



## Introduction to Light Non-Aqueous Phase Liquids

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# Ground Water Issue

## Light Nonaqueous Phase Liquids

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and Scott G. Huling\*\*

The Regional Superfund Ground-Water Forum is a group of scientists representing EPA's Regional Superfund Offices, committed to the identification and resolution of ground-water issues affecting the remediation of Superfund sites. Light nonaqueous phase liquids (LNAPLs) have been identified by the Forum as an issue of concern to decision makers. This issue paper focuses on transport, fate, characterization, and remediation of LNAPLs in the environment.

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### 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.

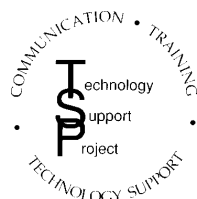
### LNAPL TRANSPORT THROUGH POROUS MEDIA

#### *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)**

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

† Values are given at 20°C unless noted.

<sup>(1)</sup> Value is at 25°C.

<sup>(2)</sup> Value is at unknown temperature but is assumed to be 20°- 30°C.

<sup>(3)</sup> Value is at 15.6°C.

<sup>(4)</sup> Value is at 38°C.

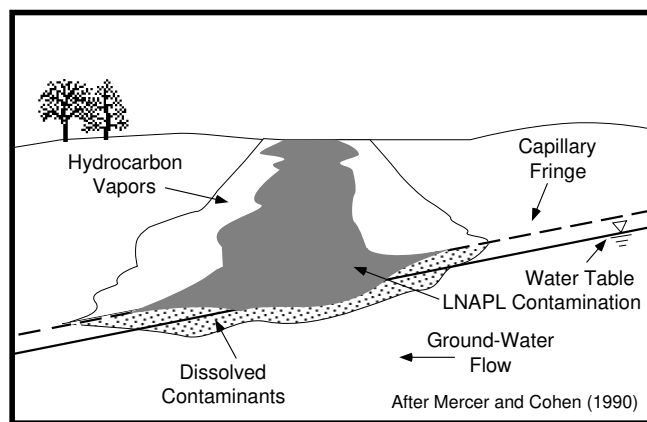
<sup>(5)</sup> Value is at 21°C.

<sup>(6)</sup> Value is at 15°C.

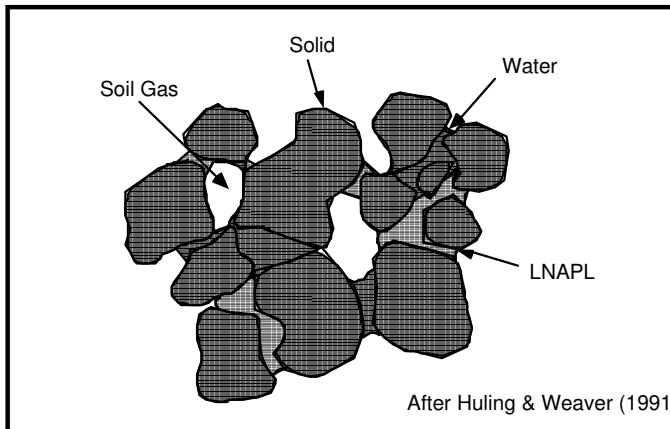
Although principal migration may be in the direction of the maximum decrease in water-table elevation, some migration may occur initially in other directions. A large continuous-phase LNAPL mass may hydrostatically depress the capillary fringe and water table. Once the source is removed, mounded LNAPL 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 LNAPL, 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 four physical states: gas, sorbed to soil materials, dissolved in water, or immiscible liquid.**

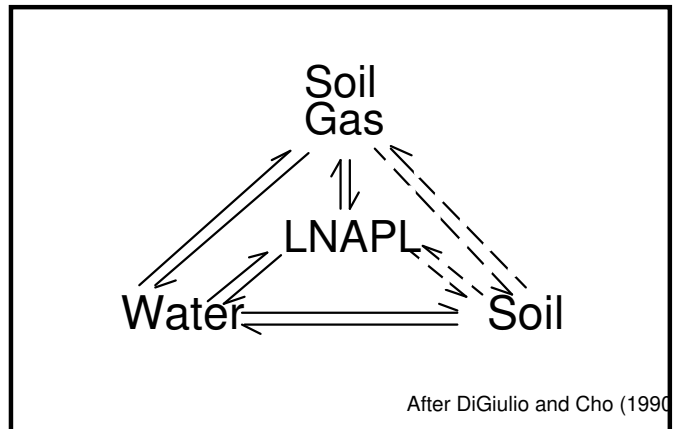
(Figure 2). In the saturated zone NAPL-related contaminants may be present in the aqueous, solid, and NAPL phases. NAPL constituents may partition, or move from one phase to another, depending on environmental conditions (Figure 3). For example, soluble components may dissolve from the NAPL into passing 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



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

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 ( $S_{r,i}$ ) and for the non-wetting fluid, generally NAPL,

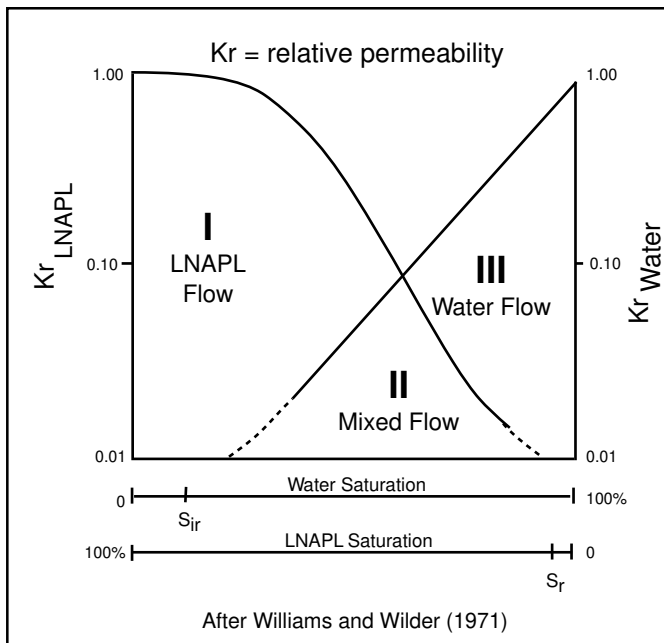
has been termed residual saturation. It should be noted that the example described above is highly simplified for purposes of this discussion. In reality, an infinite set of curves, bounded by main curves for drainage and imbibition, describe the relative permeability function.

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 found within 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:

$$v = -(k \rho g / \mu) (dh / dl) \quad (1)$$

where

- v = Darcy velocity (L/T)
- k = intrinsic permeability (L<sup>2</sup>)
- ρ = density of NAPL (M/L<sup>3</sup>)
- g = force of gravity (L/T<sup>2</sup>)
- 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

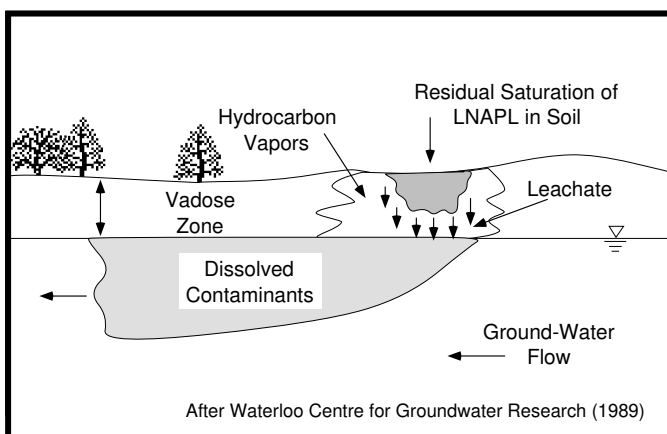
fundamental principles. However, actual release scenarios are strongly affected by numerous site-specific parameters that may not necessarily be represented in this discussion.

### **LNAPL Migration Through Vadose Zone**

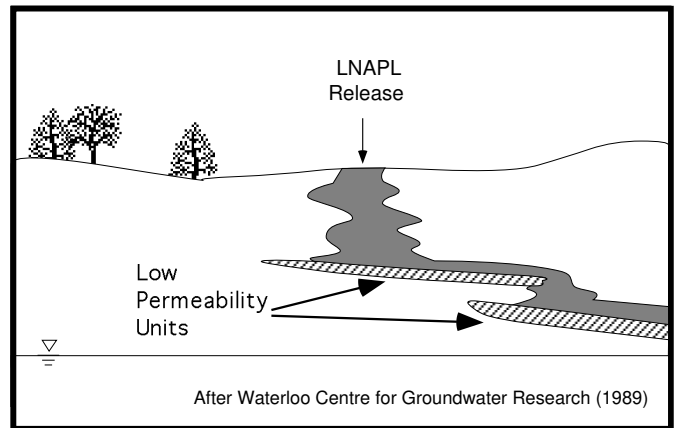
After release on the surface, LNAPL moves vertically downward under the force of gravity. For small volume LNAPL releases, all of the LNAPL may eventually be retained in pores and fractures in the unsaturated zone (Figure 5). Infiltration of water through the residual LNAPL due to recharge or increased water-table elevations slowly dissolves soluble constituents, resulting in an aqueous-phase contaminant plume. Migration of vapors may also spread contamination (Mendoza and McAlary, 1989). LNAPL migration is influenced by heterogeneity in subsurface media and may be complex. For example, it may preferentially migrate laterally through more permeable pathways or accumulate and migrate along low permeability layers above the water table (Figure 6).

### **Accumulation at the Water Table**

If a sufficient volume of LNAPL is released, it may migrate through the unsaturated zone toward the water table and zone of water held by capillary forces above the water table (i.e., capillary fringe). As LNAPL approaches the water table, entering regions of increasing water saturation, it may migrate laterally. Lateral migration is controlled by the LNAPL head distribution. In general, migration may be expected to be greatest in the direction of ground-water flow (i.e., maximum decrease in water-table elevation). However, migration may occur initially in other directions in response to the hydraulic gradients induced by an LNAPL mound (Figure 1). A relatively large LNAPL accumulation may result in compression or collapse of the capillary fringe and, potentially, depression of the water table.



**Figure 5. LNAPL is retained at residual saturation in unsaturated zone. Leaching by infiltrating water and migration of hydrocarbon vapors result in ground-water contamination.**



**Figure 6. LNAPL affected by low permeability units prior to reaching water table.**

Laboratory column experiments (Abdul, 1988) indicate LNAPL may migrate freely through the upper region of the vadose zone where water is present at irreducible saturation. Movement through regions of increasing water saturation at the capillary fringe depends on displacement of water from these zones. In general, increasing LNAPL head is required to displace water with increasing depth within these zones. Rate and volume of LNAPL release and capillary properties of subsurface materials are factors that affect the depth of LNAPL penetration within the water-saturated regions (Abdul, 1988). In general, increases in release rates and volumes lead to increased LNAPL head and increased depth of penetration. Increases in capillary forces associated with fine grained materials result in increased LNAPL head required to penetrate and displace pore water.

The conceptual model presented above is a relatively simplified representation of potential subsurface conditions. As discussed by Farr et al. (1990) and Lenhard and Parker (1990), sharp interfaces between zones saturated with LNAPL, water, and air generally do not exist in the subsurface at most sites. Porous media above the water-saturated zone are generally filled with varying saturations of LNAPL, water, and/or air (Figure 7). Thus, the conceptual model often reported in the literature indicating a discrete LNAPL-water interface should not be assumed. Instead, it is reasonable to assume that the relative saturation ranges reported for the LNAPL and water phases in the mixed flow region (i.e., region II) of Figure 4 are more representative of actual LNAPL-water interface areas. From a remediation perspective, it is apparent that LNAPL mobility is compromised due to the water saturation in this interface area.

