confirmed. **APPENDIX C-TABLES OF SAMPLING EQUIPMENT** 

	Typical perating Times	be used for as g as the battery is or for the ommended inter- ibrations, which- er is less	ip chart recorder
	ral Care and aintenance O	rge or replace Can rry lon ate immediately las re use cal eve	rge or replace 8 hou ry stri or fuel and bustion air ly gauges m routine m routine mibed in the ribed in the for leaks
	Gene M	derstand batte derstand batte inciples Calibr befo	ce to Recha batte c GC Monity on supp f Perfor main main descr man
β	Ease of Operation	Effective use requent operator un that operating procedures and procedures	Requires experier interpret data cc especially in the mode Requires calibrati for the analyst o interest for spec identification
	Limitation	Accuracy depends in part on the difference between the calibration and sampling temperatures Sensitivity is a function of the differences in the chemical and physical properties between the chemical and physical being sampled The filament can be damaged by certain compounds such as silicones, halides, tetraethyl lead, and oxygen- enriched atmospheres A valid reading under oxygen- deficient conditions is not possible	Inorganic gases and vapors or some synthetics are not detected; sensitivity depends on the compound The use at temperatures less than 40°F (4°C) is not recommended Absolute identifications are difficult High concentrations of organic compounds or oxygen-deficient atmospheres require system modification ereported relative to the calibration standard used in the survey mode
•	Detection Method	A filament, usually made of platinum is heated by burning the combustible gas or vapor, and the increase in heat is measured	Gases and vapors are ionized in a flame; a current is produced in proportion to the number of carbon atoms present
	Application	Measures the concentration of a combustible gas or vapor	In survey mode, detects the total concentrations of many organic gases and vapors; in gas chromatography (GC) mode, identifies and measures specific compounds In survey mode, ionizes and detects organic the same time In GC mode, separates volatile species
	Condition Monitored	Combustible gases and vapors	Many organic gases and vapors
	Instrument	Combustible gas indicator (CGI)	Flame Ionization detector (FID) with gas chromatography option

Table C-1-Some Direct-Reading Instruments for General Survey of Organic Vapors

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			D	'n			
Instrument	Condition Monitored	Application	Detection Method	Limitation	Ease of Operation	General Care and Maintenance	Typical Operating Times
Portable Infrared (IR) Spectrophoto- meter	Many gases and vapors	Measures concentration of many gases and vapors in air Designed to quantify one- or two-component mixtures	Passes different frequencies of IR through the sample; The frequencies adsorbed are specific for each compound	Repeated passes to achieve reliable results are necessary in the field 115-volt AC power required Use in a potentially flammable or explosive atmosphere is not permissible interference by water and vapor and carbon dioxide Certain vapors and high moisture may attack the instrument's optics, which must then be replaced	Requires personnel with extensive experience in IR spectrophotometry	As specified by manufacturer extensive	
Ultraviolet (UV) Photoionization Detector (PID)	Many organic and some inorganic gases and vapors	Total concentrations of many organic and some inorganic gases and vapors are detectable; some identifications of compounds are possible if more than one probe is used	Ionizes molecules using UV radiation; produces a current that is proportional to the number of ions	Methane is not detectable A compound is not detectable if the probe used has a lower energy level than the compound's ionization potential Response may change when gases are mixed Other voltage sources may interfere with measurements Readings can only be reported relatiave to the cultarian terported relatiave to the cultarian by high humidity	Effective use requires that the operator understand the operating principles and procedures and be competent in calibrating, reading, and interpreting the instrument	Recharge or replace battery Regularly clean lamp window Regularly clean and maintain the instrument and accessories	10 hours, 5 hours with strip chart recorder

