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Ground Water Issue

DENSE NONAQUEOUS PHASE LIQUIDS

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Background

The Regional Superfund Ground Water Forum is a group of EPA professionals representing EPA's Regional Superfund Offices, committed to the identification and the resolution of ground water issues impacting the remediation of Superfund sites. The Forum is supported by and advises the Superfund Technical Support Project. Dense nonaqueous phase liquids is an issue identified by the Forum as a concern of Superfund decision-makers. For further information contact Scott G. Huling (FTS:743-2313), Jim Weaver (FTS:743-2420), or Randall R. Ross (FTS: 743-2355).

Introduction

Dense nonaqueous phase liquids (DNAPLs) are present at numerous hazardous waste sites and are suspected to exist at many more. Due to the numerous variables influencing DNAPL transport and fate in the subsurface, and consequently, the ensuing complexity, DNAPLs are largely undetected and yet are likely to be a significant limiting factor in site remediation. This issue paper is a literature evaluation focusing on DNAPLs and provides an overview from a conceptual fate and transport point of view of DNAPL phase distribution, monitoring, site characterization, remediation, and modeling.

A nonaqueous phase liquid (NAPL) is a term used to describe the physical and chemical differences between a hydrocarbon liquid and water which result in a physical interface between a mixture of the two liquids. The interface is a physical dividing surface between the bulk phases of the two liquids, but compounds found in the NAPL are not prevented from solubilizing into the ground water. Immiscibility is typically determined based on the visual observation of a physical interface in a water- hydrocarbon mixture. There are numerous methods, however, which are used to quantify the physical and chemical properties of hydrocarbon liquids (31).

Nonaqueous phase liquids have typically been divided into two general categories, dense and light. These terms describe the specific gravity, or the weight of the nonaqueous phase liquid relative to water. Correspondingly, the dense nonaqueous phase liquids have a specific gravity greater than water, and the light nonaqueous phase liquids (LNAPL) have a specific gravity less than water.

Several of the most common compounds associated with DNAPLs found at Superfund sites are included in Table 1. These compounds are a partial list of a larger list identified by a national screening of the most prevalent compounds found at Superfund sites (65). The general chemical categories are halogenated/non-halogenated semi-volatiles and halogenated volatiles. These compounds are typically found in the following wastes and waste-producing processes: solvents, wood preserving wastes (creosote, pentachlorophenol), coal tars, and pesticides. The most frequently cited group of these contaminants to date are the chlorinated solvents.

DNAPL Transport and Fate - Conceptual Approach

Fate and transport of DNAPLs in the subsurface will be presented from a conceptual point of view. Figures have been selected for various spill scenarios which illustrate the general behavior of DNAPL in the subsurface. Following the conceptual approach, detailed information will be presented explaining the specific mechanisms, processes, and variables which influence DNAPL fate and transport. This includes DNAPL characteristics, subsurface media characteristics, and saturation dependent parameters.

Unsaturated Zone

Figure 1 indicates the general scenario of a release of DNAPL into the soil which subsequently migrates vertically under both the forces of gravity and soil capillarity. Soil capillarity is also responsible for the lateral migration of DNAPL. A point is reached at which the DNAPL no longer holds together as a continuous phase, but rather is present as isolated residual globules. The fraction of the hydrocarbon that is retained by capillary forces in the porous media is

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Table 1. Most prevalent chemical compounds at U.S. Superfund Sites (65) with a specific gravity greater than one.

Vapor[6] Compound	Density [1]	Dynamic[2] Viscosity	Kinematic Viscosity[3]	Solub.	Water[4] Constant[5]	Henry's Law Pressure
Halogenated Semi-volatiles						
1,4-Dichlorobenzene	1.2475	1.2580	1.008	8. 0 E+01	1.58 E-03	6 E-01
1,2-Dichlorobenzene	1.3060	1.3020	0.997	1. 0 E+02	1.88 E-03	9.6 E-01
Aroclor 1242	1.3850			4.5 E-01	3.4 E-04	4.06 E-04
Aroclor 1260	1.4400			2.7 E-03	3.4 E-04	4.05 E-05
Aroclor 1254	1.5380			1.2 E-02	2.8 E-04	7.71 E-05
Chlordane	1.6	1.1040	0.69	5.6 E-02	2.2 E-04	1 E-05
Dieldrin	1.7500			1.86 E-01	9.7 E-06	1.78 E-07
2,3,4,6-Tetrachlorophenol	1.8390			1. 0 E+03		
Pentachlorophenol	1.9780			1.4 E+01	2.8 E-06	1.1 E-04
Halogenated Volatiles						
Chlorobenzene	1.1060	0.7560	0.683	4.9 E+02	3.46 E-03	8.8 E+00
1,2-Dichloropropane	1.1580	0.8400	0.72	2.7 E+03	3.6 E-03	3.95 E+01
1,1-Dichloroethane	1.1750	0.3770	0.321	5.5 E+03	5.45 E-04	1.82 E+02
1,1-Dichloroethylene	1.2140	0.3300	0.27	4. 0 E+02	1.49 E-03	5 E+02
1,2-Dichloroethane	1.2530	0.8400	0.67	8.69 E+03	1.1 E-03	6.37 E+01
Trans-1,2-Dichloroethylene	1.2570	0.4040	0.321	6.3 E+03	5.32 E-03	2.65 E+02
Cis-1,2-Dichloroethylene	1.2480	0.4670	0.364	3.5 E+03	7.5 E-03	2 E+02
1,1,1-Trichloroethane	1.3250	0.8580	0.647	9.5 E+02	4.08 E-03	1 E+02
Methylene Chloride	1.3250	0.4300	0.324	1.32 E+04	2.57 E-03	3.5 E+02
1,1,2-Trichloroethane	1.4436	0.1190	0.824	4.5 E+03	1.17 E-03	1.88 E+01
Trichloroethylene	1.4620	0.5700	0.390	1. 0 E+03	8.92 E-03	5.87 E+01
Chloroform	1.4850	0.5630	0.379	8.22 E+03	3.75 E-03	1.6 E+02
Carbon Tetrachloride	1.5947	0.9650	0.605	8.0 E+02	2. 0 E-02	9.13 E+01
1,1,2,2-Tetrachloroethane	1.6	1.7700	1.10	2.9 E+03	5. 0 E-04	4.9 E+00
Tetrachloroethylene	1.6250	0.8900	0.54	1.5 E+02	2.27 E-02	1.4 E+01
Ethylene Dibromide	2.1720	1.6760	0.79	3.4 E+03	3.18 E-04	1.1 E+01
Non-halogenated Semi-volatiles						
2-Methyl Napthalene	1.0058			2.54 E+01	5.06 E-02	6.80 E-02
o-Cresol	1.0273			3.1 E+04	4.7 E-05	2.45 E-01
p-Cresol	1.0347			2.4 E+04	3.5 E-04	1.08 E-01
2,4-Dimethylphenol	1.0360			6.2 E+03	2.5 E-06	9.8 E-02
m-Cresol	1.0380	21. 0	20	2.35 E+04	3.8 E-05	1.53 E-01
Phenol	1.0576		3.87	8.4 E+04	7.8 E-07	5.293E-01
Naphthalene	1.1620			3.1 E+01	1.27 E-03	2.336E-01
Benzo(a)Anthracene	1.1740			1.4 E-02	4.5 E-06	1.16 E-09
Flourene	1.2030			1.9 E+00	7.65 E-05	6.67 E-04
Acenaphthene	1.2250			3.88 E+00	1.2 E-03	2.31 E-02
Anthracene	1.2500			7.5 E-02	3.38 E-05	1.08 E-05
Dibenz(a,h)Anthracene	1.2520			2.5 E-03	7.33 E-08	1 E-10
Fluoranthene	1.2520			2.65 E-01	6.5 E-06	E-02 E-06
Pyrene	1.2710			1.48 E-01	1.2 E-05	6.67 E-06
Chrysene	1.2740			6. 0 E-03	1.05 E-06	6.3 E-09
2,4-Dinitrophenol	1.6800			6. 0 E+03	6.45 E-10	1.49 E-05
Miscellaneous						
Coal Tar	1.028[7]	18.98[7]				
Creosote	1.05	1.08[8]				

[1] g/cc
[2] centipoise (cp), water has a dynamic viscosity of 1 cp at 20°C.
[3] centistokes (cs)
[4] mg/l
[5] atm-m^3/mol
[6] mm Hg
[7] 45° F (70)
[8] 15.5°C, varies with creosote mix (62)

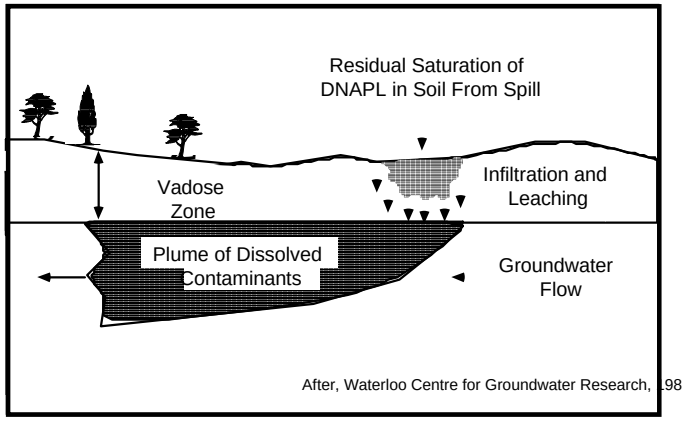

Figure 1. The entire volume of DNAPL is exhausted by residual saturation in the vadose zone prior to DNAPL reaching the water table. Soluble phase compounds may be leached from the DNAPL residual saturation and contaminate the ground water.

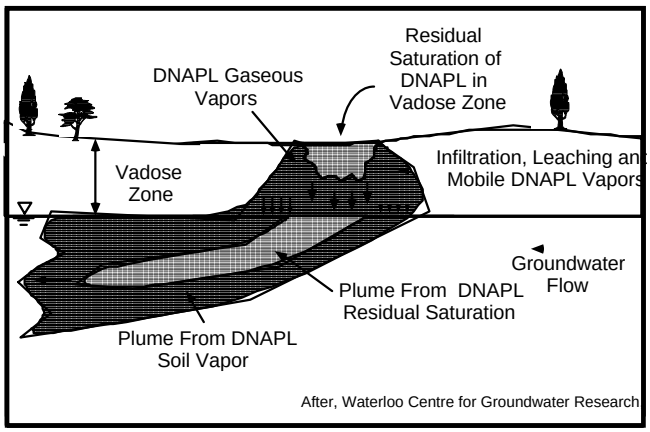

Figure 2. Migration of DNAPL vapors from the spill area and subsequent contamination of the soils and ground water.

referred to as residual saturation. In this spill scenario, the residual saturation in the unsaturated zone exhausted the volume of DNAPL, preventing it from reaching the water table. This figure also shows the subsequent leaching (solubilization) of the DNAPL residual saturation by water percolating through the unsaturated zone (vadose zone). The leachate reaching the saturated zone results in ground-water contamination by the soluble phase components of the hydrocarbon. Additionally, the residual saturation at or near the water table is also subjected to leaching from the rise and fall of the water table (seasonal, sea level, etc.).

Increasing information is drawing attention to the importance of the possibility that gaseous-phase vapors from NAPL in the unsaturated zone are responsible for contaminating the ground water and soil (18,47). It is reported that the greater “relative vapor density” of gaseous vapors to air will be affected by gravity and will tend to sink. In subsurface systems where lateral spreading is not restricted, spreading of the vapors may occur as indicated in Figure 2. The result is that a greater amount of soils and ground water will be exposed to the DNAPL vapors and may result in further contamination. The extent of contamination will depend largely on the partitioning of the DNAPL vapor phase between the aqueous and solid phases.