### **LNAPL Smearing Due to Fluctuating Water Table**

Accumulations of LNAPL at or near the water table are susceptible to "smearing" from changes in water-table elevation such as those that occur due to seasonal changes in recharge/discharge or tidal influence in coastal environments. Mobile LNAPL floating above the water-saturated zone will move vertically as the ground-water elevation fluctuates (Figure 8). As the water table rises or falls, LNAPL will be

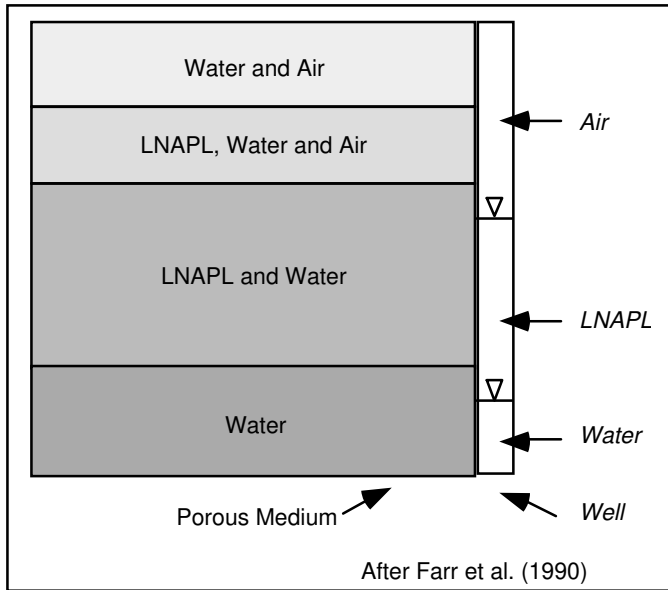


Figure 7. Conceptualization of a multiphase fluid distribution in porous medium and monitoring well screened within the medium.

retained in the soil pores, leaving behind a residual LNAPL "smear zone". If smearing occurs during a decline in ground-water elevations, residual LNAPL may be trapped below the water table when ground-water elevations rise.

A similar situation may develop during product recovery efforts. LNAPL will flow towards a recovery well or trench in response to the gradient induced by water-table depression. LNAPL residual will be retained below the water table as the water-table elevation returns to pre-pumping conditions.

#### **LNAPL Migration in Fractured Media**

LNAPL introduced into an unsaturated, fractured medium follows a complex pathway based on the characteristics of the rock, such as fracture density, orientation, and aperture distribution (Figure 9). The degree of fracture interconnectivity may not be definable due to the extreme heterogeneity of most fractured systems and the lack of economical aquifer characterization technologies (U.S.EPA, 1992a). Many clay units, once considered to be impermeable, often act as fractured media with preferential pathways for vertical and horizontal NAPL migration. Although this concern is particularly true for DNAPL, it is applicable to LNAPL in unsaturated systems.

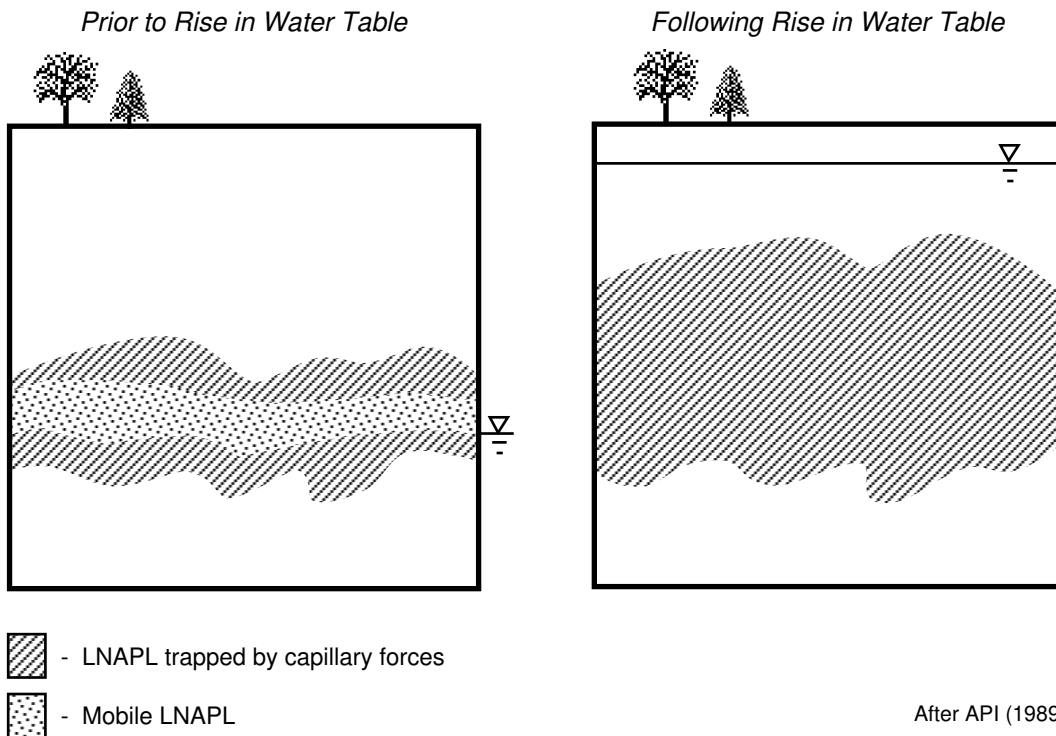


Figure 8. Effect of rising water table on LNAPL distribution in porous medium. A similar effect may be seen with a falling water table.



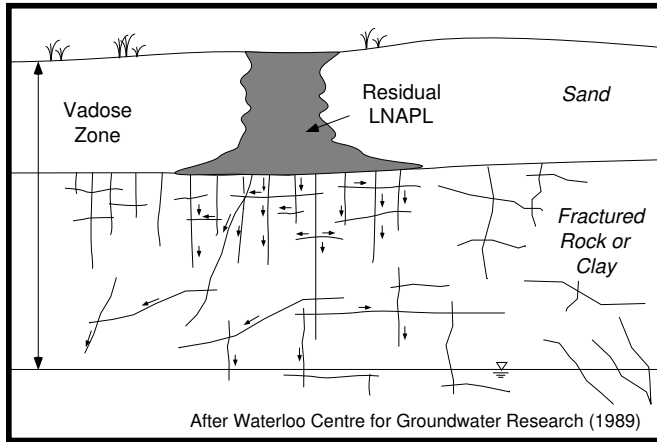


Figure 9. Potential LNAPL migration in fractured medium.

### LNAPL Migration Through Man-Made Pathways

LNAPL will move through man-made preferential pathways, such as improperly grouted monitoring wells or trenches containing distribution piping or utilities. Trenches backfilled with pea gravel or other coarse-grained material can provide a horizontal pathway for LNAPL migration in the near-surface environment.

### FATE OF LNAPLs IN THE SUBSURFACE

As illustrated in Figure 3, organic compounds which compose NAPLs may partition among four separate phases in the subsurface: gaseous, solid, aqueous, and NAPL. The subsurface fate of chemicals in these phases is largely determined by volatilization, dissolution, sorption, and degradation processes.

#### Volatilization

Volatilization of organic compounds occurs by two primary pathways: volatilization from water and NAPL. Henry's Law describes the partitioning of an organic compound between the aqueous and gaseous phases. For a dilute solution, concentrations less than approximately  $10^{-3}$  moles/l, the ideal gas vapor pressure of a volatile solute is proportional to its mole fraction in solution. More simply stated, the escaping tendency of the solute molecules from the water phase to the air phase is proportional to the concentration in the water. This relationship assumes local equilibrium between water and air and is useful for estimating the potential for organic chemical transport from water to air, and from hydrocarbon vapors to water (Mendoza and McAlary, 1989). For more concentrated solutions or pure phase compounds, volatilization is best described by Raoult's Law, which states that the vapor pressure over a solution is equal to the mole fraction of the solute times the vapor pressure of the pure phase liquid. Again, this is a measure of the escaping tendency of molecules from the NAPL to the gaseous phase.

Henry's Law and Raoult's Law are useful to describe the partitioning of organic compounds between fluid and gaseous

phases when the system is at equilibrium. Most volatilization calculations are dependent on the assumption that the LNAPL and air are in chemical equilibrium (Johnson et al., 1990a). However, it is reasonable to assume that equilibrium conditions do not occur in many volatilization-based subsurface remediation systems. The actual transfer process in a dynamic and complex subsurface system must take into account numerous parameters that are not included in these general partitioning equations. A practical approach to evaluating soil ventilating systems involves an in-depth analysis of numerous site-specific parameters and processes (Johnson et al., 1990b).

#### Dissolution

A NAPL in physical contact with ground water will dissolve (solubilize, partition) into the aqueous phase. The solubility of an organic compound is the equilibrium concentration of the compound in water at a specified temperature and pressure. For all practical purposes, the solubility represents the maximum concentration of that compound in water. The solubilities of the compounds most commonly found at Superfund sites range over several orders of magnitude. Several parameters affecting solubility include temperature, pH, cosolvents, dissolved organic matter, and dissolved inorganic compounds (salinity).

For a multicomponent NAPL in contact with water, the equilibrium dissolved-phase concentrations may be estimated using the solubility of the pure liquid in water and its mole fraction in the NAPL mixture (Feenstra et al., 1991). The maximum concentration that can be achieved in this scenario is referred to as the effective solubility, as indicated in Equation 2.

$$S_i^e = X_i S_i \quad (2)$$

where

$S_i^e$  = effective aqueous solubility of compound  $i$  in NAPL mixture

$X_i$  = mole fraction of compound  $i$  in NAPL mixture

$S_i$  = aqueous solubility of the pure-phase compound

Two examples are presented which illustrate the effect of dissolution on multicomponent LNAPLs. First, consider a two-component NAPL with equal mole fraction (0.5), where the solubilities of the pure-phase compounds are 1000 mg/l and 10 mg/l, respectively, and the effective solubilities are 500 mg/l and 5 mg/l, respectively. The more soluble compound will potentially partition into ground water 100-fold more readily than the less soluble compound. According, less soluble compounds will primarily be associated with the NAPL phase and dissolution and transport in the aqueous phase will be limited relative to more soluble components. Second, consider a "gasoline" containing numerous compounds (Johnson et al., 1990b) where the mole fractions of benzene were 0.0076 and 0.0021 for fresh and weathered gasoline, respectively. The solubility for benzene is 1780 mg/l (U.S.EPA, 1990). Yet, the predicted effective solubility would be only 13.5 mg/l and 3.78 mg/l for fresh and weathered gasoline, respectively.

The effective solubility represents the concentration that may occur at equilibrium under ideal conditions. Laboratory studies (Banerjee, 1984) indicate that effective solubilities calculated using Equation 2 are reasonable approximations for mixtures of organic liquids that are hydrophobic, structurally similar, and have low solubilities. Effective solubilities of components in more complex mixtures, such as petroleum products, appear to be in error by no more than a factor of two (Leinonen and Mackay, 1973). However, the degree to which these compounds partition to the water phase is a function of many variables including cosolvency (Rao et al., 1991). Cosolvency effects may occur in cases where dissolution of highly soluble components (e.g., alcohols) significantly increase the solubility of other components.

