CHAPTER 11

NONAQUEOUS PHASE LIQUIDS

11.1 INTRODUCTION

Nonaqueous Phase Liquids (NAPLs) are immiscible (undissolved) hydrocarbons in the sub-surface that exhibit different behavior and properties from those of dissolved contaminant plumes. While dissolved plumes are invisible to the naked eye and travel with the flow of ground water, NAPLs form a visible, separate oily phase in the subsurface whose migration is governed by gravity, buoyancy, and capillary forces. Because of the variety in their chemical composition, the behavior of NAPLs can be very different: Some light NAPLs (LNAPLs), after moving downward through the vadose zone, can float and move on top the water table, while other, more dense NAPLs (DNAPLs) can move downward past the water table and penetrate deep into the saturated zone.
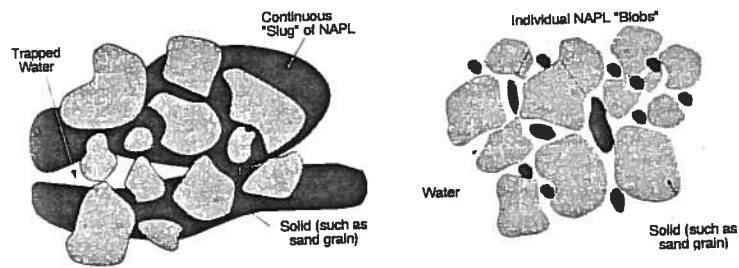
Figure 11.1 Conceptual representation of: (a) free-phase vs. (b) residual NAPL.

When released at the surface, **free-phase** or **mobile** NAPL is forced into the pores of the soil/aquifer matrix by the hydrostatic pressure on the continuous body of NAPL. Because the NAPL is under pressure, it can enter even very small pores and fractures in the subsurface as long as the original NAPL entry point, such as a waste pond or leaking underground storage tank, is active. When the supply of new NAPL is exhausted, however, the pressure on the free-phase NAPL is removed and small blobs (or "ganglia") of NAPL "snap-off" or "bypass" the once continuous NAPL body and become trapped in individual pores or small groups of pores by capillary forces (see Figure 11.1). The **residual saturation**, defined as the fraction of total pore volume occupied by residual NAPL under ambient ground water flow conditions, is an important parameter in ground water remediation problems because it indicates the amount of NAPL that is trapped in the subsurface. The actual residual saturation value at a particular location is determined by the type of chemicals that comprise the NAPL, whether the NAPLs are in the saturated zone or vadose zone, and most importantly, the structure and hydrogeologic characteristics of the soil/aquifer matrix.

NAPLs have a tremendous impact on the remediation of contaminated aquifers, because it is very difficult or impossible to remove all of the residual NAPL blobs once they are trapped in individual pores. Although many NAPL removal technologies are currently being tested, to date there have been few field demonstrations where sufficient NAPL has been successfully removed from the subsurface to restore an aquifer to drinking water quality. The NAPL that remains trapped in the soil/aquifer matrix acts as a continuing source of dissolved NAPL that remains trapped in the soil/aquifer matrix acts as a continuing source of dissolved contaminants to ground water, greatly complicating the restoration of affected aquifers for many years. Because NAPLs act so differently from dissolved constituents in ground water, several key concepts are introduced below.

11.1.1 Single Component NAPLs vs. Mixed NAPLs

NAPLs are either comprised of a single chemical or as a complex mixture of several or hundreds of chemicals. For example, a spill of pure trichloroethylene (TCE) can produce a single

component NAPL comprised of TCE. A gasoline spill, on the other hand, will yield a NAPL comprised of a number of different aromatic and aliphatic hydrocarbons. As one might expect, understanding and predicting the behavior of a mixed-NAPL is much more complex than doing so for a single-component NAPL.

11.1.2 Saturation and Residual Saturation

Saturation (S_i where "i" is an index representing a fluid, and can represent oil (o), water (w), or air (a)) is the fraction of total pore space containing a particular fluid "i" in a representative volume of a porous media:

$$S_i = V_i / V_{pore\ space} \qquad (11.1)$$

where

V_i = the volume of fluid and
$V_{pore\ space}$ = the volume of open pore space

Saturation values for free-phase, continuous masses of NAPLs have been reported as low as 15% to 25%. A controlled release of PCE at a Canadian research site indicated that the final saturations in a 3m × 3m × 3m test cell ranged from 1% to 38%, and that saturations greater than 15% appeared to be related to free-phase DNAPL (Pankow and Cherry, 1996). A study of an LNAPL site in San Diego showed typical LNAPL saturations between 5% and 20%, with several wells showing free-phase LNAPL, even in zones with LNAPL saturations less than 25% (Huntley et al. 1994).

The saturation where a continuous NAPL becomes discontinuous and is immobilized by capillary forces is known as the residual saturation (S_{or}). In unsaturated soils, residual saturation of NAPL fluids, defined as the fraction of the total pore volume occupied by NAPL under ambient condition, typically ranges from 5% to 20%. In the saturated zone, residual saturation values are typically higher because NAPL serves as a "nonwetting" fluid when in contact with water (see Section 11.3), and residual saturation values range from 15% to 50% of the total pore volume (Mercer and Cohen, 1990; Schwille, 1988). Residual saturation appears to be relatively insensitive to the type of chemicals that comprise a NAPL but is very sensitive to soil properties and heterogeneities (USEPA, 1990). Figure 11.2 describes the difference between saturation and residual saturation.

NAPL saturation can be estimated by the following equation if laboratory analysis of the total amount of organic material on the soil (such as a Total Petroleum Hydrocarbon or TPH analysis) is available (Parker et al., 1994) (see Example 11.1).

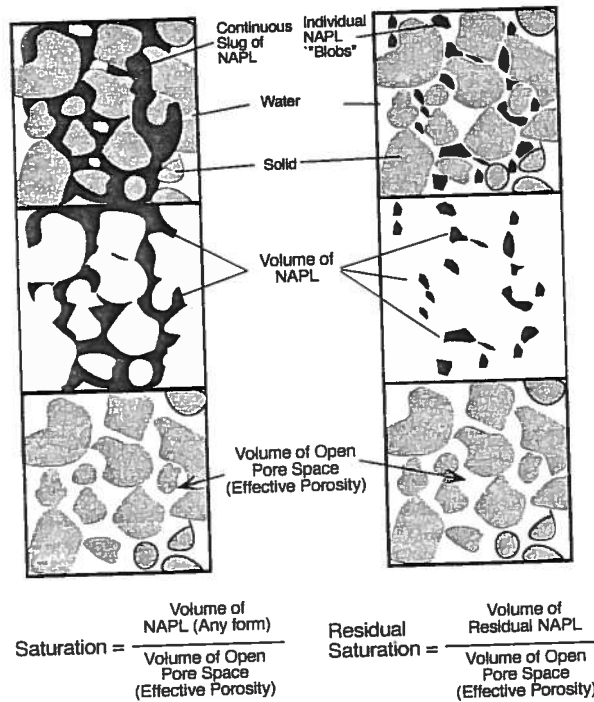$$S_o = \frac{\rho_b \cdot TPH}{\rho_n \cdot n \cdot 10^6} \qquad (11.2)$$

Figure 11.2   Saturation and residual saturation. (a) free-phase NAPL. (b) residual NAPL.

$$\text{Saturation} = \frac{\text{Volume of NAPL (Any form)}}{\text{Volume of Open Pore Space (Effective Porosity)}} \qquad \text{Residual Saturation} = \frac{\text{Volume of Residual NAPL}}{\text{Volume of Open Pore Space (Effective Porosity)}}$$

where

S_o = NAPL saturation (unitless)
ρ_b = Soil bulk density (g/cm^3)
ρ_n = NAPL density (g/cm^3)
TPH = Total Petroleum Hydrocarbons (mg$_{\text{hydrocarbon}}$/kg$_{\text{dry soil}}$)
n = porosity

Example 11.1   CONVERSION FROM TPH TO SATURATION

What is the approximate NAPL saturation of a soil with a TPH value of 10,000 mg/kg? Assume soil bulk density = 1.7 g/cm^3 and porosity = 0.40. The NAPL, gasoline, has a density of 0.75 g/cm^3. Disregard the small concentrations of hydrocarbon present in the dissolved or sorbed phases in the sample.

Solution. Apply Eq. (11.2) to calculate the NAPL saturation of this sample:

$$S_o = \frac{1.7x\,10,000}{0.75x\,0.40\,x\,10^6} \approx 0.06$$

Analysis. 6% of pore space is filled with NAPL, indicating that the NAPL is probably in a residual state and is immobile.

11.1.3 Role of NAPLs as Long-Term Sources

At many sites, the total contaminant mass in the NAPL phase is often many times larger than the total mass of even a large dissolved contaminant plume. To illustrate this point, consider that concentrations of dissolved hydrocarbon plumes are typically reported in units of **parts per million** (ppm) or **parts per billion** (ppb), which represent 1 gram of hydrocarbon per every million or billion grams of water. The amount of NAPL in an aquifer, on the other hand, is reported as a **percentage** of open pore space occupied by NAPL (the saturation value). For a comparison of the relative masses of hydrocarbon in the dissolved versus NAPL phases at a hypothetical hazardous waste site, see Example 11.2.

Because many sites involve hundreds, thousands, or even hundreds of thousands of gallons of NAPLs released to the subsurface, the relative importance of the NAPL phase should not be overlooked. While the dissolved phase is important because it can migrate off-site relatively quickly, NAPLs serve as continuing long-term sources of dissolved organic contaminants to ground water.

A detailed technical evaluation was conducted by the EPA at 24 ground water pump-and-treat sites (U.S. EPA, 1989; 1992d). This study concluded that, indeed, the key factor in the poor performance of pump-and-treat systems was the presence of NAPLs in the water-bearing units. Residual NAPLs were found to serve as continuing sources of constituents to ground water at these sites, undermining the feasibility of aquifer restoration by ground water extraction methods. In response to these findings, the EPA modified the guidelines for remedial actions at Superfund sites affected by NAPLs. In an EPA directive issued in May 1992 (U.S. EPA, 1992c), the agency recognizes that full remediation of ground water impacted by NAPLs, particularly DNAPLs, may be technically impracticable at many sites.

Example 11.2   COMPARING DISSOLVED MASS VS. NAPL MASS

A leaking underground storage tank released 1000 gal of gasoline (density approximately 0.9 g/mL and approximately 1% benzene) to the subsurface. After one year, the

resulting dissolved benzene plume is 100 ft long, 50 ft wide, and 10 ft deep. The average benzene concentration of the plume is 0.10 mg/L, and the porosity of the aquifer is 0.30. If no hydrocarbon is lost from volatilization or biodegradation, how much of the original release is in the dissolved phase, and how much is in the NAPL phase?

Solution.

1. Mass of Benzene Released in Gasoline

    NAPL Mass = [1000 gal gasoline] [3.78 L/gal] [1000 mL/L] [0.9 g/mL]

    [1 kg/1000 mg] [0.01 kg benzene/kg gasoline]

    = 34.02 kg = (74.84 lb)

2. Volume of Contaminated Ground Water in Plume

    Volume = [100 ft] [50 ft] [10 ft] [0.30] [28.3 L/ft^3]

    = 429,000 L

3. Mass of Dissolved Benzene

    Dissolved Mass = [429,000 L] [0.1 mg/L] [kg/10^6 mg]

    = 0.0429 kg Benzene

4. Comparison

    NAPL Mass   = 34.02 kg (99.9%)

    Dissolved Mass = 0.0429 kg (0.1 %)

Analysis. As this example shows, most of the organic mass at a NAPL site is found in the NAPL phase. NAPLs can act as long-term sources of dissolved contaminants to ground water.

11.1.4 Difficulty In Confirming Presence or Absence of NAPLs

Knowing whether a site is contaminated by NAPL is important in order to properly develop site characterization studies and to design reliable ground water remediation systems. At some sites the presence of NAPLs can be confirmed by visually observing if free-phase hydrocarbons have accumulated in wells or are present in soil cores. At many sites, however, the presence of NAPLs are difficult to confirm because residual NAPL will not flow into a monitoring well (it is trapped in the pores of the soil) and is even difficult to see by visual inspection of soil cores. Although several indirect methods are available to estimate the potential for NAPL occurrence, such as measuring the concentrations of hydrocarbons on soil, it is still difficult to confirm the presence or absence of NAPLs at many sites.

11.1.5 Difficulty In Removing Trapped Residual NAPLs

Capillary forces make it very difficult or impossible to remove all the NAPLs that have been released to the subsurface. For example, oil-recovery operations at oil fields that employ pumping alone typically remove less than one-third of the oil in a petroleum reservoir. Enhanced oil recovery techniques, such as waterflooding or the application of surfactants, can only bring 50% to 80% of the original in-place oil (NAPL) to the surface under optimum conditions. These recovery rates are acceptable to the oil industry, where economics determine the ultimate amount of oil recovered from a reservoir. At hazardous waste sites, however, removal of much more than 99% of NAPL is probably required in order to restore a contaminated aquifer to drinking water standards (i.e. low part-per-billion range for most organics). At most sites, this level of recovery is impractical when using pumping and injecting alone. Wilson and Conrad (1984) made a prescient summary of the problems posed by residual NAPL in 1984 when they said:

"The migration of hydrocarbon essentially immiscible with water occurs as a continuous multiphase flow under the influence of capillary, viscous, and gravity forces. Once the source of hydrocarbon is disrupted, and the main body of hydrocarbon displaced, some of it is trapped in the porous media because of capillary forces. Hydrocarbon migration halts as this lower, residual saturation is reached. The trapped hydrocarbon remains as pendular rings and/or isolated, essentially immobile blobs. Residual hydrocarbons act as a continual source of contaminants as, for example, water coming into contact with the trapped immiscible phase leaches soluble hydrocarbon components."

