Introduction to Light Non-Aqueous Phase Liquids

Course Number: EN-02-102

PDH: 3

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Light Nonaqueous Phase Liquids

Light nonaqueous phase liquids (LNAPLs) have been identified by the USEPA as an issue of concern to decision makers. This course focuses on transport, fate, characterization, and remediation of LNAPLs in the environment.

INTRODUCTION

Nonaqueous phase liquids (NAPLs) are hydrocarbons that exist as a separate, immiscible phase when in contact with water and/or air. Differences in the physical and chemical properties of water and NAPL result in the formation of a physical interface between the liquids which prevents the two fluids from mixing. Nonaqueous phase liquids are typically classified as either light nonaqueous phase liquids (LNAPLs) which have densities less than that of water, or dense nonaqueous phase liquids (DNAPLs) which have densities greater than that of water. A previous issue paper developed by the Robert S. Kerr Environmental Research Laboratory reviews processes and management issues pertaining to DNAPLs (Huling and Weaver, 1991).

Light nonaqueous phase liquids affect ground-water quality at many sites across the country. The most common LNAPL-related ground-water contamination problems result from the release of petroleum products. These products are typically multicomponent organic mixtures composed of chemicals with varying degrees of water solubility. Some additives (e.g., methyl tertiary-butyl ether and alcohols) are highly soluble. Other components (e.g., benzene, toluene, ethylbenzene, and xylenes) are slightly soluble. Many components (e.g., n-dodecane and n-heptane) have relatively low water solubility under ideal conditions. Physical and chemical properties which affect transport and fate of selected LNAPL compounds and refined petroleum products are presented in Table 1. In general, LNAPLs represent potential long-term sources for continued ground-water contamination at many sites.

LNAPL TRANSPORT THROUGH POROUS MEDIA

General Conceptual Model

Movement of LNAPLs in the subsurface is controlled by several processes described in the following simplified scenario (Figure 1). Upon release to the environment, NAPL (i.e., LNAPL or DNAPL) will migrate downward under the force of gravity. If a small volume of NAPL is released to the subsurface, it will move through the unsaturated zone where a fraction of the hydrocarbon will be retained by capillary forces as residual globules in the soil pores, thereby depleting the contiguous NAPL mass until movement ceases. If sufficient LNAPL is released, it will migrate until it encounters a physical barrier (e.g., low permeability strata) or is affected by buoyancy forces near the water table. Once the capillary fringe is reached, the LNAPL may move laterally as a continuous, free-phase layer along the upper boundary of the water-saturated zone due to gravity and capillary forces.

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Table 1. Representative properties of selected LNAPL chemicals commonly found at Superfund sites (U.S.EPA, 1990), water, and selected petroleum products (Lyman and Noonan, 1990)

Chemical	Density† (g/cm³)	Dynamic† Viscosity (cp)	Water† Solubility (mg/l)	Vapor† Pressure (mm Hg)	Henry's Law† Constant (atm-m³/mol)
Methyl Ethyl Ketone	0.805	0.40	2.68 E+05	71.2	2.74 E-05 [2]
4-Methyl-2-Pentanone	0.8017	0.5848	1.9 E+04	16	1.55 E-04 [2]
Tetrahydrofuran	0.8892	0.55	3 E+05 [1]	45.6 [2]	1.1 E-04 [2]
Benzene	0.8765	0.6468	1.78 E+03	76	5.43 E-03 [1]
Ethyl Benzene	0.867	0.678	1.52 E+02	7	7.9 E-03 [1]
Styrene	0.9060	0.751	3 E+02	5	2.28 E-03
Toluene	0.8669	0.58	5.15 E+02	22	6.61 E-03 [1]
m-Xylene	0.8642 [1]	0.608	2 E+02	9	6.91 E-03 [1]
o-Xylene	0.880 [1]	0.802	1.7 E+02	7	4.94 E-03 [1]
p-Xylene	0.8610 [1]	0.635	1.98 E+02 [1]	9	7.01 E-03 [1]
Water	0.998 [6]	1.14 [6]	----	----	----
Common Petroleum Products					
Automotive gasoline	0.72-0.76 [3]	0.36-0.49 [3]	----	----	----
#2 Fuel Oil	0.87-0.95	1.15-1.97 [5]	----	----	----
#6 Fuel Oil	0.87-0.95	14.5-493.5 [4]	----	----	----
Jet Fuel (JP-4)	~0.75	~0.83 [5]	----	----	----
Mineral Base Crankcase Oil	0.84-0.96 [6]	~275 [4]	----	----	----

† Values are given at 20°C unless noted.
[1] Value is at 25°C.
[2] Value is at unknown temperature but is assumed to be 20°- 30°C.
[3] Value is at 15.6°C.
[4] Value is at 38°C.
[5] Value is at 21°C.
[6] Value is at 15°C.

