CHAPTER III

BEHAVIOR OF HYDROCARBONS IN THE SUBSURFACE

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The purpose of this chapter is to supplement your knowledge of hydrocarbon behavior in the subsurface. This basic information lays the foundation for the principles and concepts used in the design of effective and efficient free product recovery systems.

The fate-and-transport of liquid petroleum products in the subsurface is determined primarily by the properties of the liquid and the characteristics of the geologic media into which the product has been released. Important liquid properties include density, viscosity and interfacial tension. Soil properties that influence the movement of petroleum hydrocarbons include porosity and permeability. Other additional properties, which are functions of both the liquid and the media, include capillary pressure, relative permeability, wettability, saturation, and residual saturation. Site-specific physical conditions (*e.g.*, depth to groundwater, volume of the release, direction of groundwater flow) also contribute to the migration and dispersion of released petroleum products. This chapter contains discussions of each of these factors. To put the following discussion in the context of the types of petroleum hydrocarbons commonly found at UST sites, we begin with a brief description of the classification and composition of hydrocarbons.

Classification And Composition Of Hydrocarbons

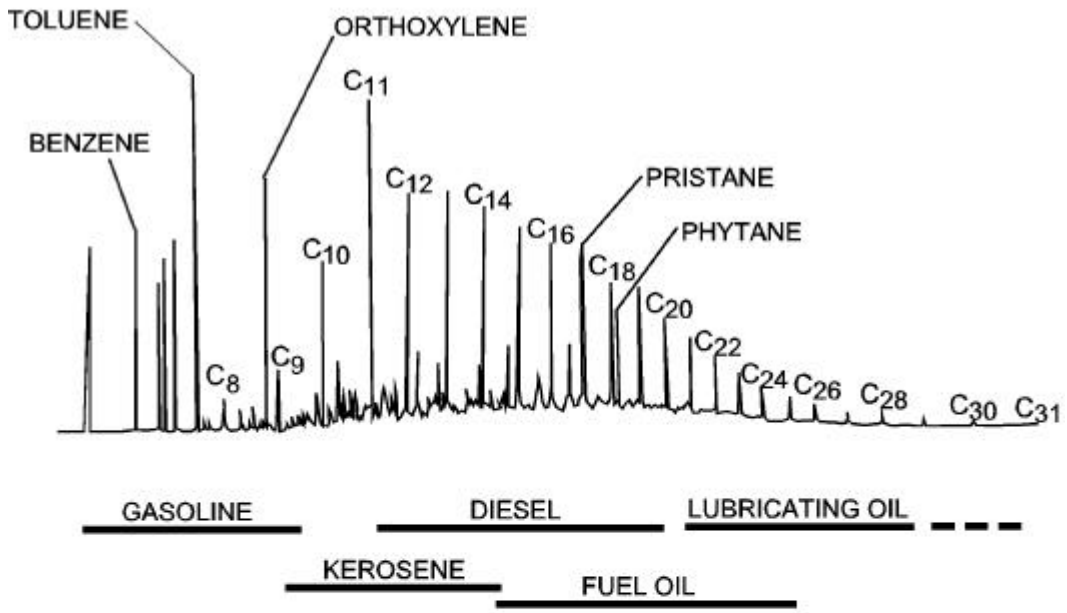
Petroleum hydrocarbons are derived from crude oil, which is refined into various petroleum products by several processes. Like the parent crude oil, refined petroleum products are also mixtures of as many as several hundred compounds. The bulk products may be classified on the basis of composition and physical properties. Products typically stored in USTs include the following main groups:

- Gasolines
- Middle Distillates
- Heavy Fuel Oils

Exhibit III-1 presents a gas chromatogram of a hydrocarbon sample with the approximate ranges in which the various constituents fall. Compounds outside the normal ranges depicted are commonly found as contaminants in other products. For example, diesel fuel may contain minor amounts of benzene and other light hydrocarbons.

Exhibit III-1

Gas Chromatogram Showing Approximate Ranges
For Individual Hydrocarbon Products



Source: Adapted from Senn and Johnson, 1985.

Gasolines

Gasolines are mixtures of petroleum hydrocarbons and other non-hydrocarbon chemical additives, such as alcohols (*e.g*., ethanol) and ethers (*e.g*., methyl tertiary-butyl ether, or MTBE). Gasolines are more mobile than either the middle distillates or the fuel oils. The higher mobility of gasoline is primarily due to the fact that its components tend to have lower molecular weights; hydrocarbon compounds usually found in gasoline have between 4 and 10 carbon atoms per molecule. The lower molecular weight results in lower viscosity, higher volatility, and moderate water solubility. Fresh gasolines contain high percentages of aromatic hydrocarbons (*i.e*., those with a 6-carbon benzene ring), which are among the most soluble and toxic hydrocarbon compounds. The most frequently encountered aromatic compounds are benzene, toluene, ethylbenzene, and xylene (BTEX). Because of their relatively high volatility, solubility, and biodegradability, BTEX compounds are usually among the first to be depleted from free product plumes. At sites of older gasoline releases, the free product plume may contain relatively little BTEX, being instead enriched in heavier, less soluble, and less readily biodegradable components. As a consequence, the product will be more viscous, slightly more dense, less volatile, and less mobile than fresh product. The non-hydrocarbon additives (*e.g*., ethanol, MTBE) are readily soluble and preferentially dissolve into groundwater, which diminishes their concentration in the free product, but results in formation of longer dissolved plumes. MTBE also moves away from the source faster than free product and because it is relatively non-degradable, it is difficult to remediate. Discussion of methods to remediate dissolved plumes are beyond the scope of this manual.

Middle Distillates

Middle distillates (*e.g*., diesel fuel, kerosene, jet fuel, lighter fuel oils) may contain 500 individual compounds, but these tend to be more dense, much less volatile, less water soluble, and less mobile than the compounds found in gasolines. The major individual components included in this category of hydrocarbons contain between 9 and 20 carbon atoms each. Lighter aromatics, such as BTEX, are generally found only as trace impurities in middle distillates, and if initially present, they are generally not present in plumes at older release sites, because they have biodegraded, evaporated, and dissolved into groundwater.

Heavy Fuel Oils

Heavy fuel oils and lubricants are similar in both composition and characteristics to the middle distillates. These types of fuels are relatively viscous and insoluble in groundwater and are, therefore, fairly immobile in the subsurface. Most of the compounds found in heavy fuel oils have more than 14 carbon atoms; some have as many as 30. Like the older releases of middle distillates and gasolines, the lighter end components are present only in trace amounts as they are more readily biodegraded and dispersed.