11.2 TYPES OF NAPLs

Although NAPLs are associated with a diverse group of industries and have a wide range of physical properties, they are generally classified by specific gravity (density relative to water) into light NAPLs (LNAPL or dense NAPLs (DNAPLs). LNAPLs have a specific gravity less than water, and will float on the water table. DNAPLs, on the other hand, have specific gravities greater than water and can sink deep into the saturated zone. This simple classification system, although based only on density, is a very useful framework for evaluating the migration pathway, related chemicals and industries, and the ultimate fate of NAPLs in the subsurface.

11.2.1 LNAPLs (Light Nonaqueous Phase Liquids)

LNAPLs are primarily associated with petroleum production, refining, and wholesale distribution and retail distribution (service stations) of petroleum products (Newell et al. 1995). Spills and accidental releases of gasoline, kerosene, diesel, and associated condensate are common sources of LNAPLs to ground water; Wiedemeier et al., (1999) summarized results

from two studies that indicated that free-phase LNAPL was found at 40% to 65% of petroleum hydrocarbon sites. When LNAPL is released at the surface, it first migrates downward through the unsaturated zone under the force of gravity. After encountering a water-bearing unit, the LNAPL forms a pancake-like pool on top of the capillary fringe and top portion of the saturated zone (see Figure 11.3). Ground water flowing past the trapped residual DNAPL dissolves soluble components of the DNAPL, forming a dissolved plume downgradient of the LNAPL zone. Typical chemicals of interest resulting from the dissolution of petroleum products include benzene, toluene, ethyl benzene, and xylene (BTEX) as well as other aromatic hydrocarbons (see Table 11.1).

Because LNAPLs do not penetrate very deep into the water table and are biodegradable under natural conditions, they are generally thought to be a more manageable environmental problem than a DNAPL release. With small-scale releases such as those associated with service stations, natural processes will usually attenuate the environmental impacts within a span of several years.

Figure 11.3 Conceptual model of LNAPL release.

TABLE 11.1 Chemicals Typically Associated with an LNAPL Release

Aromatics
Benzene
Ethyl Benzene
Toluene
Xylenes
Naphthalene
Aliphatic Alkanes
Octane
Decane

Figure 11.4 Conceptual model of DNAPL release. Source: Waterloo Centre for Groundwater Research, 1991.

11.2.2 DNAPLs (Dense Nonaqueous Phase Liquids)

DNAPLs are related to a wide variety of industrial activities, including almost any facility where degreasing, metal stripping, chemical manufacturing, pesticide production, coal gasification plants, creosote operations, or other activities involving chlorinated solvents were performed. As with LNAPLs, the main chemicals of concern are the dissolution products of the DNAPL; for solvent-type DNAPLs, these chemicals include a wide range of chlorinated aliphatic hydrocarbons and other organics such as some polyaromatic hydrocarbons (PAHs), and pentachlorobiphenyls (PCBs) (see Table 11.2).
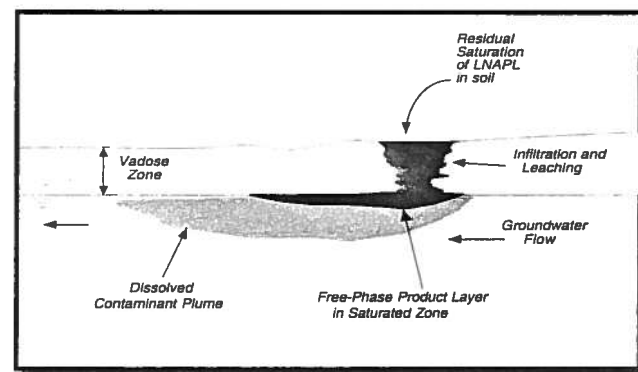
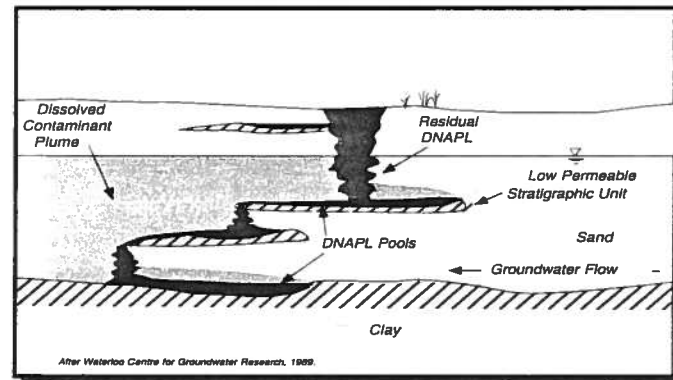After being released at the surface, DNAPLs move vertically downward through the vadose zone. If large quantities of DNAPL have been released, mobile DNAPL will continue vertical migration until it is trapped as a residual hydrocarbon or until low-permeability stratigraphic units are encountered, which can create DNAPL "pools" in the soil/aquifer matrix. However, pools are rarely observed at actual field sites.

In Figure 11.4 a perched DNAPL pool fills up and then spills over the lip of the low-

TABLE 11.2 Chemicals Typically Associated with a DNAPL Release

Halogenated Volatiles	Non-Halogenated Semi-Volatiles
Chlorobenzene	2-Methyl naphthalene
1,2-Dichloropropane	o-Cresol
1,1-Dichloroethane	p-Cresol
1,1-Dichloroethylene	2,4-Dimethylphenol
1,2-Dichloroethane	m-Cresol
Trans-1,2-Dichloroethylene	Phenol
Cis-1,2-Dichloroethylene	Naphthalene
1,1,1-Trichloroethane	Benzo(a)anthracene
Methylene chloride	Fluorene
1,1,2-Trichloroethane	Acenaphthene
Trichloroethylene	Anthracene
Chloroform	Dibenzo(a,h)anthracene
Carbon tetrachloride	Fluoranthene
1,1,2,2-Tetrachloroethane	Pyrene
Tetrachloroethylene	Chrysene
Ethylene dibromide	2,4-Dinitrophenol
Halogenated Semi-Volatiles	**Miscellaneous**
1,4-Dichlorobenzene	
1,2-Dichlorobenzene	Coal tar
Aroclor 1242, 1254, 1260	Creosote
Chlordane	
Dieldrin	
2,3,4,6-Tetrachlorophenol	
Pentachlorophenol	

permeability stratigraphic unit. This example demonstrates how the movement of DNAPL is controlled by the density forces and the structure of the subsurface, and typically not by the movement of ground water.

DNAPLs are observed much less frequently than LNAPLs. Wiedemeier et al. (1999) compiled data from two studies that showed that DNAPL was observed at only 15% to 22% of sites contaminated with chlorinated solvents in ground water. An EPA study of 310 Superfund sites found DNAPL present at only 13% of the sites (U.S. EPA, 1993). The EPA study concluded that 57% of all Superfund sites in the United States have a high or moderate potential for the presence of DNAPL, even though DNAPL was observed at only 5% of all Superfund sites in the study. In other words, DNAPL is probably an important source of ground water contamination at almost all chlorinated-solvent-contaminated sites, despite the fact that it is rarely detected in site monitoring wells.

DNAPLs, particularly if comprised of chlorinated solvents, usually present a much more formidable remediation challenge than LNAPLs for three reasons: (1) dissolved chlorinated solvents do not biodegrade as readily as petroleum hydrocarbons at some sites, and therefore can travel for longer distances in the subsurface; (2) the density and low viscosity of chlorinated solvent DNAPLs spreads the contaminated zone below the water table compared

to LNAPL releases, which remain near the surface of the water table; and (3) the chlorinated solvents density, interfacial tension, and viscosity allow them to move through small preferential flowpaths in the subsurface, so that DNAPL can move into low permeability zones that are hard to remediate. Aquifers contaminated with large quantities of DNAPLs are almost impossible to restore to original conditions using any current proven ground water clean-up technologies (Pankow and Cherry, 1996).

11.3 NAPL TRANSPORT — GENERAL PROCESSES

11.3.1 NAPL Transport at the Pore Level

At the pore level, NAPL movement occurs when enough pressure is available to force free-phase NAPL through a small pore throat and thereby displace air and/or water that once occupied the pore. The amount of pressure that is required depends on the **capillary forces** that act on the different fluids on either side of the pore throat. For example, capillary forces will draw some fluids through a pore throat and displace a second fluid residing in the pore. The way that capillary forces act on these two fluids is partially explained by wettability: The fluid drawn into the pore is referred to as the **wetting fluid** while the fluid repelled by capillary forces is the **non-wetting fluid** (Bear, 1972).

Wettability is defined as the tendency of one fluid to spread preferentially over a solid surface in favor of the second fluid. It is measured by observing the contact angle of a test fluid on a surface when surrounded by a larger volume of a background fluid (see Figure 11.5): a **contact angle** of < 70° indicates that the small amount of the test fluid is wetting and the background fluid is nonwetting. A contact angle >110° indicates that the test fluid is nonwetting, and contact angles between 70° and 110° are neutral-wetting systems (Mercer and Cohen, 1990).

Wettability is closely related to another physical property, **interfacial tension**, which is defined as the free surface energy at the interface between two immiscible fluids (Villaume, 1985). The interaction between similar molecules on one side of the interface and dissimilar molecules on either side of the interface produces capillary forces when the two fluids come in contact with a solid phase, such as a pore throat. Interfacial tension values have been reported for many organic hydrocarbons in contact with water and curves relating to capillary pressure, interfacial tension, and wettability have been developed by Mercer and Cohen, 1990.

To apply the concept of wettability to NAPL transport in specific field situations requires considerable information regarding the physical properties of each fluid in the system and the solid, that is, the soil grains or aquifer media. However, the following generalizations can be made:
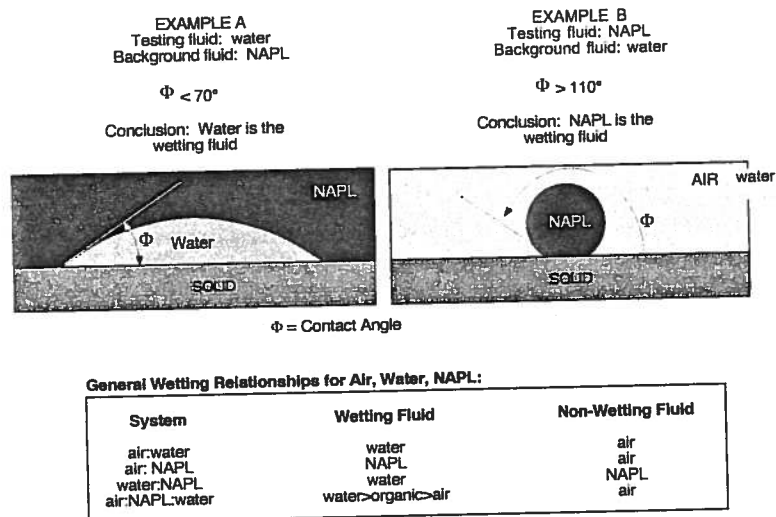
EXAMPLE A
Testing fluid: water
Background fluid: NAPL

$\Phi < 70°$

Conclusion: Water is the
wetting fluid

EXAMPLE B
Testing fluid: NAPL
Background fluid: water

$\Phi > 110°$

Conclusion: NAPL is the
wetting fluid

Φ = Contact Angle

General Wetting Relationships for Air, Water, NAPL:

System	Wetting Fluid	Non-Wetting Fluid
air:water	water	air
air: NAPL	NAPL	air
water:NAPL	water	NAPL
air:NAPL:water	water>organic>air	air

Figure 11.5 Wettability configurations for NAPL, showing a water-wet example and a NAPL-wet example.

- Water is almost always the wetting fluid when mixed with air or NAPLs in the subsurface.

- NAPLs serve as the wetting fluid when mixed with air, but act as the nonwetting fluid when combined with water in the subsurface (Domenico and Schwartz, 1990).

These general rules can be elaborated using three examples of NAPL movement: downward migration of DNAPLs through the saturated zone, NAPL movement through the vadose zone, and LNAPL behavior at the water table.

11.3.2 Downward Migration of DNAPLs in the Saturated Zone

When DNAPLs migrate through the saturated zone, a three-phase system consisting of solid, water, and DNAPL is formed. The DNAPL acts as a nonwetting fluid that must overcome capillary forces in order to squeeze through the pore throat of a pore filled with a wetting fluid, in this case water. The pressure that must be exceeded is called the **entry pressure**. To enter the pore, sufficient driving force must be provided from the combination of (1)

DNAPL density forces and (2) pressure forces present in the continuous DNAPL mass. If the driving force is greater than the entry pressure, then the DNAPL will move forward and enter the pore. When the driving force is removed, the continuous DNAPL mass can split up into countless blobs of residual NAPLs, located mostly in the larger pores of the aquifer matrix (see Figure 11.1).