Although principal migration may be in the direction of the maximum decrease in water-table elevation, some migration may occur initially in other directions. A large continuous-phase LNAPL mass may hydrostatically depress the capillary fringe and water table. Once the source is removed, mounded LNAPL migrates laterally, LNAPL hydrostatic pressure is removed, and the water table eventually rebounds. Infiltrating precipitation and passing ground water in contact with residual or mobile LNAPL will dissolve soluble components and form an aqueous-phase contaminant plume. In addition, volatilization may result in further spreading of contamination.

Contaminant Phase Distribution

LNAPL constituents may exist in any of four phases within the subsurface. The NAPL, aqueous, and gaseous phases were mentioned above. Contaminants may also partition to the solid-phase material (i.e., soil or aquifer materials). In the unsaturated zone contaminants may exist in all four phases
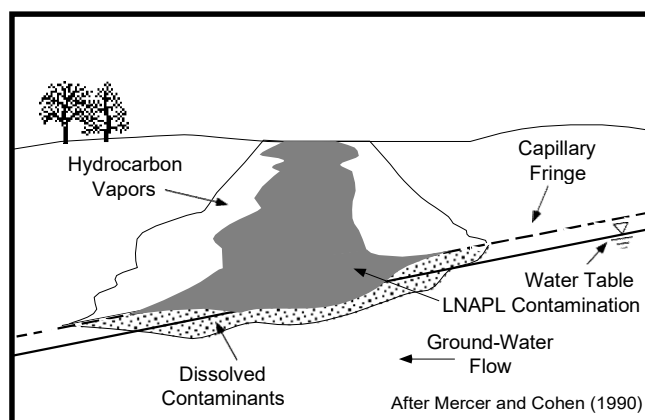
Figure 1. Simplified conceptual model for LNAPL release and migration.
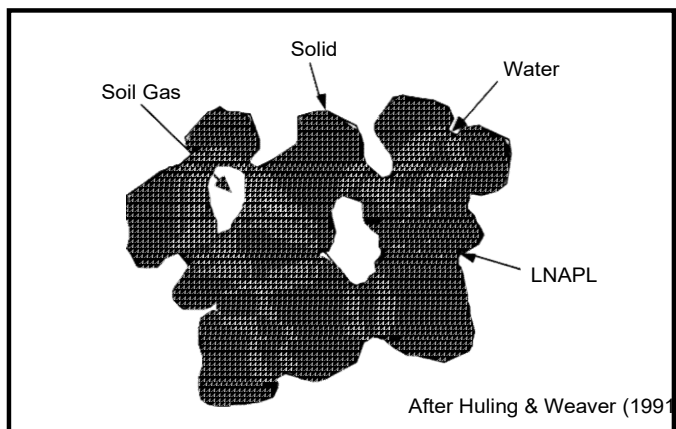
Figure 2. Contamination in the unsaturated zone may be present in the four physical states: gas, sorbed to soil materials, dissolved in water, or immiscible liquid.

Figure 3. Partitioning of LNAPL among the four phases potentially found in the unsaturated zone.

(Figure 2). In the saturated zone NAPL-related contaminants may be present in the aqueous, solid, and NAPL phases. NAPL constituents may partition, or move from one phase to another, depending on environmental conditions (Figure 3). For example, soluble components may dissolve from the NAPL into passing ground water. The same molecule may adsorb onto a solid surface, and subsequently desorb into passing ground water. The tendency for a contaminant to partition from one phase to another may be described by partition coefficients such as Henry's Law constant for partitioning between water and soil gas. These empirical coefficients are dependent on the properties of the subsurface materials and the NAPL. A clear understanding of the phase distribution of contaminants is critical to evaluating remedial decisions (Huling and Weaver, 1991). It is important to note that this distribution is not static and may vary over time due to remedial actions and natural processes.

LNAPL Transport Parameters

Characteristics of the LNAPL and subsurface materials govern transport at both the pore scale and field scale. At the pore scale, the following transport and fate parameters control LNAPL migration and distribution. At the field scale, LNAPL migration is much more difficult to predict due to such factors as complex release history and, most importantly, subsurface heterogeneity. However, the following discussion of pore-scale principles is necessary for development of conceptual models incorporating observations made at the field scale. A more detailed explanation of these concepts (Mercer and Cohen, 1990) and methods for measuring these properties (Cohen and Mercer, 1993) are available in the literature.