Phase Distribution In The Subsurface

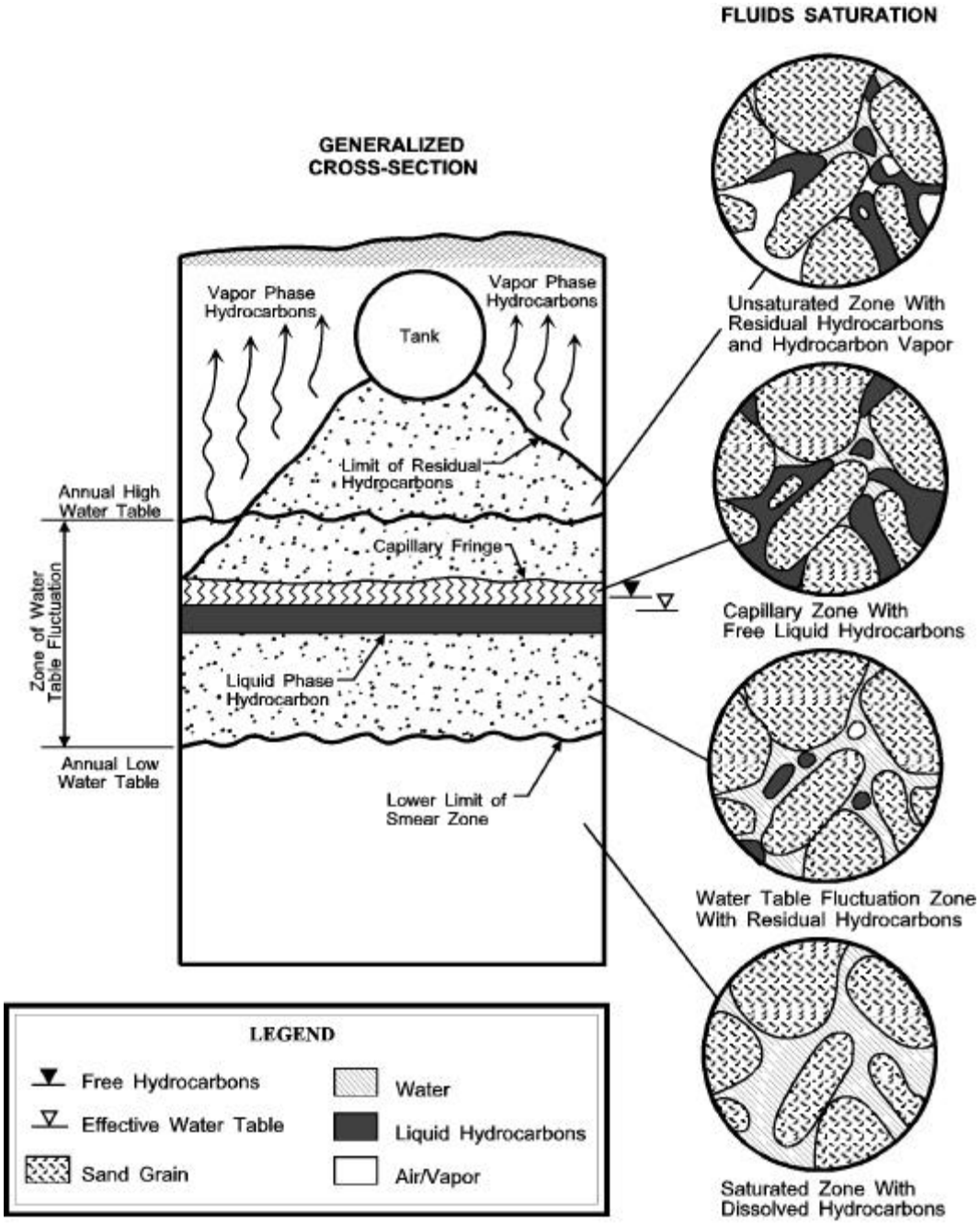
The petroleum hydrocarbon constituents that comprise free product may partition into four phases in the subsurface—vapor (in soil gas), residual (adsorbed onto soil particles including organic matter), aqueous (dissolved in water), and free or separate (liquid hydrocarbons). Exhibit III-2 illustrates the distribution of the hydrocarbon phases in the subsurface from a leaking UST. The partitioning between phases is determined by dissolution, volatilization, and sorption.

When released into the subsurface environment, liquid hydrocarbons tend to move downward under the influence of gravity and capillary forces. The effect of gravity is more pronounced on liquids with higher density. The effect of capillary forces is similar to water being drawn into a dry sponge. As the source continues to release petroleum liquids, the underlying soil becomes more saturated and the leading edge of the liquid migrates deeper leaving a residual level of immobile hydrocarbons in the soil behind and above the advancing front. If the volume of petroleum hydrocarbons released into the subsurface is small relative to the retention capacity of the soil, then the hydrocarbons will tend to sorb onto soil particles and essentially the entire mass will be immobilized. For petroleum hydrocarbons to accumulate as free product on the water table, the volume of the release must be sufficient to overcome the retention capacity of the soil between the point of release and the water table. Without sufficient accumulation of free product at the water table, there is no need for a free product recovery system. However, in either case, there may be a need for appropriate remedial action to mitigate the residual (sorbed) phase so that it does not continue to act as a lingering source of soluble groundwater contaminants or volatile, and potentially explosive, vapor contaminants. Exhibit III-3 illustrates the progression of a petroleum product release from a leaking UST. Frame A shows the hydrocarbon mass before it reaches the capillary fringe. If the release were to be stopped at this point, there would probably be no accumulation of free product. In Frame B, the release has continued and the volume of the release is sufficient for free product to begin accumulating on, and displacing, the capillary fringe. The free product is beginning to displace the capillary fringe and some of the soluble constituents are dissolving into the groundwater. The source of release has been stopped in Frame C. Residual hydrocarbons remain in the soil beneath the UST. The free product plume has spread laterally, and a plume of dissolved contaminants is migrating downgradient.

Portions of the hydrocarbon mass from both the residual and free phases will volatilize (evaporate) and solubilize (dissolve) to become components of the soil vapor and groundwater, respectively. Volatilization and solubilization of the lighter fractions tend to make the remaining hydrocarbon mass more dense and even less mobile. Hydrocarbons that are in the vapor phase are much more mobile and can migrate relatively great distances along preferential flow paths such as fractures, joints, sand layers, and utility line conduits. Accumulation of vapors in enclosed structures (*e.g.*, basements, sewers) potentially can cause fires or explosions. The more soluble components of the hydrocarbon mass will dissolve into groundwater, both above and below the water table. The dissolved hydrocarbons move with the flowing groundwater and can

Exhibit III-2

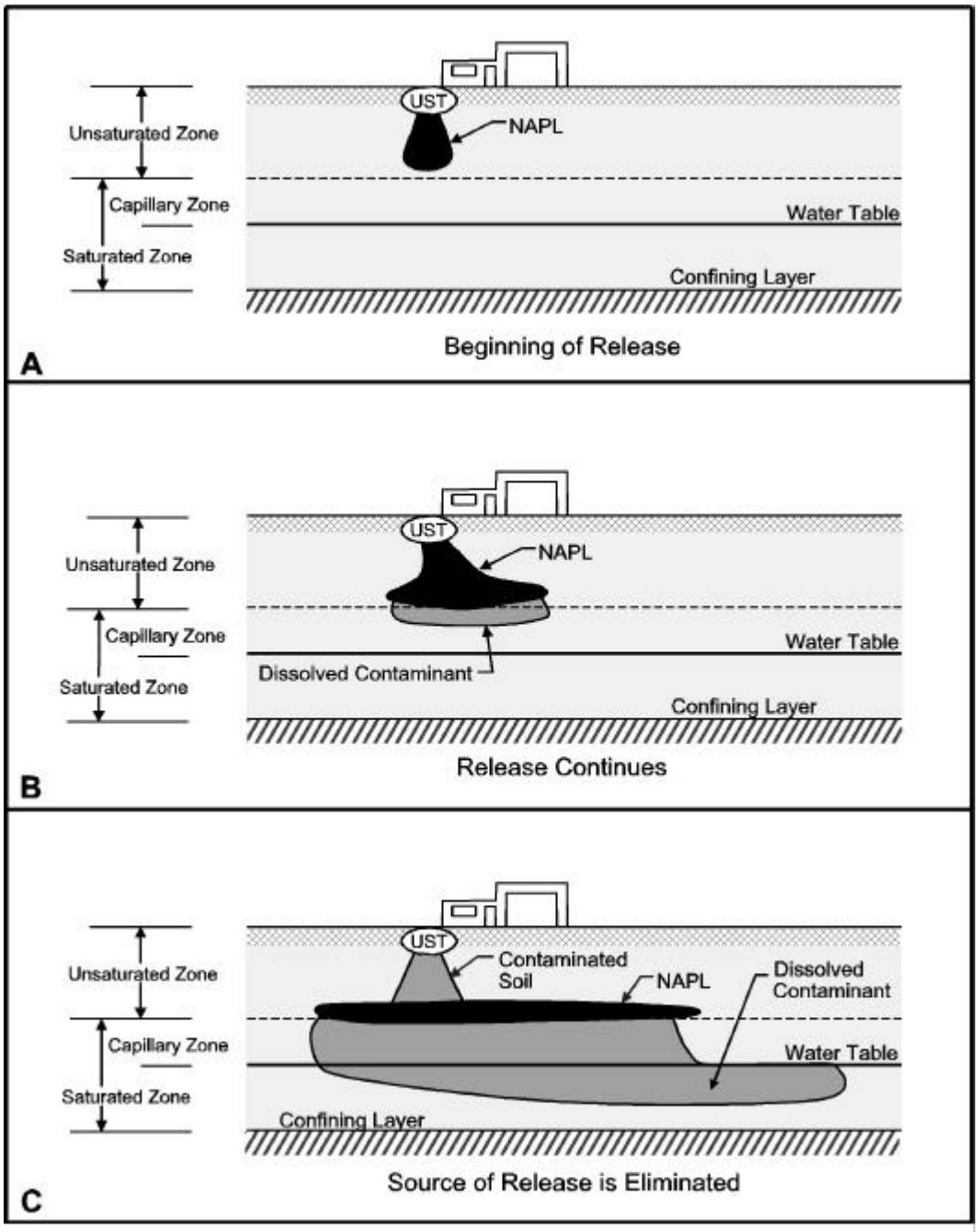
Vertical Distribution Of Hydrocarbon Phases



Source: Modified from Lundy and Gogel, 1988.