Unlike the lighter-than-water chemicals, DNAPLs will continue to move vertically downward until they reach a stratigraphic barrier or until the original supply of DNAPL is exhausted and the DNAPL mass is converted to residual DNAPL. In some cases, the downward migration can continue hundreds of feet below the surface.

11.3.3 NAPLs in the Vadose Zone

NAPL infiltration into the vadose zone results in a four-phase system consisting of the air phase, water phase, solid phase, and NAPL phase (U.S. EPA, 1990; Huling and Weaver, 1991). Water on the soil grains serves as a wetting fluid, and NAPL acts as a wetting fluid with respect to air on the water film and a nonwetting fluid with respect to the water (Domenico and Schwartz, 1998). In other words, downward migrating NAPL infiltrates relatively easily into the porous media because it is a partial wetting fluid in this four-phase system, and capillary forces do not repel the movement of NAPLs when entering a pore largely filled with air. If sufficient NAPL is available, it continues to move downward from the source area by forming (1) films between the gas and water phases and/or (2) blobs of NAPL that replace gas in the pores, or water in the pore throats (U.S. EPA, 1990). The tendency of a certain chemical to form films or blobs is dependent of the physical properties of the chemical. Chlorinated solvents, for example, will generally not to form large, continuous films when released to the vadose zone and will respond differently to remediation techniques such as soil venting and in-situ biodegradation than chemicals, which will form films (U.S. EPA, 1990).

When the original supply of NAPL is exhausted, some of the pore space in the vadose zone will be occupied by the remaining residual NAPL in films and/or blobs, with the rest of the pore space filled by air/vapor (located primarily in the larger pores) and water (spread out on the surface of the soil grains and filling the smaller pores).

The residual saturation of NAPLs (either LNAPLs or DNAPLs) in the saturated zone is usually higher than that in the unsaturated zone by a factor from two to five (Domenico and Schwartz, 1990). The reason for the higher concentration of residual NAPLs in saturated media is due to the following factors (Mercer and Cohen, 1990; U.S. EPA, 1990):

- The NAPL/air density ratio is greater than the NAPL/water density ratio, favoring drainage of NAPLs from the vadose zone.

- In the saturated zone, NAPLs are the nonwetting fluid and are trapped in the larger pores.

- NAPLs tend to spread out farther in the vadose zone because of the favorable capillary conditions.

11.3.4 LNAPL Behavior at the Water Table

The interaction between water, air, and NAPLs becomes more complex once the NAPLs approach the water table and associated capillary fringe. In a completely saturated system, water is the wetting fluid and NAPL is the nonwetting fluid whose movement is hindered by repellent capillary forces. The capillary fringe represents the transition zone between a system where NAPLs are a partial wetting fluid (the vadose zone) and where they are the non-wetting fluid (the saturated zone). If the density of a NAPL is less than water, then it will accumulate on top of the capillary fringe and eventually flow in thin sheets along the water table once a certain minimum thickness is achieved (Domenico and Schwartz, 1990). If the LNAPL flowrate through the vadose zone is fast enough, then capillary fringe will collapse and the LNAPL will move deeper and penetrate a short way past the water table. Once the LNAPL supply is exhausted, however, the continuous mass of LNAPL in the capillary fringe will begin to break up into individual blobs and convert from a free-phase mass of LNAPL to a zone containing residual LNAPL.

11.3.5 NAPL Transport Through Fractures and Heterogeneities

The previous section discussed theoretical models for movement of immiscible fluids through a porous media by moving through the primary porosity of the system, the open pore spaces. In the field, however, NAPL typically moves through preferential pathways (large pores, small-scale fractures, rootholes, etc.) in the soil and aquifer matrix. For example, many studies have shown how DNAPL will migrate preferentially through secondary porosity features in the soil/aquifer matrix, that is, larger fractures, partings, rootholes, slickensides, coarse-grained layers, and other micro-stratigraphic features rather than saturating the open pore volume of a porous media (see Pankow and Cherry, 1996). In general, heterogeneities will have the following effects on NAPL movement in the subsurface:

- **Increased residual saturation:** Even small amounts of clay or silt in a soil (as little as 2% by weight) can have a dramatic effect on NAPL migration by creating much more complex, branching migration pathways and by increasing the final residual saturation (U.S. EPA, 1990).
- **Increased penetration depth into vadose zone:** The presence of heterogeneities permit the NAPL to penetrate much deeper into the vadose zone than would be predicted from using typical residual saturation values and assuming uniform saturation of the aquifer media (see Figure 11.6). One research field study showed that even small releases of DNAPL can penetrate quickly through preferential flowpaths in the vadose zone before reaching the water table (Poulson and Kueper, 1992, Pankow and Cherry, 1996) (see Figure 11.7).
- **Make fine-grained confining units ineffective barriers to NAPL flow:** Clay aquitards that serve as effective "confining units" in the context of

ground water flow may not serve as effective barriers to migration of some DNAPLs (primarily the chlorinated solvents) because of micro-scale heterogeneities (U.S. EPA 1992d; Pankow and Cherry, 1996). Modeling studies have indicated that some low-viscosity DNAPLs can penetrate and migrate through hairline fractures as small as 20 microns wide. At one Superfund site, for example, large volumes of DNAPL were observed to have moved significant distances (~50 ft vertically and ~300 ft laterally) in the secondary porosity features of various clay and silt units underlying the site (Connor, Newell, and Wilson, 1989). Pankow and Cherry provide a detailed overview of DNAPL migration through fractures.
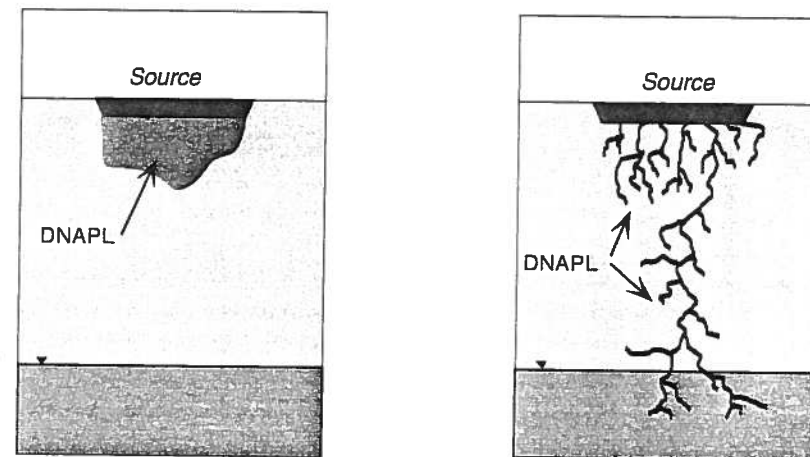

Figure 11.6 NAPL migration in primary vs. secondary porosity. (a) NAPL migration through primary porosity. (b) NAPL migration through secondary porosity features (fractures, root holes, etc.) the more common transport mechanism.

The ability of DNAPLs (primarily chlorinated solvent DNAPLs) to penetrate small fractures has enormous implications with regard to remediation. Parker et al. (1994) demonstrated how some DNAPLs that become trapped in naturally-occurring fractures in clays or rocks can dissolve relatively rapidly (on the order of a few years) into the clay or rock, leaving a geologic media that is almost impossible to restore. The physics of this type of system can be very favorable to DNAPL dissolution, as DNAPL spreads along planar fractures with very large surface areas. Large surface areas, when combined with a powerful diffusive driving
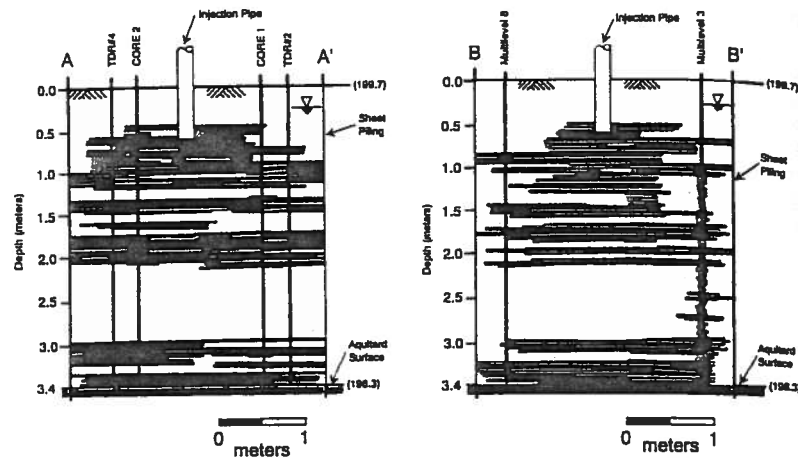
Figure 11.7 Probable distribution of PCE migration pathways after controlled release of 230.9 liters of PCE into Borden sand test cell. Shown are two perpendicular vertical cross-sections (cross-sections intersect in middle of each cross-section). Source: Kueper et al., 1993.

force between the high-concentration fracture and the lower concentration-matrix results in a rapid diffusive disappearance of DNAPLs (Parker et al., 1994; Pankow and Cherry, 1996).

Freeze and McWhorter (1997) developed a conceptual framework to qualitatively evaluate the potential benefits of DNAPL removal from fractured, low-permeability soils, a relatively common hydrogeologic setting as chlorinated solvents are often found to penetrate small fractures in clay units at site. The authors concluded that "very high mass removal efficiencies are required to achieve significant long-term risk reduction with technology applications of finite duration. Further, it is unlikely that current technologies can achieve such efficiencies in heterogeneous low-permeability soils that exhibit dual porosity properties and preferential pathways."

11.3.6 NAPL Transport at the Site Level

Beyond the scale of the individual pore, NAPL migration becomes much more difficult to predict. At the scale of an entire hazardous waste site, for example, the path taken by a NAPL as it migrates through the subsurface is dominated by factors related to the NAPL

release, physical properties of the NAPL, and most importantly geological factors (Feenstra and Cherry 1991; U.S. EPA, 1992a):

- the volume of NAPL released
- properties of the soil/aquifer media, such as pore size and permeability
- micro-stratigraphic features, such as root holes, small fractures, and slickensides found in silt/clay layers
- general stratigraphy, such as the location and topography of low-permeability units
- properties of the NAPL, such as wettability, density, viscosity, and interfacial tension
- the duration of release, such as a one-time "slug" event or a long-term continual discharge
- the area of infiltration at the NAPL entry point to the subsurface

To illustrate the movement of NAPLs at hazardous waste sites, several conceptual models are presented in Figures 11.8 to 11.15.

11.3.7 LNAPL Conceptual Models

After a spill or leak near the surface, both LNAPLs and DNAPLs move vertically downward under the force of gravity and soil capillarity. When only a small amount of NAPL was released, however, all of the free-phase NAPL is eventually trapped in pores and fractures in
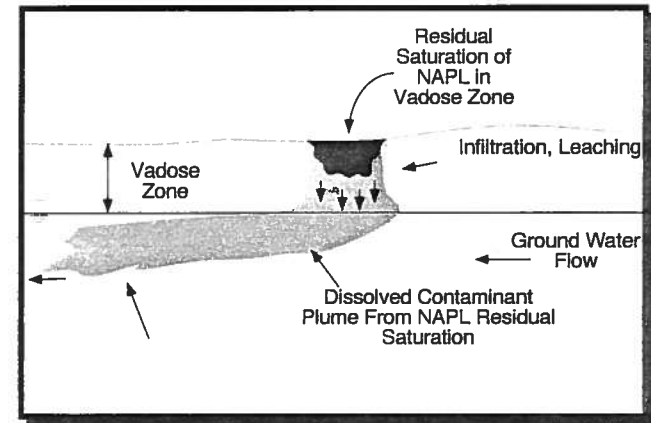

Figure 11.8 LNAPL release to vadose zone only.

the unsaturated zone (see Figure 11.8). Infiltration through the NAPL zone dissolves some of the soluble organic constituents in the NAPL, carrying organics to the water table and forming a dissolved organic plume in the aquifer. This type of release scenario is relatively rare compared to sites where NAPL has penetrated all the way to a water bearing unit (Wiedemeier et al., 1999).