DNAPL Phase Distribution - Four Phase System

It is apparent from Figures 1 and 2 that the DNAPL may be present in the subsurface in various physical states or what is referred to as phases. As illustrated in Figure 3, there are four possible phases: gaseous, solid, water, and immiscible hydrocarbon (DNAPL) in the unsaturated zone. Contaminants associated with the release of DNAPL can, therefore, occur in four phases described as follows:

1. Air phase - contaminants may be present as vapors;
2. Solid phase - contaminants may adsorb or partition onto the soil or aquifer material;
3. Water phase - contaminants may dissolve into the water according to their solubility; and
4. Immiscible phase - contaminants may be present as dense nonaqueous phase liquids.

The four phase system is the most complex scenario because there are four phases and the contaminant can partition between any one or all four of these phases, as illustrated in Figure 4. For example, TCE introduced into the subsurface as a DNAPL may partition onto the soil phase, volatilize into the soil gas, and solubilize into the water phase resulting in contamination in all four phases. TCE can also partition between the water and soil, water and air, and between the soil and air. There are six pathways of phase distribution in the unsaturated zone. The distribution of a contaminant between these phases can be represented by empirical relationships referred to as partition coefficients. The partition coefficients, or the distribution of the DNAPL between the four phases, is highly site-specific and highly dependent on the characteristics of both the soil/aquifer matrix and the DNAPL. Therefore, the distribution between phases may change with time and/or location at the same site and during different stages of site remediation.

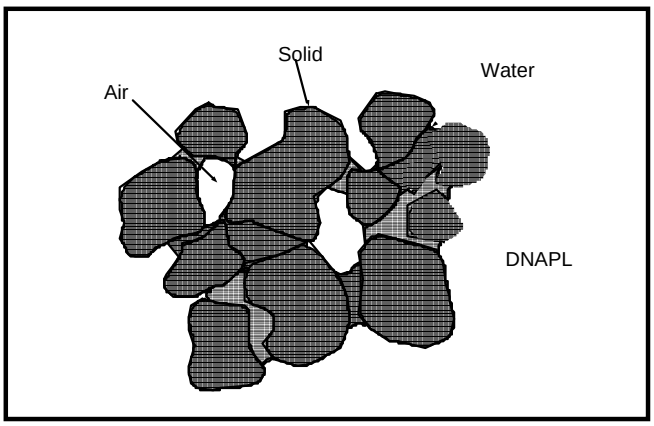

Figure 3. A DNAPL contaminated unsaturated zone has four physical states or phases (air, solid, water, immiscible). The contaminant may be present in any one, or all four phases.

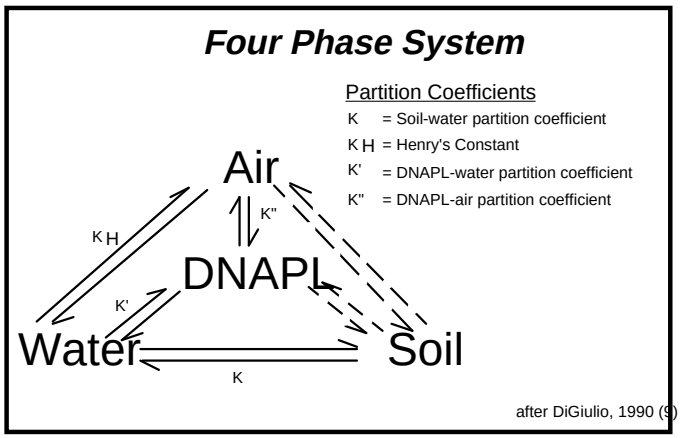

Figure 4. Distribution of DNAPL between the four phases found in the vadose zone.

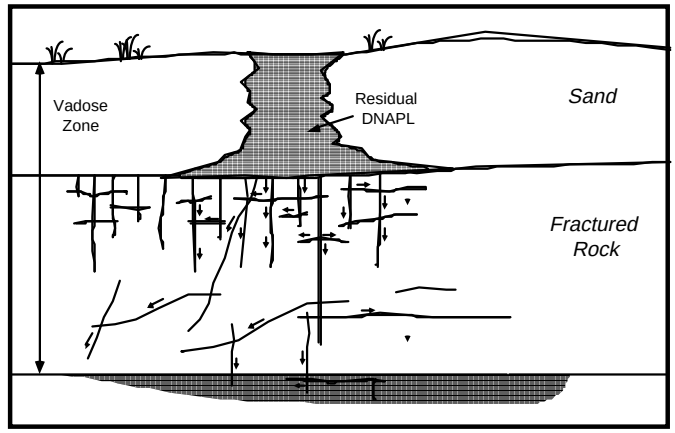

Figure 5. DNAPL spilled into fractured rock systems may follow a complex distribution of the preferential pathways.

The concept of phase distribution is critical in decision-making. Understanding the phase distribution of a DNAPL introduced into the subsurface provides significant insight in determining which tools are viable options with respect to site characterization and remediation.

DNAPL represented by residual saturation in the four phase diagram is largely immobile under the usual subsurface pressure conditions and can migrate further only: 1) in water according to its solubility; or 2) in the gas phase of the unsaturated zone (47). DNAPL components adsorbed onto the soil are also considered immobile. The mobile phases are, therefore, the soluble and volatile components of the DNAPL in the water and air, respectively.

The pore space in the unsaturated zone may be filled with one or all three fluid phases (gaseous, aqueous, immiscible). The presence of DNAPL as a continuous immiscible phase has the potential to be mobile. The mobility of DNAPL in the subsurface must be evaluated on a case by case basis. The maximum number of potentially mobile fluid phases is three. Simultaneous flow of the three phases (air, water, and immiscible) is considerably more complicated than two-phase flow (46). The mobility of three phase flow in a four-phase system is complex, poorly understood, and is beyond the scope of this DNAPL overview. The relative mobility of the two phases, water and DNAPL, in a three-phase system is presented below in the section entitled “Relative Permeability.”

Generally, rock aquifers contain a myriad of cracks (fractures) of various lengths, widths, and apertures (32). Fractured rock systems have been described as rock blocks bounded by discrete discontinuities comprised of fractures, joints, and shear zones which may be open, mineral-filled, deformed, or any combination thereof (61). The unsaturated zone overlying these fractured rock systems also contain the myriad of preferential pathways. DNAPL introduced into such formations (Figure 5) follow complex pathways due to the heterogeneous distribution of the cracks, conduits, and fractures’, i.e., preferential pathways. Transport of DNAPL may follow non-Darcian flow in the open fractures and/or Darcian flow in the porous media filled fractures. Relatively small volumes of NAPL may move deep, quickly into the rock because the retention capacity offered by the dead-end fractures and the immobile fragments and globules in the larger fractures is so small (32). Currently, the capability to collect the detailed information for a complete description of a contaminated fractured rock system is regarded as neither technically possible nor economically feasible (61).

Low permeability stratigraphic units such as high clay content formations may also contain a heterogeneous distribution of preferential pathways. As illustrated in Figure 6, DNAPL transport in these preferential pathways is correspondingly complex. Typically, it is assumed that high clay content formations are impervious to DNAPL. However, as DNAPL spreads out on low permeable formations it tends to seek out zones of higher permeability. As a result, preferential pathways allow the DNAPL to migrate further into the low permeable formation, or through it to underlying stratigraphic units. It is apparent from Figures 5 and 6 that the complexity of DNAPL transport may be significant prior to reaching the water table.

Saturated Zone

The second general scenario is one in which the volume of DNAPL is sufficient to overcome the fraction depleted by the residual saturation in the vadose zone, as illustrated in Figure 7. Consequently, the DNAPL reaches the water table and contaminates the ground water directly. The specific gravity of DNAPL is greater than water, therefore, the DNAPL migrates into the saturated zone. In this scenario, DNAPL continues the vertical migration through the saturated zone until the volume is eventually exhausted by the residual saturation process or until it is intercepted by a low permeable formation where it begins to migrate laterally.

DNAPL Phase Distribution - Three Phase System

Due to the lack of the gaseous phase, the saturated zone containing DNAPL is considered a three-phase system consisting of the solid, water, and immiscible hydrocarbon (Figure 8). Contaminant distribution in the three-phase

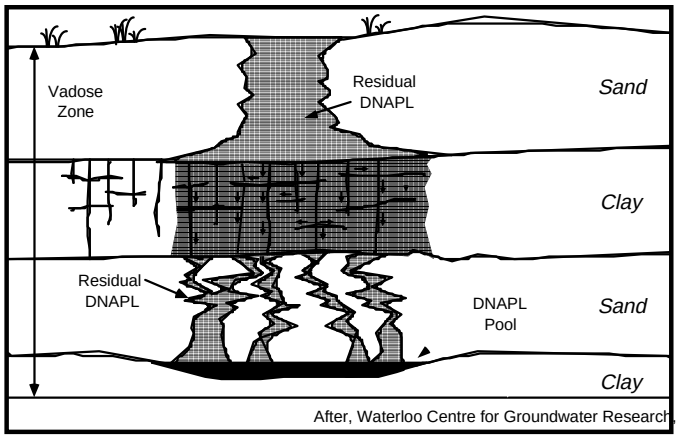

Figure 6. DNAPL spilled into a low permeable formation may follow a complex distribution of preferential pathways. The volume of DNAPL is exhausted in the vadose zone prior to reaching the water table.

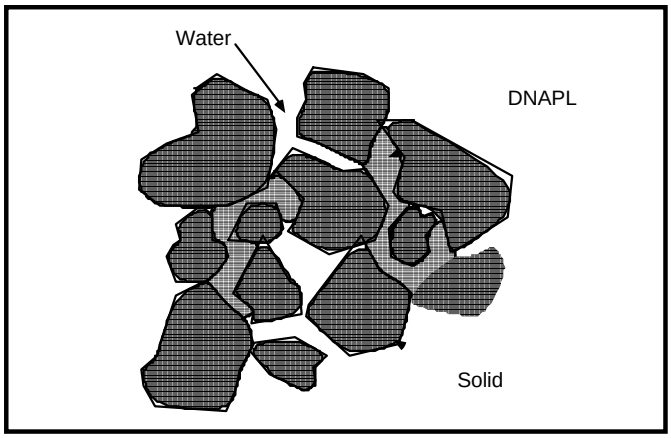

Figure 8. A DNAPL contaminated saturated zone has three phases (solid, water, immiscible). The contaminant may be present in any one, or all three phases.

system is less complex than the four-phase system. Again, this is highly dependent on the characteristics of both the aquifer matrix and the DNAPL. Figure 9 indicates the three phases and the transfer of the mass of contaminant between the phases. In this scenario, there are only three pathways of phase distribution in the saturated zone.

Note that when the DNAPL is represented by residual saturation in the three-phase system, the mobile phase of the contaminant is the water soluble components of the DNAPL and the immobile phases are the residual saturation and the adsorbed components of the DNAPL associated with the aquifer material. The main mobilization mechanism of the residual saturation is removal of soluble phase components into the ground water. When the DNAPL is present as a continuous immiscible phase, it too is considered one of the mobile phases of the contaminant. While the continuous phase DNAPL has the potential to be mobile, immobile continuous phase DNAPL may also exist in the subsurface. Although the saturated zone is considered a three-phase system, gaseous vapors from DNAPL in the unsaturated zone does have the potential to affect ground-water quality, as was indicated earlier in Figure 2.