# Table C-1—Some Direct-Reading Instruments for General Survey of Organic Vapors (Continued)

A GUIDE TO THE ASSESSMENT AND REMEDIATION OF UNDERGROUND PETROLEUM RELEASES

Not for Resale

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Instrument	Condition Monitored	Application	Detection Method	Limitation	Ease of Operation	General Care and Maintenance	Typical Operating Times
Direct reading colorimetric Indicator Tube	Specific gases and vapors	Measures concentrations of specific gases and vapors	The compound reacts with the indicator chemical in the tube, producing a stain whose length or color change is proportional to the compounds concentrations	The measured concentration of the same compound may vary arnong different manufacturer's tubes Many similar chemicals interfere Greatest sources of error are (a) how the operator judges stain's end-point, and (b) the tube's limited accuracy High humidity has adverse effects	Minimal operator traning expertise required	Do not use a previously opened tube even if the indicator chemical is not stained Check pump for leaks before and after use Refrigerate prior to use to maintain shelf life of about 2 years Check expiration date of tubes Calibrate pump volume at least quarterly Avoid rough handling which may cause channeling	
Oxygen Meter	Oxygen (O2)	Measures the percentage of O <sub>2</sub> in air	Uses an electrochemical sensor to measure the partial pressures of O <sub>2</sub> in the air and converts that reading to O <sub>2</sub> concentration	Calibration is necessary before use to compensate for altitude and baronnetric pressure Certain gases especially oxidants, such as ozone, can affect readings; can be ozone, carbon dioxide (CO <sub>2</sub> ) adversely affects the detector cell	Effective use requires that the operator understand the operating principals and procedures	Replace detector cell according to manufacturer's recommendation Recharge or replace batteries as specified by the manufacturer Replace or rejuvenate the O <sub>2</sub> detector cell frequently if the ambient air is more than 0.5% CO <sub>2</sub>	8 to 12 hours

Table C-1—Some Direct-Reading Instruments for General Survey of Organic Vapors (Continued)

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### Table C-2—Advantages and Disadvantages of Groundwater Sample Collection Methods Disadvantage Advantage DOWN-HOLE COLLECTION DEVICES General Most down-hole collection devices are unsuitable for flushing because Greater potential of preserving sample integrity than many other they provide only discrete and often very small volumes of water; methods because water is not driven by pressure differences this situation can be avoided by using another method, which may be disruptive, to flush the installation before using the down-hole collection device for sampling Bailers Usually bailer is very time consuming for flushing installations, Inexpensive to purchase or fabricate and economical to operate; especially at great depths; lowering and raising the bailer by hand this may permit the assignment of one collection device for can be physically taxing for the operator each installation to be sampled, thereby circumventing issues of cross-contamination Can cause chemical alterations due to degassing, volatilization or atmospheric invasion when transferring the sample to the storage Very simple to operate and require no special skills container Easily cleaned, though cleaning of ropes and/or cables may be more difficult Produceable from inert materials Very portable and requires no power source MECHANICAL DEPTH-SPECIFIC SAMPLERS Some of the materials used can cause sample contamination Inexpensive to construct (for example, rubber stoppers) Very portable, and requires no power source Activating mechanism is prone to malfunctions Stratified sampler is well suited for sampling distinct layers of immiscible fluids May be difficult to operate at great depths Producible from inert materials Can cause chemical alterations when transferring sample to storage container Stratified sampler is easily cleaned Difficult to transfer sample to storage container Kemmerer sampler is difficult to clean thoroughly **Pneumatic Depth-Specific Samplers** Producible from inert materials Types that are commercially available are moderately expensive Easily portable and requires only a small power source Westbay sampler is compatible only with the Westbay casing system (for example, a hand pump) Solinst, and Westbay samplers are difficult to clean Solinst sampler and syringe sampler can be flushed down-hole Materials used in disposable syringes of syringe samplers can with the water to be sampled contaminate the water sample Syringe of the syringe sampler can be used as a short term Water sample comes in contact with pressurizing gas in Solinst, and storage container Westbay samplers (but not in syringe samplers) Syringe sampler is very inexpensive Suction-Lift Methods Simple, convenient to operate, and easily portable Limited to situations where the water level is less than 23-26 feet (7-8 meters) below Inexpensive to purchase and to operate ground surface. Easily cleaned Can cause sample bias through degassing and agitation of the sample, especially if the sample is taken from an in-line vacuum flask. Components can be of inert materials Can cause sample contamination if water is allowed to touch pump Very efficient in removing standing water from the sampling components installations, depending on the pumping mechanism Provide a continuous and variable flow rate

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# Table C-2—Advantages and Disadvantages of Groundwater Sample Collection Methods (Continued)

