Introduction to Light Non-Aqueous Phase Liquids

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PDH: 3

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Module 1: Light Nonaqueous Phase Liquids

Learning Objectives

By the end of this section, you will be able to:

- **Identify** the physical and chemical properties of LNAPLs that govern transport, fate, and phase distribution in the subsurface.
- **Evaluate** site characterization data to differentiate between mobile and residual LNAPL and calculate corrected hydraulic heads.
- **Select** appropriate remediation technologies and "treatment train" sequences based on site-specific hydrogeologic constraints.

Executive Summary: Light Nonaqueous Phase Liquids (LNAPLs) are immiscible hydrocarbons less dense than water that pose long-term contamination risks to ground water. Effective management requires a phased characterization to understand the four-phase distribution (NAPL, aqueous, gaseous, and solid) and the complex relationship between apparent and actual thickness. Successful remediation typically necessitates a treatment train approach, as single technologies rarely achieve complete removal of both mobile and residual phases.

Introduction

Nonaqueous phase liquids (NAPLs) are hydrocarbons that exist as a separate, immiscible phase when in contact with water and/or air. Differences in physical and chemical properties result in a physical interface that prevents mixing. LNAPLs have densities less than that of water, while dense nonaqueous phase liquids (DNAPLs) have densities greater than water.

The most common LNAPL-related ground-water contamination problems result from the release of petroleum products. These are typically multicomponent mixtures with varying solubilities:

- **Highly Soluble**: Additives like MTBE and alcohols.
- **Slightly Soluble**: Benzene, toluene, ethylbenzene, and xylenes (BTEX).
- **Low Solubility**: Components like n-dodecane and n-heptane.

LNAPL Transport Through Porous Media

General Conceptual Model

Movement in the subsurface is controlled by gravity and capillary forces.

- **Initial Migration**: Upon release, LNAPL migrates downward under gravity.
- **Residual Globules**: In small releases, hydrocarbon is retained by capillary forces as residual globules, eventually ceasing movement.
- **Lateral Migration**: If sufficient volume is released, LNAPL reaches the water table and moves laterally as a continuous, free-phase layer.

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/cm*^{3})	*Dynamic† Viscosity* (*cp*)	*Water† Solubility* (*mg/l*)	*Vapor† Pressure* (*mm Hg*)	*Henry's Law† Constant* (*atm-m*^{3}*/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.

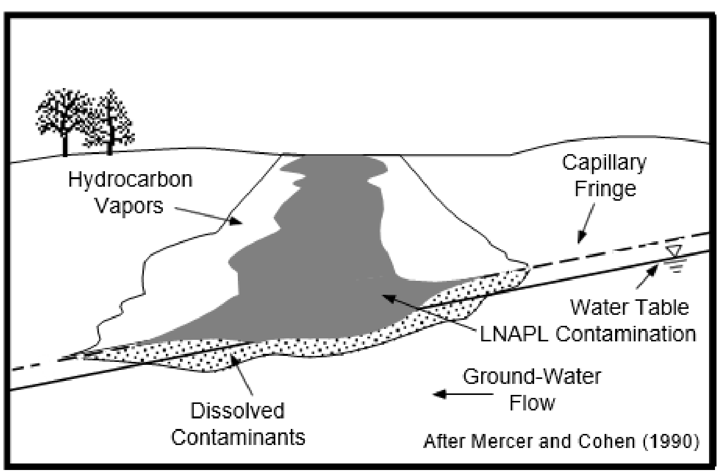

Figure 1. Simplified conceptual model for LNAPL release and migration.

Contaminant Phase Distribution

LNAPL constituents exist in four phases:

1. **NAPL**: Immiscible liquid.
2. **Aqueous**: Dissolved in water.
3. **Gaseous**: Volatilized in soil gas.
4. **Solid**: Partitioned/sorbed to soil or aquifer materials.

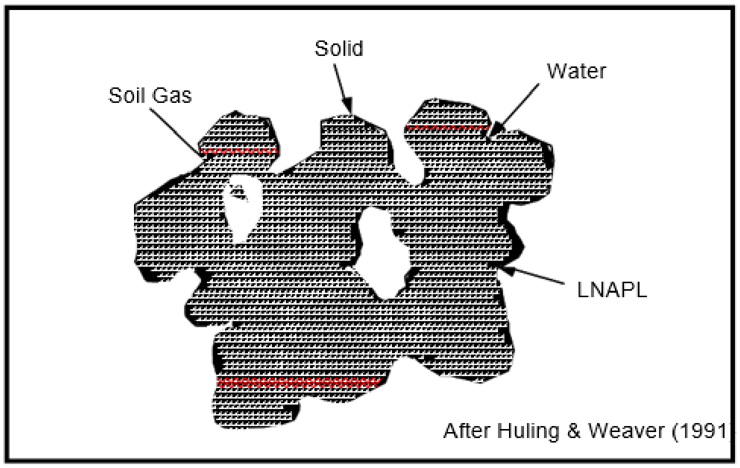

Figure 2. Contamination in the unsaturated zone may be present in four physical states: gas, sorbed to soil materials, dissolved in water, or immiscible liquid.