Density

Density is defined as the mass of a substance per unit volume. One way to express density of a fluid is the specific gravity (S.G.) which is the ratio of the mass of a given volume of substance at a specified temperature to the mass of the same volume of water at the same temperature. If a NAPL has an S.G. less than water, generally less than 1.0, it is less dense than water (i.e., LNAPL) and will float on water. If it has an S.G. greater than water, generally greater than 1.0, it is denser than water (DNAPL). The density of most fluids
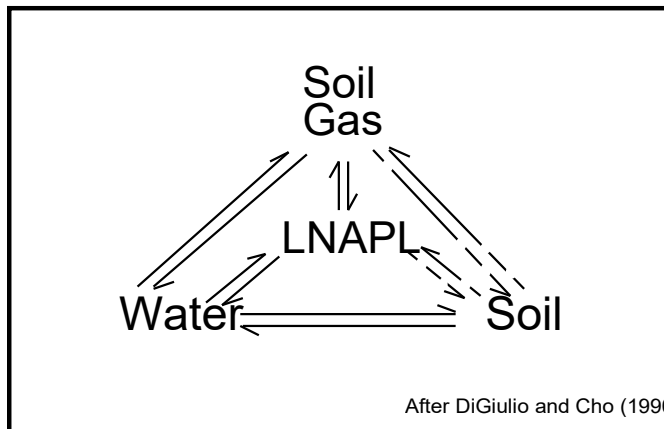
generally, decreases as temperature increases. Consequently, the density of fluids considered to be DNAPLs under normal subsurface conditions may decrease during remedial actions which impart heat to the subsurface (e.g., Johnson and Leuschner, 1992). A decrease in density of DNAPLs which have densities near that of water (e.g., some coal tar residues) may result in sufficient reduction to temporarily convert the DNAPL to an LNAPL. Density not only affects the buoyancy of a liquid but also the subsurface mobility. The hydraulic conductivity of a porous medium is a function of the density and viscosity of the liquid. As the density increases, the hydraulic conductivity with respect to the liquid also increases.

Viscosity

Viscosity is the resistance of a fluid to flow. Dynamic, or absolute, viscosity is expressed in units of mass per unit length per unit time. This resistance is also temperature dependent. The viscosity of most fluids will decrease as the temperature increases. The lower the viscosity, the less energy required for a fluid to flow in a porous medium. The hydraulic conductivity increases as the fluid viscosity decreases.

Interfacial Tension

When two liquids, which are immiscible, are in contact, an interfacial energy exists between the fluids, resulting in a physical interface. Interfacial tension is the surface energy at the interface that results from differences in the forces of molecular attraction within the fluids and at the interface (Bear, 1972). It is expressed in units of energy per unit area. In general, the greater the interfacial tension, the greater the stability of the interface between the liquids. Interfacial tension is affected by temperature (Davis and Lien, 1993), changes in pH and the presence of surfactants and dissolved gases. It is an important factor affecting wettability (Mercer and Cohen, 1990).

Wettability

Wettability is generally defined as the overall tendency of one fluid to spread on or adhere to a solid surface (i.e.,

preferentially coat) in the presence of another fluid with which it is immiscible. This concept has been used to describe fluid distribution at the pore scale. In a multiphase system, the wetting fluid will preferentially coat (wet) the solid surfaces and tend to occupy smaller pore spaces. The non-wetting fluid will generally be restricted to the largest interconnected pore spaces. In the vadose zone, where air, water, and LNAPL are present, liquids, usually water, preferentially wet solid surfaces. However, under conditions where only LNAPL and air are present, LNAPL will preferentially coat the mineral surfaces and displace air from pore spaces. In the saturated zone, with only water and LNAPL present, water will generally be the wetting fluid and will displace LNAPL from pore spaces. Wettability is affected by such factors as NAPL and aqueous-phase composition, presence of organic matter, surfactants, mineralogy, and saturation history of the porous medium (Mercer and Cohen, 1990). Some researchers have concluded that wetting of subsurface media by NAPL may be heterogeneous due to subsurface variability and the many factors that influence wettability (Anderson, 1986). In summary, wettability is a qualitative indicator useful to understand the general behavior of NAPLs in multiphase systems and has been used extensively in the petroleum industry (Anderson, 1986). Actual wettability measurements of NAPLs on solid surfaces are usually reported for flat, homogeneous material which is unrepresentative of complex aquifer and soil material. Refined petroleum products typically found at Superfund sites can generally be considered the non-wetting fluid in water: LNAPL systems, and the wetting fluid in LNAPL: air systems.