Exhibit III-3

Progression Of A Typical Petroleum Product Release
From An Underground Storage Tank



Source: EPA, 1990

contaminate drinking water supplies. Also, if groundwater is recovered as a result of pumping or skimming, it may require treatment or disposal if the concentration of dissolved hydrocarbons is higher than the applicable groundwater or drinking water standard. Vapors may be released from the groundwater or be drawn directly from the subsurface if vacuum-enhanced free product recovery systems are employed. These vapors may require treatment to mitigate fire or explosion potential and to comply with air quality criteria.

Exhibit III-4 presents estimates of phase distribution from a gasoline release into the subsurface consisting of medium sand. Most of the amount spilled (64 percent) remains in the free phase; however, the volume contaminated by residual phase and dissolved phase hydrocarbons represents nearly 99 percent of the total contaminated volume. Perhaps the most important point to note is that a very small quantity of petroleum hydrocarbons (1 to 5 percent of the original release volume) can contaminate a significant amount of groundwater (79 percent of the total contaminated volume). Hence, recovery of as much free product as possible is important, but only a portion (up to 50 percent) of the free phase hydrocarbon is actually recoverable with the balance remaining in the residual phase acting as a continuous source of groundwater contamination. Where a water supply is threatened by a release, recovery of free product may be only the first step. An adequate remedial action may require aggressive remediation of the residual phase as well.

Exhibit III-4

Phase Distribution At A 30,000-Gallon Gasoline Spill
Site In An Aquifer Of Medium Sand

Phase	Contaminant Volume (gal)	% of Total	Contaminated Volume (yd^3)	% of Total
Free Phase	18,500	64	7,100	1
Residual Phase	10,000	35	250,000	20
Dissolved (Water)	333	1	960,000	79

Source:Modified from Wilson and Brown, 1989.

Properties Of Geologic Media

The extent and rate of petroleum hydrocarbon migration depends in part on the properties of the subsurface medium in which it is released. The subsurface medium may be naturally occurring geologic materials (*e.g.*, sedimentary, metamorphic, or igneous rock or sediments) or

artificial fill that has been imported to the site by human activity. In order to design effective and efficient free product recovery systems, you need to characterize both the type and the distribution of geologic media (or fill material) so that you can determine the likely migration routes and travel times.

In the context of fluid flow in the subsurface, geologic media can be classified on the basis of the dominant characteristics of pore space, fractures, or channels through which fluids move. In porous media, fluids move through the interconnected voids between solid grains of soil. Fractured media are those in which fluids migrate readily through fractures rather than the adjacent soil or rock matrix. Fracturing is usually associated with consolidated materials, but it can also occur in unconsolidated clays due to desiccation. Karst media are those in which fluids flow through solution features and channels (*e.g.*, caves associated with carbonate rocks such as limestone).

Porosity and permeability are the two most important media-specific properties of a natural geologic material. Porosity characterizes the ability of media to store fluids, and permeability characterizes the ability of the media to transport fluids. Exhibit III-5 summarizes the significance of geologic properties and their relevance to free product recovery.

EXHIBIT III-5

Functional Characteristics
Of Geologic Media Properties

Property	Significance
Porosity	Porosity is required for calculation of the amount of free product and immobile (residual) product. The relevant parameter for determining recoverable free product is the “drainable” or “effective” porosity, which is always less than total porosity.
Permeability	Permeability controls the rates of groundwater flow and free product migration. It is also used to calculate pumping rates required for hydraulic control.
Anisotropy	Anisotropy is a condition of the geologic media in which measurement of a property (*e.g.*, hydraulic conductivity) depends upon the direction of measurement. Anisotropy can cause groundwater flow to not be in the same direction as the hydraulic gradient.
Heterogeneity	Heterogeneous media often provides preferential pathways for fluid migration—these pathways are difficult to locate and to characterize.

Porosity

Porosity, or more specifically effective ("drainable") porosity, is an important factor to be considered in the evaluation of a free product recovery system. Calculation of the amount of free and immobile product in the subsurface requires a value or estimate of effective porosity.

Porosity defines the storage capacity of a subsurface media. All rocks and unconsolidated media contain pore spaces. The percentage of the total volume of an unconsolidated material or rock that consists of pores is called porosity. Porosity is classified as either primary or secondary. Primary porosity, which is created when sediments are deposited (or crystalline rocks are formed), depends on the shape, sorting, and packing of grains. Primary porosity is greatest when grains are nearly equal in size (i.e., are well graded or sorted) and nonspherical in shape. Unconsolidated sediments that contain a wide range of grain sizes (*i.e*., are poorly graded or sorted) tend to have a low primary porosity because smaller grains fill the pore spaces between the larger grains.

Secondary porosity develops after rocks have been formed or sediments deposited. Examples are joints, foliations, fractures, and solution openings. Also included in this category are animal burrows, root holes, and desiccation cracks in clay soils. While the latter examples typically facilitate free product migration only very locally, the former examples can exert a much more regional influence. Characterization of the flow of groundwater and free product through solution channels, fractures, and joints can be especially problematic. Wells completed at sites underlain by these features may not accurately (or completely) define flow directions or rates. The flow of groundwater and free product through the larger openings can sometimes even be under conditions of open channel flow. Once free product enters these larger openings, it can migrate undetected over relatively great distances (miles in some cases) in a matter of weeks or months. Although it would potentially be easier to recover free product in such a setting, it is much more difficult (and in many cases impossible) to locate recoverable accumulations.

Total porosity is based on the volume of all voids (primary and secondary), whether or not the pores are connected. When pores are not connected and dead-end pores exist, groundwater cannot move through the rock or sediments. Effective porosity is the term that characterizes the ratio of the volume of interconnected pores to the total volume of unconsolidated materials or rock.

There is no direct correlation between effective and total porosity. Effective porosity is approximated by drainable porosity and can be significantly less than total porosity. In general, the smaller the grains in the rock, the smaller the effective porosity (and the greater the retention capacity or residual saturation). For example, clays and limestones can have an upper range of total porosity that is in excess of 55 percent (see Exhibit III-6), but a lower range of drainable porosity of 1 percent or less.

Exhibit III-6

Porosity Of Various Geologic Materials

MATERIAL	NO. OF ANALYSES	RANGE	ARITHMETIC MEAN
Total Porosity			
Sedimentary Materials			
Sandstone	65	0.14 - 0.49	0.34
Siltstone	7	0.21 - 0.41	0.35
Sand (fine)	243	0.26 - 0.53	0.43
Sand (coarse)	26	0.31 - 0.46	0.39
Gravel (fine)	38	0.25 - 0.38	0.34
Gravel (coarse)	15	0.24 - 0.36	0.28
Silt	281	0.34 - 0.61	0.46
Clay	74	0.34 - 0.57	0.42
Limestone	74	0.07 - 0.56	0.30
Metamorphic Rocks			
Schist	18	0.04 - 0.49	0.38
Drainable Porosity			
Sedimentary Materials			
Sandstone (fine)	47	0.02 - 0.40	0.21
Sandstone (medium)	10	0.12 - 0.41	0.27
Siltstone	13	0.01 - 0.33	0.12
Sand (fine)	287	0.01 - 0.46	0.33
Sand (medium)	297	0.16 - 0.46	0.32
Sand (coarse)	143	0.18 - 0.43	0.30
Gravel (fine)	33	0.13 - 0.40	0.28
Gravel (medium)	13	0.17 - 0.44	0.24
Gravel (coarse)	9	0.13 - 0.25	0.21
Silt	299	0.01 - 0.39	0.20
Clay	27	0.01 - 0.18	0.06
Limestone	32	0.00 - 0.36	0.14
Metamorphic Rocks			
Schist	11	0.22 - 0.33	0.26

Source: Modified from McWhorter and Sunada, 1977 (Original Reference Morris and Johnson, 1967).

Permeability

Permeability is one of the most critical properties to be considered in the design of any recovery system for free product recovery. The rates of groundwater flow and free product migration are related directly to permeability. The rate of free product migration also depends on other parameters, but permeability exhibits the greatest range in values (varying over 5 or 6 orders of magnitude for common geologic media).