In general, higher dissolution rates may be associated with higher ground-water velocities, higher LNAPL saturation in the subsurface, increased contact area between LNAPL and water, and LNAPLs with a high fraction of soluble components (Mercer and Cohen, 1990; Miller et al., 1990). However, recent studies (e.g., Powers et al., 1992) indicate that non-equilibrium effects may limit contaminant mass transfer by dissolution under certain conditions such as high ground-water velocity. Laboratory and modeling studies conducted by many researchers (e.g., Borden and Kao, 1992; Geller and Hunt, 1993; Powers et al., 1991) indicate that complete dissolution of an LNAPL may require hundreds or thousands of pore volumes of water under ideal field conditions. These studies observed initially high aqueous contaminant concentrations which were followed by a period of rapid decline and an asymptotic period during which concentrations declined slowly.

### **Sorption**

Sorption is defined as the interaction of a contaminant with a solid (Piwoni and Keeley, 1990). In soil or aquifer material contaminated with LNAPL, contaminants from the LNAPL will partition onto solid phase material. The primary pathway in which this process occurs is through the water phase, as indicated in Figure 3. For example, when LNAPL is released into the subsurface, components will dissolve into the aqueous phase, then partition onto aquifer material. Numerous parameters affect sorption at hazardous waste sites including solubility, polarity, ionic charge, pH, redox potential, and the octanol/water partition coefficient (Piwoni and Keeley, 1990).

In general, solid-phase (adsorbed) contaminants may represent a small fraction of the total contaminant mass in soil and aquifer material where continuous phase or residual LNAPL exists. The majority of the contaminant mass in these systems is typically present in the nonaqueous liquid phase. Desorption of the contaminant (i.e. mass transfer of contaminant from the solid phase to the water phase) is often a rate-limited step and is partially responsible for the tailing effect commonly observed in ground-water pump-and-treat systems.

Analytical results from an LNAPL-contaminated aquifer or soil sample extracted and analyzed in the laboratory represent the total contaminant mass associated with the sample. Careful evaluation of the chemical and physical properties of the contaminant(s) and soil/aquifer sample is necessary to

evaluate the phase(s) in which the contaminant exists. A practical approach has been developed to evaluate contaminant phase distribution by applying equilibrium partitioning theory (Feenstra et al., 1991).

### **Biodegradation**

Many of the LNAPL-related compounds are amenable to biological degradation in the aqueous phase by naturally occurring microorganisms in the subsurface. However, there is an important distinction between aqueous-phase and LNAPL biodegradation. The distinction is the inability to create and maintain conditions that are conducive to microbial activity within a LNAPL. In brief, biodegradation of pure phase hydrocarbon does not appear to be practical and has not been demonstrated. Considerable research has focused on evaluating aerobic and anaerobic biodegradation and transformation processes. These processes play an important role in the ultimate fate of LNAPLs in the subsurface, both in the form of naturally occurring and actively engineered remediation processes (Norris et al., 1994).

### **LNAPL SITE CHARACTERIZATION**

Success or failure of an LNAPL remediation program depends in large measure on the remediation objectives and adequacy of the site characterization. This section will focus on issues pertaining to LNAPL investigations. Discussion of strategies and techniques for characterization of aqueous-phase and sorbed contamination will be limited. More information regarding site characterization concepts, techniques, and strategies is provided by U.S.EPA (1991) and Cohen and Mercer (1993).

The focus of site characterization is often to provide information necessary to define and evaluate potential remedial options. Specific objectives may include determination/delineation of subsurface contamination in the aqueous, gaseous, solid, and LNAPL phases; mobile and residual LNAPL; migration rates/directions of the mobile phases; geologic controls on LNAPL movement; LNAPL properties; and other pertinent fluid/media properties. The level of detail and the type of data required will be site-specific, partially dictated by the remedial technologies under consideration and practical economic constraints, and often restricted by available characterization technologies. Such limitations include lack of practicable methods for detailed delineation of many parameters of interest including LNAPL distribution and saturation and hydraulic conductivity distributions.

### **Conceptual Model**

The conceptual model is the interpretation and assimilation of all site-related information into assumptions and hypotheses regarding contaminant sources, subsurface contaminant distribution, and dominant transport/fate processes. The basis for this conceptual model may include one or more of the conceptual models discussed in the previous section.

Characterization is best conducted in a phased approach, beginning with a review of site history, contaminant properties, and regional/local studies. This review should include the following (API, 1989):

1. Information on storage, transportation, use, monitoring, and disposal of LNAPLs at the site;
2. Locations, volumes, and timing of any known LNAPL releases;
3. Locations of underground piping, structures, or utilities which might influence LNAPL flow;
4. Regional/local geologic and hydrogeologic studies, soil surveys, climatic data, and pertinent maps/historic photographs of the site; and
5. Preliminary information, available from the literature, concerning pertinent contaminant transport and fate parameters for the site-specific contaminants.

An initial conceptual model for contaminant distribution, transport, and fate at the site is then formulated and used to plan further characterization. Each characterization phase is designed to test and refine this model. The iterative process continues throughout remedial design and during remedial operations.

### ***Soil/Aquifer Material***

Lithologic, stratigraphic, and structural features may often be dominant influences on LNAPL movement. As expected, LNAPLs migrate faster through relatively permeable features (e.g., root holes, fractures, sandy layers, utility trenches, etc.) in the unsaturated zone than through less permeable materials. Characterization of subsurface heterogeneity to the extent practicable may provide valuable information concerning potential LNAPL migration and distribution. Analyses of geologic materials exposed in trenches and obtained from borings may be used at some sites to improve the conceptual model and identify features that potentially serve as preferential pathways for LNAPL. Non-invasive geophysical methods may also provide information regarding the distribution of geologic materials and stratigraphic or structural features that may control contaminant migration. However, detailed characterization of heterogeneity and LNAPL distribution often will not be possible due to subsurface complexity and limitations in characterization tools and techniques (U.S.EPA, 1992a).

Fractured rock and karstic settings may represent extreme examples of heterogeneous environments. These settings pose exceptionally difficult problems in site characterization due to the complexity of transport pathways. Efficient techniques for characterizing contaminant transport (i.e., LNAPL, aqueous phase, and gaseous phase) at such sites are not available currently.

### **Hazards of Invasive Characterization Methods**

Certain hazards may exist during invasive characterization at LNAPL contamination sites. The potential for increasing the vertical extent of contamination should be considered when evaluating drilling and well installation programs. Drilling through mobile LNAPL (e.g., liquids perched on low permeability units above the water table) may result in contaminating deeper intervals. Such risks may be reduced using appropriate techniques such as detailed observation and screening of geologic materials. The risk of explosion or fire (API, 1989) may exist at sites contaminated with flammable materials (e.g., most liquid petroleum products).

During drilling operations, LNAPL, contaminated soil and aquifer material, and vapors are brought to the surface where conditions for ignition may exist. LNAPL is not only a concern as a fire and explosion hazard, but also with regard to chemical exposure to the driller and sampling crews. Monitoring and mitigation of explosion and exposure risks should be considered when planning field operations.

### **Information from Borings and Excavations**

Multiple borings with continuous sampling of subsurface media or excavation of pits/trenches will generally be required to define stratigraphy and estimate properties of the subsurface media and fluids. Media properties useful in contaminant fate and transport studies at NAPL sites include texture, porosity, permeability, organic carbon content, isotropy, and heterogeneity. Estimation of fluid/media properties, such as fluid saturation and capillary pressure-saturation relationships, may also be useful. Such data may provide the basis for evaluating potential LNAPL distribution and mobility at the macro scale. Various laboratory methods for measuring such properties are discussed in Cohen and Mercer (1993). Applicability of these methods will be site specific. Hydrogeologic information, including the depth to ground water, delineation of perched ground water or LNAPL, hydraulic gradient, and hydraulic conductivity of saturated materials, is also essential. This information may be used to evaluate ground-water flow directions which will also be the potential flow directions for the LNAPL. Characterization of temporal as well as spatial variations in many of these parameters generally will be required. For example, information on seasonal variations in water-table elevations may aid in evaluating mobile LNAPL flow directions and LNAPL distribution above and below the average water-table elevation. Installation of wells will be required to obtain much of this information. These data will provide the basis for evaluating LNAPL mobility on the site scale.

Methods for direct detection of NAPL in soil samples are relatively limited. Visual observation often has been relied upon to make this determination in the field. However, it may be difficult or impossible to observe NAPLs which are colorless or clear, heterogeneously distributed in the sample, or present at low saturations (Huling and Weaver, 1991).

Recently, qualitative techniques to enhance rapid, visual observations of NAPL in drill cuttings or cores have been evaluated (Cohen et al. 1992). Centrifugation, examination under ultraviolet light, soil-water separation tests, and addition of hydrophobic dye to preferentially stain NAPL (i.e., Sudan IV) were studied. Of these methods, the use of hydrophobic dye and ultraviolet light examination for fluorescent NAPLs were found to be the simplest and most effective methods. These methods provide only limited, qualitative information concerning the presence of LNAPLs. However, this information may be useful to delineate the presence of LNAPL along a vertical profile when limited resources prevent the use of more expensive, quantitative techniques.

Screening of soil headspace vapors using a flame ionization detector was also found useful in evaluating the presence of volatile NAPL (Cohen et al., 1992). However, a poor correlation between NAPL saturation in the samples and

headspace vapor concentrations was obtained. This result was principally due to physical constraints on contaminant concentrations in the vapor phase.

Chemical analysis of soil samples will generally be required to identify individual compounds and their concentrations and aid in evaluating NAPL present at low residual saturations (Huling and Weaver, 1991). Chemical analyses do not directly distinguish between gaseous, aqueous, sorbed, and NAPL contaminants. However, relatively high constituent concentrations indicate the constituent may be present as a NAPL or sorbed to subsurface materials (Huling and Weaver, 1991). An example of sampling and analysis techniques applied at the site of an aviation gasoline spill to determine the LNAPL distribution in the capillary fringe is described by Ostendorf et al. (1992).

Feenstra et al. (1991) proposed a method to indirectly assess the presence of NAPL in soil samples by applying equilibrium partitioning theory. Application of this method to DNAPL assessments is explained in U.S.EPA (1992b). In the absence of NAPL, there is a theoretical maximum contaminant mass which can be present in a sample. The maximum constituent concentration in the sample is dependent on the constituent solubility in water, the sorptive capacity of the soil, and the saturated soil gas concentration. If NAPL is present, the constituent concentration detected in the sample will exceed the calculated maximum concentration and the calculated constituent concentration in pore water would exceed the effective constituent solubility. This method requires determination of soil moisture content, organic carbon content, porosity, potential LNAPL composition, sorption parameters, effective solubilities, and total constituent concentrations in soil samples. The methods are most useful when relatively large quantities of NAPL are present, pore water/soil partitioning coefficients are determined rather than estimated from available literature, and effective solubilities are measured. However, many of these data may be unavailable at many sites and the methods are less reliable when parameters are estimated rather than measured (Cohen and Mercer, 1993; Feenstra et al., 1991).