Capillary Pressure

Capillary pressure is the pressure difference across the interface between the wetting and non-wetting phases and is often expressed as the height of an equivalent water column. It determines the size of the pores in which an interface can exist. It is a measure of the relative attraction of the molecules of a liquid (cohesion) for each other and for a solid surface (adhesion). Capillary pressure is represented by the tendency of the porous medium to attract the wetting fluid and repel the non-wetting fluid (Bear, 1972). The capillary pressure of the largest pore spaces must be exceeded before the non-wetting fluid (generally NAPL) can enter the porous medium. The minimum pressure required for the NAPL to enter the medium is termed the entry pressure.

In general, capillary pressure increases with decreasing pore size, decreasing initial moisture content, and increasing interfacial tension. Capillary conditions affect the configuration and magnitude of trapped residual NAPL. Field observations of the effects of capillary pressure include preferential LNAPL migration through coarse-grained materials (e.g., sands and gravels), rather than fine-grained materials (e.g., silts and clays). Analytical expressions describing relationships between capillary pressure and NAPL movement under hydrostatic and hydrodynamic conditions are compiled by Mercer and Cohen (1990). Although these approximate expressions do not account for complicated pore geometries and distributions present in most systems, evaluation of site conditions using such expressions may often be useful in refining the conceptual model for NAPL transport.

Although the capillary forces that hold residual NAPL in pores are relatively strong, they can be overcome to some degree by viscous forces associated with ground-water flow. However, complete mobilization of residual hydrocarbons is very difficult or impossible to achieve in most aquifers by manipulating hydraulic gradient alone (Wilson and Conrad, 1984). The required hydraulic gradients are so high for many aquifers (greater than 1 ft/ft) that no reasonable configuration of pumping and injection wells could sweep all of the residual NAPL trapped in the pores of the aquifer.

Saturation and Residual Saturation

Saturation is the relative fraction of total pore space containing a particular fluid (e.g., NAPL) in a representative volume of a porous medium. The mobility of an LNAPL is related to its saturation in the medium as described by the relative permeability function discussed below. The saturation level where a continuous NAPL becomes discontinuous and is immobilized by capillary forces is known as the residual saturation (S_r). Residual saturation of LNAPL represents a potential source for continued ground-water contamination that is tightly held in the pore spaces and not readily removed using currently available remediation technologies. The magnitude of residual saturation is affected by several factors including pore-size distribution, wetting properties of the fluids and soil solids, interfacial tension, hydraulic gradients, ratios of fluid viscosities and densities, gravity, buoyancy forces, and flow rates (Mercer and Cohen, 1990; Demond and Roberts, 1991). Due to the known heterogeneity of subsurface systems with regard to these factors, it follows that residual saturation in the subsurface is also highly variable.

Data compiled by Mercer and Cohen (1990) indicate the residual saturation of most NAPLs in these studies ranged from about 10% to 20% in the unsaturated zone and about 15% to 50% of the total pore volume in the saturated zone. The potential for higher retention of NAPLs in the saturated zone than in the unsaturated zone is due to several factors including: 1) potential existence of the NAPL as the wetting fluid relative to air in the unsaturated zone resulting in NAPL spreading to adjacent pores with residual held in small pore spaces, 2) existence of the NAPL as the non-wetting fluid in the saturated zone resulting in NAPL present as blobs in larger pore spaces, and 3) the relatively high fluid density ratio of NAPL to air in the vadose zone resulting in drainage (Anderson, 1988).

Relative Permeability

Relative permeability is the ratio of the effective permeability of the medium to a fluid at a specified saturation and the permeability of the medium to the fluid at 100% saturation. Values for relative permeability range between 0 and 1. A simplified relative permeability diagram for a hypothetical LNAPL/water system (Figure 4) illustrates how two fluids interfere with each other to reduce mobility. Similar, yet more complex relationships exist in the unsaturated zone where three fluids (air, water, and NAPL) may be present (van Dam, 1967; Ferrand et al., 1989). At most points on the curves, the relative permeabilities of NAPL and water do not sum to one because interference reduces the overall mobility of both fluids in the porous medium. The curves also illustrate that a minimum saturation must be attained before the permeability to a fluid is non-zero (Schwille, 1988). The minimum saturation for the wetting fluid has been termed irreducible saturation (S_{ir}) and for the non-wetting fluid, generally NAPL,

has been termed residual saturation. It should be noted that the example described above is highly simplified for purposes of this discussion. In reality, an infinite set of curves, bounded by main curves for drainage and imbibition, describe the relative permeability function.