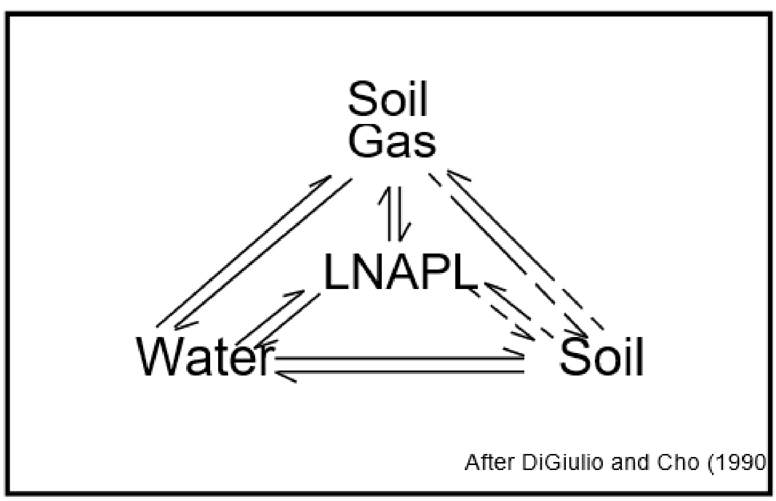

Figure 3. Partitioning of LNAPL among the four phases potentially found in the unsaturated zone.

LNAPL Transport Parameters

Density

Density is the mass per unit volume, often expressed as specific gravity (S.G.).

- **Buoyancy**: Fluids with S.G. < 1.0 float on water.
- **Mobility**: Density affects hydraulic conductivity; as density increases, conductivity increases.

Viscosity

Viscosity is the resistance of a fluid to flow.

- **Temperature Effect**: Viscosity decreases as temperature increases.
- **Flow Efficiency**: Lower viscosity requires less energy for a fluid to flow.

Interfacial Tension

This is the surface energy at the interface resulting from molecular attraction differences. Higher interfacial tension generally leads to greater interface stability.

Wettability

The tendency of one fluid to spread on or adhere to a solid surface in the presence of an immiscible fluid.

- **Wetting Fluid**: Preferentially coats solid surfaces and occupies smaller pores.
- **Non-wetting Fluid**: Restricted to larger interconnected pore spaces.

Capillary Pressure

The pressure difference across the interface between wetting and non-wetting phases.

💡 **Design Tip**: Capillary pressure must be exceeded (entry pressure) before LNAPL can enter a porous medium.

Saturation and Residual Saturation

Saturation is the fraction of pore space containing a specific fluid. Residual saturation (Sr) is the level where LNAPL becomes discontinuous and immobilized.

- **Unsaturated Zone Sr**: 10% to 20%.
- **Saturated Zone Sr**: 15% to 50%.

Relative Permeability

The ratio of effective permeability at a specified saturation to the permeability at 100% saturation.

- **Zone I**: High LNAPL saturation; potentially mobile continuous phase.
- **Zone II**: Both LNAPL and water are continuous; relative permeability of each is reduced.
- **Zone III**: LNAPL is discontinuous/trapped; flow is almost exclusively water.

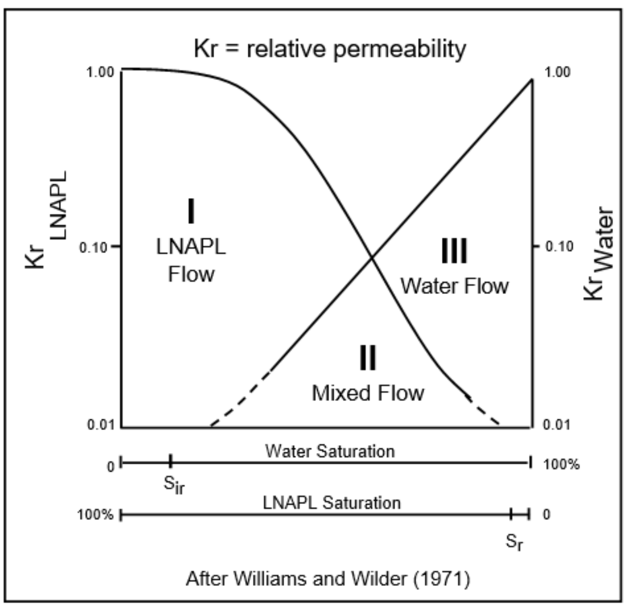

Figure 4. Hypothetical relative permeability curves for water and an LNAPL in a porous medium.