Assuming the residual saturation in the saturated zone does not deplete the entire volume of the DNAPL, the DNAPL will continue migrating vertically until it encounters a zone or stratigraphic unit of lower permeability. Upon reaching the zone of lower permeability, the DNAPL will begin to migrate laterally. The hydraulic conductivity in the vertical direction is typically less than in the horizontal direction. It is not uncommon to find vertical conductivity that is one-fifth or one-tenth the horizontal value (4). It is expected that DNAPL spilled into the subsurface will have a significant potential to migrate laterally. If the lower permeable boundary is “bowl shaped”, the DNAPL will pond as a reservoir (refer to Figure 10). As illustrated in Figure 11, it is not uncommon to observe a perched DNAPL reservoir where a discontinuous impermeable layer; i.e., silt or clay lens, intercepts the vertical migration of DNAPL. When a sufficient volume of

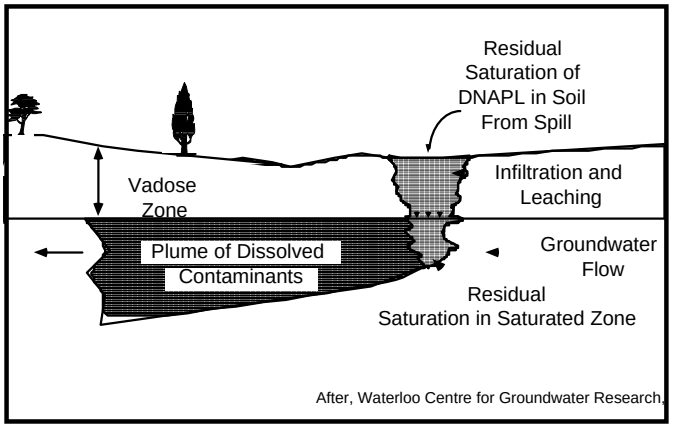

Figure 7. The volume of DNAPL is sufficient to overcome the residual saturation in the vadose zone and consequently penetrates the water table.

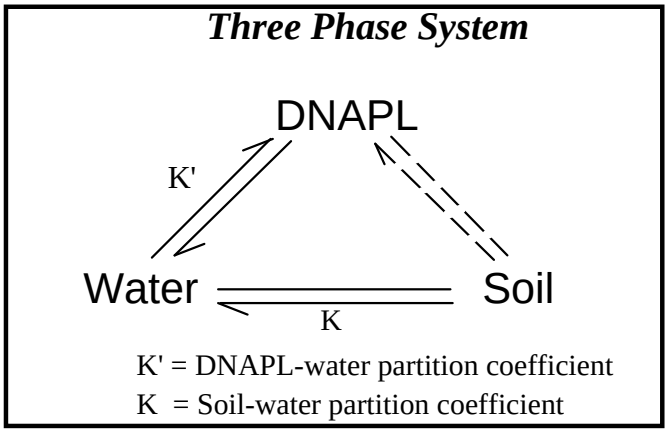

Figure 9. Distribution of DNAPL between the three phases found in the saturated zone.

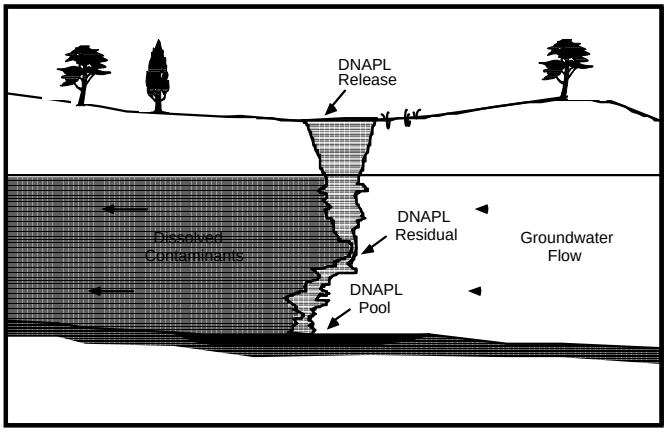

Figure 10. Migration of DNAPL through the vadose zone to an impermeable boundary.

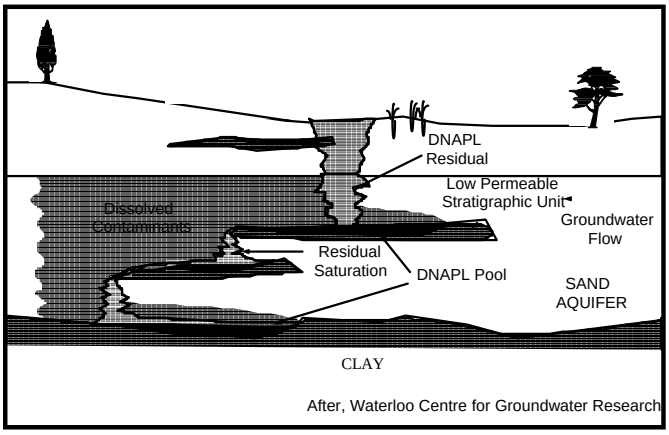

Figure 12. Perched and deep DNAPL reservoirs.

DNAPL has been released and multiple discontinuous impermeable layers exist, the DNAPL may be present in several perched reservoirs as well as a deep reservoir (refer to Figure 12). Lateral migration continues until either the residual saturation depletes the DNAPL or an impermeable depression immobilizes the DNAPL in a reservoir type scenario. Soluble-phase components of the DNAPL will partition into the ground water from both the residual saturation or DNAPL pools. The migration of DNAPL vertically through the aquifer results in the release of soluble-phase components of the DNAPL across the entire thickness of the aquifer. Note, that ground water becomes contaminated as it flows through, and around, the DNAPL contaminated zone.

As indicated earlier, DNAPL will migrate laterally upon reaching a stratigraphic unit of lower permeability. Transport of DNAPL will therefore be largely dependent on the gradient of the stratigraphy. Occasionally, the directional gradient of an impermeable stratigraphic unit may be different than the direction of ground-water flow as illustrated in Figure 13a. This may result in the migration of the continuous phase DNAPL in a direction different from the ground-water flow. Nonhorizontal stratigraphic units with varying hydraulic conductivity may also convey DNAPL in a different direction than ground-water flow, and at different rates (refer to Figure 13b). Determination of the direction of impermeable stratigraphic units will therefore provide useful information concerning the direction of DNAPL transport.

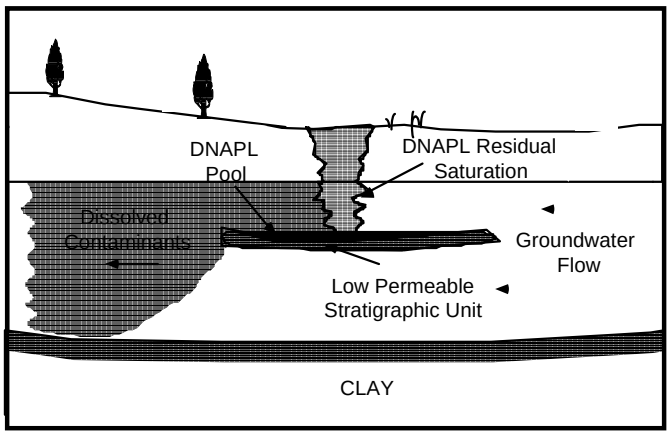

Figure 11. Perched DNAPL reservoir.

Similar to the unsaturated zone, the saturated zone also contains a complex distribution of preferential pathways from cracks, fractures, joints, etc. DNAPL introduced into such formations correspondingly follow the complex network of pathways through an otherwise relatively impermeable rock material. Other pathways which may behave as vertical conduits for DNAPL include root holes, stratigraphic windows, disposal wells, unsealed geotechnical boreholes, improperly sealed hydrogeological investigation sampling holes and monitoring wells, and old uncased/unsealed water supply wells (72). Transport of the DNAPL may migrate very rapidly in these open conduits or follow Darcian flow in the surrounding porous media or porous media filled fractures. A relatively small volume of DNAPL can move deep into a fractured system due to the low retentive capacity of the fractured system. Consequently, fractured clay or rock stratigraphic units, which are often considered lower DNAPL

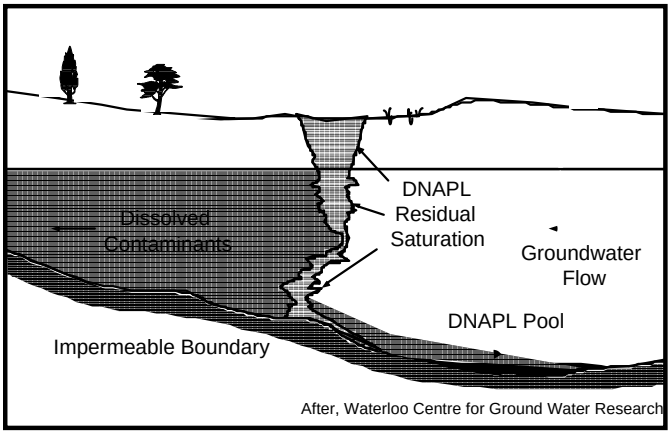

Figure 13a. Stratigraphic gradient different from ground water gradient results in a different direction of flow of the ground water and continuous phase DNAPL.

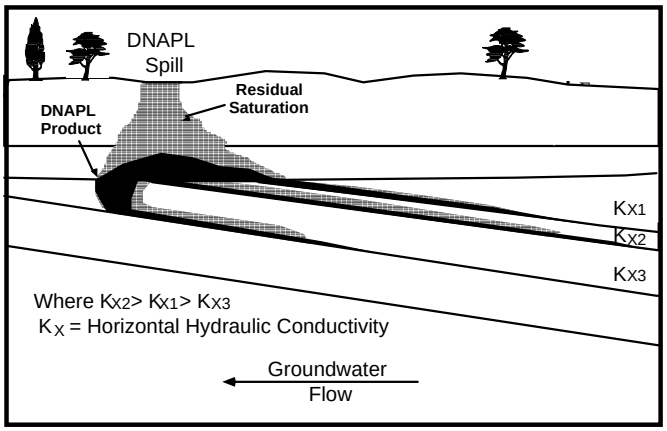

Figure 13b. Non-horizontal stratigraphic units with variable hydraulic conductivity may convey DNAPL in a different direction than the ground water flow direction.

boundary conditions, may have preferential pathways leading to lower formations, as depicted in Figure 14. Careful inspection of soil cores at one Superfund site indicated that DNAPL flow mainly occurred through preferential pathways and was not uniformly distributed throughout the soil mass (8). Due to the complex distribution of preferential pathways, characterization of the volume distribution of the DNAPL is difficult.

Important DNAPL Transport and Fate Parameters

There are several characteristics associated with both the subsurface media and the DNAPL which largely determine the fate and transport of the DNAPL. A brief discussion of these parameters is included to help identify the specific details of DNAPL transport mechanisms. Several of the distinctive DNAPL phenomena observed on the field-scale relates back to phenomena at the pore-scale. Therefore, it is important to understand the principles from the pore-scale level to develop an understanding of field-scale observations, which is the scale at which much of the Superfund work occurs. A more complete and comprehensive review of these parameters is available (2,36,71).

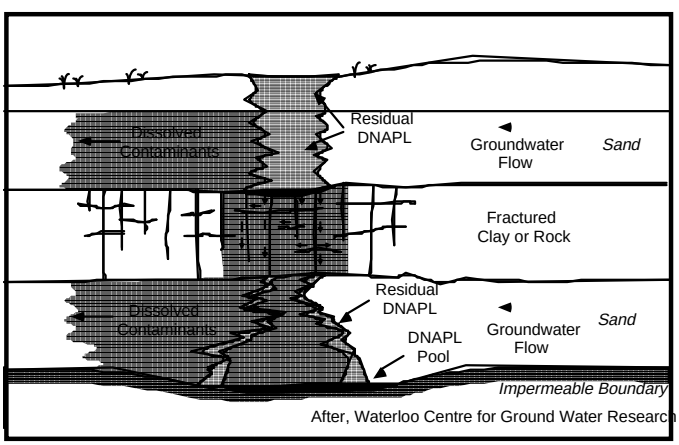

Figure 14. DNAPL transport in fracture and porous media stratigraphic units.