When enough LNAPL is released to reach the water table, the LNAPL will spread along the capillary fringe and the top of the water table because of buoyancy forces. Moving ground water will move past this thin, pancake-like LNAPL layer will dissolve soluble contaminants to form a dissolved hydrocarbon plume (see Figure 11.3).
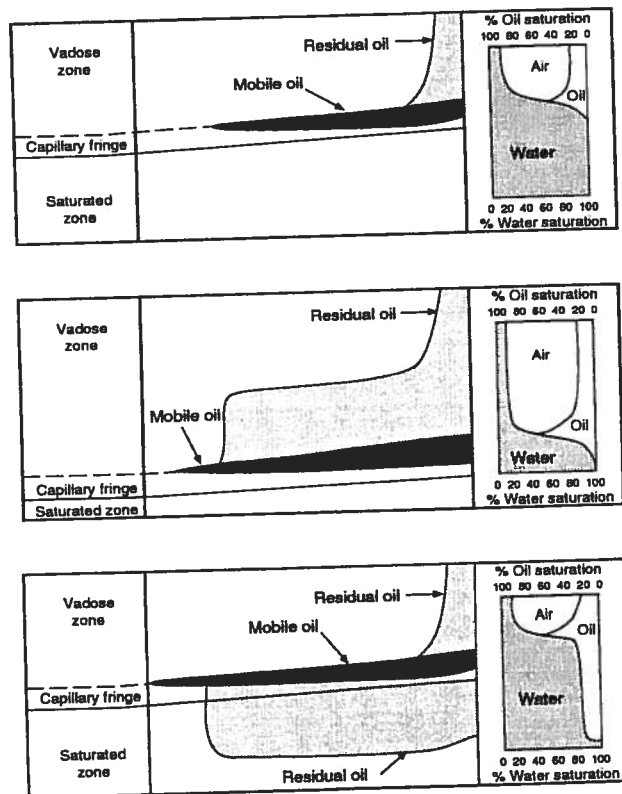

Figure 11.9 Effect of falling and rising water table on the distribution of mobile and residual phases on an LNAPL. Source: Fetter, 1993.

If a free-phase LNAPL is present, a falling water table will lower the floating LNAPL layer, leaving an emplaced source of residual NAPL behind in the saturated zone when the water table recovers (see Figure 11.9). Similarly, a rising water table will lift the free-phase layer into the vadose zone and can increase the residual saturation of the affected soils after the water table drops. This movement is a cause for concern because it will increase the residual hydrocarbon zone, and therefore greatly increase the concentration of dissolved organics.

As shown in Figure 11.10, LNAPL that is forced into confined aquifers by high-entry pressures can migrate under buoyancy forces in directions other than the direction of ground water flow. This phenomenon is very similar to the trapping of oil in petroleum reservoirs. To increase the recovery of LNAPL, recovery wells should be installed near the tops of any stratigraphic traps and screened through the confining unit/aquifer boundary.
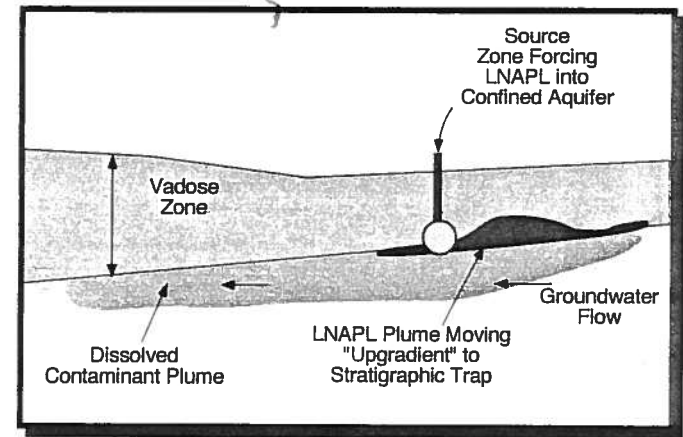

Figure 11.10 LNAPL accumulating in stratigraphic trap in confined aquifer.

11.3.8 DNAPL Conceptual Models

A DNAPL release at the surface can migrate all the way through the unsaturated zone and then continue downward until the mobile DNAPL is exhausted and is trapped as a residual hydrocarbon in the porous media (see Figure 11.4). Ground water flowing past the trapped residual DNAPL dissolves soluble components of the DNAPL, forming a dissolved plume downgradient of the DNAPL zone.

Mobile DNAPL will continue vertical migration until it is converted a residual state or until low-permeability stratigraphic units are encountered which can create DNAPL "pools"

in the soil/aquifer matrix (see Figure 11.4), although pools are rarely observed at field sites. In this figure, a perched DNAPL pool fills up and then spills over the lip of the low-permeability stratigraphic unit. The spill-over point (or points) can be some distance away from the original source, greatly complicating the process of tracking the DNAPL migration. Pankow and Cherry (1996) concluded that lateral movement from the input location can be large.

DNAPL introduced into a fractured rock or fractured clay system follows a complex pathway based on the distribution of fractures in the original matrix (see Figure 11.11). The number, density, size, and direction of the fractures usually cannot be determined due to the extreme heterogeneity of a fractured system and the lack of economical aquifer characterization technologies. Relatively small volumes of DNAPL can penetrate deeply into fractured systems due to the low retention capacity of the fractures and the ability of some DNAPLs
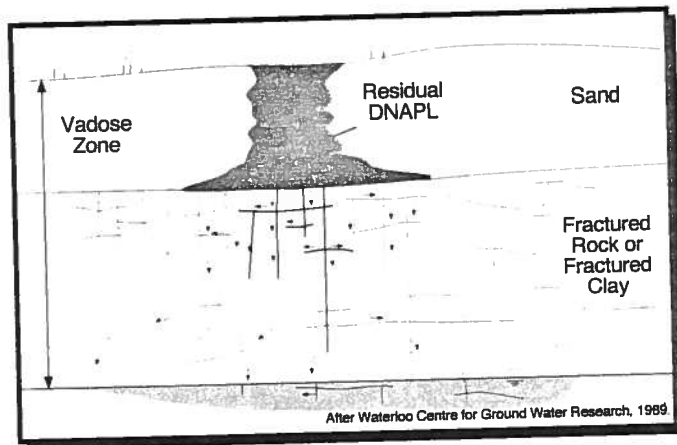

Figure 11.11 Fractured rock or fractured clay system. Waterloo Centre for Groundwater Research, 1991.

to migrate through very small (< 20 microns) fractures. Many clay units, once considered to be relatively impermeable to DNAPL migration, often act as fractured media with preferential pathways for vertical and horizontal DNAPL migration (Pankow and Cherry, 1996).

In the case of a composite DNAPL site, mobile DNAPL migrates vertically downward through the unsaturated zone and the first saturated zone, producing a dissolved constituent plume in the upper aquifer (see Figure 11.12). Although a DNAPL pool is formed on the fractured clay unit, the fractures are large enough to permit vertical migration downward to the deeper aquifer. The DNAPL then pools in a topographic low in the underlying impermeable unit, and a second dissolved constituent plume is formed.
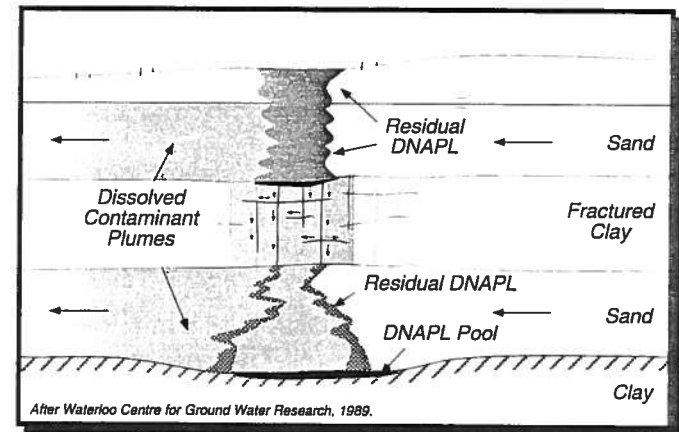
Figure 11.12 Composite DNAPL site. Source: Waterloo Centre for Groundwater research.

The reader should note that these diagrams depict general patterns of NAPL behavior only. The actual path taken by NAPLs at actual hazardous waste sites is usually much more complex due to the large-scale and small-scale heterogeneities found at the site. At many sites the final distribution of NAPLs in the subsurface may never be fully characterized due the complex distribution of countless small-scale heterogeneities in the subsurface.

11.3.9 Conceptual Models — Scale Effects

Wiedemeier et al. (1999) developed a group of conceptual models of NAPL source zones that telescope from the site level (typically hundreds of feet in size) down to the sub-pore level (typically millimeters or smaller in size). This model, shown in Figure 11.13, is described below (adapted with permission from Wiedemeier et al., 1999). The **site-wide models** for LNAPL and DNAPL (top "a" panels) are quite similar, as both LNAPL and DNAPL migrate down through the vadose zone, spread out at changes in soil texture, and then penetrate further downward in fingers. When the LNAPL hits the water table, however, buoyancy forces cause the LNAPL to spread out in a thin, pancake-like layer, and later to smear vertically with the changing water table, leaving residual LNAPL throughout the smear zone. An aqueous-phase plume flows from the smear zone, migrating with the moving ground water close to the water table.
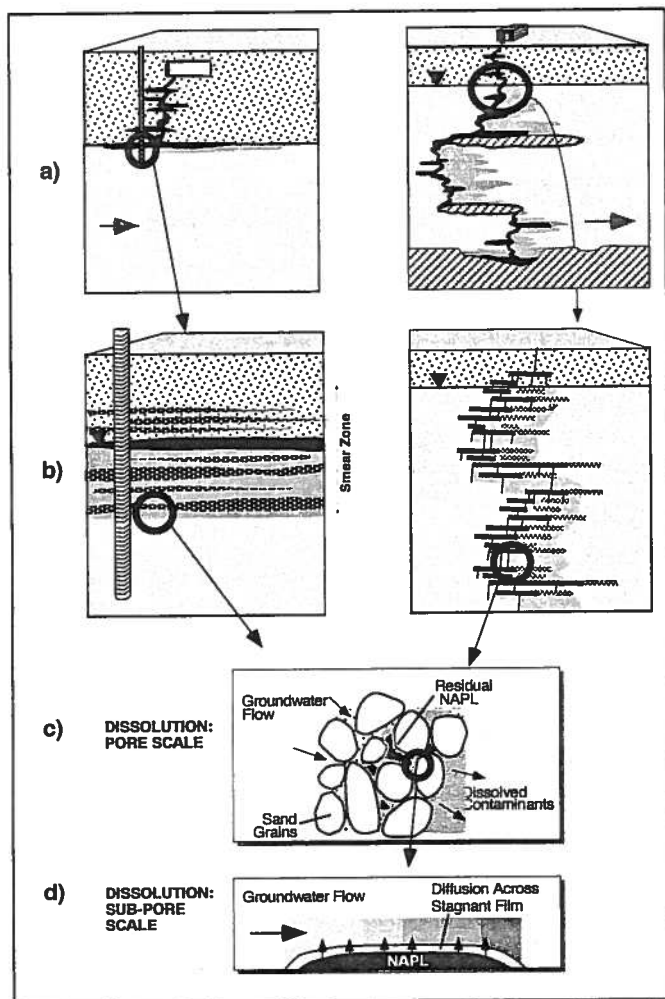
Figure 11.13 Conceptual model of NAPL dissolution at different scales. Source: Wiedemeier et al., 1999 and Pankow and Cherry, 1996.

DNAPL penetrates through the water table and fingers into the saturated zone, forming lenses at subtle changes in aquifer material and more major, macro-scale heterogeneities. In the conceptual model, the DNAPL spills down from the lenses and eventually forms a pool on a capillary barrier (in this case, an unfractured clay layer) at the bottom of the water-bearing unit. Based on a theoretical treatment of fingering phenomena, Kueper and Frind (1988) suggested that the fingers formed by chlorinated solvent DNAPLs in saturated sands or finer media are often less than 10 cm wide. Dissolved plumes are created by every finger and pool, with the plumes associated with the discrete fingers being very thin in the y direction (the direction coming out of the page), and the plumes created by the pools being very thin in the z direction (vertically up and down).

In the second "b" panels of the conceptual model, closer, **core-scale views** on the order of a few feet are shown for the LNAPL and DNAPL releases, corresponding to the size observed when a typical saturated soil core is brought to the surface for evaluation. Note that NAPL can be present, but not observed, in a core, as the amount of NAPL can be small and lack a strong color contrast with the soil. With the LNAPL release, the entire smear zone is visible, and it is apparent that subtle changes in the aquifer material cause a nonuniform distribution of residual LNAPL. In the DNAPL conceptual model, a similar process occurs where subtle changes in the aquifer materials cause the DNAPL to form an apparently random sequence of fingers leading down to thin horizontal lenses from which more fingers emanate.

The amount of dissolution that occurs at this scale is dependent on (1) the surface area of the NAPL that is exposed to moving ground water, (2) the size of the NAPL blobs, and (3) the chemical characteristics of the NAPL (e.g., the mole fraction of soluble components and the solubility of NAPL compounds). Note that the presence of residual NAPL in a porous medium can reduce the relative permeability of the residual NAPL zone. In one laboratory experiment performed by Anderson et al. (1992a), the flow through the residual DNAPL zone was reduced by about 20%. Kueper and Frind (1992), using a range of residual saturations between 14% and 40%, estimated that the corresponding reduction in relative permeability (and therefore ground water flow) for a PCE/water system is between 20% and 70%.

In the **pore scale** (millimeters or less) conceptual model, either residual LNAPL and DNAPL blobs are shown in panel "c"). Both the LNAPL and DNAPL residual blobs have the same general appearance, and ground water flow between the sand grains of the porous medium will come into contact with a NAPL blob, and dissolve the soluble contaminants. Note that the LNAPL and DNAPL will usually be "nonwetting" in the saturated system. In this case, water (the wetting agent) will be in direct contact with the solid (sand grains in this case) and occupy the smallest pore spaces, whereas the NAPL blobs will occupy the larger pores. In a LNAPL smear zone or a DNAPL pool, the percentage of the pore space occupied by the NAPL (called saturation) will be greater than that occupied by water, such that the NAPL may form a continuous mass that could migrate as a body. Under most conditions, however, water will continue to occupy some fraction of the pore space (called the residual water content), and it is rare for large volumes of the porous media to be completely occupied by the NAPL at most contaminated sites.