### **Cone Penetrometer**

The cone penetrometer (ASTM Standard D3441) is a geotechnical tool that originated in the construction industry. This tool is capable of rapidly providing valuable stratigraphic information useful in assessing potential LNAPL distribution. Data collected during penetrometer testing have also been used to evaluate soil saturation, potentiometric surfaces, and horizontal soil permeability. In its simplest form, truck-mounted hydraulic rams force a cone-shaped instrument containing strain gages through the soil, sending back continuous readings of tip resistance, sliding friction, and inclination. Correlations developed between subsurface materials cored in adjacent borings and corresponding penetrometer measurements may allow rapid interpretations of stratigraphy in each test hole (Chiang et al., 1992). Penetration depths depend on the subsurface material properties but are often limited to less than approximately thirty meters.

Modified penetrometers have been equipped to collect subsurface samples of fluids and aquifer materials useful in delineating LNAPL (Chiang et al., 1992). Other researchers

are incorporating additional in situ sensing technology into cone penetrometers (Seitz, 1990) for real-time detection of organic contaminants which may eventually provide a rapid means for defining LNAPL distribution. It should be noted that such methods are still in the developmental stage and should be applied with caution.

### **Geophysical Methods for Hydrogeologic Characterization**

Surface geophysical methods, where applicable, allow non-invasive investigation of subsurface physical and chemical properties. Certain techniques, including seismic, electrical, magnetic, and ground-penetrating radar, have been applied successfully to site characterization (e.g., Benson et al., 1982; Walther et al., 1986). These methods may provide valuable hydrogeologic information concerning lithologic and stratigraphic boundaries, fracture orientation, locations of underground utilities, and depths to ground water and bedrock. Variations of these and other methods are useful borehole techniques for hydrogeologic site characterization (Keys and MacCary, 1971; Keys, 1989). Use of such techniques should be considered as part of an integrated approach to delineation of hydrogeologic controls on ground-water flow and potential LNAPL migration.

### **LNAPL**

Light nonaqueous phase liquids may exist as continuous, free-phase liquids and/or as residual liquids trapped by capillary forces above and below the water table. Evaluation of LNAPL remedial options requires delineation of LNAPL distribution, composition, and properties. Installation of wells and excavations coupled with previously discussed soil sampling and analysis generally will be required to estimate distribution and potential mobility. LNAPL fate, transport, and distribution has been presented from a theoretical and conceptual model perspective. However, site characterization may be technically challenging due to the heterogeneity of subsurface media and variability of subsurface conditions. It is not uncommon to observe a "patchy" distribution of LNAPL over a relatively small area at a site, or the transient presence of LNAPL in a well.

### **Mobile LNAPL**

Monitoring wells, borings, and test pits installed in areas of potential LNAPL releases are one of the key sources of information concerning the distribution of mobile LNAPL. Wells used for this purpose must be screened across the air/LNAPL interface and the water table to provide uninhibited access for floating LNAPL (API, 1989). The screen generally should encompass the water table and LNAPL during seasonal fluctuations in ground-water elevations. Additional design considerations include use of appropriate construction materials. In general, conventional construction practices use a filter pack coarser than the surrounding formation to allow entry of the LNAPL. However, research regarding construction materials specifically designed for LNAPL monitoring is relatively limited. Recent studies (Hampton and Heuvelhorst, 1990; Hampton et al., 1991) of filter packs for LNAPL recovery wells indicated traditional design practices may not produce an optimum recovery well. These studies indicated LNAPL recovery rates were increased using packs with a grain size approximately half of conventional recommendations for recovery wells. Based on such results,



thickness is measured. LNAPL thickness in the bailer may be slightly greater than the apparent thickness present in the well due to fluid displacement by the bailer walls (API, 1989; Mercer and Cohen, 1990). Detection of clear or colorless LNAPLs may be enhanced by addition of a hydrophobic dye that preferentially stains the organic liquid (Cohen et al., 1992).

### **Recharge and Bail-Down Tests**

Methods used to estimate mobile LNAPL thickness in the formation have included studies referred to as bail-down, recovery, or recharge tests (e.g., Hughes et al., 1988; Gruszczenski, 1987). These tests involve monitoring LNAPL recharge to a well following its removal by pumping or bailing. The mobile LNAPL thickness in the formation at each well is then estimated by various interpretations of depth-to-product, depth-to-water, and product thickness as a function of time. Several potential sources for error exist in the performance and interpretation of these tests. In general, these procedures have not been adequately proven in a variety of field situations (Testa and Paczkowski, 1989) and do not provide information concerning LNAPL trapped by capillary forces (Durnford et al., 1991). However, the performance of such tests may provide qualitative information concerning the potential for LNAPL recovery using conventional pumping technology (API, 1989).

### **Apparent LNAPL Thickness Relationships**

Studies regarding the relationship between apparent LNAPL thickness and in situ LNAPL distribution have been reported by many researchers (e.g., Ballesterio et al., 1994; Blake and Hall, 1984; Farr et al., 1990; Gruszczenski, 1987; Hall et al., 1984; Hampton and Miller, 1988; Kembrowski and Chiang, 1990; Lenhard and Parker, 1990; Pantazidou and Sitar, 1993; Testa and Paczkowski, 1989; Yaniga, 1984; Yaniga and Warburton, 1984). Methods proposed for estimating in situ mobile LNAPL thickness and, ultimately, LNAPL volume range from simple relationships based on hydrocarbon density (e.g., De Pastrovich et al., 1979) to more complex relationships incorporating properties of the porous media (e.g., Farr et al., 1990). Commercial software packages implementing some of these methods are currently available.

Based on laboratory studies and a review of many of these methods, Hampton and Miller (1988) concluded that the relationships investigated in their study were not sufficient to reliably predict hydrocarbon thickness in the formation. Of these relationships, the De Pastrovich et al. (1979) equation was found to yield crude, order-of-magnitude approximations of mobile LNAPL thickness. Wagner et al. (1989) compared estimates using various techniques including simple and complex relationships, bail-down tests, and chemical analysis of soil samples. The study indicated that estimates from bail-down tests, analysis of soil samples from a test pit, a developmental hydrocarbon-sensing probe, and the relationship proposed by De Pastrovich et al. (1979) yielded comparable results at one field site. However, none of the aforementioned methods have been adequately evaluated under a variety of controlled and field conditions.

Farr et al. (1990) and Lenhard and Parker (1990) developed methods for evaluating LNAPL volume in porous media under equilibrium conditions based on fluid and media properties

and apparent LNAPL thickness. In a controlled study, Wickramanayake et al. (1991) compared the methods proposed by De Pastrovich et al. (1979), Hall et al. (1984), and Lenhard and Parker (1990) to estimate LNAPL volume from a known release. A known quantity of JP-4 fuel was released into a model aquifer equipped with observation wells. In this study, the method proposed by Lenhard and Parker (1990) provided the best estimate of LNAPL release after the system had reached equilibrium. However, all estimates were within an order of magnitude of the actual release volume.

Durnford et al. (1991) identified several potential limitations in applying many of these relationships. These problems include:

1. Water table fluctuations can result in differences in apparent LNAPL thickness without significant in situ changes. This is a major source of uncertainty in estimating in situ distribution.
2. Several of these relationships are based on soil and fluid properties that require measurements of capillary pressure-saturation curves which are difficult to obtain and may not be representative of actual field conditions.
3. Spatial variability in subsurface properties (i.e., heterogeneity) and the effects on apparent and in situ LNAPL thickness are not easily evaluated using these relationships.
4. LNAPL held by capillary forces above and below the water table, which is an important potential source for ground-water contamination, is not addressed using many of these methods.

In addition, many of the methods are based on an assumed equilibrium distribution of the fluids. Such assumptions will not be applicable at many sites. This implies that simple relationships and proportionalities may not be sufficient to estimate mobile LNAPL thickness or volume from apparent thickness information. In addition, methods requiring estimates of subsurface media properties may be subject to much uncertainty due to heterogeneity and uncertainty in parameter estimates. However, the techniques described above may yield order-of-magnitude estimates of mobile LNAPL distribution at some sites. In summary, proven field methods for accurate and reliable estimation of mobile LNAPL volume using well thickness information are not currently available. Further research and development of methods for directly assessing subsurface LNAPL distribution are warranted.

### **Geophysical Methods for Contaminant Detection**

Application of geophysical methods for direct detection of organic contamination, including LNAPL, is currently an area of research and development (U.S.EPA, 1992a). Surface geophysical methods which have been applied with limited success at a small number of sites include ground penetrating radar, complex resistivity, electromagnetic induction, and direct current resistivity (e.g., Olhoeft, 1986; King and Olhoeft, 1989; Holzer, 1976). Borehole techniques which have been studied include dielectric logging (Keech, 1988) and a driven probe equipped with galvanic and conductivity circuits for sensing soil moisture and a hydrocarbon indicator for sensing LNAPL (Hampton et al., 1990). Such techniques are currently in the developmental stage and should generally be

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considered research applications. The utility of geophysics at most sites will not be in the direct detection of LNAPL, but in hydrogeologic site characterization (U.S.EPA, 1992a).

### **LNAPL Samples**

Determination of physical and chemical properties of LNAPL obtained from wells or separated from soil samples will often be required to evaluate many aspects of LNAPL site characterization and remedial design. For example, information concerning physical properties such as density and viscosity may be used to assess LNAPL mobility and distribution (Reidy et al., 1990; Cohen and Mercer, 1993) and potential extraction designs. Analyses of LNAPL will be necessary to determine the chemical composition which may be used to compute the effective solubility of LNAPL components, identify potential LNAPL sources, and evaluate applicability of certain remedial technologies such as soil vapor extraction.

Depending on the study objectives and potential LNAPL composition, many analytical methodologies may be applicable for chemical analysis of LNAPL samples. Common techniques include infrared spectrometry, gas and liquid chromatography, mass spectrometry, and nuclear magnetic resonance spectrometry. Such techniques are used to qualitatively and quantitatively determine hydrocarbon composition. Cohen and Mercer (1993) describe many of these techniques in the context of characterizing DNAPL samples. This information is also applicable to LNAPL sample characterization. Multiple techniques may be required to characterize complex, multicomponent LNAPL mixtures. In addition, analyses for indicator parameters such as total petroleum hydrocarbons and total organic carbon may be useful in screening level investigations at some sites.

Current guidance dictates LNAPL samples should be obtained prior to purging of the well. Purging of the LNAPL from the well prior to sampling may be conceptually desirable to obtain a more representative sample. However, in many cases purging may result in an inability to sample due to slow or no LNAPL recharge and emulsification of the sample. Specific sampling techniques should be evaluated with regard to study objectives and site conditions. A bailer will generally be adequate for LNAPL sample collection from wells (API, 1989). Additional equipment such as a bladder pump, peristaltic pump, or specialized equipment used for LNAPL recovery may be useful at many sites.

### **Soil Gas**

Depending on site conditions, soil gas analysis for volatile organic compounds may be useful in locating contaminants present in the subsurface. Several techniques have been developed for conducting such surveys (e.g., Marrin and Kerfoot, 1988; Thompson and Marrin, 1987). However, limitations in the use and interpretation of data from soil gas surveys exist (Kerfoot, 1988; Marrin, 1988). Soil gas surveys may provide qualitative information useful as a screening tool in delineating areas of LNAPL contamination as well as aqueous-phase contamination (e.g., Evans and Thompson, 1986; Devitt et al., 1987). Anomalously high soil gas concentrations may be an indication of NAPL in the vadose zone near the sample location.