DNAPL Characteristics

Density

Fluid density is defined as the mass of fluid per unit volume, i.e. g/cm^3 . Density of an immiscible hydrocarbon fluid is the parameter which delineates LNAPL's from DNAPL's. The property varies not only with molecular weight but also molecular interaction and structure. In general, the density varies with temperature and pressure (2). Equivalent methods of expressing density are specific weight and specific gravity. The specific weight is defined as the weight of fluid per unit volume, i.e. lb/ft^3. The specific gravity (S.G.) or the relative density of a fluid is defined as the ratio of the weight of a given volume of substance at a specified temperature to the weight of the same volume of water at a given temperature (31). The S.G. is a relative indicator which ultimately determines whether the fluid will float (S.G.< 1.0) on, or penetrate into (S.G.>1.0) the water table. Table 1 contains a list of compounds with a density greater than one that are considered DNAPL's. Note, however, that while the specific gravity of pentachlorophenol and the non-halogenated semi-volatiles is greater than 1.00, these compounds are a solid at room temperature and would not be expected to be found as an immiscible phase liquid at wood preserving sites but are commonly found as contaminants. Pentachlorophenol is commonly used as a wood preservant and is typically dissolved (4-7%) in No. 2 or 3 fuel oil.

Viscosity

The viscosity of a fluid is a measure of its resistance to flow. Molecular cohesion is the main cause of viscosity. As the temperature increases in a liquid, the cohesive forces decrease and the absolute viscosity decreases. The lower the viscosity, the more readily a fluid will penetrate a porous media. The hydraulic conductivity of porous media is a function of both the density and viscosity of the fluid as indicated in equation [1]. It is apparent from this equation that fluids with either a viscosity less than water or fluids with a density greater than water have the potential to be more mobile in the subsurface, than water.

$$K = \frac{k \rho g}{\mu} \quad \text{where,} \quad \begin{array}{lcl} K & = & \text{hydraulic conductivity} \\ k & = & \text{intrinsic permeability} \\ \rho & = & \text{fluid mass density} \\ g & = & \text{gravity} \\ \mu & = & \text{dynamic (absolute) viscosity} \end{array} \qquad [1]$$

Results from laboratory experiments indicated that several chlorinated hydrocarbons which have low viscosity (methylene chloride, perchloroethylene, 1,1,1-TCA, TCE) will infiltrate into soil notably faster than will water (47). The relative value of NAPL viscosity and density, to water, indicates how fast it will flow in porous media (100% saturated) with respect to water. For example, several low

viscosity chlorinated hydrocarbons (TCE, tetrachloroethylene, 1,1,1-TCA, Methylene Chloride, Chloroform, Carbon Tetrachloride, refer to Table 1) will flow 1.5-3.0 times as fast as water and higher viscosity compounds including light heating oil, diesel fuel, jet fuel, and crude oil (i.e. LNAPL's) will flow 2-10 times slower than water (45). Both coal tar and creosote typically have a specific gravity greater than one and a viscosity greater than water. It is interesting to note that the viscosity of NAPL may change with time (36). As fresh crude oils lose the lighter volatile components from evaporation, the oils become more viscous as the heavier components compose a larger fraction of the oily mixture resulting in an increase in viscosity.

Solubility

When an organic chemical is in physical contact with water, the organic chemical will partition into the aqueous phase. The equilibrium concentration of the organic chemical in the aqueous phase is referred to as its solubility. Table 1 presents the solubility of several of the most commonly found DNAPL's at EPA Superfund Sites. The solubility of organic compounds varies considerably from the infinitely miscible compounds, including alcohols (ethanol, methanol) to extremely low solubility compounds such as polynuclear aromatic compounds.

Numerous variables influence the solubility of organic compounds. The pH may affect the solubility of some organic compounds. Organic acids may be expected to increase in solubility with increasing pH, while organic bases may act in the opposite way (31). For example, pentachlorophenol is an acid which is ionized at higher pH's. In the ionized form, pentachlorophenol would be more soluble in water (59). Solubility in water is a function of the temperature, but the strength and direction of this function varies. The presence of dissolved salts or minerals in water leads to moderate decreases in solubility (31). In a mixed solvent system, consisting of water and one or more water-miscible compounds, as the fraction of the cosolvent in the mixture increases, the solubility of the organic chemical increases exponentially (12). In general, the greater the molecular weight and structural complexity of the organic compound, the lower the solubility.

Organic compounds are only rarely found in ground water at concentrations approaching their solubility limits, even when organic liquid phases are known or suspected to be present. The observed concentrations are usually more than a factor of 10 lower than the solubility presumably due to diffusional limitations of dissolution and the dilution of the dissolved organic contaminants by dispersion (74). This has also been attributed to: reduced solubility due to the presence of other soluble compounds, the heterogeneous distribution of DNAPL in the subsurface, and dilution from monitoring wells with long intake lengths (10). Detection of DNAPL components in the subsurface below the solubility should clearly not be interpreted as a negative indicator for the presence of DNAPL.

In a DNAPL spill scenario where the DNAPL or its vapors are in contact with the ground water, the concentration of the soluble phase components may range from non-detectable up to the solubility of the compound. The rate of dissolution has been expressed as a function of the properties of the DNAPL components (solubility), ground water flow conditions, differential between the actual and solubility concentration, and the contact area between the DNAPL and the ground water (10). The contact area is expected to be heterogeneous and difficult to quantify. Additionally, as the time of contact increases between the DNAPL and the water, the concentration in the aqueous phase increases.

Vapor Pressure

The vapor pressure is that characteristic of the organic chemical which determines how readily vapors volatilize or evaporate from the pure phase liquid. Specifically, the partial pressure exerted at the surface by these free molecules is known as the vapor pressure (30). Molecular activity in a liquid tends to free some surface molecules and this tendency towards vaporization is mainly dependent on temperature. The vapor pressure of DNAPL's can actually be greater than the vapor pressure of volatile organic compounds. For example, at 20 C, the ratio of the vapor pressures of TCE and benzene is 1.4 (1).

Volatility

The volatility of a compound is a measure of the transfer of the compound from the aqueous phase to the gaseous phase. The transfer process from the water to the atmosphere is dependent on the chemical and physical properties of the compound, the presence of other compounds, and the physical properties (velocity, turbulence, depth) of the water body and atmosphere above it. The factors that control volatilization are the solubility, molecular weight, vapor pressure, and the nature of the air-water interface through which it must pass (31). The Henry's constant is a valuable parameter which can be used to help evaluate the propensity of an organic compound to volatilize from the water. The Henry's law constant is defined as the vapor pressure divided by the aqueous solubility. Therefore, the greater the Henry's law constant, the greater the tendency to volatilize from the aqueous phase, refer to Table 1.

Interfacial Tension

The unique behavior of DNAPLs in porous media is largely attributed to the interfacial tension which exists between DNAPL and water, and between DNAPL and air. These interfacial tensions, result in distinct interfaces between these fluids at the pore-scale. When two immiscible liquids are in contact, there is an interfacial energy which exists between the fluids resulting in a physical interface. The interfacial energy arises from the difference between the inward attraction of the molecules in the interior of each phase and those at the surface of contact (2). The greater the interfacial tension between two immiscible liquids; the less likely emulsions will form; emulsions will be more stable if formed, and the better the phase separation after mixing. The magnitude of the interfacial tension is less than the larger of the surface tension values for the pure liquids, because the mutual attraction of unlike molecules at the interface reduces the large imbalance of forces (31). Interfacial tension

decreases with increasing temperature, and may be affected by pH, surfactants, and gases in solution (36). When this force is encountered between a liquid and a gaseous phase, the same force is called the surface tension (66).

The displacement of water by DNAPL and the displacement of DNAPL by water in porous media often involves a phenomena referred to as immiscible fingering. The lower the interfacial tension between immiscible fluids, the greater the instability of the water:DNAPL interface and thus the greater the immiscible fingering (27). The distribution of the fingering effects in porous media has been reported to be a function of the density, viscosity, surface tension (27) and the displacement velocity (13) of the fluids involved as well as the porous media heterogeneity (28).

Wettability

Wettability refers to the relative affinity of the soil for the various fluids - water, air, and the organic phase. On a solid surface, exposed to two different fluids, the wettability can be inferred from the contact angle (66), also referred to as the wetting angle, refer to Figure 15. In general, if the wetting angle is less than 90 degrees, the fluid is said to be the wetting fluid. In this scenario, water will preferentially occupy the smaller pores and will be found on solid surfaces (14). When the wetting angle is near 90 degrees, neither fluid is preferentially attracted to the solid surfaces. If the wetting angle is greater than 90 degrees, the DNAPL is said to be the wetting fluid. The wetting angle is an indicator used to determine whether the porous material will be preferentially wetted by either the hydrocarbon or the aqueous phase (71). Wettability, therefore, describes the preferential spreading of one fluid over solid surfaces in a two-fluid system. The wetting angle, which is a measure of wettability, is a solid-liquid interaction and can actually be defined in terms of interfacial tensions (71). Several methods have been developed to measure the wetting angle (36,71). In most natural systems, water is the wetting fluid, and the immiscible fluid is the non-wetting fluid. Coal tar may be the exception (i.e. contact angle greater than 90 degrees), which is mainly attributed to the presence of surfactants (70). The wetting fluid will tend to coat the surface of grains and occupy smaller spaces (i.e. pore throats) in porous media, the non-wetting fluid will tend to be restricted to the largest openings (47).

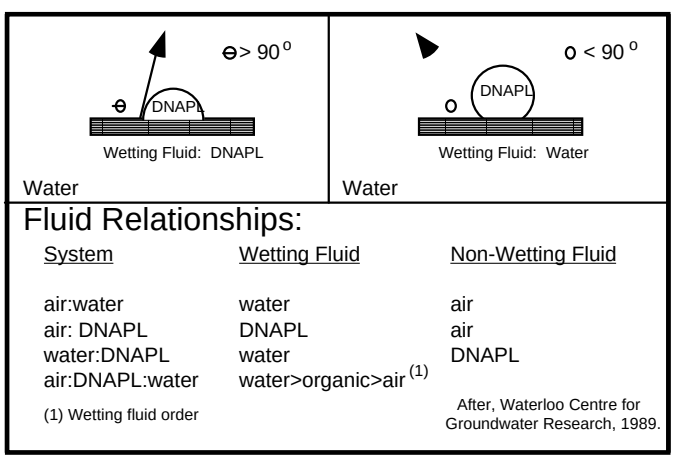

Figure 15. Wetting angle and typical wetting fluid relationships.

The wetting angle depends on the character of the solid surface on which the test is conducted. The test is conducted on flat plates composed of minerals which are believed representative of the media, or on glass. Contact angle measurements for crude oil indicates that the wetting angles vary widely depending on the mineral surface (53). Soil and aquifer material are not composed of homogeneous mineral composition nor flat surfaces. The measured wetting angle can only be viewed as a qualitative indicator of wetting behavior.

The reader is recommended to refer to reference No. 31 for review of the basic principles and for various techniques to measure the following DNAPL parameters: density, viscosity, interfacial tension, solubility, vapor pressure, and volatility.

Subsurface Media Characteristics

Capillary Force/Pressure

Capillary pressure is important in DNAPL transport because it largely determines the magnitude of the residual saturation that is left behind after a spill incident. The greater the capillary pressure, the greater the potential for residual saturation. In general, the capillary force increases in the following order; sand, silt, clay. Correspondingly, the residual saturation increases in the same order. Capillary pressure is a measure of the tendency of a porous medium to suck in the wetting fluid phase or to repel the nonwetting phase (2). Capillary forces are closely related to the wettability of the porous media. The preferential attraction of the wetting fluid to the solid surfaces cause that fluid to be drawn into the porous media. Capillary forces are due to both adhesion forces (the attractive force of liquid for the solids on the walls of the channels through which it moves) and cohesion forces (the attraction forces between the molecules of the liquid) (32). The capillary pressure depends on the geometry of the void space, the nature of solids and liquids, the degree of saturation (2) and in general, in-creases with a decrease in the wetting angle and in pore size, and with an increase in the interfacial tension (71). All pores have some value of capillary pressure. Before a nonwetting fluid can enter porous media, the capillary pressure of the largest pores (smallest capillary pressure) must be exceeded. This minimum capillary pressure is called the entry pressure.