At the **sub-pore scale** (see the "d" panel), the surface of the LNAPL or DNAPL blob is in contact with ground water, and dissolution is actively taking place. Here a thin film of stagnant water is formed on the blob, and diffusion occurs through the stagnant film to transport soluble contaminants to the film's surface. Moving ground water mixes with the dissolved compounds leaving the film, forming a dissolved plume. At many parts of each residual NAPL blob, however, there is no moving ground water near the blob (e.g., the part of the blob adjacent to sand grains) and, therefore, there is little or no mass transport across the film.

If the NAPL consists of a single compound, the NAPL blob will slowly shrink over time as dissolution continues. If the NAPL consists largely of nonsoluble components with a small fraction of soluble compounds (such as gasoline), dissolution will be affected by effective solubility considerations (see below), and the residual NAPL blob will not shrink appreciably.

11.4 NAPL TRANSPORT — COMPUTATIONAL METHODS

Although the exact path of NAPL movement through the subsurface is difficult or impossible to predict, several general relationships are available for planning and conceptual design purposes.

11.4.1 Pore Level Calculations

Capillary Pressure. Several researchers have summarized the relationships between capillary forces and NAPL movement under hydrostatic and hydrodynamic conditions (Mercer and Cohen, 1990; Bear, 1979). A simple definition of capillary pressure is that it is the pressure difference between the nonwetting and wetting fluid:

$$P_c = P_{nw} - P_w \qquad (11.3)$$

where,

P_c = capillary pressure
P_{nw} = pressure of nonwetting fluid (such as a NAPL)
P_w = pressure of wetting fluid (such as water)

Bear (1979) provides a more detailed definition of capillary pressure for the case of a nonwetting NAPL sphere in a water-filled porous media:

$$P_c = (2\sigma \cos \phi)/r \qquad (11.4)$$

where

P_c = capillary pressure

σ = interfacial tension between NAPL and water
ϕ = contact angle
r = radius of the water filled pore that the NAPL must move through to exit or enter pore

Using this relationship, one can see that as the radius of the soil pores gets smaller, the capillary pressure required to force NAPL into or out of the pore increases. In other words, NAPLs have more difficulty moving through fine-grained soils such as silts and clays than through coarse-grained sands and gravels, corresponding to observations from numerous field sites.

The capillary pressure relationship shown in Eq. (11.4) can be expanded to provide estimates of the hydrostatic and hydrodynamic conditions required for NAPL migration. Some of the more important NAPL migration relationships, listed below, are presented in Table 11.3 (Mercer and Cohen, 1990):

- Critical NAPL height required for NAPL penetration into the vadose zone (see Eq. (11.5)
- Critical NAPL height required for DNAPL penetration into a saturated aquifer (Eq. (11.6)
- Critical NAPL height required for DNAPL penetration from a coarse-grained material into a fine-grained material (Eq. (11.7) and Example 11.3)
- Minimum hydraulic gradient required to prevent downward DNAPL migration or upward LNAPL migration (Eq. (11.8))

TABLE 11.3   Additional Capillary Pressure Relationships

$$Z_n(est) = \frac{2\sigma \cos \phi}{r_t g \rho_n} \qquad (Eqn. 11.5)$$

where: Zn (est) = Critical NAPL height required for NAPL penetration into the vadose zone

$$Z_n(est) = \frac{2\sigma \cos \phi}{r_t g (\rho_n - \rho_w)} \qquad (Eqn. 11.6)$$

where: Zn (est) = Critical NAPL height required for DNAPL penetration into a saturated aquifer

TABLE 11.3 *continued*

$$Z_n(est) = \frac{2\sigma \cos\phi\left(\frac{1}{r_t} - \frac{1}{r}\right)}{gabs(\rho_n - \rho_w)} \quad \text{(Eqn. 11.7)}$$

$$= \frac{P_{c(fine)} - P_{c(coarse)}}{gabs(\rho_n - \rho_w)}$$

$$= \frac{P_{c(fine)} - P_{c(coarse)}}{gabs(\rho_n - \rho_w)}$$

where: Zn (est) = Critical NAPL height required for downward DNAPL penetration or upward LNAPL migration from a coarse-grained material into a fine-grained material

$$\frac{\Delta h}{\Delta z_n} = \frac{\rho_n - \rho_w}{\rho_w} \quad \text{(Eqn. 11.8)}$$

where: $\Delta h / \Delta z_n$ = Minimum hydraulic gradient required to prevent downward DNAPL migration or upward LNAPL migration

σ = interfacial tension between NAPL and water

ϕ = contact angle

r = radius of the water filled pore that the NAPL must move through to exit or enter pore

r_1 = radius of the water filled pore throat that the NAPL must move through to exit or enter pore

ρ_n = density of NAPL (gm/cc)

ρ_w = density of water (1 gm/cc)

g = force of gravity (980 cm/sec2)

μ = dynamic viscosity (centipoise)

Example 11.3 illustrates how to apply a capillary force relationship to a NAPL problem.

Example 11.3 CRITICAL NAPL HEIGHT REQUIRED FOR NAPL PENETRATION INTO THE VADOSE ZONE

Assume that a mobile DNAPL pool is perched above an unsaturated fine-grained silt layer with a pore radius of 0.005 mm. The DNAPL has a specific gravity of 1.3, an interfacial tension with water of 0.04 N/m, and a contact angle to a mineral solid phase of 35°. How thick must the DNAPL have to be before it penetrates the fine-grained silt layer? Assume the residual DNAPL saturation is located above the DNAPL pool.

Solution. Apply Eq. 11.5.

$$Z_n(est) = \frac{2s \cos f}{r_{fine}g(r_n - r_w)}$$

$$= \frac{2(0.040 \text{ N/m})(\cos 35°)}{(0.000005 \text{ m})(9.8 \text{ m/sec}^2)(1300 \text{ kg/m}^3 - 1000 \text{ kg/m}^3)}$$

$$= 4.5 \text{ m}$$

Analysis. Based on this theoretical analysis, substantial accumulation (i.e., 4.5 m) of DNAPL on top of the silt layer is required to penetrate the silt. Because the capillary pressure relationships are dependent on pore radius, microscale heterogeneities (such as fractures) will often control the overall migration pathway taken by mobile DNAPL. At actual sites, the above can overpredict DNAPL ponding on acquitards (Stephens et al., 1998; Tuck et al., 1999).

Darcy's Law. Movement of free-phase NAPLs through a porous medium can be evaluated by using Darcy's equation. If all or almost all of the open pore space is filled with a continuous, free-phase NAPL mass, then Darcy's equation can be applied to NAPL movement in a similar way that Darcy's equation is used for ground water flow. The most important exception, however, is that hydraulic conductivity (K) must be replaced by the intrinsic permeabilities (k) to account for the different hydraulic characteristics differences related to the NAPL fluid. For the simple one-dimensional (1-D) case:

$$v = -(k\rho g/\mu)(dh/dl) \quad (11.9)$$

where

$$dh/dl = \frac{z + P}{\rho g} dl \quad (11.10)$$

v = darcy velocity (cm/sec)

k = intrinsic permeability (cm²; 1 cm² = 10^8 darcies)

ρ = density of NAPL (g/cm³)

g = force of gravity (980 cm/sec²)

μ = dynamic viscosity (poise; 1 poise = 1 g/cm-sec)

dh/dl = hydraulic gradient of NAPL mass

z = reference elevation

P = pressure (atm)

Relative Permeability. When both water and NAPL are present in the aquifer, however, multiphase flow regime is established. Multiphase flow occurs when two different fluids flow through a porous medium, compete for available pore space, and thereby reduce the mobility of both fluids (Mercer and Cohen, 1990). This reduction in mobility is defined by the **relative permeability**, the ratio of the effective permeability of a fluid at a given saturation to the intrinsic permeability of the medium. In a specific porous medium, relative permeability of a fluid ranges from 0 to 1.0 based on a complex function of the saturation of the fluid, whether the fluid is wetting or nonwetting, and whether a wetting fluid is displacing a nonwetting fluid (called **imbibition**) or a nonwetting fluid is displacing a wetting fluid (called **drainage**). NAPL moving into the saturated zone is an example of drainage (the water is draining away from the pore). Forcing NAPL out of the pore with water pressure is an example of imbibition.

Figure 11.14 shows a typical relative permeability diagram for a two-fluid system comprised of NAPL and water and illustrates how the two fluids interfere with each other to reduce mobility. At most parts of the relative saturation curve, adding the relative permeabilities of the NAPL (the nonwetting fluid in a NAPL/water mixture) and the water (the wetting fluid) do not equal one; thus the interference reduces the overall mobility of both fluids in the porous medium (see Example 11.4). One additional point shown on this relative permeability curve is the difference in relative permeability for NAPLs undergoing drainage versus imbibition. As one might expect, it is easier for NAPL to enter a pore than it is to leave a pore, meaning that a relatively permeability diagram for drainage will show higher relative permeability than will the relative permeability diagram for imbibition.

Example 11.4 RELATIVE PERMEABILITY

A NAPL has entered an aquifer and a laboratory study of cores taken from the site yielded the relative permeability curves shown in Figure 11.14. If the average NAPL saturation (S_{ln}) is 0.50, what are the relative permeabilities of the NAPL and the water? What are the implications of those relative permeability numbers?

Solution. From Figure 11.14, the relative permeability of NAPL is 0.25, and the relative permeability of water is 0.05. A relative permeability of 0.25 means that the NAPL will flow through the current mixture of sand/water/NAPL at only 25% the rate that it would flow through a sand/NAPL mixture with no water present. Similarly, water will flow through this sand/water/NAPL mixture at a rate that is only 5% of the flowrate for a sand/water mixture (i.e., no NAPL).

Analysis. The movement of NAPL and water through a porous media slows down significantly when oil and water are mixed together. To maximize the removal of a
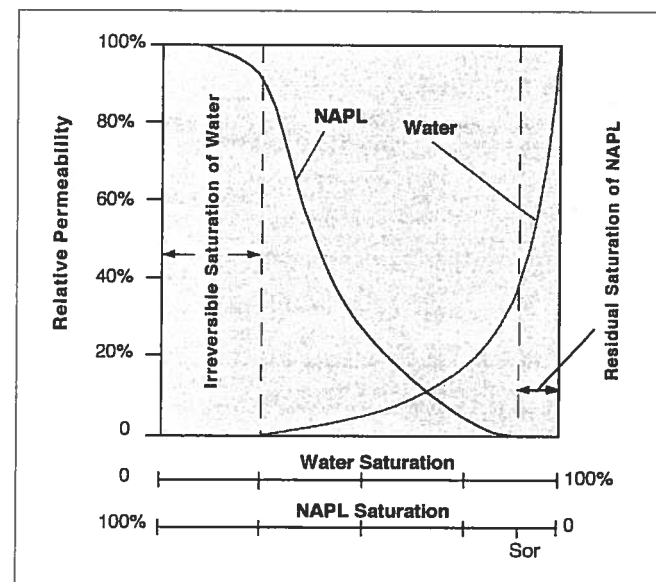
Figure 11.14 Residual Saturation curve. Source: Schwille, 1998. 1999 by Lewis Publishers, a subsidiary of CRC Press.

large free-phase NAPL pool, keep the NAPL pool intact for as long as possible to avoid the interference caused by pumping a combined NAPL and water mixture.

With the same relative permeability curve, the type of flow regime can be described as a function of saturation, as shown in Figure 11.15 (Williams and Wilder, 1971). When the NAPL saturation is high (Zone I), the NAPL mass is continuous and NAPL transport dominates. Because the water is trapped in small, isolated pores, water phase is noncontinuous and the relative permeability of water is very low or zero. In Zone II, both NAPL and water are continuous but do not share the same pore spaces. Due to interference, however, the relative permeabilities of both fluids are greatly reduced. Zone III represents the case where the NAPL is discontinuous and is trapped as a residual hydrocarbon in isolated pores. Water movement in this region dominates flow, and there is little or no NAPL flow under these conditions. The saturation where the relative permeability of the NAPL phase becomes zero is defined as the residual saturation for NAPL; all of the NAPL is discontinuous and no NAPL flow is observed.
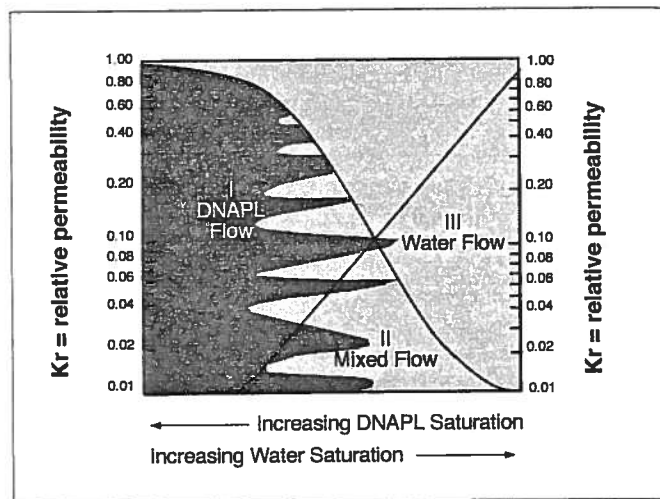
Figure 11.15 Different flow regimes in NAPL/water system. Source: Williams and Wilder, 1971.