### **Ground Water**

Ground-water elevations in wells containing LNAPL require correction for the depression of the LNAPL/water interface in the well to obtain total hydraulic head. The depression is caused by the weight of the hydrocarbon. The correction is accomplished by multiplying the apparent LNAPL thickness in the well by the specific gravity of the LNAPL. The result is then added to the elevation of the LNAPL/water interface to obtain the total hydraulic head (API, 1989; Hudak et al., 1993). The computed hydraulic head facilitates a more accurate assessment of hydraulic gradient which leads to better conclusions regarding potential contaminant sources, extent of free-product accumulation, and optimal areas for focusing remediation efforts (Hudak et al., 1993). It should be noted that this approach may be inappropriate for conditions in which LNAPL enters the well from a low-permeability unit perched above the water table.

The influence of this correction on data interpretation is dependent on several factors, including apparent LNAPL thickness and hydraulic gradient. The greater the thickness of LNAPL in the well and the lower the hydraulic gradient, the greater the potential influence of this correction. The necessity of performing this calculation should be evaluated on a site-specific basis. Accumulation of LNAPL in a well introduces an additional degree of uncertainty into the calculation of hydraulic head and gradient. Density of the LNAPL obtained from the well must be measured and, often, will not be constant across a site due to such factors as LNAPL release history and differences in the degree of "weathering" following release. Measurement of the apparent thickness using any of the methods previously described is subject to a higher degree of uncertainty than measurement of ground-water elevation in a well which does not contain LNAPL. The additional uncertainty introduced by LNAPL accumulation in wells is site specific and should be evaluated during any investigation.

Although contaminant concentrations in ground-water samples may not approach the effective solubility of each compound, analyses for LNAPL components may aid in evaluating the potential presence of LNAPL and delineating potential source areas. Several factors may account for lower-than-expected concentrations of constituents in ground water from LNAPL zones. First, the effective solubility of a single chemical from a multicomponent LNAPL is less than the solubility of the pure chemical in water. The difference is often an order of magnitude or more. Other explanations for the relatively low concentrations of dissolved constituents in LNAPL zones may include variability in subsurface LNAPL distribution, mixing of ground water from different intervals in a well during sampling, and effects resulting from non-uniform ground-water flow (Cohen et al., 1992). Non-equilibrium dissolution may also be a factor at some sites (Powers et al., 1991).

### **REMEDICATION**

Applicability of potential remedial technologies depends on site-specific hydrogeologic characteristics, nature/distribution of contaminants, and remedial objectives. Technologies for removal of mobile LNAPL exist and may be applicable at some sites. However, technologies for removal of residual LNAPL, particularly those liquids trapped in the saturated zone, are not well developed. Subsurface restoration to pre-

contamination conditions may require removal of virtually all LNAPL and much of the contamination sorbed to aquifer material. Technological limitations to complete LNAPL removal may exist at many sites.

### Excavation

The remedial alternative(s) selected for an LNAPL site may depend on the volume of LNAPL released. If the volume is small enough to be retained within the upper portion of the vadose zone, excavation and above-ground treatment/disposal may be selected in lieu of in situ remediation. Some of the advantages of excavation are:

- Costs of shallow excavation are generally low compared to other remediation technologies.
- Remediation time is relatively short.
- Experienced contractors are more readily available.
- A wide variety of contaminants often can be remediated with a high degree of reliability.

The potential disadvantages include:

- Contamination may not be completely removed due to inability to delineate LNAPL distribution in detail.
- Structures, roads, or other features can restrict the area available for excavation.
- Air emissions of volatile constituents may be significant.
- Costs of deep excavation may be high.

### Mobile LNAPL Recovery - Trenches/Drains/Wells

Recovery potential for mobile LNAPL is controlled by such factors as LNAPL viscosity and density and relative permeability (Testa and Paczkowski, 1989). Liquids trapped by capillary forces are not recoverable using conventional trench, drain, or well systems. High LNAPL viscosity, high residual water saturation, and low permeability reduce LNAPL recovery rates. Under optimum circumstances, these systems may remove less than 50% of the total LNAPL volume in the subsurface (Abdul, 1992). It is estimated that only 20% to 30% of the total release volume is typically recovered (Testa and Paczkowski, 1989). The remaining LNAPL will generally be sufficient to result in continued ground-water contamination. However, there may be important benefits to mobile LNAPL recovery other than simple contaminant mass removal.

Some of the other potential reasons for recovery of these liquids include:

- Mobility reduction. Residual LNAPL held by capillary forces is relatively immobile under normal hydrogeologic conditions. Recovery of mobile LNAPL will limit the migration of these liquids.
- Increase LNAPL transformation. Reduction in LNAPL saturation may increase LNAPL surface area and may result in more rapid dissolution, degradation, and volatilization of the LNAPL. This may be an advantage to the remediation program at some sites.

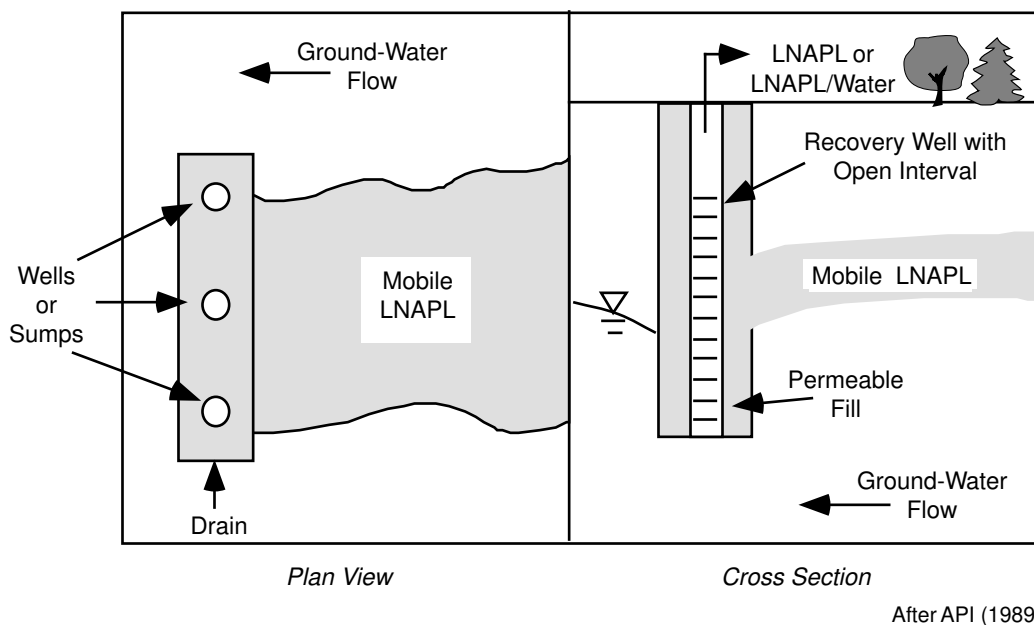


Figure 11. Plan and cross sectional views of a drain designed for mobile LNAPL recovery.



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## **Trench/Drain Systems**

Trenches/drains may be used to recover mobile LNAPL at shallow depths. Generally, they are used at sites where the LNAPL is located within 15 to 20 feet of the surface with access for construction equipment (U.S.EPA, 1988). Depending on available excavation equipment, costs, and soil stability, deeper drains may be cost effective (API, 1989). Trench/drain systems provide the most hydraulically efficient means for removing fluids from the aquifer. Therefore, these systems often are well suited for low-permeability units and heterogeneous sites which would require a large number of wells to control LNAPL flow (API, 1989). Trenches are usually excavated perpendicular to the general direction of ground-water flow, downgradient and/or within mobile LNAPL (Figure 11). The trench generally should be as long as the width of the mobile LNAPL to provide containment. It should be excavated to a depth several feet below the lowest expected seasonal water-table elevation to prevent the migration of LNAPL below the collection system. However, trenches for recovery of LNAPL perched on low permeability layers should not penetrate the supporting unit allowing further downward migration to the water table. In general, trench width is not a factor in LNAPL recovery (U.S.EPA, 1988) and may be as narrow as possible to reduce costs (API, 1989). A low permeability barrier may be installed on the downgradient side of the trench to limit hydrocarbon migration while allowing water to flow underneath. However, such a barrier may not be an essential component of the design. In case of a trench/drain constructed in fine-grained native materials using a coarse grained fill, a capillary barrier effect may exist. Even without installation of an artificial barrier, the non-wetting LNAPL may tend to be trapped in the trench due to the higher elevation of the capillary fringe in the formation on each side of the trench. As long as product is removed from the trench, LNAPL migration beyond the trench may be limited.

Open trenches may be converted to drains by backfilling with appropriate graded filter materials (e.g., gravel). Sumps or wells may be installed along the drain to collect LNAPL (API, 1989). Perforated pipe installed in the trench and connected to the sumps may be used to improve system efficiency. Recovery of LNAPL from trenches/drains or wells may be accomplished using several options including pumps for collecting total fluids (i.e., LNAPL and water) and skimming systems and pumps for collecting only LNAPL (API, 1989; U.S.EPA, 1988).

Trenches/drains may be operated to recover only LNAPL migrating under the influence of the natural hydraulic gradient. A system operated in this manner would generally result in a relatively low recovery rate. Recovery time frames may also be relatively long unless multiple trenches/drains are used. Such systems should generally use continuous LNAPL recovery to prevent accumulation and migration around the ends of the trench (API, 1989). Ground-water extraction to increase hydraulic gradients toward the trench/drain may be used to increase LNAPL recovery rate and establish hydrodynamic control. However, depressing the water table may also result in LNAPL migration into deeper portions of the saturated zone previously uncontaminated by these liquids. In this situation, residual LNAPL will remain trapped below the water table following mobile LNAPL recovery. The potential

consequences of such system operation should be carefully considered before implementation.

## **Recovery Wells**

Wells used to recover mobile LNAPL offer more flexibility in system design and operation than trench/drain systems. Wells may be most useful at sites with moderate to high hydraulic conductivities, but may be used in less conductive materials. Conventional recovery well designs have relied on modified water-well design procedures to maximize well efficiency and increase LNAPL recovery rates (Blake and Lewis, 1983). However, well construction materials and recovery equipment compatible with the LNAPL should be used (Mercer and Cohen, 1990). Potential fire and explosion hazards should also be considered.

Wells may be designed to remove only LNAPL, LNAPL and water separately, or a combined fluid mixture (API, 1989; Blake and Lewis, 1983; U.S.EPA, 1988). Well construction depends on system design. Screens generally are set across the air/LNAPL/water interfaces in the well. Such screens should be long enough to encompass the anticipated changes in position of these interfaces due to pumping and other influences. Maximization of open screen area through use of continuous wire-wrapped designs has been recommended (Blake and Lewis, 1983) to maximize well efficiency and extend intervals between maintenance. Well diameter depends, in part, on the proposed pumping equipment. Many conventional designs have used wells of 6-inch diameter or larger. However, recent equipment innovations have allowed use of smaller diameter wells.

Standard water-well design procedures traditionally have been used for gravel pack design. However, studies by Sullivan et al. (1988) indicate that filter packs which are too coarse may reduce hydrocarbon recovery efficiency. Laboratory studies reported by Hampton and Heuvelhorst (1990) indicate that LNAPL recovery may be enhanced using hydrophobic filter packs and a grain size approximately half as large as traditional designs. Further laboratory studies (Hampton et al., 1991) again indicated that hydrophobic materials were superior to other materials for filter pack construction. Of the remaining materials which were tested, the mixture containing the least quartz, most angular grain shape, and least uniform size distribution produced the most efficient filter pack. Further research, including field studies, regarding well construction for LNAPL recovery appear to be warranted.