In the unsaturated zone, pore space may be occupied by water, air (vapors), or immiscible hydrocarbon. In this scenario, capillary pressure retains the water (wetting phase) mainly in the smaller pores where the capillary pressure is greatest. This restricts the migration of the DNAPL (non-wetting phase) through the larger pores unoccupied by water. Typically, DNAPL does not displace the pore water from the smaller pores. It is interesting to note that the migration of DNAPL through fine material (high capillary pressure) will be impeded upon reaching coarser material (low capillary pressure).

The capillary fringe will obstruct the entry of the DNAPL into the saturated zone. When a sufficient volume of DNAPL has been released and the “DNAPL pressure head” exceeds the water capillary pressure at the capillary fringe (entry pressure), the DNAPL will penetrate the water table. This is why DNAPL is sometimes observed to temporarily flatten out

on top of the water table. Similarly, laboratory experiments have been conducted in which DNAPL (tetrachloroethylene) infiltrating through porous media was found to flow laterally and cascade off lenses too fine to penetrate (28), (refer to Figure 11). This was attributed to the inability of the DNAPL to overcome the high capillary pressure associated with the lenses. Logically, when “DNAPL pressure head” exceeds the capillary pressure, the DNAPL will penetrate into the smaller pores. These laboratory experiments are important because they illustrate that small differences in the capillary characteristics of porous media can induce significant lateral flow of non-wetting fluids.

A comprehensive investigation of capillary trapping and multiphase flow of organic liquids in unconsolidated porous media revealed many intricacies of this process in the vadose and saturated zone (66). An important note is that while capillary pressure is rarely measured at hazardous waste sites, the soil texture (sand, silt, clay) is usually recorded during drilling operations and soil surveys. This information, along with soil core analyses will help to delineate the stratigraphy and the volume distribution of NAPL.

Pore Size Distribution/Initial Moisture Content

In natural porous media, the geometry of the pore space is extremely irregular and complex (2). The heterogeneity of the subsurface environment i.e. the variability of the pore size distribution, directly affects the distribution of the capillary pressures along the interfaces between the aqueous and immiscible phases (50). In saturated column experiments, it was observed that NAPL preferentially traveled through strings of macropores, almost completely by-passing the water filled micropores (66). In the same study, a heterogeneous distribution of coarse and fine porous material was simulated. Most of the incoming organic liquid preferentially traveled through the coarse lens material.

In short term column drainage experiments, results indicated that the particle grain size is of primary importance in controlling the residual saturation of a gasoline hydrocarbon (19). Fine and coarse sands (dry) were found to have 55% and 14% residual saturation, respectively. The finer the sand, the greater the residual saturation. During these experiments, the residual saturation was reduced 20-30% in a medium sand and 60% in a fine sand when the sands were initially wet. Soil pore water held tightly by capillary forces in the small pores will limit the NAPL to the larger pores, and thus, result in lower residual saturation. In a similar laboratory (unsaturated) column study, the smaller the grain size used in the experiment, the greater the residual saturation of the NAPL (74). The residual saturation in the saturated column experiments was found to be greater than the unsaturated columns and was independent of the particle size distribution.

These observations follow traditional capillary force theory. Residual saturation resulting from a DNAPL spill in the unsaturated zone is highly dependent on the antecedent moisture content in the porous media. When the moisture content is low, the strong capillary forces in the smaller pores will tenaciously draw in and hold the DNAPL. When the moisture content is high, the capillary forces in the smaller pores will retain the soil pore water, and DNAPL residual saturation will mainly occur in the larger pores. Therefore, greater residual saturation can be expected in dryer soils. Correspondingly, NAPL will migrate further in a wetter soil, and displacement of NAPL from small pores is expected to be more difficult than from large pores.

Stratigraphic Gradient

DNAPL migrating vertically will likely encounter a zone or stratigraphic unit of lower vertical permeability. A reduction in the vertical permeability of the porous media will induce lateral flow of the DNAPL. The gradient of the lower permeable stratigraphic unit will largely determine the direction in which the DNAPL will flow. This is applicable to both the saturated and unsaturated zones. As depicted in Figures 13a and 13b, the lateral direction of DNAPL flow may be in a different direction than ground-water flow.

Ground Water Flow Velocity

The ground water flow velocity is a dynamic stress parameter which tends to mobilize the hydrocarbon (39). As the ground water velocity increases, the dynamic pressure and viscous forces increase. Mobilization of DNAPL occurs when the viscous forces of the ground water acting on the DNAPL, exceeds the porous media capillary forces retaining the DNAPL.

Saturation Dependent Functions

Residual Saturation

Residual saturation is defined as the volume of hydrocarbon trapped in the pores relative to the total volume of pores (38) and therefore is measured as such (74). Residual saturation has also been described as the saturation at which NAPL becomes discontinuous and is immobilized by capillary forces (36). The values of residual saturation vary from as low as 0.75 - 1.25% for light oil in highly permeable media to as much as 20% for heavy oil (50). Residual saturation values have also been reported to range from 10% to 50% of the total pore space (39,74). Other researchers reported that residual saturation values appear to be relatively insensitive to fluid properties and very sensitive to soil properties (and heterogeneities) (66). Laboratory studies conducted to predict the residual saturation in soils with similar texture and grain size distribution yielded significantly different values. It was concluded that minor amounts of clay or silt in a soil may play a significant role in the observed values.

In the unsaturated zone during low moisture conditions, the DNAPL residual saturation will wet the grains in a pendular state (a ring of liquid wrapped around the contact point of a pair of adjacent grains). During high moisture conditions, the wetting fluid, which is typically water, will preferentially occupy the pendular area of adjacent grains and the hydrocarbon will occupy other available pore space, possibly as isolated droplets. In the saturated zone, the DNAPL residual saturation will be present as isolated drops in the open pores (47). Furthermore, results of laboratory experimentation indicated that residual saturation increased with decreasing hydraulic conductivity in both the saturated

and unsaturated zones and that the residual saturation is greatest in the saturated zone. Laboratory experiments indicated that vadose zone residual saturation was roughly one third of the residual saturation in the saturated zone (66). The increase in residual saturation in the saturated zone is due to the following: [1] the fluid density ratio (DNAPL:air versus DNAPL:water above and below the water table, respectively) favors greater drainage in the vadose zone; [2] as the non-wetting fluid in most saturated media, NAPL is trapped in the larger pores; and, [3] as the wetting fluid in the vadose zone, NAPL tends to spread into adjacent pores and leave a lower residual content behind, a process that is

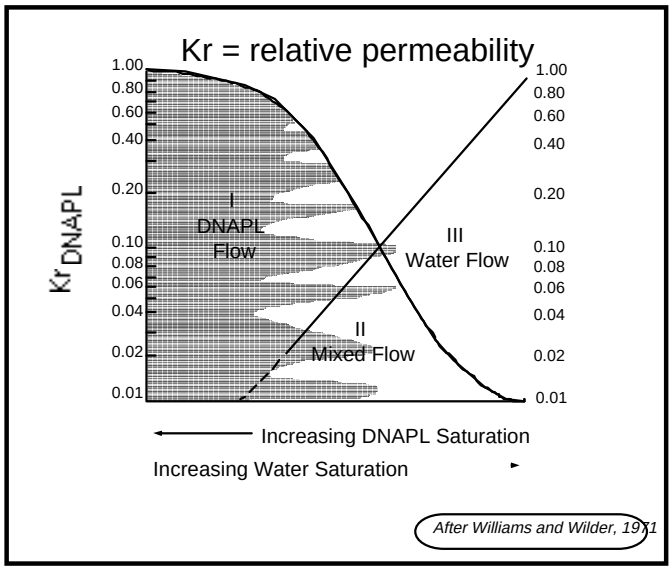

Figure 16. Relative permeability graph.

inhibited in the saturated zone (36). Thus, the capacity for retention of DNAPLs in the unsaturated zone is less than the saturated zone.

Relative Permeability

Relative permeability is defined as the ratio of the permeability of a fluid at a given saturation to its permeability at 100% saturation. Thus it can have a value between 0 and 1 (71). Figure 16 illustrates a relative permeability graph for a two fluid phase system showing the relationship between the observed permeability of each fluid for various saturations to that of the observed permeability if the sample were 100% saturated with that fluid (73). The three regions of this graph are explained as follows (71): Region I has a high saturation of DNAPL and is considered a continuous phase while the water is a discontinuous phase, therefore, water permeability is low. Assuming the DNAPL is the non-wetting fluid, water would fill the smaller capillaries and flow through small irregular pores. In Region II, both water and DNAPL are continuous phases although not necessarily in the same pores. Both water and NAPL flow simultaneously. However, as saturation of either phase increases, the relative permeability of the other phase correspondingly decreases. Region III exhibits a high saturation of water while the DNAPL phase is mainly discontinuous. Water flow dominates

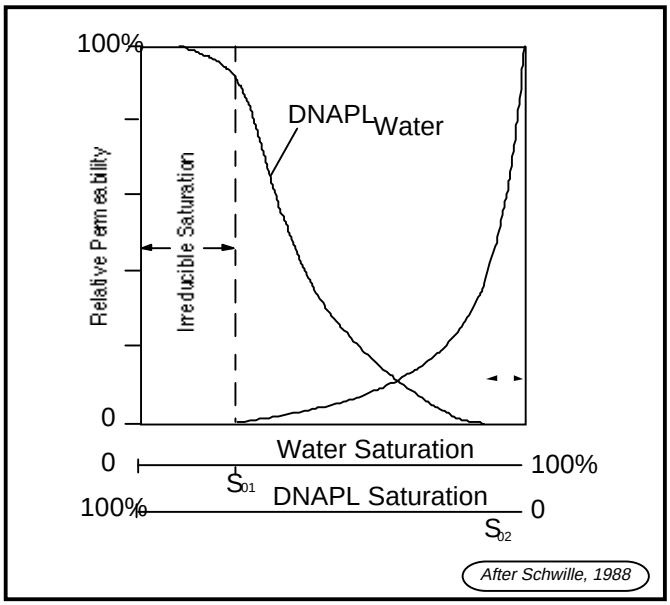

Figure 17. The relative permeability curves for water and a DNAPL in a porous medium as a function of the pore space saturation.

Site Characterization for DNAPL

Characterization of the subsurface environment at hazardous waste sites containing DNAPL is complex and will likely be expensive. Specific details associated with the volume and timing of the DNAPL release are usually poor or are not available and subsurface heterogeneity is responsible for the complicated and unpredictable migration pathway of subsurface DNAPL transport. As discussed previously, slight changes in vertical permeability may induce a significant horizontal component to DNAPL migration.

Site characterization typically involves a significant investment in ground-water analyses. Although analysis of ground water provides useful information on the distribution of the soluble components of the DNAPL, the presence of other phases of the DNAPL may go unrecognized. The investigation must, therefore, be more detailed to obtain information concerning the phase distribution of the DNAPL at a site. Site characterization may require analyses on all four phases (aqueous, gaseous, solid, immiscible) to yield the appropriate information (refer to Table 2). In brief, data collected on the various phases must be compiled, evaluated and used to help identify: where the contaminant is presently located; where it has been; what phases it occurs in; and what direction the mobile phases may be going. A comprehensive review of site characterization for subsurface investigations is available (68). Development of monitoring and remediation strategies can be focused more effectively and efficiently after a clear definition of the phase distribution has been completed.

Ground Water

Ground water analyses for organic compounds, in conjunction with ground water flow direction data, has repeatedly been used to: delineate the extent of ground

Table 2 - Phase Distribution of DNAPL in the Subsurface

MATRIX	PHASE
1. ground water	aqueous - soluble components of DNAPL
2. soil/aquifer material	solid - adsorbed components of DNAPL on solid phase material
3. DNAPL	immiscible - continuous phase (mobile), residual saturation (immobile)
4. soil gas	gaseous - volatile components

water contamination from DNAPL; determine the direction of plume migration; and to identify probable DNAPL source area(s). While this approach has been used successfully to characterize the distribution of contaminants in the subsurface, there are limitations. For example, since DNAPL and ground water may flow in different directions, as indicated in Figures 13a and 13b, ground water analyses may not necessarily identify the direction of DNAPL migration.