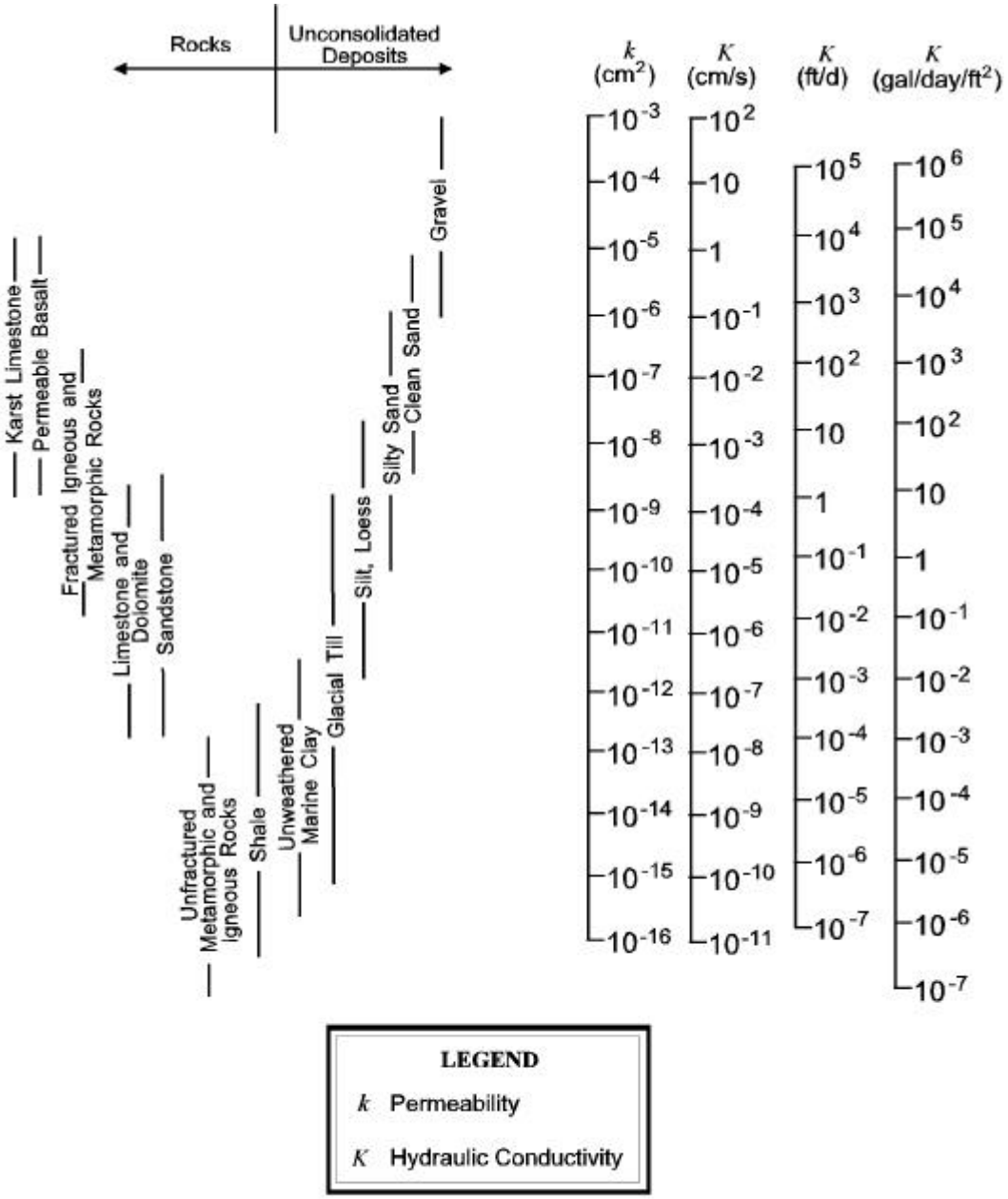
The intrinsic permeability of the geologic media is independent of the nature of the fluid flowing through the media. Intrinsic permeability is related to hydraulic conductivity, which is a measure of the ability of the geologic medium to transmit water, but the terms are not interchangeable. Hydraulic conductivity is a function of properties of both the media and the fluid. Although confusing, hydraulic conductivity is often referred to as simply "permeability". Geologic media with high hydraulic conductivities are highly permeable and can easily transmit non-viscous fluids, especially water and many types of petroleum products. Various geologic media tend to have hydraulic conductivity values within predictable ranges (Exhibit III-7).

A geologic medium is described as "isotropic" if the measured permeability is the same in all directions. Flow through an isotropic medium is parallel to the hydraulic gradient. This condition might exist in a uniform, well-graded sand. The permeability of a geologic medium is often observed to vary depending upon the direction in which it is measured. Known as "anisotropy", this condition can cause the flow of groundwater and free product to occur in a direction that is not necessarily the same as the principle direction of the hydraulic gradient. Because of anisotropy, a cone-of-depression formed around a pumping well may be asymmetrical (*e.g.*, elliptical) rather than circular. Sediments that are comprised of a high proportion of flat, plate-like particles (*e.g.*, silt, clay) which can pack tightly together and foliated metamorphic rocks (*e.g.*, schist) often exhibit anisotropy. Anisotropy may occur in three dimensions. For example, in flat-lying sedimentary units, horizontal permeability is usually much greater than vertical permeability.

The nature of geologic processes results in the nonuniform deposition and formation of rocks and sediments. Geologic media often are characterized by the degree of uniformity in grain size and properties such as permeability. Geologic media with uniform properties over a large area are referred to as being homogeneous. By contrast, geologic media that vary in grain size from place to place are called heterogeneous. In nature, heterogeneity is much more common than homogeneity. Soil properties (*e.g.*, permeability, texture, composition) can be dramatically different over short distances. These changes strongly influence the direction and rate of the flow of groundwater, free product, and vapor through the subsurface. For example, free product may migrate farther and faster than it would in homogeneous media because hydrocarbons tend to move through the most permeable pathways and bypass extremely low permeability zones. Fine-grained fractured media are heterogeneous in the extreme. Migration distances in fractured media can be large because of the very small storage capacity of the fractures.

Exhibit III-7

Range Of Values Of Hydraulic Conductivity And Permeability



Source: Modified from Freeze & Cherry, 1979

Properties Of Fluids

The physical properties of fluids that are most significant to free product recovery and migration are density and viscosity. Density determines the tendency of free product to accumulate above the water table or to sink to the bottom of the aquifer. Common petroleum hydrocarbons tend to accumulate above the water table because of their low density. Viscosity is a factor controlling the mobility and recoverability of liquid hydrocarbons. Petroleum hydrocarbons with low viscosity are more mobile and are more easily recovered than those with high viscosity. A third fluid property is interfacial tension, which is important because it determines how easily a geologic media will be wetted with a fluid and also controls (with pore size) the height of the capillary rise in a porous media. All three properties are inversely related to temperature. Exhibit III-8 summarizes the significance of fluid properties and their relevance to free product recovery.

EXHIBIT III-8

Functional Characteristics
Of Fluid Properties

Property	Significance
Density	Density values are used to determine whether free product will float on top of water or sink through it. Products that float are called LNAPLs (light non-aqueous phase liquids). Most fuel hydrocarbons are LNAPLs. Water levels measured in monitor wells containing free product must be corrected to account for the density and thickness of the product layer (see Exhibit III-10).
Viscosity	Viscosity is a measure of how resistant a fluid is to flow—viscous fluids resist flow. Higher viscosity fluids are more resistive to flow than lower viscosity fluids. For example, gasoline, which is less viscous than diesel fuel, flows faster than diesel fuel. Diesel fuel, which is less viscous than fuel oil #2, flows faster than the fuel oil.
Interfacial Tension	Interfacial tension is responsible for the capillary rise exhibited by fluids in fine-grained media. Interfacial tension is inversely related to the size of the pores. Fine-grained media retain more free product (residual saturation) than coarse-grained media.

Density

Density, which refers to the mass per unit volume of a substance, is often presented as specific gravity (the ratio of a substance's density to that of some standard substance, usually water). The densities of petroleum hydrocarbons typically found in USTs are less than 1.0 and typically range from 0.75 g/ml to as high as 0.99 g/ml. Density varies as a function of several parameters, most notably temperature, however, in most subsurface environments the temperature (and hence the density) remains relatively constant. The density of water is about 1.0 g/ml at normal groundwater temperatures. Densities of some common petroleum hydrocarbons are presented in Exhibit III-9. For a more detailed list of hydrocarbons and their properties, see Eastcott *et al*. (1988).