Fluid recovery rate for wells designed to recover only LNAPL generally will be relatively low. Thus, the reduction in hydraulic head due to removal may be minimal. This results in a relatively small capture zone around each well and, generally, hydrodynamic control is not maintained. Conditions in which such systems may be most applicable include situations where water-table depression is not necessary or desired and water treatment/disposal capacities are limited (API, 1989).

Equipment designed for recovery of only LNAPL operates using a variety of mechanisms (API, 1989) including:

1. top mounted intakes allowing fluid collection from the LNAPL/water interface,
2. density-sensitive float valves,
3. conductivity sensors for pump activation, and
4. hydrophobic filters that preferentially allow hydrocarbons to pass.

Such equipment can recover LNAPL to a thickness of a fraction of an inch for systems equipped with conductivity sensors and to a sheen for systems using a hydrophobic membrane (U.S.EPA, 1988).

Wells designed to recover total fluids (i.e., LNAPL and water) may use surface mounted suction-lift or submersible pumps (API, 1989). Recent applications of this technology are similar to wellpoint dewatering systems used in the construction industry (Hayes et al., 1989). In this application, several closely spaced driven or drilled wells may be manifolded to a single high volume vacuum pump. However, practical recovery depths using suction-lift pumps are limited to approximately 20 feet. Total fluids recovery systems generally require LNAPL/water separation which may be difficult due to emulsification. Emulsification problems can be minimized by proper pump selection. Centrifugal pumps generally will emulsify the LNAPL/water mixture more than surface

diaphragm pumps or down-hole pneumatic pumps (API, 1989). Aqueous-phase constituent concentrations in recovered water are also relatively high due to LNAPL/water mixing. Although relatively high yields are possible (Hayes et al., 1989), total fluids removal may be effectively used in situations where the hydraulic conductivity is too low to permit the efficient use of higher capacity pumps (API, 1989; Blake and Lewis, 1983).

Operation of recovery well systems using total fluids recovery may sometimes be enhanced by sealing the wellhead and creating a vacuum within the well (API, 1989; Hayes et al., 1989). Vacuum generation enhances recovery by reducing pressure within the casing, increasing the effective head difference between the formation and the well. Wells constructed using this design may be installed with the top of the screen below the mobile LNAPL (Hayes et al., 1989). The water table is depressed sufficiently during pumping to allow LNAPL to enter the well. This results in less vacuum loss through minimal screening of the unsaturated zone.

Dual pump systems (Figure 12) use one pump located near the bottom of the well to extract only water, creating a cone of depression to initiate LNAPL movement towards the well (API, 1989; Blake and Lewis, 1983; U.S.EPA, 1988). A separate

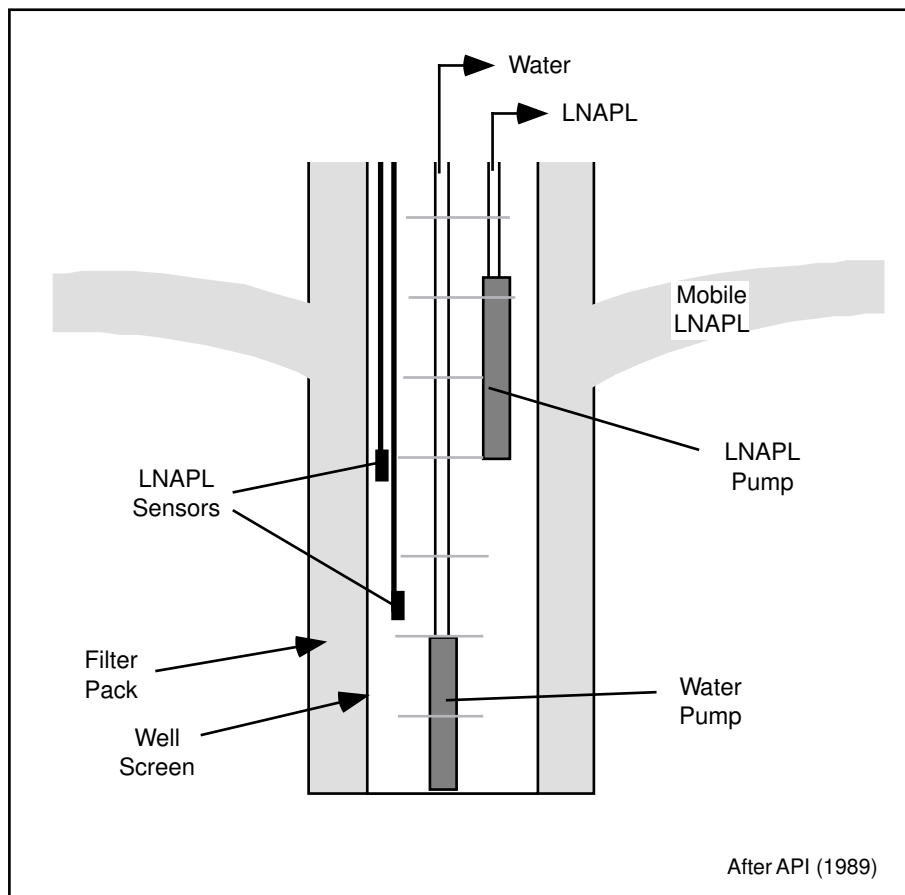


Figure 12. Conceptual system design for separate recovery of LNAPL and water in a single well.

pump located in the upper portion of the screened interval is used to remove LNAPL. Both pumps rely on sensors to ensure that only water and only LNAPL are extracted in their respective pumps (API, 1989). Dual pump systems may also use submersible or surface mounted pumps. Positioning of the water pump generally should be well below the LNAPL/water interface to minimize constituent concentrations and treatment requirements for recovered ground water. Single units, combining separate LNAPL and water pumps, equipped with sensors to prevent pumping mixed fluids are also available (U.S.EPA, 1988).

Dual well LNAPL recovery systems extract water and LNAPL from separate wells. As with single well/dual pump systems, one well produces only water and induces a hydraulic gradient to promote LNAPL movement. The adjacent well is used to recover LNAPL that accumulates in the cone of depression. Conditions under which dual pump and dual well systems are normally used include (API, 1989):

1. Water-table depression to increase LNAPL recovery rates is desirable and not detrimental to the remediation objectives.
2. Hydraulic conductivity and saturated thickness are large enough to sustain flows of separate fluid streams.
3. LNAPL/water separation and treatment capacities are limited.

Installation of horizontal wells is an emerging technology in the environmental field (Morgan, 1992). Such wells could greatly increase contaminant removal efficiency, including LNAPL removal, at some sites. Reported use of this technology at contamination sites (e.g., Looney et al., 1992; Oakley et al., 1992) has been limited. Additional information regarding construction and use of horizontal wells is available in U.S.EPA (1994).

### **System Design and Operation**

At sites where a systematic design approach has been used, traditional LNAPL extraction system designs generally have relied on estimation of the recovery well capture zone. Well locations are then selected to capture and remove hydrocarbons (e.g., API, 1989; Blake and Lewis, 1983). Injection of recovered ground water also has been used to increase LNAPL recovery rates by increasing hydraulic gradients and provide a hydraulic barrier to LNAPL migration (e.g., Zinner et al., 1991). Careful evaluation of the effects of reinjecting treated/untreated ground water is recommended to minimize the potential for increasing subsurface contamination.

Much of the optimization of LNAPL recovery has been conducted in the field through manipulation of LNAPL and water pumping rates. Several factors should be considered during system design and operation. One important design consideration is the effect of water-table depression used to increase LNAPL recovery rates (API, 1989; Blake and Lewis, 1983; Chiang et al., 1990). Although high water extraction rates initially may yield a higher hydrocarbon recovery rate, the ultimate recovery may be greatly reduced. Much of the LNAPL that was originally mobile may be smeared into uncontaminated portions of the aquifer as the water table is

depressed, trapping it as immobile, residual LNAPL in soil pores. This residual LNAPL will remain trapped below the water table when the recovery system is turned off providing a continuing source for ground-water contamination. At many sites, multiple wells pumping water and LNAPL at lower rates may ultimately recover more LNAPL than fewer wells pumping water at higher rates to create large water-table depressions (API, 1989). In addition, if the recovery rate exceeds the LNAPL migration rate to the well, water saturation around the well may increase, resulting in lower relative permeability with respect to LNAPL and reduced recovery (Abdul, 1988; Chiang et al., 1990).

Similar considerations exist for systems using water injection to increase LNAPL recovery rates. Water-table mounding may result in pushing LNAPL upward into previously uncontaminated intervals (Testa et al., 1992). Injection may also cause undesired lateral LNAPL migration. These potential effects should be considered during system design.

Additional variables which may affect optimal LNAPL recovery rates include thickness of the mobile LNAPL and formation permeability to the LNAPL (Charbeneau et al., 1989; Chiang et al., 1990). As the mobile LNAPL thickness increases, the transmissivity of the formation with respect to LNAPL also increases resulting in increased recovery. In low permeability situations, the overall system recovery rate may become a linear function of the number of wells. This is often due, in part, to a lack of hydraulic interference between wells.

In recent studies, several researchers have recommended strategies for maximizing the overall recovery of LNAPL from systems using LNAPL and water extraction. One recommended strategy is to pump the LNAPL layer at relatively low rates in order to maintain the LNAPL as a flowing continuous mass (Abdul, 1988; Charbeneau et al., 1989; Chiang et al., 1990). Water pumping, if used, is carefully controlled to minimize smearing of the LNAPL layer and to prevent upconing of the water table. As expected, these studies indicate that this approach results in a relatively small capture zone for each pumping well. Although this implies that the total LNAPL recovery rate may be a linear function of the number of wells which are used, a greater volume of LNAPL may be recoverable than is possible using other approaches such as maximizing water-table depression.

Based on mathematical simulations, Chiang et al. (1990) produced a series of nomographs to aid in estimating the optimal LNAPL recovery rate for a well under various conditions of hydraulic conductivity, LNAPL thickness, density, and viscosity. However, assumptions such as homogeneity of subsurface materials and LNAPL thickness were used in development of the nomographs, limiting their applicability at many sites. Comparison with site-specific data would be required to verify the utility of these nomographs for a specific site. Charbeneau et al. (1992) also proposed a general method for selecting the optimum hydrocarbon pumping rate in dual water/LNAPL pumping systems as a function of water pumping rate. However, this method only aids in estimating an LNAPL pumping rate and does not indicate an optimal pumping rate for water.

The time frame required for mobile LNAPL recovery using extraction wells, trenches, or drains depends on many factors

including LNAPL and porous media properties, LNAPL volume and distribution, and recovery system design. Time frames generally will be difficult to estimate due to heterogeneity and uncertainty in the values of pertinent parameters. At many sites the time frame required for recovery will be a direct function of the number of wells, trenches, and drains installed.