Ground water analyses may be useful to identify probable DNAPL source areas, but, estimating the volume of DNAPL in the subsurface is limited using this approach. Soluble phase components of DNAPL are rarely found in excess of 10% of the solubility even when organic liquids are known or suspected to be present. The concentration of soluble DNAPL components in the ground water is not only a function of the amount of DNAPL present, but also the chemical and physical characteristics of the DNAPL, the contact area and time between the ground water and DNAPL, and numerous transport and fate parameters (retardation, biodegradation, dispersion, etc.). One technique has been developed using chemical ratios in the ground water as a means of source identification and contaminant fate prediction (18).

Soil/Aquifer Material

Exploratory Borings

Physical and chemical analyses of soil and aquifer material (drill cuttings, cores) from exploratory borings will provide useful information in the delineation of the horizontal and vertical mass distribution of DNAPL. While simple visual examination for physical presence or absence of contamination might seem like a worthwhile technique, it can be deceiving and does nothing to sort out the various liquid phases and their relationship to each other (71). A quantitative approach is necessary to determine DNAPL distribution.

Drill cuttings or core material brought to the surface from exploratory borings can be screened initially to help delineate the depth at which volatile components from the various phases of the hydrocarbon exists. The organic vapor analyzer and the HNU are small portable instruments that can detect certain volatile compounds in the air. These methods are used to initially screen subsurface materials for volatile components of DNAPL. Identification of individual compounds and their concentrations may be confirmed by other, more precise, analyses.

Analysis of the soil or aquifer material by more accurate means, such as gas chromatography or high pressure liquid chromatography, will take longer but will provide more specific information on a larger group of organic compounds, i.e., volatile/non-volatile, and on specific compounds. This information is necessary to help fix the horizontal and vertical mass distribution of the contaminant and to help delineate the phase distribution. These analyses do not distinguish between soluble, sorbed or free-phase hydrocarbon, however; a low relative concentration indicates that the contaminant may mainly be present in the gaseous or aqueous phases; and a high relative concentration indicates the presence of sorbed contaminant or free phase liquid either as continuous-phase or residual saturation. A more rigorous set of analyses is required to distinguish between the various phases.

Additional tests to identify the presence of NAPL in soil or aquifer core sample are currently undeveloped and research in this area is warranted. Squeezing and immiscible displacement techniques have been used to obtain the pore water from cores (40). Other methods of phase separation involving vacuum or centrifugation may also be developed for this use. A paint filter test was proposed in one Superfund DNAPL field investigation where aquifer cores were placed in a filter/funnel apparatus, water was added, and the filtrate was examined for separate phases. These core analysis techniques have potential to provide valuable field data to characterize NAPL distribution.

Cone Penetrometer

The cone penetrometer (ASTM D3441-86)(69) has been used for some time to supply data on the engineering properties of soils. Recently, the application of this technology has made the leap to the hazardous waste arena. The resistance of the formation is measured by the cone penetrometer as it is driven vertically into the subsurface. The resistance is interpreted as a measure of pore pressure, and thus provides information on the relative stratigraphic nature of the subsurface. Petroleum and chlorinated hydrocarbon plumes can be detected most effectively when the cone penetrometer is used in conjunction with in-situ sensing technologies (48). Features of the cone penetrometer include: a continuous reading of the stratigraphy/permeability; in-situ measurement; immediate results are available; time requirements are minimal; vertical accuracy of stratigraphic composition is high; ground-water samples can be collected in-situ; and the cost is relatively low.

Data from the cone penetrometer can be used to delineate probable pathways of DNAPL transport. This is accomplished by identifying permeability profiles in the subsurface. A zone of low permeability underlying a more permeable stratigraphic unit will likely impede vertical transport of the DNAPL. Where such a scenario is found, a collection of DNAPL is probable and further steps can be implemented to more accurately and economically investigate and confirm such an occurrence. This general approach has successfully been implemented at one Superfund site (8).

DNAPL

Well Level Measurements

In an effort to delineate the horizontal and vertical extent of the DNAPL at a spill site, it is important to determine the elevation of DNAPL in the subsurface. Monitoring DNAPL elevation over time will indicate the mobility of the DNAPL. There are several methods that can be used to determine the presence of DNAPL in a monitoring well. One method relies on the difference in electrical conductivity between the DNAPL and water. A conductivity or resistivity sensor is lowered into the well and a profile is measured. The interface of the DNAPL is accurately determined when the difference in conductivity is detected between the two fluids. This instrument may also be used to delineate LNAPL. A transparent, bottom-loading bailer can also be used to measure the thickness (and to sample) of DNAPL in a well (36). The transparent bailer is raised to the surface and the thickness of the DNAPL is made by visual measurement.

Several laboratory and field studies have been performed which investigate the anomaly between the actual and measured LNAPL levels in ground-water wells (15,16,24,25). The anomaly between actual and measured NAPL thickness in the subsurface is also applicable to DNAPL, but for different reasons. The location of the screening interval is the key to understanding both scenarios. First, if the well screen interval is situated entirely in the DNAPL layer, and the hydrostatic head (water) in the well is reduced by pumping or bailing, then to maintain hydrostatic equilibrium, the DNAPL will rise in the well (36,44,71) (refer to Figure 18). Secondly, if the well screen extends into the barrier layer, the DNAPL measured thickness will exceed that in the formation by the length of the well below the barrier surface (36) (refer to Figure 19). Both of these scenarios will result in a greater DNAPL thickness in the well and thus a false indication (overestimate) of the actual DNAPL thickness will result. One of the main purposes of the monitoring well in a DNAPL

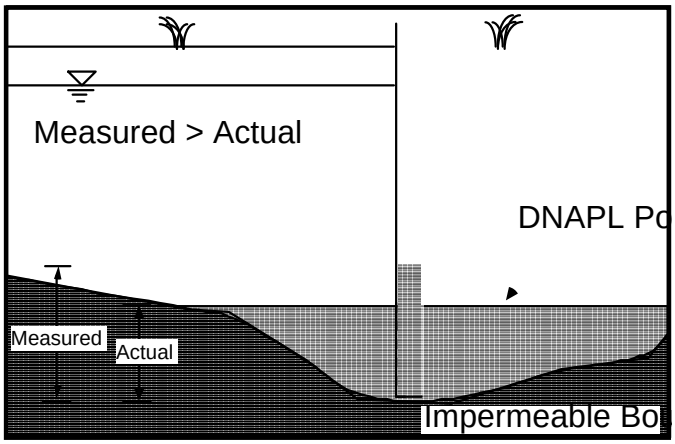

Figure 18. A well screened only in the DNAPL in conjunction with lower hydrostatic head (i.e. water) in the well may result in an overestimation of DNAPL thickness.

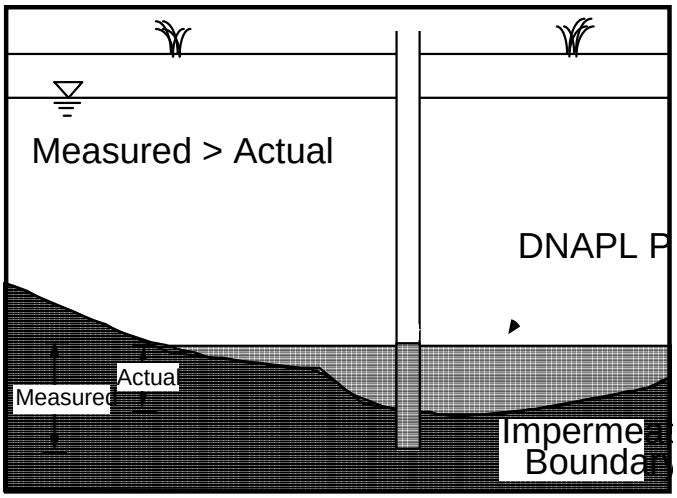

Figure 19. A well screened into an impermeable boundary may result in an over-estimation of the DNAPL thickness.

investigation is to provide information on the thickness of the DNAPL in the aquifer. Therefore, construction of the well screen should intercept the ground water:DNAPL interface and the lower end of the screen should be placed as close as possible to the impermeable stratigraphic unit.

DNAPL Sampling

Sampling of DNAPL from a well is necessary to perform chemical and physical analyses on the sample. Two of the most common methods used to retrieve a DNAPL sample from a monitoring well are the peristaltic pump and the bailer. A peristaltic pump can be used to collect a sample if the DNAPL is not beyond the effective reach of the pump, which is typically less than 25 feet. The best method to sample DNAPL is to use a double check valve bailer. The key to sample collection is controlled, slow lowering (and raising) of the bailer to the bottom of the well (57). The dense phase should be collected prior to purging activities.

Soil-Gas Surveys

A soil-gas survey refers to the analysis of the soil air phase as a means to delineate underground contamination from volatile organic chemicals and several techniques have been developed (34,52). This investigative tool is mainly used as a preliminary screening procedure to delineate the areal extent of volatile organic compounds in the soil and ground water. This method is quick, less expensive than drilling wells and can provide greater plume resolution (33).

Data from a soil-gas survey is a valuable aid in the development of a more detailed subsurface investigation where ground water monitoring wells and exploratory borings are strategically located for further site characterization. There are limitations to soil-gas surveys (26,52) and data interpretation must be performed carefully (35,49). Soil-gas investigations have mainly been conducted to identify the location of the organic contaminants in ground water. At the

time of this publication, the scientific literature did not contain information specifically applicable to the delineation of DNAPL from soil-gas survey data. However, it is surmisable that soil- gas surveys can be used to help delineate DNAPL residual saturation in the unsaturated zone or the location of perched DNAPL reservoirs.

Miscellaneous

The vertical migration of DNAPL in the saturated zone will eventually be challenged by a low permeability stratigraphic unit. According to the principles of capillary pressure, the lower permeability unit will exhibit a greater capillary pressure. Displacement of water by DNAPL requires that the hydrostatic force from the mounding DNAPL exceed the capillary force of the low permeability unit. The Hobson formula is used to compute the critical height calculation to overcome the capillary pressure under different pore size conditions (70).

In an effort to minimize further DNAPL contamination as a result of drilling investigations, precautionary steps should be taken. Penetration of DNAPL reservoirs in the subsurface during drilling activities offers a conduit for the DNAPL to migrate vertically into previously uncontaminated areas. It is very easy to unknowingly drill through a DNAPL pool and the bed it sits on, causing the pool to drain down the hole into a deeper part of the aquifer or into a different aquifer (32). Special attention to grouting and sealing details during and after drilling operations will help prevent cross-contamination.

Precautionary efforts should also be considered when a DNAPL reservoir is encountered during drilling operations. The recommended approach is to cease drilling operations and install a well screen over the DNAPL zone and cease further drilling activities in the well. If it is necessary to drill deeper, construction of an adjacent well is recommended. Alternatively, if it is not necessary to screen off that interval, it is recommended to carefully seal off the DNAPL zone prior to drilling deeper.

Well construction material compatibility with DNAPL should be investigated to minimize downhole material failure. A construction material compatibility review and possible testing will prevent the costly failure of well construction material. The manufacturers of well construction material are likely to have the most extensive compatibility data and information available.

Remediation

Remediation of DNAPL mainly involves physical removal by either pumping or trench-drainline systems. Removal of DNAPL early in the remediation process will eliminate the main source of contaminants. This step will substantially improve the overall recovery efficiency of the various DNAPL phases including the long term pump and treat remediation efforts for soluble components. Remediation technologies such as vacuum extraction, biodegradation, ground water pumping, and soil flushing is mainly directed at the immobile DNAPL and the various phases in which its components occur. Physical barriers can be used in an effort to minimize further migration of the DNAPL.