Petroleum hydrocarbons that are less dense than water will float; these are also referred to as light non-aqueous phase liquids, or LNAPLs. It is important to know the density of free product at a release site because water levels measured in monitor wells that also contain free product must be corrected to account for the different densities of water and the product and the thickness of the product layer. The correction procedure is demonstrated in Exhibit III-10. Density is also a required parameter for some volume estimation methods, which are discussed in Chapter IV and in the Appendix.

Viscosity

Viscosity, which describes a fluid's resistance to flow, is caused by the internal friction developed between molecules within the fluid. For most practical applications, viscosity can be considered to be a qualitative description in that the higher a fluid's viscosity, the more resistive it is to flow. Fluids with a low viscosity are often referred to as "thin", while higher viscosity fluids are described as "thick". Thinner fluids move more rapidly through the subsurface than thicker fluids. This means that a thinner petroleum product (*i.e.*, gasoline) is generally more easily recovered from the subsurface and leaves a lower residual saturation than a thicker petroleum product (*e.g.*, fuel oil). Viscosity is inversely proportional to temperature: As the temperature of the fluid increases, the viscosity decreases. The efficiency of free product recovery may be reduced at sites in northern areas if temperatures in the shallow subsurface decrease significantly during the winter months. The viscosity of free product in the subsurface environment typically changes over time, becoming thicker as the thinner, more volatile components evaporate and dissolve from the liquid hydrocarbon mass.

Three different terms are commonly used to describe viscosity: *absolute*, *dynamic*, and *kinematic*. Absolute and dynamic are synonymous terms and are typically reported in units of centipoise (cP). Kinematic viscosity, which is equal to dynamic (or absolute) viscosity divided by density, is typically reported in units of centistokes (cSt). Because viscosity is relative, the term selected for use when comparing viscosities for various petroleum hydrocarbons, does not matter as long as it is the same for all the products being compared. If a flow equation is being solved, be sure to use a term that expressed in units which are consistent with the equation.

Absolute (or dynamic) viscosities of common petroleum hydrocarbons are presented in Exhibit III-9.

Exhibit III-9

Density And Dynamic Viscosity Of Selected Fluids

Fluid	Density, r (g/ml)	Dynamic (Absolute) Viscosity, m (centipoise, cP)
Water	0.998	1.14
Automotive gasoline	0.729	0.62
Automotive diesel fuel	0.827	2.70
Kerosene	0.839	2.30
No. 5 jet fuel	0.844	-
No. 2 fuel oil	0.866	-
No. 4 fuel oil	0.904	47.20
No. 5 fuel oil	0.923	215.00
No. 6 fuel oil or Bunker C	0.974	-
Norman Wells crude	0.832	5.05
Avalon crude	0.839	11.40
Alberta crude	0.840	6.43
Transmountain Blend crude	0.855	10.50
Bow River Blend crude	0.893	33.70
Prudhoe Bay crude	0.905	68.40
Atkinson crude	0.911	57.30
LaRosa crude	0.914	180.00

Notes: all measurements at 15°C.
g/ml = grams per milliliter
C = Celsius

Source: API, 1996. A Guide to the Assessment and Remediation of Petroleum Releases, 3rd edition. API Publication 1628, Washington, DC. Reprinted courtesy of the American Petroleum Institute.

Exhibit III-10

Correction To Compute Hydraulic Head In Wells Containing Free Product

Equation: To obtain a corrected hydraulic head value when free product (liquid hydrocarbon) is present in a well:

$$h_c = h_m + \left(H_o \frac{r_o}{r_w} \right)$$

where:

h_c	=	hydraulic head corrected (ft)
h_m	=	measured elevation of hydrocarbon-water interface (ft)
H_o	=	thickness of hydrocarbon layer (ft)
r_o	=	hydrocarbon density (g/ml)
r_w	=	water density (g/ml); usually assumed = 1.0

Example: The distance from the well head to the hydrocarbon-air interface is 15.00 feet. The hydrocarbon-water interface is measured at 19.75 feet. The elevation of the top of the well head is 100.00 feet above sea level. The density of the hydrocarbon is 0.73.

What is the hydraulic head in this well?

Solution: The elevation of the air/hydrocarbon interface is 85 feet above sea level (100.00 feet - 15.00 feet). The elevation of the hydrocarbon-water interface is 80.25 feet above sea level. The hydrocarbon thickness is 4.75 feet (19.75 feet - 15.00 feet). Substituting the appropriate values into the equation:

$$h_c = 80.25\ ft + 4.75\ ft \times \frac{0.73\ g/ml}{1.0\ g/ml}$$

$$= 83.72\ ft$$

Note that the hydraulic head elevation (83.72 feet) is significantly different from the measured hydrocarbon-water interface (80.25) and from the measured air-hydrocarbon interface (85.00 feet). Groundwater elevations based on uncorrected measurements are incorrect and flow directions should not be determined using these values. Because the flow directions are incorrect, a recovery system designed based on them would likely be inefficient or even ineffective.

Interfacial Tension

The characteristics of free hydrocarbon movement are largely determined by interfacial tension that exists at the interface between immiscible fluids (*e.g.*, hydrocarbon, air, and water). Interfacial tension causes a liquid to rise in a capillary tube (or porous medium) and form a meniscus. The height of the capillary rise is inversely proportional to the radius of the tube (or pore spaces), which explains why the capillary rise is greater in fine-grained porous media than in coarse-grained material. In general, higher surface tensions result in higher capillary pressure, which may produce higher residual saturation (Mercer and Cohen, 1990). The interfacial tension between a liquid and its own vapor is called surface tension.

Interfacial tension is the primary factor controlling wettability. The greater the interfacial tension, the greater the stability of the interface between the two fluids. The interfacial tension for completely miscible liquids is 0 dyne cm^{-1}. Water (at 25°C) has a surface tension of 72 dyne cm^{-1}. Values of interfacial tension for petroleum hydrocarbon-water systems fall between these two extremes (Mercer and Cohen, 1990). Interfacial tension decreases with increasing temperature and may be affected by pH, surface-active agents (surfactants), and gas in solution (Schowalter, 1979). Some of the theoretical methods for estimating free product volume in the subsurface and some multiphase flow models require values of interfacial tension as input. Obtaining accurate values is difficult for a couple of reasons. First, measurement of interfacial tension in the field is generally not practical. Second, although values for some petroleum hydrocarbons may be obtained from the literature, these values tend to be for pure compounds under ideal conditions and may not be representative of free product plumes in the subsurface environment.

Properties Of Fluids And Geologic Media

The movement of free product in the subsurface also depends upon several factors which are functions of properties of both the fluid and the geologic media. These factors are capillary pressure, relative permeability, wettability, saturation, and residual saturation. Although all of these factors are interrelated, the most important are capillary pressure and relative permeability. Exhibit III-11 summarizes the most significant properties of both the fluid and the geologic media and illustrates how these properties relate to free product recovery.

EXHIBIT III-11

Functional Characteristics Of
Properties Dependent On Both The Fluid
And The Geologic Media

Property	Significance
Capillary Pressure	Capillary forces restrict the movement of free product--movement tends to occur through pathways where capillary pressures are low, as in coarser-grained media. Capillary pressure is inversely related to saturation. It is not practical (or necessary) to measure capillary pressure in the field.
Relative Permeability	Relative permeability is a function of saturation and also controls the mobility of liquids in a porous medium. Relative permeability and saturation are directly proportional. In media with two liquids present, the permeability of the media is reduced for each liquid due to the presence of the other liquid.
Wettability	Most geologic materials are preferentially wet by water as opposed to free product (or air)--this means that water, rather than free product will be more mobile.
Saturation	Saturation controls the mobility of liquids (water and free product) through a porous medium--for a liquid to be mobile, the liquid phase must be continuous and the media must be at least partially saturated. Saturation levels are also used to determine the volumes of free and residual product.
Residual Saturation	Liquids drain from a porous medium until a certain minimum saturation level is reached (for free product this is “residual saturation”) and flow ceases.

Capillary Pressure

Capillary pressure is the difference in pressure observed between two phases (*e.g.*, hydrocarbon liquid and water) that occupy the same pore space. As the result of interfacial tension, the boundary between two immiscible phases is a curved surface, or interface. Capillary pressure is the change in pressure across this curved interface. In the vadose zone capillary pressure is negative (*i.e.*, less than atmospheric) and is referred to as suction or tension. Capillary pressures are larger in fine-grained media (*e.g.*, silt, clay)

than in coarse-grained media (*e.g.*, gravel). The capillary fringe above the water table is a familiar consequence of capillary pressure. Because capillary pressure resistance is inversely proportional to pore size, the height of the capillary fringe is greater in finer grained media.