### LNAPL Modeling

Several multiphase flow models have been developed which are capable of simulating LNAPL transport (e.g., API, 1988; Charbeneau et al., 1989; Faust et al., 1989; Huyakorn et al., 1992; Kaluarachchi and Parker, 1989; Kaluarachchi et al., 1990; Katyal et al., 1991; van der Heijde and Elnawawy, 1993; Weaver et al., 1994). Such models have been used in site characterization to simulate potential contaminant distribution and LNAPL recovery system design. However, multiphase flow is a complex problem, particularly in a heterogeneous environment. Models incorporate simplifying assumptions to facilitate utility. Recognition of the underlying assumptions and evaluation of the site-specific applicability of the model is required. Data requirements may also be extensive. Certain parameters may not be readily measured in the field due to site characterization technology limitations. Many of the models are sensitive to parameters such as permeability, porosity, and LNAPL spill history that are often unknown or poorly defined. Thus, significant uncertainty in the accuracy of the results may exist, even at relatively well characterized sites.

The applicability of these models at many sites may be limited. Objectives of modeling, required quality/quantity of characterization data, and required confidence in the model results should be evaluated prior to initiation of the exercise (Huling and Weaver, 1991). Use of models as screening level and site characterization tools may be beneficial at some sites. For example, Weaver et al. (1994) developed a simple collection of integrated models called the Hydrocarbon Spill Screening Model to help predict the environmental impact on ground water from LNAPL spills. Included are models for simulating the downward migration of LNAPL through the unsaturated zone, radial transport of the oil lens on the water table, and advection and dispersion of the dissolution products in ground water. The modeling package is intended to be used as a screening tool for estimating the effects of parameters such as LNAPL loadings, adsorption, ground-water velocity, and other major factors. Results of simulations using other appropriate models may also aid in designing LNAPL recovery systems. However, as in any simulation of subsurface processes, significant uncertainty in the accuracy of the results generally exists and should be considered in the modeling and remedial design processes.

### Soil Vapor Extraction

Soil vapor extraction (SVE) is a rapidly developing technology with applications for removal of volatile contaminants from the vadose zone. In a simple system, air is drawn through the affected area by applying a vacuum to vapor extraction wells (Figure 13), stripping volatile organic compounds into the moving air stream. The air containing the organic vapors is then treated, if necessary, and discharged to the atmosphere. More complex systems may incorporate trenches, air injection wells, and surface seals to direct the air flow through the

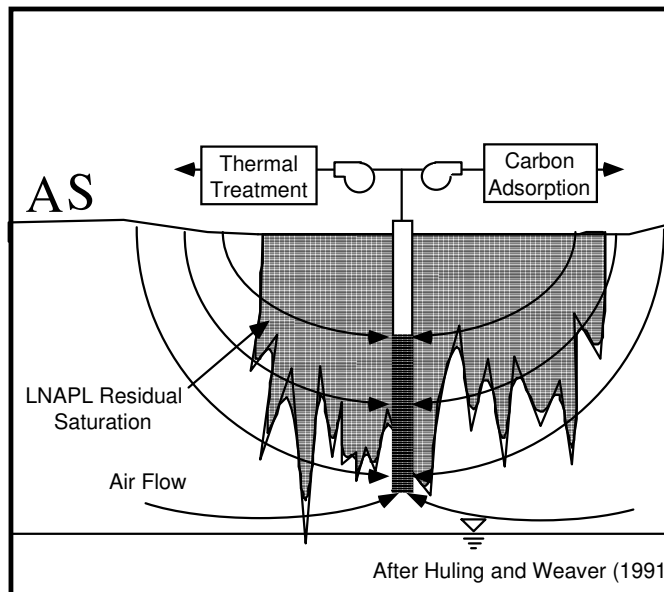


Figure 13. Conceptual design of soil vapor extraction system with vapor treatment prior to discharge.

desired remediation zone (e.g., Johnson et al., 1990b; Lyman and Noonan, 1990; Pedersen and Curtis, 1991).

Success of the SVE system at LNAPL removal is based on three factors: 1) chemical composition of the LNAPL, 2) vapor flow rates through the unsaturated zone, and 3) flow path of the carrier vapors relative to the zone of contamination (Johnson et al., 1990a). In general, SVE may be best suited for the removal of compounds with vapor pressures greater than approximately 14 mm Hg at 20° C (Sims, 1990). With multiple component LNAPLs, preferential removal is observed for chemical compounds with higher vapor pressures and higher mole fractions in the LNAPL mixture.

Subsurface media must be permeable enough to allow adequate vapor movement. Vapor flow rates are dependent on the vacuum drawn in the SVE wells and the properties of the unsaturated zone (e.g., soil moisture content, soil texture, macropores, and LNAPL distribution). The ability to direct flow through the contaminated zone is another primary concern. Vapor flow paths to wells are affected by the degree of short-circuiting from the surface that occurs, locations of subsurface heterogeneities, and the presence of preferential flow paths. A design process based on vapor pressure data for the contaminants and soil/air permeability data was developed by Johnson et al. (1990a, 1990b) to determine if a site is amenable to SVE and to estimate the size of the required system. Additional information concerning design and application of SVE systems is available from DiGiulio (1992), Pedersen and Curtis (1991), and U.S.EPA (1992c).

Ground-water extraction may be used with SVE systems to counteract upconing of the water table near the SVE well caused by pressure reduction (Johnson et al., 1990a). Increased ground-water extraction may dewater deeper intervals exposing contaminated materials for recovery by

SVE at some sites. Controlled studies conducted in a model aquifer by Johnson et al. (1992) indicate this application of SVE may be very effective in removing much of the residual NAPL previously trapped below the water table.

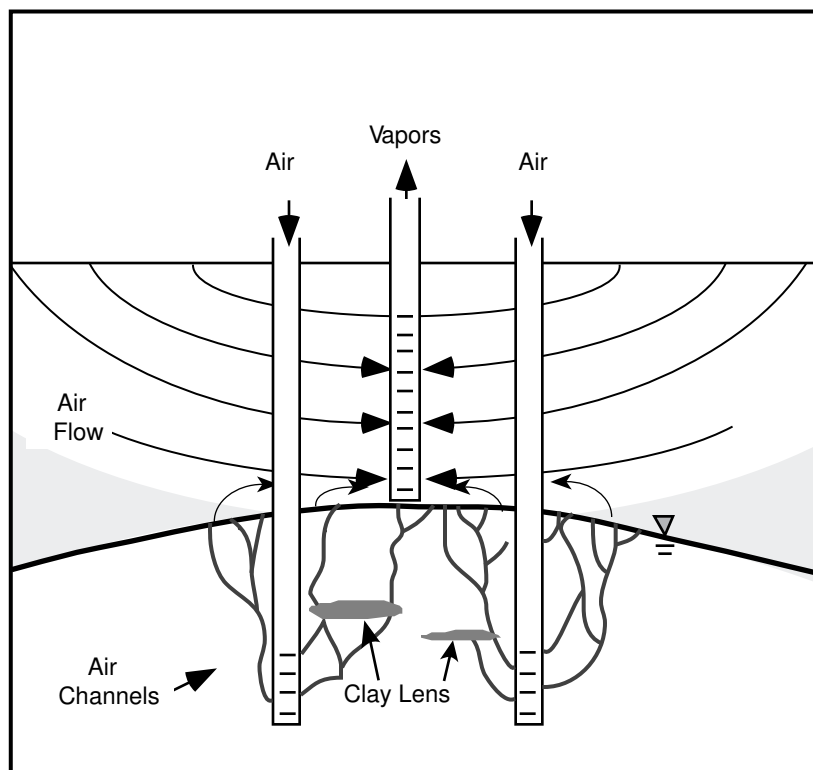
Enhancements which have been applied to SVE systems include in situ soil heating and induced fracturing. Contaminant volatility, which can be one of the limitations to the effectiveness of SVE, increases with increasing temperature. Steam or hot air injection has been investigated for use in increasing removal of volatile and semivolatile constituents (DePaoli and Hutzler, 1992; Sittler et al., 1992; U.S.EPA, 1992a). Studies using radio-frequency heating have also been performed (U.S.EPA, 1992a). Field scale trials have been relatively limited to date. Hydraulic and pneumatic methods for inducing fractures in fine grained vadose zone materials have also resulted in increased vapor yields and contaminant removal during field trials (U.S.EPA, 1993a; U.S.EPA, 1993b).

Another recent enhancement to the SVE concept is the use of induced air flow to increase biodegradation of contaminants in the vadose zone (e.g., Kampbell, 1992; van Eyk, 1992). The term "bioventing" has been applied to such systems. The system is operated to deliver oxygen to the indigenous microbes, thereby promoting degradation of contaminants. Research efforts are currently focusing on design issues such as the need for nutrient addition and the kinetics of the biological reactions.

There are practical limitations to the effectiveness and efficiency of SVE at many sites. For example, site conditions resulting in vapor flow around but not through contaminated zones will result in contaminant mass transfer limitations (Johnson et al., 1990a; Travis and Macinnis, 1992). Situations in which such conditions may occur include; 1) contaminated low permeability materials surrounded or layered with higher permeability materials, and 2) LNAPL removal from a relatively thick layer with a high liquid saturation and a correspondingly low vapor permeability. Contaminant mass transfer in these cases is limited by diffusion from the contaminated zone. The effectiveness of SVE in removing contaminants from the water-saturated zone is similarly limited by diffusive transfer. In general, soil vapor extraction may be applicable for removal of much of the LNAPL located above the water table, including liquids retained by capillary forces, at many sites. Selection of SVE or conventional pumping technology for removal of mobile LNAPL will depend on site conditions and remedial objectives.

### **Air Sparging**

Air sparging is a relatively new technology that is being implemented to remove volatile contaminants below the water table in unconfined aquifers (e.g., Loden, 1992; Marley et al., 1992a; U.S.EPA, 1992a). Air is injected from a well screened in the saturated zone (Figure 14). Two potential objectives cited for such systems are: 1) strip volatile hydrocarbons from the aqueous phase and from any NAPLs present along the



**Figure 14. Conceptual design of air sparging system.**

path of air flow, and 2) add oxygen to the water to encourage biodegradation of amenable constituents. The compounds must be volatile to be stripped and transported to the surface. Additionally, the compounds must be biodegradable for the biodegradation component of this technology to be effective. In the case of multicomponent LNAPLs, a certain fraction of the LNAPL may be volatile and biodegradable. However, a certain fraction of the LNAPL may be relatively unaffected by air sparging. After the air makes its way to the unsaturated zone, a soil vapor extraction system is used to remove the vapors for treatment prior to release to the atmosphere.

Air sparging generally is proposed in conjunction with vacuum extraction, therefore, design limitations, and concerns associated with vacuum extraction are also applicable in air sparging systems. Specific design parameters for air sparging are numerous and detailed discussions are beyond the scope of this review. Generally, these parameters fall under three categories: hydrogeological constraints, contaminant properties and distribution, and system operations (Marley et al., 1992a; Brown, 1994). However, the primary design consideration is contaminant volatility, (i.e., volatilization from the water phase (Henry's Law) or from the NAPL (Raoult's Law)).

One limitation of air sparging is the vulnerability to preferential pathways and heterogeneities. Short circuiting along manmade and natural pathways (sheet piles, wells, sparge points, root holes, high hydraulic conductivity layers, stratigraphic windows, etc.) reduces the overall effectiveness of air sparging. Subsurface heterogeneity results in channeling air flow through preferential pathways (Ji et al., 1993; Johnson et al., 1993). Sparging below an impervious stratigraphic unit may direct air laterally, spreading contamination (Brown, 1994). As with other technologies, overall effectiveness may be reduced due to rate limited mechanisms such as contaminant desorption and slow contaminant diffusion from low permeability materials. Consequently, the radius of influence of a sparge well is difficult to evaluate, and may be relatively small.