Clean-up of DNAPL can involve sizable expenditures: they are difficult to extract and the technology for their removal is just evolving (43). Historically, field recovery efforts usually proceed with a poor understanding of the volume distribution of the DNAPL. This reflects the difficulties involved in adequate site characterization, poor documentation of the release, and the complexity associated with the DNAPL transport in the subsurface.

Pumping Systems

Pumping represents an important measure to stop the mobile DNAPL from migrating as a separate phase by creating a hydraulic containment and by removal of DNAPL (44). Very simply, DNAPL recovery is highly dependent on whether the DNAPL can be located in the subsurface. The best recovery scenario is one in which the DNAPL is continuous and has collected as a reservoir in a shallow, impermeable subsurface depression. Once the DNAPL has been located and recovery wells are properly installed, pumping of pure phase DNAPL is a possible option but depends largely on site specific conditions which include, but are not limited to: DNAPL thickness, viscosity, and permeability.

Many DNAPL reservoirs in the subsurface are of limited volume and areal extent. Therefore, it can be expected that both the level of DNAPL (saturated thickness) in the well will decline from the prepumping position and the percentage of DNAPL in the DNAPL:water mixture will decrease rather rapidly. Correspondingly, DNAPL recovery efficiency decreases. Field results indicate that recovery wells screened only in the DNAPL layer will maintain maximum DNAPL:water ratios (44). Well diameter was not found to influence long term DNAPL recovery; however, large diameter wells allow high volume pumping for short durations; and small diameter wells result in lower DNAPL:water mixtures and greater drawdown.

An enhanced DNAPL recovery scheme may be used to improve recovery efficiency. An additional well is constructed with a screen interval in the ground water zone located vertically upward from the DNAPL screen intake. Ground

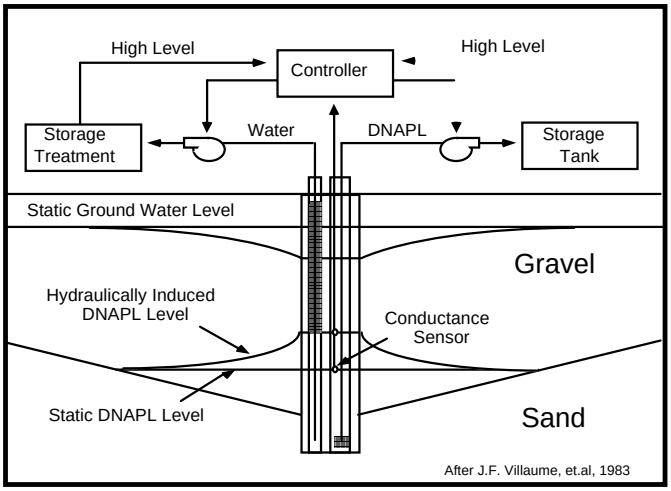

Figure 20. A DNAPL recovery system where deliberate upwelling of the static coal-tar surface is used to increase the flow of product into the recovery wells.

water is withdrawn from the upper screen which results in an upwelling of the DNAPL (70), refer to Figure 20. The upwelling of the DNAPL, coal tar in this case, improved the rate (twofold) at which the coal tar was recovered resulting in a more efficient operation. The ground water withdrawal rate must be carefully determined; too much will result in the coal tar from rising excessively and being either mixed (emulsions) with or suppressed by the higher water velocity above; too low will not caused upwelling. An estimate of this upwelling can be calculated using the simplified Ghyben-Herzberg Principle under ideal conditions (4). Laboratory studies indicated that dimethyl phthalate (1.19 g/cc) recovery rate was doubled or tripled over the conventional, non-upconing, recovery scheme (75). A similar application of this technique was used to increase the level of DNAPL (solvents) in a sandstone bedrock formation (11). Other enhanced DNAPL recovery techniques were implemented utilizing both water flooding and wellbore vacuum. Essentially, this minimized drawdown, allowing a maximum pumping rate of the DNAPL:water mixture. Both techniques offered significant advantages in terms of the rate and potential degree of DNAPL removal (8).

The highly corrosive nature of some DNAPL's may increase maintenance problems associated with the recovery system. A design consideration during any DNAPL recovery program should include a material compatibility review to minimize downhole failures. This is applicable to the well construction material and the various appurtenances of the recovery system. Manufacturers of the construction material would most likely have the best compatibility information available.

While most scientists agree that the residual saturation of immiscible hydrocarbon droplets in porous media are immobile, researchers have investigated the mobility of residual saturation in porous media for enhanced oil recovery and for NAPL remediation at spill sites. Specifically, this includes a complex interplay between four forces (viscous, gravity, capillary, buoyancy). These forces are dependent on both the chemical and physical characteristics of the DNAPL and porous media. The mobilization of residual saturation mainly hinges on either increasing the ground water velocity which increases the viscous forces between the residual saturation and the ground water, or decreasing the interfacial tension between the residual saturation and the ground water which decreases the capillary forces.

The capillary number is an empirical relationship which measures the ratio between the controlling dynamic stresses (absolute viscosity and ground water velocity) and static stresses (interfacial tension) of the residual saturation (39). The former are the viscous stresses and the dynamic pressure in the water which tend to move the oil. The latter are the capillary stresses in the curved water/oil interfaces which tend to hold the oil in place. As the capillary number is increased, the mobility of the residual saturation increases. In a laboratory column study, the capillary number had to be increased two orders of magnitude from when motion was initiated to complete displacement of the hydrocarbon in a sandstone core (74). In a glass bead packed column, only one order of magnitude increase was required. However, a higher capillary number was required to initiate mobility. The difference in mobility between the two columns was attributed to the pore geometry, i.e. size, shape.

There are limitations to residual saturation mobilization. The ground water gradient (dh/dl) necessary to obtain the critical capillary number to initiate blob mobilization would be 0.24. To obtain complete NAPL removal would require a gradient of 18 (3). Ground water gradients of this magnitude are unrealistic. Another estimate of the gradient necessary to mobilize carbon tetrachloride in a fine gravel and medium sand was 0.09 and 9.0 respectively (74). The former gradient is steep but not unreasonable and the latter gradient is very steep and impractical to achieve in the field. The same researchers concluded from more recent, comprehensive studies, that the earlier predictions were optimistic, and that the gradient necessary to mobilize residual organic liquid is clearly impractical (66). Another limitation is that along with residual saturation mobilization, the NAPL blobs disperse into smaller blobs and that the blob distribution was dependent on the resulting capillary number (6). Recovery of the NAPL residual saturation by pumping ground water may be more feasible where the porous media is coarse and capillary forces are low, i.e. coarse sands and gravel. However, even in this scenario, it is expected that the radius of residual saturation mobilization would be narrow.

It is held in petroleum engineering theory that the only practical means of raising the capillary number dramatically is by lowering the interfacial tension (39) and that this can be achieved by using surfactants (66). Surfactants reduce the interfacial tension between two liquids, and therefore, are injected into the subsurface for enhanced recovery of immiscible hydrocarbons. In laboratory experiments, surfactant flushing solutions produced dramatic gains in flushing even after substantial water flushing had taken place (54). Unfortunately, surfactants can be quite expensive and cost prohibitive in NAPL recovery operations. Surfactants are usually polymeric in nature and a surfactant residue may be left behind in the porous media which may not be environmentally acceptable. Additionally, surfactants may be alkaline and thus affect the pH of the subsurface environment. It has been suggested that such a surfactant may inhibit bacterial metabolism and thus preclude subsequent use of biological technologies at the site. Significant research in this area is currently underway which may uncover information improving the economics and feasibility of this promising technology.

In summary, practical considerations and recommendations concerning the mobilization and recovery of residual saturation include the following: greater effectiveness in very coarse porous media i.e. coarse sands and gravel; recovery wells should be installed close to the source to minimize flow path distance; a large volume of water will require treatment/ disposal at the surface; compounds with high interfacial tension or viscosity will be difficult to mobilize; and implementation of linear one-dimensional sweeps through the zones of residual saturation (74) and surfactants will optimize recovery.

Pumping the soluble components (aqueous phase) of DNAPL from the immiscible (continuous and residual saturation), solid (sorbed), and gaseous phases has been perhaps one of the most effective means to date to both recover DNAPL from the subsurface and to prevent plume migration. Recovery of soluble components quite often has been the only remediation means available. This is largely

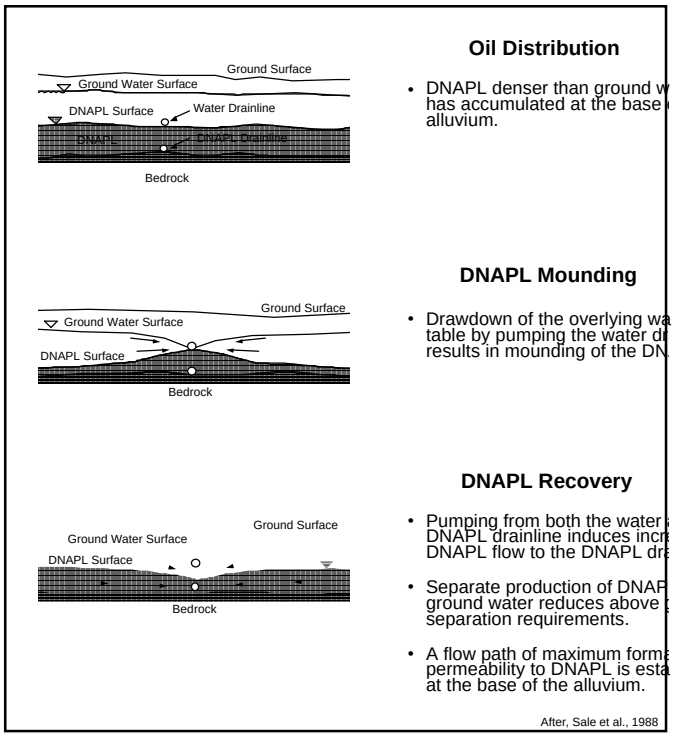

Figure 21. Trench recovery system of DNAPL utilizing the dual drainline concept.

attributed to the inability to locate DNAPL pools and due to low, DNAPL yielding formations. The basic principles and theory of pump and treat technology and the successes and failures have been summarized in other publications (64,67) and is beyond the scope of this publication.

Pumping solubilized DNAPL components from fractured rock aquifers historically has been plagued with a poor recovery efficiency. Although the rock matrix has a relatively small intergranular porosity, it is commonly large enough to allow dissolved contaminants from the fractures to enter the matrix by diffusion and be stored there by adsorption (32). The release of these components is expected to be a slow diffusion dominated process. This is because little or no water flushes through dead-end fracture segments or through the porous, impervious rock matrix. Therefore, clean-up potential is estimated to be less than that expected for sand and gravel aquifers.

Trench Systems

Trench systems have also been used successfully to recover DNAPL and are used when the reservoir is located near the ground surface. Trench systems are also effective when the DNAPL is of limited thickness. Recovery lines are placed horizontally on top of the impermeable stratigraphic unit. DNAPL flows into the collection trenches and seep into the recovery lines. The lines usually drain to a collection sump where the DNAPL is pumped to the surface. Similar to the pumping system, an enhanced DNAPL recovery scheme may be implemented using drain lines to improve recovery efficiency. This “dual drain line system” (41) utilizes a drain line located in the ground water vertically upward from the DNAPL line. Ground water is withdrawn from the upper screen which results in an upwelling of the DNAPL which is collected in the lower line, refer to Figure 21. This increases the hydrostatic head of the DNAPL. Excessive pumping of either single or dual drain line systems may result in the ground water “pinching off” the flow of DNAPL to the drain line. An advantage of the dual drain system is that the oil:water separation requirements at the surface are reduced.