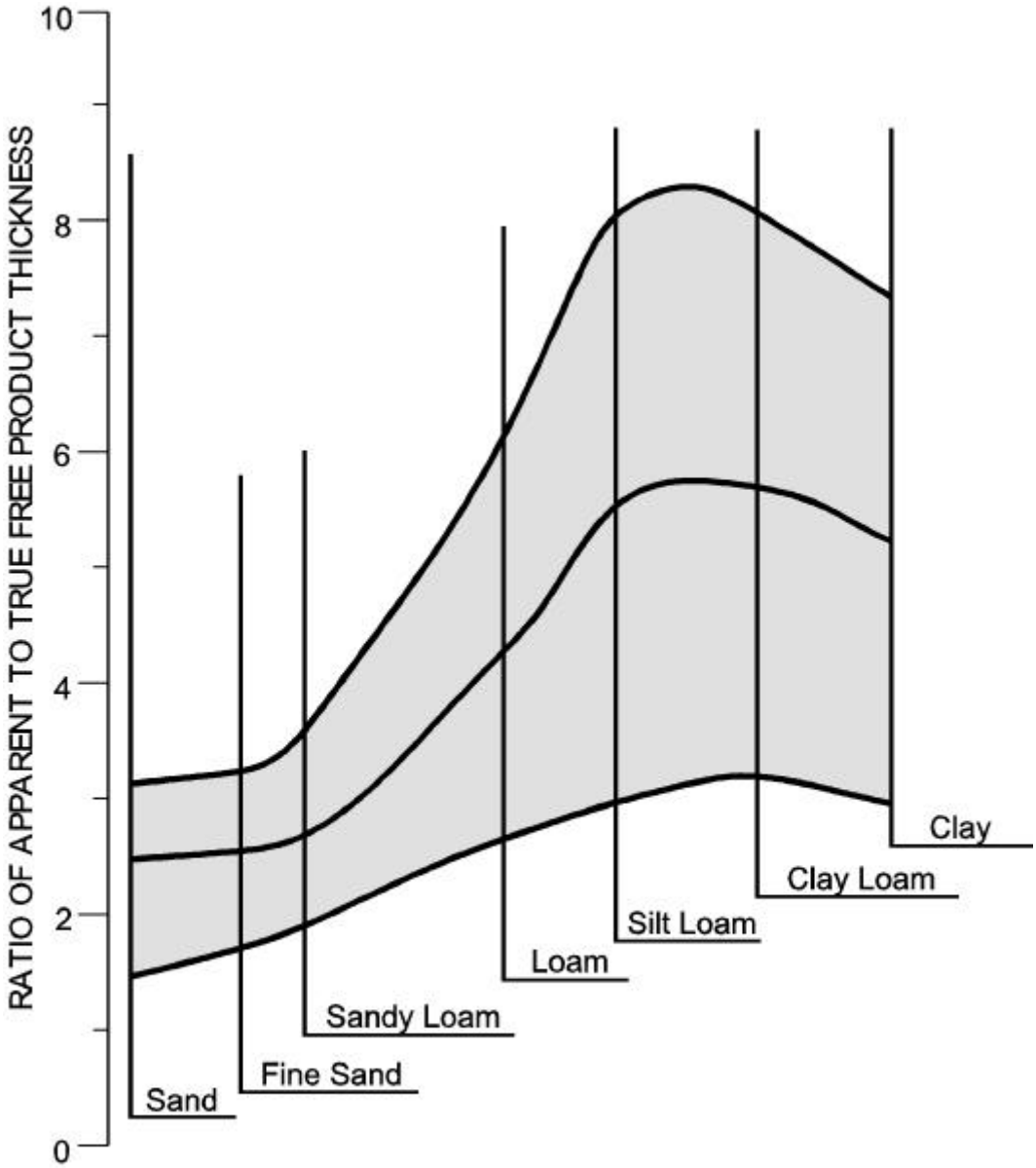
The distribution and accumulation of free product in the subsurface is influenced by capillary pressure. Soil water content and the size and orientation of pore spaces affect the penetration of free product in the vadose zone. Penetration of free product into the subsurface is enhanced by dry soil conditions and facilitated by inclined, relatively permeable pathways such as those provided by secondary permeability features (*e.g.*, fractures, root holes, and bedding plane laminations). Upon reaching the capillary fringe, resistance to downward movement will be increased and hydrocarbons will spread laterally and accumulate above the saturated media. This accumulation is sometimes referred to as a "lens" or "pancake". As long as there is a sufficient supply of hydrocarbons from above, the lens thickness and downward pressure will continue to increase. Eventually, the petroleum product (the nonwetting fluid) will begin to displace water (the wetting fluid) and enter the largest pores. The pressure required for this to occur is referred to as the "threshold entry pressure" (Schwille, 1988; Cary *et al.*, 1991).

Similarly, in the saturated zone, hydrocarbons will tend to spread laterally over fine-grained capillary barriers and move through fractures and coarser media wherever possible. The thickness or height of a hydrocarbon column required to develop sufficient hydrocarbon pressure head to exceed capillary force resistance is known as the critical hydrocarbon thickness (or height). Because capillary forces can restrict the migration of free product into water-saturated media, fine-grained layers can act as capillary barriers. That is, before free product can penetrate a water-saturated porous medium, the hydrocarbon pressure head must exceed the resistance of the capillary forces (Schwille, 1988). In heterogeneous media, free product tends to move through pathways where capillary effects are weak, such as lenses of sand and gravel or large fractures.

Although capillary pressure is not measured in the field (it can be measured in the laboratory or estimated from grain size data [Mishra *et al*., 1989]), the effects of capillary pressure should be considered in the analysis of field data. A commonly measured field parameter is the thickness of product in a well, however, this thickness is usually much greater than the true thickness of free product in the aquifer. This exaggeration is most pronounced in media with strong capillary effects (*e.g.*, fine grained silts and clays) and least pronounced in media with weak capillary effects (*e.g.*, sands and gravels). Exhibit III-12 illustrates this effect, however, the exhibit is not intended to be used to estimate the amount of free product at a particular site. This effect obviously is of great practical significance in the design of a free product recovery system. For example, thick oil accumulations in monitor wells may be caused by either significant amounts of free product or small amounts of free product in fine grained media. A conventional recovery system (*e.g.*, skimmer) may be appropriate in coarser-grained media with thick

Exhibit III-12

Ratio Of Apparent To True Free Product Thickness
Measured In A Monitor Well For Various Soil Types



Source: EPA, 1990

accumulations of free product. In the case of thinner accumulations in finer-grained media, a vacuum-enhanced recovery system, rather than a conventional recovery system, may be required.

Relative Permeability

The effectiveness of a recovery system to collect free product depends upon the mobility of the free product through the geologic media. Mobility is strongly controlled by the relative permeability of the petroleum hydrocarbons and water, which in turn is dependent upon saturation. Relative permeability is the ratio of the effective permeability of a fluid at a specified saturation to the intrinsic permeability of the medium at 100-percent saturation (Mercer and Cohen, 1990). The relative permeability of a particular geologic media that is completely saturated with a particular fluid is equal to the intrinsic permeability. When more than one fluid (*i.e.*, air, water, petroleum hydrocarbon) exists in a porous medium, the fluids compete for pore space thereby reducing the relative permeability of the media and the mobility of the fluid. This reduction can be quantified by multiplying the intrinsic permeability of the geologic media by the relative permeability. As with saturation, the mobility of each fluid phase present varies from zero (0 percent saturation) to one (100 percent saturation).

An example of relative permeability curves for a water-hydrocarbon system is shown in Exhibit III-13. The curves representing water saturation and hydrocarbon saturation are contrary to one another and divide the figure into three flow zones. Zone I, where hydrocarbon saturations are relatively high, is dominated by hydrocarbon flow. Water saturations are relatively high in Zone III, and water flow is dominant. Mixed flow characterizes Zone II. Refer to the exhibit explanation for more details.