Typical relative permeability data are available in the technical literature (Saraf and McCafferty, 1982 and Honarpour et al. 1987) and are useful for illustrating the general relationship between permeability and saturation. The shape of the relative permeability curve is related to (1) intrinsic permeability, (2) pore-size distribution, (3) ratio of fluid viscosity, (4) interfacial tension, and (5) wettability (Domenico and Schwartz, 1990; Demond and Roberts, 1987). In actual practice, however, relative permeability relationships are rarely developed from individual field studies (Mercer and Cohen, 1990).

11.4.2 NAPL Computations At The Site Level

Computer Models for Continuous-Phase NAPL Migration. The petroleum industry pioneered the development of computer models that simulated the migration of NAPLs in the subsurface in the 1960s, and during the 1980s environmental scientists and engineers began to adapt these types of codes to ground water problems. While the current family of environmental multiphase models can simulate a variety of ground water problems, the data requirements are significant and difficult to estimate accurately (Mercer and Cohen, 1990). Due to extreme field complexity associated with NAPL migration, most models are used for conceptual studies only or for prediction of general migration patterns of NAPL in the subsurface. Pankow and Cherry (1996) provide reviews of existing computer models for simulating NAPL flow for ground water problems.

Residual NAPL Relationships for Design of Remediation Systems. While the capillary forces that hold residual NAPL in pores are relatively strong, they can be overcome by gravity forces associated with buoyancy/density forces, or by viscous forces associated with ground water flow. The ratio of capillary forces to gravity forces is known as the bond number (N_b) while the ratio of capillary forces to viscous forces is called the capillary number (N_c):

$$N_b = k\Delta\rho g/\sigma \tag{11.11}$$

$$N_c = (k\rho g/\sigma)(\Delta h/\Delta l) \tag{11.12}$$

$$N_c = (K\mu/\sigma)(\Delta h/\Delta l) \tag{11.13}$$

where,

k	=	intrinsic permeability (cm^2)
ρ	=	density of water (g/cm^3)
σ	=	interfacial tension (dyne/cm)
g	=	gravitational acceleration (g/cm^2)
$\Delta\rho$	=	fluid-fluid density difference (g/cm^3)
$\Delta h/\Delta l$	=	hydraulic gradient
μ	=	dynamic viscosity of water (g/cm-sec)
K	=	hydraulic conductivity (cm/sec)

The bond and capillary number relationships can be used with empirical data to estimate the change in residual saturation due to gravity or viscous forces. Figure 11.16 shows an example of a residual saturation/capillary number curve for a sandstone material. As the capillary number increases, either from an increase in ground water velocity or a reduction in interfacial tension, the amount of residual saturation decreases. On this curve, the change in residual saturation is represented by the ratio of current saturation (S_l) to initial residual saturation (S_{lr}). The first residual hydrocarbon blobs are mobilized when $N_c = 2 \times 10^{-5}$, and all the residual hydrocarbon blobs are mobilized when $N_c = 2 \times 10^{-3}$. Please note that this curve is for one particular sandstone, and that other porous media will have curves with different shapes and endpoints.

Capillary numbers can be used to estimate the potential efficiency of a hydrocarbon removal scheme employing either high hydraulic gradients or reduced interfacial tension, or both. With the empirical data from the sandstone material in Figure 11.16, Wilson and Conrad (1986) showed the magnitude of the hydraulic gradient required to mobilize NAPL
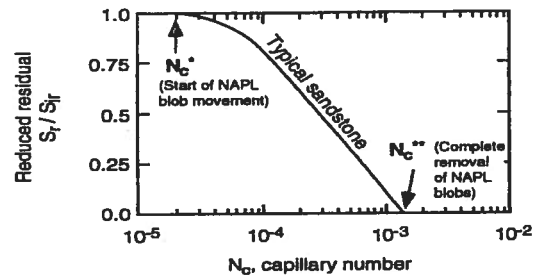
Figure 11.16 Residual hydrocarbon saturation ration, relating final residual saturation to initial residual saturation as a function of capillary number Nc. Source: Wilson and Conrad, 1984.

blobs (see Figure 11.17). These data show that complete mobilization of residual hydrocarbons is very difficult or impossible to achieve in most aquifers using hydraulic gradient alone (Wilson and Conrad, 1986). The required hydraulic gradients are so high for many aquifers (> 1 ft/ft) that no reasonable configuration of pumping and injection wells could be designed to sweep all of the residual NAPL trapped in the pores of the aquifer. In a few cases where permeability is exceptionally high, such as aquifers comprised of coarse-grained material such as gravel, it may be possible to remove all or most of the residual hydrocarbons using the force of water alone.

Addition of surfactants and cosolvents (agents such as polymers, alcohols, or detergents) can also increase the capillary number by reducing the interfacial tension of the NAPL/water blobs. See Chapter 13 for additional information regarding the use of surfactant agents.

1.5 FATE OF NAPLs IN THE SUBSURFACE

As indicated by the transport relationships described in the preceding section, much of the NAPL that is released in the subsurface becomes tightly trapped by capillary forces in the pores and fractures of the soil/aquifer matrix. Eventually, however, the hydrocarbons that comprise the NAPLs are either (1) transferred to the air, (2) transformed to carbon dioxide and water, or (3) transferred to the water. These three processes are called **volatilization, in-situ biodegradation/hydrolysis**, and **dissolution**.
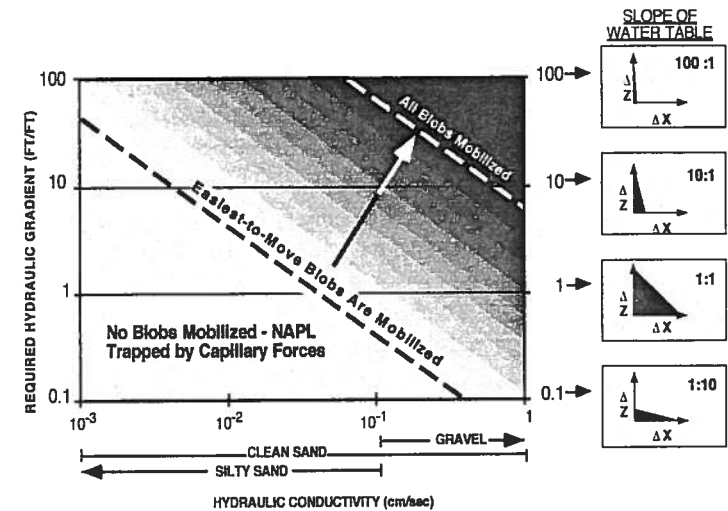
Figure 11.17 Hydraulic gradient required to initiate or completely mobilize residual NAPL blobs vs. hydraulic conductivity of porous media. Note the median hydraulic gradient from a nation-wide survey of 400 aquifers was 0.007 ft/ft, and the median hydraulic conductivity was 0.005 cm/sec. These conditions are well below the values required for blob mobilization. Source: Wiedemeier et al., 1999.

11.5.1 Volatilization

In the vadose zone, volatilization can occur when contaminated water, soil containing sorbed hydrocarbons, or NAPL comes in contact with air. As described in Chapter 7, one of the most important volatilization relationship is Henry's law, which is based on a local equilibrium assumption and yields the concentration of an organic in air if one knows the total concentration of the organic in water.

NAPLs in the subsurface will also volatilize, but in a different fashion than that of a mixture of dissolved organics in water. For a pure-phase NAPL, the vapor pressure defines the equilibrium between the NAPL phase and air phase. For NAPL mixtures, equilibrium conditions for a hydrocarbon are described by principles from Raoult's law:

$$P_a = X_a P_0^a \tag{11.14}$$

where

$\quad P_a \quad =$ vapor pressure of the hydrocarbon "a" in the NAPL mixture (atm)

X_a = mole fraction of hydrocarbon "a" in the NAPL mixture
P_0^a = vapor pressure of a pure hydrocarbon "a" NAPL (atm)

Note that if the NAPL is a single component, the mole fraction equals 1.0 and the pure phase vapor pressure can be used to estimate the vapor pressure in the system of interest. See Example 11.5 for more details on the application of Raoult's Law.

Example 11.5   RAOULT'S LAW

A NAPL of pure benzene is released to the unsaturated zone. What is the *theoretical* concentration of benzene in an air stream that passes through the contaminated zone? What is the concentration of benzene in the air if the NAPL is comprised of only 20% by mole fraction NAPL and 80% nonvolatile organics?

Solution. The theoretical concentration of benzene in air for the pure benzene NAPL can be expressed in two ways, either as a volumetric concentration in units of parts per million volume (ppmv) or as a unit of mg/L (note this is not equivalent to ppm when air is the solvent). To calculate a volumetrically-based concentration for the pure benzene, convert from the vapor pressure expressed in atmospheres using Eq. 11.14:

$$P_a = X_a P_0^a$$
$$P_a = (1)\,(0.10 \text{ atm})$$
$$P_a = 0.10 \text{ atm}$$
$$C = P_a \text{ (atm)} \times 1{,}000{,}000 = 100{,}000 \text{ ppmv}$$

where

X_a = mole fraction of benzene in NAPL (1.0 for a pure benzene NAPL)
P_0^a = vapor pressure of pure-phase component (0.10 atm or 76 mm Hg)
C = volumetric concentrations of benzene in air (ppmv)

To calculate the concentration in mg of benzene per liter of air, use the expression

$$C \text{ (mg/l)} = \frac{[X_a][P_0^a][MW]}{RT}$$

$$= \frac{[1.0 \text{ mole/mole}][0.10 \text{ atm}][78.1 \text{ g/mole}][1000 \text{ mg/g}]}{[0.0821 \text{ L} - \text{atm/mole} - \text{K}][293 \text{ K}]}$$

$$= 325 \text{ mg/L}$$

If the NAPL contains only 20% mole fraction of benzene, use Raoult's law to estimate the actual vapor pressure:

$$P_a = X_a P_0^a$$
$$= 0.20(0.10 \text{ atm})$$
$$= 0.02 \text{ atm}$$

To convert to a mass-based concentration, use this expression:

$$C \text{ (mg/l)} = \frac{[X_a][P_0^a][MW]}{RT}$$

$$= \frac{[0.2 \text{ mole/mole}][0.10 \text{ atm}][78.1 \text{ g/mole}][1000 \text{ mg/g}]}{[0.0821 \text{ L} - \text{atm/mole} - \text{K}][293 \text{ K}]}$$

$$= 65 \text{ mg/L}$$

Analysis: Different concentrations have different practical applications: Volumetric concentrations are often compared against health-based standards, while the mass-based concentrations are important for remediation design.

Vapor transport through the soil under ambient conditions is usually limited by diffusion because there is considerable "dead end" spaces in the subsurface that will be partially filled with NAPL but will not allow air to pass by directly. Therefore, volatilization occurs as the vapors leave the NAPL and move to diffusion towards the zones with lower concentrations, that is, the pathways carrying air. Several software packages are available to describe diffusion-limited volatilization from contaminated soils that are exposed to the atmosphere (e.g., Connor and Bowers, 1998). A simple diffusion model developed by Hamaker (Lyman et al., 1982) assumes the soil column to be semi-infinite (the total depth of the zone undergoing removal of organics by volatilization is small compared to the total contaminated depth) and estimates mass loss over time in soils with:

$$Q_t = 2C_0 \left(D_t / \pi \right)^{-0.5} \tag{11.15}$$

where

Q_t = mass loss over time per unit area of exposed soil for some time t [M/L^2]
C_0 = initial concentration of soil [M/L^3]
D_t = Diffusion coefficient of vapor through soil [L^2/T]

11.5.2 Chemical And Biological Degradation

Hydrolysis. Hydrolysis (see Chapter 7) is probably the most important nonbiological reaction for many NAPL-related chemicals, and is probably the most significant environmental fate process for certain families of chemicals, such as selected chlorinated solvents

(i.e., 1,1,1-trichlorethane, chloroethane). Hydrolysis is a nonbiological transformation where an organic chemical reacts with water (or a component ion of water) to form a derivative organic chemical (Domenico and Schwartz, 1990):

$$R-X \Rightarrow R-OH + X^- + H^+ \qquad (11.16)$$

In this reaction, $R-X$ is a hydrocarbon with X representing an attached halogen, carbon, phosphorous, or nitrogen group. Lyman et al. (1982) lists functional groups that are particularly susceptible to hydrolysis reactions and groups that are resistant to hydrolysis. When considering the effect of hydrolysis on NAPLs, note that only the molecules on the surface of a NAPL blob are in contact with water, thereby preventing the hydrolysis of the hydrocarbon molecules on the inside of the blob. Similarly, NAPLs in the vadose zone will not undergo hydrolysis when they are only in contact with air (see Chapter 7).