Vacuum Extraction

Soil vacuum extraction (SVE) is a remediation technology which involves applying a vacuum to unsaturated subsurface strata to induce air flow. Figure 22 illustrates that the volatile contaminants present in the contaminated strata will evaporate and the vapors are recovered at the surface and treated. Common methods of treatment include granular activated carbon, catalytic oxidation, and direct combustion. SVE can effectively remove DNAPL present as residual saturation or its soluble phase components in the unsaturated zone. In general, vacuum extraction is expected to be more applicable for the chlorinated solvents (PCE, TCE, DCE) than the polycyclic aromatic compounds (wood preserving wastes, coal tars, etc.). When DNAPL is present in perched pools (Figure 12) it is more effective to remove the continuous phase DNAPL prior to the implementation of SVE. The same strategy is applicable in the saturated zone where DNAPL removal by SVE is attempted concomitantly with lowering the water table. Upon lowering the water table, SVE can be used to remove the remnant volatile wastes not previously recovered. Often, the precise location of the DNAPL is unknown; therefore, SVE can be used to remediate the general areas where the presence of DNAPL is suspected. Removal of DNAPL by SVE is not expected to be as rapid as direct removal of the pure phase compound. One advantage of SVE however, is that the precise location of the DNAPL need not be known.

Important parameters influencing the efficacy of SVE concern both the DNAPL and porous media. Porous media specific parameters include: soil permeability, porosity, organic carbon, moisture, structure, and particle size distribution. DNAPL specific parameters include: vapor pressure, Henry’s constant, solubility, adsorption equilibrium, density, and viscosity (20). These parameters and their relationships must be evaluated on a site specific basis when considering the feasibility of vacuum extraction and a practical approach to the design, construction, and operation of venting systems (22). Additionally, soil gas surveys which delineate vapor concentration as a function of depth is critical in locating the contaminant source and designing an SVE system.

Historically, SVE has been used to remove volatile compounds from the soil. Recently it has been observed that SVE enhances the biodegradation of volatile and semivolatile organic compounds in the subsurface. While SVE removes volatile components from the subsurface, it also aids in supplying oxygen to biological degradation processes in the unsaturated zone. Prior to soil venting, it was believed that biodegradation in the unsaturated zone was limited due to inadequate concentrations of oxygen (17). In a field study where soil venting was used to recover jet fuel, it was

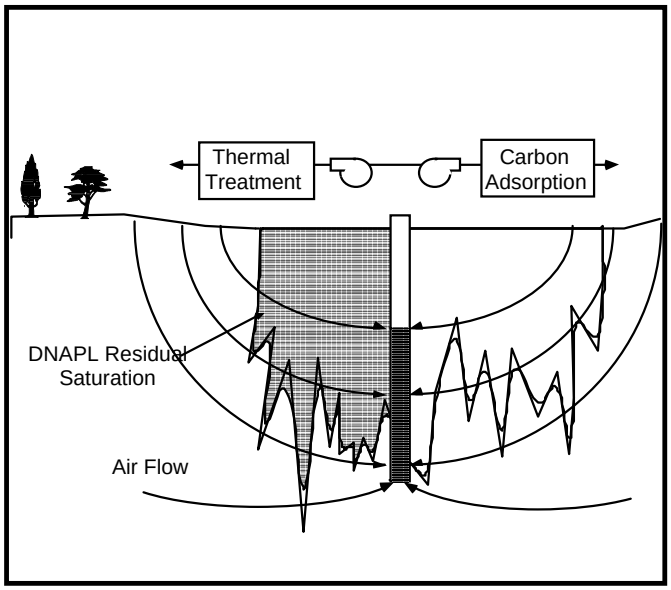

Figure 22. Vacuum extraction of DNAPL volatile components in the unsaturated zone. As shown here, vapors are treated by thermal combustion or carbon adsorption and the air is discharged to the atmosphere.

observed that approximately 15% of the contaminant removal was from the result of microbial degradation. Enhanced aerobic biodegradation during SVE increases the cost effectiveness of the technology due to the reduction in the required above ground treatment.

Vacuum extraction is one form of pump and treat which occurs in the saturated zone where the fluid is a gas mixture. Therefore, many of the same limitations to ground water pump and treat are also applicable to vacuum extraction. While the application of vacuum extraction is conceptually simple, its success depends on understanding complex subsurface chemical, physical, and biological processes which provide insight into factors limiting its performance (9).

Biodegradation

The potential for biodegradation of immiscible hydrocarbon is highly limited for several reasons. First, pure phase hydrocarbon liquid is a highly hostile environment to the survival of most microorganisms. Secondly, the basic requirements for microbiological proliferation (nutrients, electron acceptor, pH, moisture, osmotic potential, etc.) is difficult if not impossible to deliver or maintain in the DNAPL. A major limitation to aerobic bioremediation of high concentrations of hydrocarbon is the inability to deliver sufficient oxygen. A feasible remediation approach at sites where immiscible hydrocarbon is present is a phased technology approach. Initial efforts should focus on pure phase hydrocarbon recovery to minimize further migration and to decrease the volume of NAPL requiring remediation. Following NAPL recovery, other technologies could be phased into the remediation effort. Bioremediation may be one such technology that could be utilized to further reduce the mass of contaminants at the site. NAPL recovery preceding bioremediation will improve bioremediation feasibility by reducing the toxicity, time, resources, and labor.

Similar to other remediation technologies, a comprehensive feasibility study evaluating the potential effectiveness of bioremediation is critical and must be evaluated on a site specific basis. A comprehensive review of biodegradation of surface soils, ground water, and subsoils of wood preserving wastes, i.e. PAH's (29,37,51,62,63) are available. A comprehensive review of microbial decomposition of chlorinated aromatic compounds is also available (58).

Soil Flushing

Soil flushing utilizing surfactants is a technology that was developed years ago as a method to enhance oil recovery in the petroleum industry. This technology is new to the hazardous waste arena and available information has mainly been generated from laboratory studies. Surfactant soil flushing can proceed on two distinctly different mechanistic levels: enhanced dissolution of adsorbed and dissolved phase contaminants, and displacement of free-phase nonaqueous contaminants. These two mechanisms may occur simultaneously during soil flushing (42).

Surfactants, alkalis, and polymers are chemicals used to modify the pore-level physical forces responsible for immobilizing DNAPL. In brief, surfactants and alkalis reduce the surface tension between the DNAPL and water which increases the mobility. Polymers are added to increase the viscosity of the flushing fluid to minimize the fingering effects and to maintain hydraulic control and improve flushing efficiency. Based on successful laboratory optimization studies where an alkali-polymer-surfactant mixture was used, field studies were conducted on DNAPL (creosote) which resulted in recovery of 94% of the original DNAPL (42). Laboratory research has also been conducted which indicated that aqueous surfactants resulted in orders of magnitude greater removal efficiency of adsorbed and dissolved phase contaminants than water flushing (55).

Depth to contamination, DNAPL distribution, permeability, heterogeneities, soil/water incompatibility, permeability reduction, and chemical retention are important factors when considering soil flushing (42). Prior to this technology being cost effective in the field, surfactant recycling will be necessary to optimize surfactant use (55). Soil flushing is complex from a physical and chemical point of view; is relatively untested in the field; and will likely be challenged regulatorily. Considerable research currently being conducted in this area may result in the increased use of this technology to improve DNAPL recovery in the future.

Thermal methods of soil flushing involve injecting hot water or steam in an effort to mobilize the NAPL. The elevated temperature increases volatilization and solubilization and decreases viscosity and density. A cold-water cap is used to prevent volatilization. The mobile phases of the DNAPL are then recovered using a secondary approach, i.e. pumping, vacuum extraction etc. This approach (Contained Recovery of Oily Wastes) to enhance recovery of DNAPL is currently under EPA's Superfund Innovative Technology Evaluation Program and a pilot-scale demonstration is forthcoming (21). A limitation in the use of thermal methods is that the DNAPL

may be converted to LNAPL due to density changes (36). The adverse effects from this are that the DNAPL, existing as a thin layer, becomes buoyant and mobilizes vertically resulting in a wider dispersal of the contaminant. Other limitations involve the high energy costs associated with the elevated water temperature and the heat loss in the formation (36).

Physical Barriers

Physical barriers may be used to prevent the migration of DNAPL's in the subsurface and are typically used in conjunction with other recovery means. One feature of physical barriers is the hydraulic control it offers providing the opportunity to focus remediation strategies in treatment cells. Unfortunately, physical barriers, while satisfactory in terms of ground water control and containment of dissolved-phase plumes, may contain small gaps or discontinuities which could permit escape of DNAPL (7). Chemical compatibility between physical barriers and construction material must agree to insure the physical integrity of the barrier. The history of the performance of these containment technologies is poorly documented and is mainly offered here for completeness of review. A more complete review of these physical barriers is available (5,56).

Sheet piling involves driving lengths of steel that connect together into the ground to form an impermeable barrier to lateral migration of DNAPL. Ideally, the bottom of the sheet pile should be partially driven into an impermeable layer to complete the seal. Slurry walls involve construction of a trench which is backfilled with an impermeable slurry (bentonite) mixture. Grouting is a process where an impermeable mixture is either injected into the ground or is pumped into a series of interconnected boreholes which together form an impermeable boundary. Again, the main feature of these techniques is to physically isolate the DNAPL.

In summary, site characterization and remediation options for sites containing DNAPL are limited. Field data from site characterization and remediation efforts are also limited. This is largely due to the complexity of DNAPL transport and fate in the subsurface, poorly developed techniques currently available to observe and predict DNAPL in the subsurface, and to the fact that this issue has not been widely recognized until recently. Clearly, there is a growing realization within the scientific and regulatory community that DNAPL is a significant factor in limiting site remediation. Correspondingly, current research efforts within the private, industrial, and public sectors are focusing on both the fundamentals and applications aspects of DNAPL behavior in subsurface systems. Additionally, the number of field investigations reflecting an increased awareness of DNAPLs, is growing.

DNAPL Modeling

A modeling overview report identified nineteen (numeric and analytic) multiphase flow models which are currently available (60). Most of these models were developed for salt water intrusion, LNAPL transport, and heat flow. Four models are qualitatively described as immiscible flow models but do not specifically indicate DNAPL. A more recent model has been developed which simulates density driven, three phase flow, that is capable of modeling DNAPL transport (23). Presently, very little information is available on DNAPL modeling in the scientific literature.

Multiphase flow modeling involves modeling systems where more than one continuous fluid phase (NAPL, water, gaseous) is present. Modeling any subsurface system requires a conceptual understanding of the chemical, physical, and biological processes occurring at the site. Modeling of simultaneous flow of more than one fluid phase requires a conceptual understanding of the fluids and the relationship between the fluid phases. The significance of multiphase flow over single phase flow is the increased complexity of fluid flow and the additional data requirements necessary for modeling. As presented earlier, numerous variables strongly influence DNAPL transport and fate, and consequently, the mathematical relationship of these variables is complex. Therefore, it follows that DNAPL modeling presents paramount technical challenges.

Presently, it is exceedingly difficult to obtain accurate field data which quantitatively describes DNAPL transport and fate variables within reasonable economic constraints. DNAPL transport is highly sensitive to subsurface heterogeneities (8,27,28) which compounds the complexity of modeling. Heterogeneities are, by nature, difficult to identify and quantify and models are not well equipped to accommodate the influence of heterogeneities. Additionally, relative permeability and capillary pressure functions must be quantified to identify the relationship between fluids and between the fluids and the porous media. Unfortunately, these parameters are very difficult to measure, particularly in three phase systems. Prior to an investment of time and money to model a given site, a careful evaluation of the specific objectives and the confidence of the input and anticipated output data should be performed. This will help illuminate the costs, benefits, and therefore, the relative value of modeling in the Superfund decision making process.

In summary, DNAPL modeling at Superfund sites is presently of limited use. This is mainly due to: the fact that very little information is available in the scientific literature to evaluate previous work; accurate and quantitative input data is expected to be costly; the sensitivity of DNAPL transport to subsurface heterogeneities; and, the difficulty in defining the heterogeneities in the field and reflecting those in a model. However, multiphase flow models are valuable as learning tools.

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