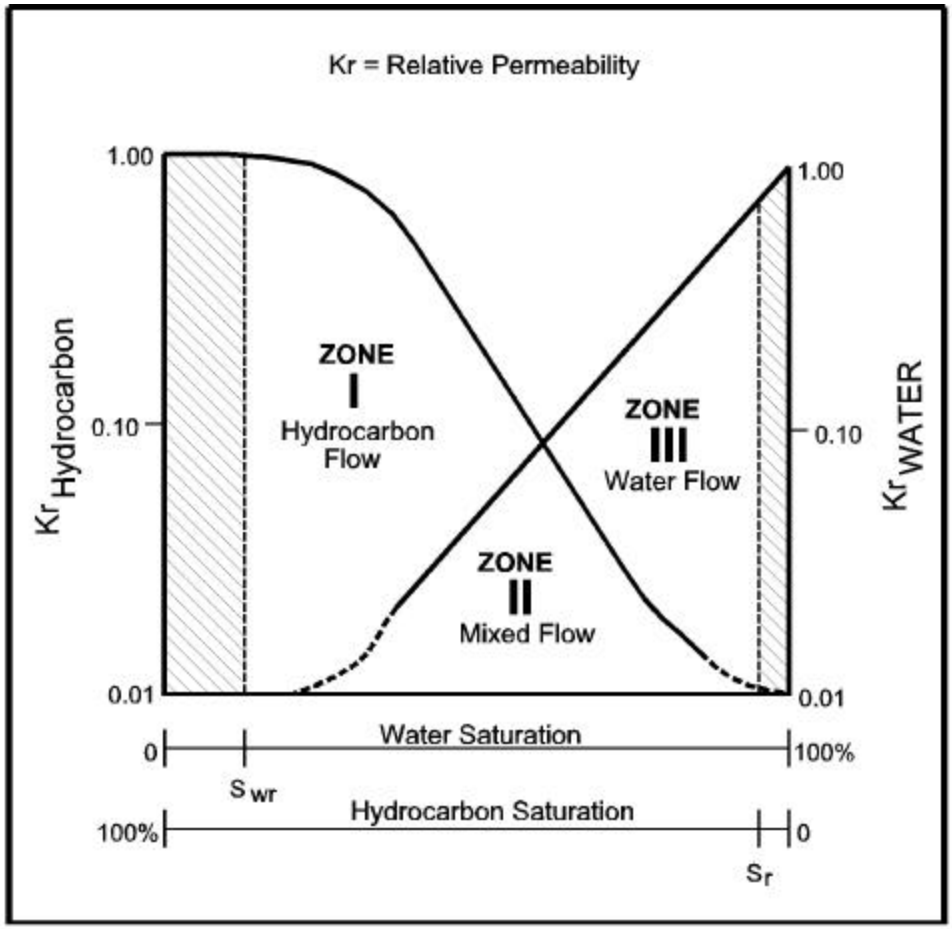
Because of the difficulties associated with laboratory and field measurement of relative permeability, alternative theoretical approaches can be utilized to estimate this function from the more easily measured capillary pressure data (Mualem, 1976; Lenhard and Parker, 1987; Luckner *et al.*, 1989; and Busby *et al*., 1995). Relative permeability relationships can be estimated from grain size data for unconsolidated materials (Mishra *et al*., 1989).

Wettability

Wettability, which depends on interfacial tension, refers to the preferential spreading of one fluid over solid surfaces in a two-fluid system (Mercer and Cohen, 1990). Because of the dependence on interfacial tension, the size of the pore spaces in a geologic medium strongly influences which fluid is the wetting fluid and which fluid is

Exhibit III-13

Hypothetical Relative Permeability Curves
For Water And A Liquid Hydrocarbon In A Porous Medium



ZONE	EXPLANATION
I	Liquid hydrocarbon occurs as a potentially mobile, continuous phase and saturation is high. Water is restricted to small pores. The relative permeability of water is very low or zero. Such conditions may be observed within large mobile product accumulations.
II	Both liquid hydrocarbon and water occur as continuous phases, but generally they do not necessarily share the same pore spaces. However, the relative permeability of each fluid is greatly reduced by the saturation of the other fluid. Such conditions may be representative of zones of smaller mobile product accumulations at the water table.
III	Liquid hydrocarbon is discontinuous and trapped as residual in isolated pores. Flow is almost exclusively the movement of water, not LNAPL. Examples of such conditions may be found within zones of residual LNAPL retained below the water table.

Source: Newell et. al., 1995

the nonwetting fluid. The dominant adhesive force between the wetting fluid and media solid surfaces causes porous media to draw in the wetting fluid (typically water) and repel the nonwetting fluid (typically hydrocarbon or air) (Bear, 1972). Liquids (hydrocarbon or water), rather than air, preferentially wet solid surfaces in the vadose zone. In the saturated zone, water will generally be the wetting fluid and displace LNAPL (Newell, *et al*., 1995). Whereas the wetting fluid (usually water in a hydrocarbon-water system) tends to coat solid surfaces and occupy smaller openings in porous media, the nonwetting fluid tends to be constricted to the largest openings (*i.e.*, fractures and relatively large pore spaces). When a formerly saturated porous media drains, a thin film of adsorbed wetting fluid will always remain on the solid.

The factors affecting wettability relations in immiscible fluid systems include mineralogy of the geologic media, the chemistry of the groundwater and the petroleum hydrocarbon, the presence of organic matter or surfactants, and the saturation history of the media. Sometimes, such factors can lead to the preferential wetting of only a portion of the total surface area; this is called fractional wettability. With the exception of soil containing a high percentage of organic matter (*e.g*., coal, humus, peat), most geologic media are strongly water-wet if not contaminated by NAPL (Mercer and Cohen, 1990). This means that free product will be less mobile and generally leave a higher residual saturation in the soil, than will water.

Anderson (1986a, 1986b, 1986c, 1987a, 1987b, and 1987c) prepared an extensive literature review on wettability, its measurement, and its effects on relative permeability, capillary pressure, residual hydrocarbon saturation, and enhanced hydrocarbon recovery.

Saturation

The level of saturation possible in a subsurface media has several implications for recovering free product. First, it controls the mobility of fluids; second, it defines the volumetric distribution of petroleum hydrocarbons (discussed in Chapter IV); and third, it is a function of other properties (*e.g*., capillary pressure, relative permeability). The mobility of a particular phase is reduced with decreasing saturation until flow ceases to occur. Saturation of a porous medium may be defined as the relative fraction of total pore space containing a particular fluid (Newell *et al*., 1995). The saturation level for each of the fluids ranges between zero (the fluid is not present in the porespace and saturation is 0 percent) and one (the fluid completely occupies the porespace and saturation is 100 percent). Of course, a given pore space can only be filled to a maximum of 100 percent, and the proportions of each phase saturation must sum to 1 (or 100 percent saturation).

The mobility of a liquid through a porous medium is a function of the saturation of the porous medium with respect to that liquid. In order for it to flow through a porous medium, a liquid must be continuous through the area where flow occurs. As liquid

drains from the media, the liquid phase becomes discontinuous. The point at which the saturation level for a continuous liquid phase other than water (*i.e.*, petroleum hydrocarbon) becomes discontinuous (and hence immobile) is known as the residual saturation (Newell, *et. al.*, 1995). The corresponding saturation level for water is called the irreducible water saturation. At these low saturations, capillary pressures are very high.

The wetting and draining cycles of a porous media differ from one another as the result of differences in saturation, wettability, and capillary pressure. During drainage, the larger pores drain the wetting fluid (*i.e.*, water) quickly while the smaller pores drain slowly, if at all. During wetting, the smaller pores fill first, and the larger pores fill last. The consequence of this phenomenon is that the vadose zone will retain less residual petroleum hydrocarbon than the saturated zone.

Residual Saturation

Residual saturation refers to the saturation level at which a continuous mass of petroleum hydrocarbons (NAPL) becomes discontinuous and immobilized by capillary forces (Newell, *et al.*, 1995). Residual saturation is important to free product recovery, because it represents the amount of petroleum that cannot be recovered by pumping or gravity drainage. Following a release of petroleum hydrocarbons into the subsurface, the hydrocarbon mass seeps downward into the unsaturated zone. If the volume of the release is enough to sufficiently saturate the soil, the leading edge of the hydrocarbon mass continues to move deeper into the subsurface. Behind and above the leading edge, a significant portion of the hydrocarbon mass is retained in pore spaces by capillary forces. The amount of hydrocarbon that is retained against the force of gravity is referred to as the residual saturation. The corresponding term for water is irreducible water saturation.