Dissolution. The transfer of soluble organics from an immiscible liquid (such as a NAPL) to the water is called **dissolution** (see Figure 11.18). In the vadose zone, infiltration water moving past NAPL will dissolve soluble hydrocarbons and transport them to the saturated zone. In aquifers, dissolution occurs when NAPL slowly dissolves as ground water flows past residual NAPL blobs or a large continuous-phase NAPL pool. Because most sites are probably affected by NAPLs, the dissolved plumes are a symptom of NAPL contamination either in the vadose zone or the saturated zone (Weidemeier et al. 1999).

The most important factors controlling the dissolution rate are the saturation of the NAPL in the subsurface and the **effective solubility** of the dissolving hydrocarbons. Simply put, higher dissolution rates are associated with more soluble hydrocarbons in a NAPL and/or large amounts of NAPL in the subsurface. Secondary parameters that influence the dissolution rate include ground water seepage velocity and porosity. With several of these key values estimated from engineering judgment or obtained from the field, an estimate of dissolution rate can be obtained and used for the purpose of predicting how long the NAPL will serve as an active source of dissolved hydrocarbons to ground water.
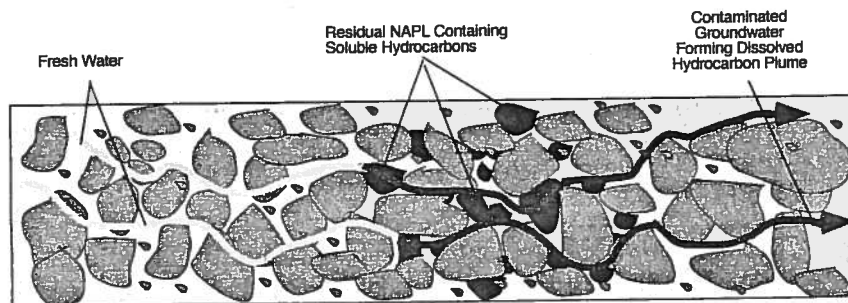

Figure 11.18 NAPL dissolution of residual NAPL, forming dissolved hydrocarbon plume.

Effective Solubility Relationship. For single-component NAPLs, the pure-phase solubility of the organic constituent can be used to estimate the theoretical upper-level concentration of organics in aquifers or for performing dissolution calculations. For NAPLs comprised of a mixture of chemicals, however, the **effective solubility** concept should be employed. **Effective solubility** is defined as the theoretical aqueous solubility of an organic constituent in ground water that is in chemical equilibrium with a mixed NAPL (a NAPL containing several organic chemicals). The effective solubility of a particular organic chemical can be estimated by multiplying its mole fraction in the NAPL mixture by its pure phase solubility, based on principles from Raoult's law (see Borden, et al., 1992; Feenstra, Mackay, and Cherry, 1991; Pankow and Cherry, 1996):

$$S_i^e = X_{oi}S_i \qquad (11.17)$$

where

S_i^e = the effective solubility of indicator constituent i in the water phase (mg/L)

X_{oi} = the mole fraction of indicator constituent i in the DNAPL phase (unitless)

S_i = the solubility of indicator constituent i in water (mg/L)

Effective solubilities can be calculated for all components in a DNAPL mixture (see Example 11.6). Insoluble organics in the mixture (such as long-chained alkanes) will reduce the mole fraction and effective solubility of more soluble organics but will not contribute dissolved-phase organics to ground water. Please note that this relationship is approximate and does not account for nonideal behavior of mixtures, such as cosolvency, etc.

The initial mole fraction of the soluble organic in the NAPL phase is determined through laboratory analysis.

Example 11.6 EFFECTIVE SOLUBILITY

Calculate the effective solubility of a DNAPL with a mole fraction of trichloroethylene (TCE) equal to 0.10.

Solution. Apply Eq. (11.17):

$$S_i^e = X_{oi}S_i$$
$$S_i^e = (0.10)(1100 \text{ mg/l})$$
$$S_i^e = 110 \text{ mg/l}$$

Analysis. When soluble organics are found in mixed DNAPLs, they have a lower theoretical solubility in water than they would if the organics were found as a pure-component DNAPL. This is one reason why near-solubility concentrations are never found in the field, as many of the DNAPLs causing dissolved plumes are mixed DNAPLs. The other main reason for never observing near-saturation conditions in the

field is dilution with clean water. Even in an area of high DNAPL saturation, there are still some streamlines that never come into contact with the DNAPL (see Anderson et al., 1992a; Anderson et al., 1992b; Pankow and Cherry, 1996; Wiedemeier et al., 1999).

Predicting Dissolution Rates Over Time. As with the volatilization of NAPLs, the dissolution rate of a mixed NAPL will decline over time, due to the reduction in mole fraction of soluble components in the NAPL. Simple models (e.g., see discussion in Wiedemeier et al., 1999) can be used to simulate the slow decline in dissolved hydrocarbon concentration over time that is originating from a NAPL zone. A method developed by Feenstra (Pankow and Cherry, 1996) uses dissolution data from multi-component NAPLs to estimate the mass of NAPL in a source zone.

In-Situ Biodegradation. Current conceptual models of biodegradation assume that significant biological transformation does not occur in the NAPLs themselves. However, vigorous biodegradation reactions can serve to reduce dissolved contaminants that result from dissolution, thereby increasing the driving force for dissolution and increasing the rate that NAPLs are depleted. The dissolution products from fuel NAPLs, such as the BTEX compounds from gasoline, are readily biodegradable both aerobically and anaerobically (Wiedemeier et al. 1999). Computer models such as BIOPLUME and BIOSCREEN (see Chapter 8) account for the available biodegradation capacity (also called the expressed assimilative capacity) of the ground water to simulate the biodegradation of fuel components (e.g., see Newell et al., 1996). Example 11.7 illustrates the mass balance between available electron acceptors that flow through a residual NAPL source zone and the mass of dissolvable contaminants in the source zone.

Many chlorinated solvents are now known to biodegrade in the subsurface. For example, the chlorinated ethenes (PCE, TCE, DCE, and VC) and chlorinated ethenes (TCE, DCA) are biodegraded by dechlorinating bacteria called halorespirators that consume dissolved hydrogen along with chlorinated solvents. The dissolved hydrogen itself is either produced by naturally occurring bacteria that ferment nonchlorinated organics, or can be added directly (Newell et al., 1998).

Example 11.7   IN-SITU BIODEGRADATION OF LNAPL SOURCE ZONE

How long does it take to for clean ground water to biodegrade the mass in an LNAPL source zone? Use the following assumptions:

Depth of LNAPL penetration into saturated zone: 2 m

Width of LNAPL release in saturated zone: 10 m

LNAPL mass: 1000 gallons of gasoline (~2500 kg)

Fraction of BTEX in gasoline: 10%

Ground water darcy velocity: 0.1 m/day

Equivalent amount of BTEX that can be consumed by clean ground water flowing through source zone (this is based on the expressed assimilative capacity of the clean ground water, such as the amount of oxygen and other electron acceptors available for biodegradation) : 10 mg/l

Solution.

Time to degrade (t) may be calculated as follows:

$$t = \frac{\left[2500 \text{ kg LNAPL}\right] \cdot \left[\dfrac{0.1 \text{ kg BTEX}}{1 \text{ kg LNAPL}}\right] \cdot \left[\dfrac{10^6 \text{ mg BTEX}}{\text{kg BTEX}}\right]}{\left[\dfrac{0.1 \text{ m}}{\text{day}} \cdot 10 \text{ m} \cdot 2 \text{ m}\right] \cdot \left[\dfrac{10^3 \text{ L}}{\text{m}^3}\right] \cdot \left[\dfrac{10 \text{ mg e}^- \text{ acceptors}}{1 \text{ L clean water}}\right]\left[\dfrac{1 \text{ mg BTEX removed}}{3.14 \text{ mg e}^- \text{ acceptor}}\right] \cdot \left[\dfrac{365 \text{ day}}{\text{yr}}\right]}$$

$= 34$ years

Analysis. This calculation indicates that clean ground water has the capacity to biodegrade all of the dissolved BTEX contaminants in the LNAPL source zone in 34 years at this site. The actual time may be longer, however, if the rate of BTEX dissolution is slower than the rate that the clean ground water delivers electron acceptors to the source zone.

11.6 CHARACTERIZING NAPLs AT REMEDIATION SITES

Although the presence of NAPLs can dominate the remediation process at a site, it is often difficult to locate NAPL zones or even to confirm that NAPL is present at site. The following sections summarize the most important techniques, both direct and indirect, that can be employed to characterize the distribution of NAPLs at a hazardous waste site. Cohen and Mercer (1993) provide a rich collection of procedures for evaluating DNAPL sites, many of which can also be applied to investigation of LNAPL problems. The U.S. EPA (1992a) provides a worksheet and flowcharts to help determine the potential for occurrence of DNAPL at hazardous waste sites.

11.6.1 Direct Measure

Apparent vs. Actual LNAPL Thickness. Analysis of free-phase hydrocarbons in a well is the best evidence that NAPLs are present in the subsurface. As would be expected, a floating layer in a monitoring well indicates the presence of a LNAPL layer floating on top of the water table, while a dense layer at the bottom of a well indicates a heavy DNAPL in the formation. The thickness of the LNAPL layer in the well can provide an order-of-

magnitude indication of the thickness of the LNAPL floating layer, with the "apparent thickness" in the well usually being two to ten times thicker than the actual product thickness in the aquifer (Cohen and Mercer, 1993). The primary reason for this difference is seen in Figure 11.19, where the LNAPL in the formation is shown floating on top of the capillary fringe while the LNAPL in the well floats on top of, and partially depresses, the actual water table.

The actual relationship between the apparent and true LNAPL thickness is very difficult to predict. Based on a review of many of these methods, Hampton and Miller (1988) proposed the use of the following simplified relationship for approximating the true thickness of LNAPL-saturated formation. LNAPL thickness in a formation (h_f) may be approximated by:

$$h_f \approx h_w (\rho_{water} - \rho_{LNAPL})/\rho_{LNAPL} \qquad (11.18)$$

where

    h_f is the thickness of LNAPL in formation
    h_w is the thickness of LNAPL in well
    ρ_{water} is the density of water
    ρ_{LNAPL} is the density of LNAPL

Note that this relationship is only an approximation of actual conditions in the field. Some specialized field procedures, such as dielectric logging, may be more useful for estimating the true product thickness in the formation (Kemblowski and Chiang, 1989; Keech, 1988).

DNAPL Thickness in Wells. While apparent product thickness can provide a general indication of the amount of LNAPL conditions in the field, DNAPL thickness data is much more difficult to interpret and use. Unless the DNAPL observation well is screened
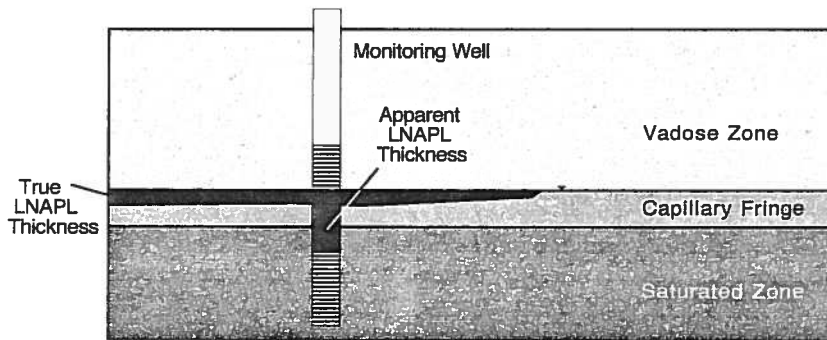
Figure 11.19 LNAPL floating on top of capillary fringe in formation and accumulating on top of water table in well.

Screen Too High
Below Confining Unit
No Accumulation

Screen Too Deep
Above Confining Unit
Too Much Accumulation

Screen Penetrates Lense
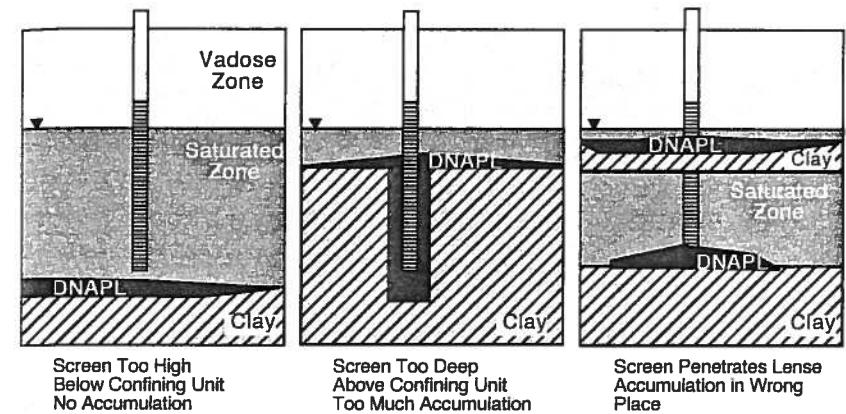Accumulation in Wrong
Place

Figure 11.20 Problems with measuring DNAPL in monitoring wells.

directly within a DNAPL pool or lens and is constructed correctly, the apparent DNAPL thickness can give erroneous indications of the quantity of DNAPL in the formation (see Figure 11.20). In general, DNAPL accumulation in wells only proves that mobile DNAPL is present in the subsurface (Pankow and Cherry, 1996).