Relative permeability curves (Figure 4) can be used to describe different types of multiphase flow regimes, all of which may exist at any particular site (Williams and Wilder, 1971):

Zone I: LNAPL occurs as a potentially mobile, continuous phase and saturation is high. Water is restricted to small pores. The relative permeability of water is low. Such conditions may be observed within large mobile product accumulations.

Zone II: Both LNAPL and water occur as continuous phases, but, generally, do not 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.

Zone III: LNAPL 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.
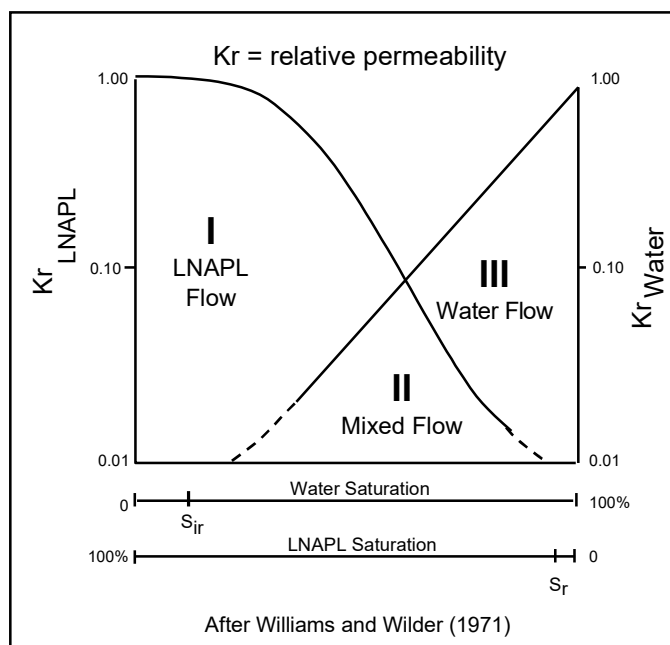
Figure 4. Hypothetical relative permeability curves for water and an LNAPL in a porous medium.

LNAPL Migration at the Field Scale

Darcy's Law

Various forms of Darcy's Law may be used to describe fluid migration in porous media under many conditions. For example, a form of Darcy's Law, including relative permeability as a function of saturation, may be used to describe LNAPL flow when LNAPL saturation is less than 100%. However, movement of LNAPL can be examined using a simple conceptual model to understand the effects of LNAPL physical properties on mobility. The one-dimensional migration of LNAPL in an LNAPL-saturated system can be represented using the following form:

$$v = - (k \, \rho \, g \, / \, \mu) \;\; (dh \, / \, dl) \qquad (1)$$

where

v = Darcy velocity (L/T)
k = intrinsic permeability (L^2)
ρ = density of NAPL (M/L^3)
g = force of gravity (L/T^2)
μ = dynamic (absolute) viscosity ($M/L*T$)
dh/dl = hydraulic gradient of NAPL mass (L/L)

Hydraulic conductivity of the medium is proportional to the density and inversely proportional to the viscosity of the LNAPL. The potential mobility of various fluids may be compared using the ratio of density to viscosity. High ratios correspond to greater potential mobility. In the subsurface, LNAPLS are subjected to biotic and abiotic (volatilization and solubilization) weathering processes which change the composition (mass fraction) of product (Johnson et al., 1990b). The weathering process may alter the overall LNAPL properties, such as increasing the viscosity. A significant change in these properties will affect the potential mobility of the LNAPL.

Field Scale Versus Pore Scale

While LNAPL migration at the pore scale can be described using some of the physical relationships presented above, migration and distribution of LNAPL at the field scale is controlled by a complex combination of release factors, soil/ aquifer properties, and LNAPL characteristics (Mercer and Cohen, 1990) including:

- volume of LNAPL released;
- release rate (e.g., one-time "slug" event vs. long-term continual discharge);
- LNAPL infiltration area at the release site;
- properties of the LNAPL (e.g., density, viscosity);
- properties of the soil/aquifer media (e.g., permeability, pore size distribution);
- fluid/porous media relationships (e.g., wettability);
- lithology and stratigraphy; and
- macro-scale features (e.g., fractures, root holes).

To illustrate how these factors can combine to control LNAPL migration, a series of conceptual models is presented below which describe a general LNAPL release scenario. These conceptual models are intended to convey several

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