Generally, the finer-grained the soil, the higher the residual saturation. Residual saturation for the wetting fluid is conceptually different from that for the nonwetting fluid. When the wetting fluid (*i.e.*, water) drains from a porous media, even at the level of the irreducible water saturation, there is a thin, continuous layer of water occupying the smallest pores and coating the grains of the media. As the nonwetting fluid (*i.e.*, petroleum hydrocarbon or NAPL) drains from a porous media, the pores drain incompletely because of the residual water that remains in the smallest pores. The result is that discontinuous blobs of immobile petroleum hydrocarbon remain in the soil at the level of the residual saturation. More viscous fluids tend to have higher residual saturations than less viscous fluids. Fluids that are more dense for a given viscosity drain to a greater degree under the influence of gravity than do less dense fluids. Fluids that have high interfacial tension also tend exhibit higher capillary pressure, which may result in higher residual saturation. Although field-scale values for residual saturation are difficult to either measure or accurately estimate, in general, residual saturation levels

tend to be much higher in the saturated zone (0.15 to 0.50) than in the unsaturated zone (0.10 to 0.20) (Mercer and Cohen, 1990).

Because residual hydrocarbons are both tightly bound and discontinuous in pore spaces, they are essentially immobile and, therefore, not amenable to collection by standard free product recovery methods. However, the residual phase often represents a potential long-term source for continued groundwater contamination. Although some portion of the residual mass will be slowly diminished (*i.e.*, will naturally attenuate) over time as the result of dissolution, volatilization, and biodegradation, more aggressive remedial action may be required to mitigate this source within a reasonable amount of time.

Groundwater Flow Conditions

The subsurface can be divided into two zones based on water content: The unsaturated zone and the saturated zone. The movement of petroleum hydrocarbons in the subsurface is fundamentally different in the unsaturated and saturated zones. The boundary between these two zones is commonly accepted to be the water table, which is the surface where water pressure equals atmospheric pressure. Below the water table, in the saturated zone, all pore and void spaces are filled with water and water pressure is greater than atmospheric pressure. Water pressures above the water table, in the unsaturated zone, are less than atmospheric pressure, and the water may be considered to be under tension or suction. Directly above the water table is a relatively thin zone—the capillary fringe—that is saturated with water but the water pressure is less than atmospheric pressure. The capillary fringe is thicker in fine-grained media and thinner in coarse-grained media. Above the capillary fringe in the unsaturated zone, voids and pore spaces are filled primarily with air and varying amounts of water as either liquid or vapor.

Petroleum hydrocarbon migration is strongly affected by essentially the same factors that govern groundwater flow. In general, liquid hydrocarbons move in the same direction as groundwater but at a reduced rate because of the higher viscosity of the hydrocarbons (except for gasoline) and the lower relative permeability of the porous medium. Important characteristics of the groundwater flow system that influence free product are depth to water and hydraulic head variations across the site. Direct measurements of depth to water and water table elevations/head are necessary to design or evaluate most free product recovery systems. Exhibit III-14 summarizes the characteristics of the groundwater flow system that are most relevant to free product recovery.

EXHIBIT III-14

Functional Characteristics Of
Groundwater Conditions

Property	Significance
Depth to Water Table	Mass of free product required to reach the water table increases with depth; options to recover free product become more limited (*e.g.*, depth must be less than 20 feet for trenching); costs to recover free product increase with depth.
Groundwater Elevation	Groundwater elevation (hydraulic head) determines hydraulic gradient and direction of groundwater flow and free product migration—presence of free product requires that measured groundwater elevations be corrected to account for the density and thickness of the free product layer (see Exhibit III-10).

Depth To Water Table

The depth to water table is an important factor that affects how the free product migrates and how its recovery should be approached. Except for very deep water tables, the depth to the water table can be determined through relatively inexpensive borings or monitoring wells (or well points). The depth to water table will indicate the potential for petroleum hydrocarbons to reach the water table, where the free product can then be collected in wells or trenches. All other factors being equal, a greater depth to water table requires a greater volume of liquid petroleum hydrocarbons to reach the water table.

The depth to water table, or the top of the free product layer in a well or trench, is a critical consideration in the selection of a recovery approach and equipment specification. For example, excavation depth is constrained by equipment limitations, and excavation costs increase substantially with depth in nearly all cases. Thus, recovery systems utilizing drains or gravel-filled trenches are typically limited to sites with water tables less than 20 feet deep and preferably closer to 10 feet deep. Excavated material may be highly contaminated and require appropriate handling and disposal. In most cases where the depth to the water table is greater than 20 feet, wells must be installed.

Groundwater Elevation (Hydraulic Head)

Measurements of groundwater elevations in wells and piezometers (a well open to a narrow interval) are the basic response data that characterize the direction of groundwater flow. The basic principle of groundwater hydrology is described by Darcy's Law, which relates flow through porous media to the hydraulic gradient. Groundwater flows downgradient; that is, from areas of higher head to areas of lower head. The hydraulic gradient is the change in head per unit distance at a given point and given direction. In an unconfined aquifer, the hydraulic gradient is defined by the slope and direction of dip of the water table. A common observation at many UST sites is a groundwater mound created by the influence of the tank excavation. These excavations are typically filled with pea gravel which has a much higher permeability than the native soils at the site. As a result, tank excavations tend to accumulate and hold water, usually at a higher hydraulic head than the local water table. This can cause the formation of a localized groundwater mound that can influence the hydraulic gradient at the site, possibly inducing free product to migrate outward in all directions from the source of the release.

Because petroleum hydrocarbons have a density different from that of water, neither the measured elevation of free product nor the measured elevation of water in a well containing free product represents hydraulic head. Measured fluid elevations in monitoring wells must be corrected to determine groundwater flow directions and rates. The equation for this correction and an example calculation are presented in Exhibit III-10.

Relevance To Free Product Recovery

This chapter has presented many factors that influence the occurrence and movement of free product in the subsurface. This section presents a discussion limited to those factors that are most relevant to the recovery of the principal types of petroleum products typically stored in USTs (*i.e.*, gasolines, middle distillates, and heavy fuel oils). A summary of these factors is provided in Exhibit III-15.

The majority of petroleum hydrocarbons stored in USTs are lighter than water, which means that they float. Free product generally moves in the same direction as the flow of groundwater. This movement is strongly influenced by soil heterogeneity and anisotropy, and the design and operation of an effective free product recovery system is dependent upon accurate characterization of the hydrogeologic conditions at the site. It is extremely important to realize that the elevations of liquid surfaces in a monitoring well containing both groundwater and free product is not representative of hydraulic head at that location. The measurement must first be corrected to account for the thickness of the free product and its density. Other critical factors to consider are the total volume of the

Exhibit III-15

Most Important Factors Influencing
Free Product Recovery

Factor	Significance
Soil Heterogeneity and Anisotropy	Controls direction of free product migration and the flow of groundwater
Product Viscosity	Affects mobility, ease of recoverability, and level of residual saturation
Soil Permeability	Controls rate of free product migration and the flow of groundwater
Depth to Water Table	Coupled with volume of release, determines which remedial technologies may be effective at the site
Volume of Release	Coupled with depth to water table, determines whether free product recovery is practical or necessary

release and the depth to groundwater. If the volume of release is so small that there is no accumulation at the water table, then recovery of free product is not practical.

Gasolines are significantly less viscous than water. They can move more rapidly through geologic media than water and subsurface accumulations can be relatively easily recovered. Many of the principal components of gasoline are volatile and somewhat soluble. Because of their high mobility and vapor generation potential, recovery measures should be initiated as soon as possible after a gasoline release has been discovered. The lighter components also tend to be more soluble and groundwater supplies can easily be contaminated. Residual soil saturation is lower than for the heavier and thicker petroleum products. Older gasoline plumes will be enriched in the heavier, less volatile fractions; they may behave more like a fresh middle distillate plume. As a result of the absence of the volatile fractions, vacuum technologies will be less effective in recovering petroleum hydrocarbons due to volatilization (evaporation), but vacuum-enhancement may be effective in recovering a greater proportion of the plume than would be possible without the enhancement.

Middle distillates and heavy fuel oils are significantly more viscous than water. Their movement through the subsurface is typically slow. Although not as volatile as gasoline, vapors emanating from middle distillate plumes can create situations in which

fire, explosion, or toxicity threatens human health and safety. Because of the higher viscosity and lower volatility, residual soil saturation is higher for plumes comprised of middle distillates and heavy fuel oils than for gasoline plumes.

Recovery of free product to the maximum extent practicable is merely the first step in a typical remedial action. Regardless of what type of petroleum product was released and the characteristics of the subsurface materials, a significant portion of the total release volume will not be recoverable by any existing remedial technology. Appropriate treatment of the residual hydrocarbon mass may require application of a combination of alternative remedial technologies.

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