One important point to remember is that the absence of NAPL in a well does not confirm that the subsurface is free of NAPL, however. If a screen is set below the surface of the water table, for example, the floating LNAPL layer will ride above the screen and buoyancy forces will prevent the LNAPL from entering the well. Similarly, a well that does not intersect any DNAPL-flowing zones, or is screened above a DNAPL pool or lens, will not indicate the presence of DNAPL. Considerable care must be taken to make sure that the well screen will intersect the zone that may have NAPLs. Most importantly, a well will not exhibit any NAPL if the screened interval contains only residual NAPL. The residual NAPL is trapped in the porous media and is prevented by capillary forces from migrating into the well.

Visual examination of soil samples. In cases of gross NAPL contamination, a visual inspection of a soil core can prove that NAPLs are present in the subsurface. A core that is saturated with oil, for example, is usually fairly easy to discern with the naked eye. NAPL that is present in small secondary porosity features or tied up as small residual blobs may be very difficult to observe, however, particularly if the NAPL has a similar color to the soil matrix. Some field investigators recommend shaking the soil core in a jar with water to separate the DNAPL from the soil or performing a paint filter test to increase the chance for visual detection. In addition, use of a black light will help to identify many NAPLs containing aromatic and other florescent hydrocarbons, and Sudan IV hydrophobic dye can be used to help see NAPLs in soil samples (Cohen and Mercer, 1993).

11.6.2 Indirect Measures

Ground Water Concentration and Distribution. Although one might expect that concentrations of dissolved chemicals in NAPL zones would be near the solubility of these chemicals, in actual practice concentrations this high are rarely observed in the field. Two main explanations are often given for this phenomenon: (1) the effective solubility relationship limits the actual concentration of dissolved constituents in ground water in contact with mixed NAPLs; and (2) the typical monitoring well, constructed with a 10 to 20 ft-long screen, intersects many "clean" flowlines that do no contact NAPL, resulting in a dilution of the "dirty" NAPL-related flowlines that are sampled.

Because of these factors, an often-employed rule of thumb for NAPL states that if concentrations of NAPL-related chemicals in ground water are greater than 1% of the pure-phase or effective solubility, then NAPLs are probably present at the site (U.S. EPA, 1992a, Pankow and Cherry, 1996) (Example 11.8). Note that this is a general rule and therefore it should be used in conjunction with other indicators of NAPL presence. The EPA (1992) states "however, certain concentrations are generally accepted as indicating a highly likelihood of a subsurface DNAPL source across a wide range of sites (i.e., 1% or more of a compounds solubility). However, concentrations representing less than 1% of a compounds solubility do not indicate the absence of a subsurface DNAPL source." A modified version of the rule that considers the presence of multi-component NAPLs was used by the U.S. EPA (1992a).

Example 11.8   INDIRECT MEASURES OF DNAPL PRESENCE: 1% RULE

Site A has a monitoring well with dissolved trichloroethene concentrations on the order of 15 mg/L. What does the 1% rule indicate for DNAPLs at this site?

Solution.

Pure-phase solubility of TCE = 1100 mg/L
1% of pure phase solubility = 11 mg/L
Concentrations at this well exceed 1% of the pure phase solubility

Analysis. The site concentrations at this well suggest that DNAPL is present at the site, even though free-phase DNAPL was not observed in the well. Although the presence of DNAPL cannot be proven explicitly at this site, the data from this well indicate a likelihood of DNAPL presence.

The distribution of dissolved constituents at a site can also be used as an indicator of the presence of NAPLs. If dissolved NAPL-related chemicals appear in an anomalous upgradient/across gradient location, or are variable over time, then either a free-phase floating LNAPL layer or DNAPL mass may have been moving across the site and that NAPLs are

currently serving as a source of dissolved constituents to ground water. Finally, if DNAPL-related chemical concentrations appear to increase with depth, then the presence of DNAPLs is indicated.

Chemical Analysis of Soil/Aquifer Matrix Samples. A general rule of thumb for soil samples is that if greater than 10,000 mg/kg of hydrocarbon contamination (1% of soil mass) is observed in the soil or aquifer matrix sample, then that sample probably contains some NAPL (Feenstra et al., 1991). A more exact method employs a partitioning calculation based on the chemical analyses of soil samples from the saturated zone and the effective solubility concept. This method tests the initial hypothesis that all of the organics in the subsurface are either dissolved in ground water or adsorbed to soil (assuming dissolved-phase sorption, not the presence of NAPL). By using the concentration of organics on the soil and the partitioning calculation, a theoretical pore-water concentration of organics in ground water is determined. If the theoretical pore-water concentration is greater than the estimated solubility of the organic constituent of interest, then NAPL may be present at the site (Feenstra et al., 1991):

Step 1: Calculate S_i^e, the effective solubility of organic constituent of interest.

Step 2: Determine K_{oc}, the organic carbon-water partition coefficient from literature sources or from empirical relationships based on K_{ow}, the octanol-water partition coefficient, which is also found in the literature. For example, K_{oc} can be estimated from K_{ow} using the following expression developed for polyaromatic hydrocarbons (Karickhoff et al, 1979):

$$\log K_{oc} = \log K_{ow} - 0.21 \tag{11.19}$$

Other empirical relationships between K_{oc} and K_{ow} are presented in Chapter 7.

Step 3: Determine f_{oc}, the fraction of organic carbon on the soil, from a laboratory analysis of clean soils from the site. Values for f_{oc} typically range from 0.03 to 0.00017 mg/mg (Domenico and Schwartz, 1990). Convert values reported in percent to mg/mg.

Step 4: Determine or estimate ρ_b, the dry bulk density of the soil, from a soil analysis. Typical values range for ρ_b from 1.8 to 2.1 g/mL (kg/L). Determine or estimate θ_w, the water-filled porosity.

Step 5: Determine K_d, the partition (or distribution) coefficient between the pore water (ground water) and the soil solids:

$$K_d = K_{oc} \cdot f_{oc} \tag{11.20}$$

Step 6: Using C_t, the measured concentration of the organic compound in saturated soil in mg/kg, calculate the theoretical pore water concentration assuming no NAPL (i.e., C_w in mg/L):

$$C_w = (C_t \cdot \rho_b)/(K_d \cdot \rho_b + \theta_w) \qquad (11.21)$$

Step 7: Compare C_w and S_i^e (from Step 1):

$$C_w < S_i^e \text{ suggests possible absence of NAPL} \qquad (11.22)$$

$$C_w > S_i^e \text{ suggests possible presence of NAPL} \qquad (11.23)$$

Example 11.9 shows how this partitioning procedure is applied to field data to help determine whether NAPLs are present in the subsurface.

Example 11.9 INDIRECT MEASURES OF DNAPL PRESENCE: SOILS DATA

A soil sample extracted from a site with a gasoline release shows 100 mg/kg benzene. Does this indicate that the benzene is present as a NAPL? The fraction of natural organic carbon on the soil (f_{oc}) is 0.1% or 0.001 gm/gm. Assume that the gasoline is 2% benzene, the K_{oc} for benzene is 38 L/kg, and the soil bulk density is 1.8 kg/L.

Solution. Using Eqs. (11.20) and (11.21):

Pure-phase solubility of benzene = 1,740 mg/L

Effective solubility = $S_i^e = 0.02 \cdot 1740 = 34.8$ mg/L

$K_d = f_{oc} \cdot K_{oc} = (0.001)\ (38\ \text{L/kg}) = 0.038$ L/kg

$$C_w = \frac{\left(100\ \frac{\text{mg}}{\text{kg}}\right)\left(1.7\frac{\text{kg}}{\text{L}}\right)}{\left[\left(0.038\frac{\text{L}}{\text{kg}}\right)\left(1.7\frac{\text{kg}}{\text{L}}\right) + 0.35\right]}$$

$C_w = 414$ mg/L

$S_i^e = 34.8$ mg/L

$C_w > S_i^e$ (the presence of NAPL is indicated in this soil sample)

Analysis. Because the residual NAPL blobs are so small, often they cannot be seen. This simple analysis can be used to help determine whether NAPL is present in the soil. C_w represents the theoretical pore water concentration if there were no NAPL present. S_i^e represents the effective solubility in the presence of NAPL, that is, the lowest concentration that would be expected if NAPL were there. Since C_w is greater than S_i^e then the presence of NAPL is indicated.

Geophysics. Because of the difficulty in locating NAPLs in the subsurface, borehole and surface geophysics are becoming more popular for site characterizations. Ground penetrating radar, complex resistivity, and electromagnetic induction have been applied to detect aqueous and nonaqueous hydrocarbons at some sites (U.S. EPA, 1992b). The value of these methods increases with the number of applications at a particular site; these geophysical techniques are better suited for detecting subtle changes in subsurface composition, such as a moving free-phase NAPL mass, than in assessing static conditions. Currently the application of geophysics at hazardous waste sites is limited by the paucity of results from research sites and by the small number of personnel that are trained to use geophysics for ground water remediation problems.

11.6.3 Integrated Approach for Determining Potential Occurrence of DNAPLs

In practice, data from several sources are used together to determine whether NAPLs are present at a hazardous waste site. One example of an integrated approach for determining whether DNAPL is present at Superfund sites uses both direct and indirect evidence (U.S. EPA, 1992a). This preliminary screening approach can be employed to determine the need for implementation of a full-scale DNAPL detection/delineation program.

11.6.4 Special Considerations for Designing DNAPL Delineation Programs

Special precautions are required to avoid inadvertent creation or enhancement of DNAPL migration pathways during the course of hydrogeologic investigations conducted at DNAPL-contaminated sites. Given the ability of DNAPL materials to move downward through very small fractures (e.g., 20 microns) within the soil mass, conventional grouting procedures may not prove effective for soil borings or wells drilled directly through a DNAPL perching stratum and into an underlying, clean unit. In developing a DNAPL detection / delineation workplan, the following concepts should be applied:

- "Outside-In" Approach: Prior to penetrating a suspected DNAPL zone, critical stratigraphic features should first be identified by investigations conducted outside of the area of concern. These preliminary data should be analyzed to identify potential perching strata or "safety nets" beneath the DNAPL zone. All drilling

subsequently conducted within the area of DNAPL occurrence must be terminated at the depth of the uppermost, continuous "safety net" stratum. In thick, fractured rock settings, such perching strata may not be present, and the risks associated with drilling inside the DNAPL zone must be carefully weighed against the need for vertical delineation data.

- Soil Borings and Wells: To avoid inadvertent penetration of perching layers within DNAPL zones, soil borings should be sampled continuously with depth and terminated at or near the surface of such confining strata. For detection of free-phase DNAPL, observation wells must be screened across the upper surface of a perching layer (see Figure 11.5). However, under no conditions should the well boring penetrate the full thickness of the base stratum. Wells should be constructed with short screen sections and double-cased through the depth of any overlying DNAPL -contaminated sections.

- Non-Invasive Site Investigation Techniques: Where applicable, non-invasive techniques should be employed to indicate DNAPL presence or characterize site stratigraphy. Geophysical methods can be applied to define the presence and topography of perching strata. In addition, shallow soil gas sampling above the zone DNAPL occurrence has proven a useful indicator of DNAPL presence in some cases.

In general, the risks involved with LNAPL delineation techniques are much smaller than for DNAPL, largely because the downward migration of LNAPL is restricted by the water table and associated capillary fringe.

SUMMARY

Nonaqueous phase liquids (NAPLs) are contaminants that exist in a separate immiscible (nondissolved) phase in the subsurface. Because they are a separate phase, NAPLs have different fate and transport properties from those of dissolved contaminant plumes. NAPLs migrate through the subsurface under gravity and buoyancy forces and do not move along the general flow of ground water. While NAPLs can migrate through the subsurface as a continuous organic mass, it is almost impossible to extract all the NAPL. The NAPL breaks up into countless blobs in individual pores that are trapped so tightly by capillary forces that typical pumping measures cannot dislodge them. Because of this phenomenon, it is common to never observe NAPL during site investigations. Therefore, indirect indicators are often be used to determine if NAPL is present or not.

NAPLs can be divided into two major types based on density: LNAPLs (lighter-than-water NAPLs) will move downward and then float on top of the water table, whereas DNAPLs (denser-than-water NAPLs) can sink far below the water table. Although this classification system is based on density, it is also a good predictor of where NAPLs come from and their fate in the subsurface. In general, LNAPLs are associated with petroleum product

spills and have chemicals that, once dissolved, are readily biodegraded by naturally occurring microorganisms at almost all sites. Many DNAPL releases are related to the manufacture and use of chlorinated solvents, once dissolved these chemicals appear to biodegrade under some but not all natural conditions.

Sites containing NAPLs usually have many times the contaminant mass as a site with only a dissolved plume. Therefore, it is much more difficult to restore ground water at NAPL-affected sites, particularly if a DNAPL comprised of chlorinated solvents is present. These solvent sites cannot be restored to drinking-water standards using any proven technologies, so the trapped DNAPL can act as a continuing source of ground water contamination for tens or hundreds of years. To effectively manage ground water problems at hazardous-waste sites, the effects of NAPLs should be considered very carefully during site characterization and remediation system design.

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