Advantage	Disadvantage
POSITIVE-DISPLACE	MENT METHODS
Gener	al
Reduced possibility of degassing and volatilization because the sample is delivered to ground surface under positive pressure; in some situations the pressure at ground surface may be substantially less than the natural water pressure in the formation and thus	Cost of the commercially available pumps is substantial (roughly \$2,000 to \$5,000); it would, therefore, not be feasible to dedicate a sampling pump to each sampling point
the degassing concern can not be entirely ignored	Cleaning between sampling sessions can be difficult
Sample does not contact the atmosphere	Cleaning of cables and delivery tubing is required between sampling points
Sampling pumps for use in monitoring wells as small as 1.5–2 inches (3.8–5 centimeters) are commercially available	Commercially available devices are too large for very small-diameter
Most of the commercially available devices have a sufficient flow rate for flushing sampling installations	instantations such as buildle piezometers
Submersible Centr	rifugal Pumps
Can pump at large and variable flow rates	Subject to excessive wear in abrasive or corrosive waters
Johnson-Keck pumps can fit down wells as small as 2 inches (5 centimeters)	Conventional submersible pumps cannot be used in installations less than 4 inches (12 centimeters) in diameter
Johnson-Keck pump is easily portable	Potential for contaminating water samples because contact with metals and lubricants is more extensive than in conventional pumps
Conventional pumps are usually much cheaper than the Johnson-Keck pump	Johnson-Keck pump has intermittent flow (15 minutes on, 15 minutes off)
Johnson-Keck pump offers little potential for sample contamination because it is made mostly of stainless steel and Teflon <sup>®</sup>	
Submersible Pie	ston Pumps
Gas-drive piston pumps have small power requirements	Rod pumps require large power source and are permanently mounted
Gas-drive piston pump of Gillham and Johnson (1981) is inexpensive and can be assigned permanently to sampling point, thereby eliminating questions of cross-contamination	Difficult to clean When used as part of an installation, the gas drive pump of Gillham
	and Johnson (1981) cannot be retrieved for servicing or repair
Double-acting pumps have continuous, adjustable flow rates	Single-acting pumps have intermittent flow
Can be built of inert materials (most commercially available pumps are not, however)	
Gas-Squeez	e Pump
- Can be built of inert materials	Intermittent but adjustable flow
Commercially available pumps can fit in installations as small as 2 inches (5 centimeters)	Requires large but portable power source
Can easily be taken apart for cleaning but can be inconvenient to clean between sampling sessions	
Advantage	Disadvantage
GAS-LIFT M	ETHODS
Simple to construct or are available commercially at relatively low cost	Can only be used efficiently when roughly one third of the under- ground portion of the device is submerged
Can be used in very narrow installations	Contamination of the sample with the driving gas, atmospheric contamination of the sample, or degassing is unavoidable.
Easily portable	
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# Table C-2—Advantages and Disadvantages of Groundwater Sample Collection Methods (Continued)

Advantage	Disadvantage
GAS-DRIVE	METHODS
Can offer good potential for preserving sample integrity because very little of the driving gas comes in contact with the water sample, and because the sample is driven by a gradient of positive	Not very efficient for flushing installations larger than about 1 inch (2.5 centimeters)
pressure	Can be difficult to clean between sampling sessions
Can be incorporated as part of the sampling installation, thereby removing the possibility of cross-contamination	The driving gas comes in contact with the water, and therefore the beginning and the end of the sample of water obtained at the surface can be contaminated
The triple-tube sampler is well suited for installations of very	
narrow diameter (e.g., $\frac{3}{8}$ inch [0.95 centimeters]) where the only other possible sampling method is to use narrow-tube bailers or suction-lift (when applicable)	When used as part of a permanent sampling installation gas drive samplers cannot be retrieved for repair or servicing
Inart metarials can be used	Pump intermittently and at a variable flow rate
Advantage	Disadvantage
JET-PU	JMPS
Can be used at great depths	Use circulating water which mixes with the pumped water; a large amount of water needs to be pumped before the circulating water has a composition that approximates that of the water in the installation
Useful to flushing monitoring installations	
	The water entering the verturi assembly is subjected to a pressure drop (which may be large), and can therefore undergo degassing or volatilization, or both
	The circulating pump at the surface can contaminate the pumped water because of its materials and lubricants
Advantage	Disadvantage
DESTRUCTIVE SAM	IPLING METHODS
Can provide very useful information in the reconnaissance surveys and	Because no permanent installation is left in the ground, these methods
in other specific field situations	in most cases, however, they do not interfere with the construction
Most of the techniques are used during the drilling operation and will not interfere with the construction of a permanent installation	of permanent installations
-	Can result in large drilling costs
Coring-extraction methods are the only convenient means of obtaining	
several parameters related to both the liquid and solid phases (for example, exchangeable cations, total microbial population	water contained in cores can be contaminated with drilling fluids and
(for example, exchangeable cations, total interobial population, samples of the formation, and so forth), and in certain situations	can undergo degassing and volatilization at the ground sufface
they may induce the least bias(such as, in very fine-grained formations)	
Using temporary installations can in some situations be the most	
cost-effective way of obtaining preliminary and reconnaissance data	



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