Additional potential concerns with use of this technology include increased contaminant migration and in situ precipitation of dissolved minerals (Marley et al., 1992b). Mechanisms such as formation of gas pockets may result in lateral displacement of contaminated ground water or LNAPL into previously clean areas. Uncontrolled vapor migration in the vadose zone may also spread contamination. Clearly, control of both the vapor emissions in the unsaturated zone and the ground-water plume generally must be monitored and maintained. Mineral precipitation due to changes in geochemical conditions may result in undesired permeability reduction at some sites. Adequate site characterization, system design, and monitoring would be required to mitigate such concerns.

Controlled studies of the effectiveness of this technology are relatively limited. In a study conducted in a model aquifer (Johnson et al., 1992) contaminant mass removal using air sparging was observed. However, significant contaminant mass appeared to remain following sparging. Preferential pathways and a limited radius of influence were also observed. The overall performance of this technology has not been adequately assessed under a variety of field conditions. Carefully monitored field demonstrations are required to better determine applicability and effectiveness.

## ***Enhanced Oil Recovery Technologies***

Methods for enhancing oil recovery which were pioneered by the petroleum industry are being developed for environmental applications. Technologies under investigation include injection of hot water or steam, cosolvents (e.g., ethanol), surfactants, alkaline agents, and polymers. Currently many researchers are evaluating the applicability of enhanced oil recovery (EOR) technology to the remediation of LNAPL sites. Most of these technologies are still experimental. Very little information regarding field applications is available. Current reviews of the development of EOR technologies for DNAPL removal (U.S.EPA, 1992a) and other hazardous waste site remediations (Sims, 1990) are available. Information from these sources is also applicable to LNAPL site remediation.

Primary LNAPL recovery systems (e.g., drains, pumping wells) will generally result in the removal of significantly less than 50% of the total LNAPL volume. Enhanced oil recovery may remove more of the LNAPL. However, there are practical limitations to the effectiveness of these techniques. Conditions such as subsurface heterogeneity, low permeability units, and relative permeability reductions caused by the presence of NAPL can prevent remediation fluids from making contact with the NAPL. Significant quantities of LNAPL may remain in place following EOR applications (Mercer and Cohen, 1990).

Recovery of LNAPL may be enhanced by injecting fluids to increase hydraulic gradients, reduce the NAPL/water interfacial tension, reduce NAPL viscosity, increase wetting-phase viscosity, and/or increase NAPL solubility (U.S.EPA, 1992a). The application of heat to viscous LNAPL will enhance mobility by decreasing viscosity and may result in increased solubility. Volatile NAPL components may also volatilize and condense in advance of a steam or hot water flood increasing NAPL saturation and relative permeability. Steam/hot water/hot air flooding, electrical heating, radio frequency heating, and conduction heating are possible techniques which have been investigated (e.g., Davis and Lien, 1993; Fulton et al., 1991; Hunt et al., 1988a; Hunt et al., 1988b; Johnson and Leuschner, 1992; Sims, 1990; Udell, 1992; U.S.EPA, 1992a). Thermal techniques have potential application for increased removal of LNAPL in both the saturated and unsaturated zones. These techniques have been evaluated in a relatively limited number of field scale studies (U.S.EPA, 1992a).

Chemically enhanced recovery techniques appear to be promising technologies for increasing LNAPL solubility and mobility (U.S.EPA, 1992a). Injection of surfactant solutions has been investigated for use in increasing the solubility of NAPL constituents and increasing NAPL mobility through reduction of interfacial tension (Fountain, 1992). Surfactants are potentially capable of increasing NAPL solubility by several orders of magnitude. Injection of alkaline agents has been used in the petroleum industry to increase NAPL mobility through in situ surfactant production resulting from reaction with organic acids in the NAPL. Polymer flooding has been used as a component of water flooding technology by the petroleum industry. Polymers are used to displace some portion of the residual NAPL by increasing the viscosity of the water flood. Application of these technologies in the environmental field has been very limited (U.S.EPA, 1992a). In addition, use of cosolvents has been proposed for increasing solubility of NAPL compounds (e.g., Augustijn et

al., 1992; Boyd and Farley, 1992; Rao et al., 1991; U.S.EPA, 1992a). In general, chemically enhanced recovery of hydrocarbons for environmental applications is in the developmental stage (U.S.EPA, 1992a).

### **Bioremediation**

Practical biological degradation of LNAPL pools has not been demonstrated. Bioremediation of immiscible hydrocarbon is limited due to the following: (1) NAPLs present a highly hostile environment to the survival of most soil microbes, (2) the basic requirements for microbial proliferation (nutrients, terminal electron acceptor, pH, moisture, osmotic potential, etc.) are difficult if not impossible to deliver or maintain in the NAPL (Huling and Weaver, 1991). Correspondingly, bioremediation may be limited to the periphery of the NAPL zone in both saturated and unsaturated media. It has been postulated that biologically-produced surfactants resulting from microbial activity near a NAPL have increased the rate of NAPL solubilization (Wilson and Brown, 1989). However, this has not been proven. Through degradation of the solubilized constituents, microbes may also increase contaminant mass transfer rates from the NAPL by creating steeper concentration gradients than solubilization alone.

Many aqueous-phase compounds dissolved from LNAPL sources are amenable to degradation by naturally occurring microorganisms in the subsurface (Norris et al., 1994; Wilson et al., 1986). While in situ biodegradation occurs naturally at most sites, the overall rate of the reaction may be limited by a lack of nutrients, electron acceptors, or both (Thomas and Ward, 1989). Therefore, in situ biodegradation projects attempt to reduce limitations by injecting necessary nutrients and electron acceptors into the contaminated zone and stimulating naturally-occurring microorganisms. Effectiveness of this approach may be limited by the inability to deliver nutrients and electron acceptor into heterogeneously contaminated and low permeability materials. Although limitations exist, biodegradation of aqueous-phase contaminants derived from many LNAPL sources, such as petroleum products, is a process that is potentially applicable as one component of site management at many LNAPL sites. The greatest utility of enhanced biodegradation may be as a polishing step following removal, to the extent practicable, of mobile and residual NAPL. More comprehensive discussions of the application of biodegradation to contaminant removal from soils and ground water are available (Norris et al., 1994; Sims et al., 1989; Sims et al., 1992).

### **Ground-Water Pump-and-Treat**

Traditional pump-and-treat systems extract contaminated ground water for above-ground treatment. Such systems have primarily been designed to recover aqueous-phase contaminants. Flushing of hundreds or thousands of pore volumes of ground water may be required to significantly diminish contaminant levels at some sites (e.g., Borden and Kao, 1992; Geller and Hunt, 1993; Hunt et al., 1988a; Newell et al., 1990). Complete mobilization of LNAPL trapped below the water table using increased hydraulic gradients alone is not practical under conditions encountered in the field (Hunt et al., 1988a; Wilson and Conrad, 1984). Many of the more soluble LNAPL components may continue to dissolve in ground water resulting in ground-water contamination at unacceptable concentrations, potentially necessitating

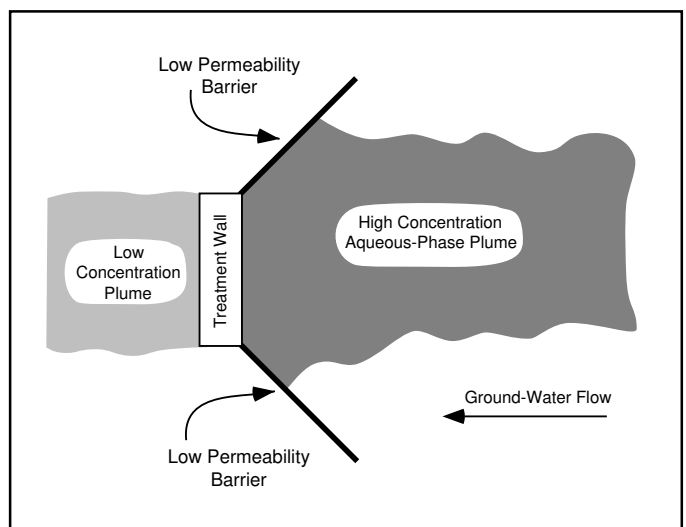
containment operations. Depending on site conditions, time frames of many decades or centuries may be required to remove LNAPLs trapped in the saturated zone using dissolution alone.

Despite the limitations, ground-water extraction and injection technology will be an applicable component of the overall remediation strategy at most sites. Pump-and-treat systems may be most useful for establishing hydrodynamic control to prevent contaminant migration and for remediation of aqueous-phase contamination in some situations in which contaminant sources, including NAPLs, have been removed or isolated. However, many factors, including subsurface heterogeneities, may limit the effectiveness of contaminant removal.

### **Physical Barriers**

Low permeability barriers (e.g., grout curtains, slurry walls, sheet piling) for control of ground-water and LNAPL flow (Mitchell and van Court, 1992) may be applicable as components of remedial operations at many sites. Potential uses include containment of ground-water and/or mobile LNAPL during remediation. However, several of the concerns cited regarding difficulties in DNAPL containment (Huling and Weaver, 1991) will exist for LNAPL containment. Concerns regarding difficulty in assessing barrier integrity and materials compatibility issues should always be considered.

Permeable treatment walls (e.g., Brown et al., 1992; Gillham and Burris, 1992) are an emerging technology for passive control of aqueous-phase contaminant migration. The technology is in its infancy with very few field-scale trials reported to date. Conceptually, reactive materials or substances creating a reactive zone are placed to form a vertical wall (Figure 15). The reactive materials remove or transform dissolved contaminants in ground water that passes through the wall. Low permeability barriers may be incorporated to channel ground water through the reactive



**Figure 15. Map view of reactive treatment wall and low permeability barriers used to channel ground-water flow.**

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wall. A biological treatment wall, for example, may slowly allow dissolution of oxygen and nutrients into ground water, encouraging in situ biodegradation to proceed at an accelerated pace.

### **Treatment Train**

Remediation may require the use of more than one technology. It is likely that several remediation techniques, used in series and/or parallel applications, will be required for maximum contaminant removal. This collaborative effort may be referred to as a treatment train approach (U.S.EPA, 1992a). A conceptual example of a treatment train which might be effective at an LNAPL site includes use of conventional pumping technology for mobile LNAPL removal. This phase might be followed by vapor extraction for removal of residual LNAPL and possibly coupled with ground-water extraction to lower the water table for increased contaminant removal. Additional technologies such as bioremediation might be used to further reduce contaminant concentrations.

Optimum sequencing of remedial actions in a treatment train will be site specific and will depend on such factors as LNAPL migration rates and distribution, remedial objectives, and applicable remedial technologies. Containment of migrating LNAPL may be an appropriate objective of initial actions at many sites. Removal of LNAPL to the extent practicable will also be an objective during early stages of remediation at many sites.

The treatment train concept acknowledges the strengths and weaknesses of various remediation strategies and couples promising technologies to overcome limitations. A successful treatment train will require a thorough understanding of the hydrogeologic and geochemical characteristics of the site. Detailed site characterization efforts and an in-depth understanding of the processes which affect the transport and fate of LNAPLs in the subsurface will permit the optimization of all possible remedial actions, maximize predictability of remediation effectiveness, minimize remediation costs, and make cost estimates more reliable (API, 1989; U.S.EPA, 1992a; Wilson et al., 1986).

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