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SUBSURFACE CONTAMINATION BY DENSE NON-AQUEOUS PHASE LIQUID (DNAPL) CHEMICALS
CONCEPTS AND IMPLICATIONS

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TABLE OF CONTENTS

	Page
1. Introduction	1
2. Groundwater Contamination by DNAPL Chemicals	3
3. DNAPL Migration in the Subsurface	9
4. Dissolution of DNAPL into the Groundwater	17
5. Significance of Subsurface DNAPL Chemical Sources	22
6. References	25

LIST OF TABLES

	Page
1. Solubility of selected DNAPL chemicals compared to US EPA Drinking Water Standards.	1
2. Density of selected DNAPL chemicals	2

LIST OF FIGURES

	Page
1. Groundwater contamination from a residual DNAPL source in the vadose zone.	5
2. Groundwater contamination from residual DNAPL sources in the vadose and saturated zones.	7
3. Groundwater contamination from residual DNAPL and DNAPL layers.	8
4. Relative permeability relationships for a DNAPL-water system.	12
5. Increase in mass transfer coefficient for DNAPL dissolution with increasing groundwater velocity.	20
6. Decrease in tetrachloroethylene (PCE) dissolution rate with the fraction PCE removed in soil column dissolution tests.	21

1. Introduction

Substances such as many halogenated aliphatic hydrocarbons, halogenated benzenes, phthalate esters and polychlorinated biphenyls (PCB) comprise a group of organic chemicals which in their pure form can be categorized as dense non-aqueous phase liquid (DNAPL) chemicals. DNAPL chemicals are analogous to petroleum hydrocarbons in that they are immiscible in water, but unlike petroleum hydrocarbons, DNAPL chemicals have densities greater than that of water. Approximately one quarter of the organic chemicals on the US EPA List of Priority Pollutants are DNAPL chemicals at typical subsurface temperatures.

Although DNAPL chemicals are immiscible in water and have relatively low solubilities in water (typically several hundred to several thousand milligrams per litre), their solubilities can often be many orders of magnitude higher than their respective drinking water standards (see Table 1).

TABLE 1. Solubility of selected DNAPL chemicals compared to proposed US EPA Drinking Water Standards.

Chemical	Solubility in Water (mg/L)	Drinking Water Standard (mg/L)
Carbon tetrachloride	785	0.005
1,2-Dichloroethane	8,700	0.005
1,1-Dichloroethylene	400	0.007
1,1,1-Trichloroethane	4,400	0.20
Trichloroethylene	1,100	0.005

Because drinking water standards for many DNAPL chemicals are so low, even small quantities introduced into the subsurface can result in large-scale groundwater contamination problems. For example, 200 L or 294 kg (53 gal. or 647 lb.), equivalent to one drum of trichloroethylene, could potentially contaminate approximately 60 billion L (16 billion gal.) of groundwater to the drinking water standard at a concentration of 0.005 mg/L.

The potential for groundwater contamination by DNAPL chemicals is also significant because of their distinctive physical and chemical properties. As previously noted, DNAPL chemicals are immiscible in water and have densities greater than water (See Table 2). The combination of low solubility and high density can enable DNAPL chemicals from waste disposal facilities or chemical spill sites to penetrate downward into the subsurface through the unsaturated and saturated zones as a separate non-aqueous phase. The tendency for DNAPL chemicals to sink through the saturated zone differs from that of petroleum hydrocarbons which will float on the groundwater in the saturated zone due to their lower densities. In the subsurface, small but significant quantities of chemicals can be dissolved by groundwater in contact with the DNAPL chemicals and can result in groundwater contamination.

TABLE 2. Density of selected DNAPL chemicals.

Chemical	Density (g/cm^3)
Carbon tetrachloride	1.58
1,2-Dichloroethane	1.26
1,1-Dichloroethylene	1.25
1,1,1-Trichloroethane	1.35
Trichloroethylene	1.47

The following sections describe:

- Basic conceptualizations for groundwater contamination by DNAPL chemicals,
- The principal factors influencing the behaviour of DNAPL chemicals in the subsurface,
- The general implications of the presence of DNAPL chemicals in the subsurface on remediation at chemical spill and waste disposal sites.

2. Groundwater Contamination by DNAPL Chemicals

Pioneering research into the behaviour of DNAPL chemicals in the subsurface was conducted starting in the mid-1970's by Friedrich Schwille at the Federal Institute of Hydrology in Koblenz, Federal Republic of Germany. Schwille's work has primarily involved small-scale and large-scale laboratory simulations of the penetration of DNAPL chemical into unsaturated and saturated granular geologic materials. These studies and concepts of subsurface contamination by DNAPL chemicals have been described by Schwille (1981), Schwille (1984a and 1984b) and Feenstra (1986). The latest of Schwille's studies have been translated into English and will be included in a volume entitled "Dense Organic Solvents in Groundwater" which is currently being prepared by John Cherry of the University of Waterloo and James Pankow of the Oregon Graduate Centre.

Based on the laboratory studies of Schwille and observations at a variety of chemical spill and waste disposal sites in North America, several general conceptualizations for the development of groundwater contamination from DNAPL chemicals can be described.

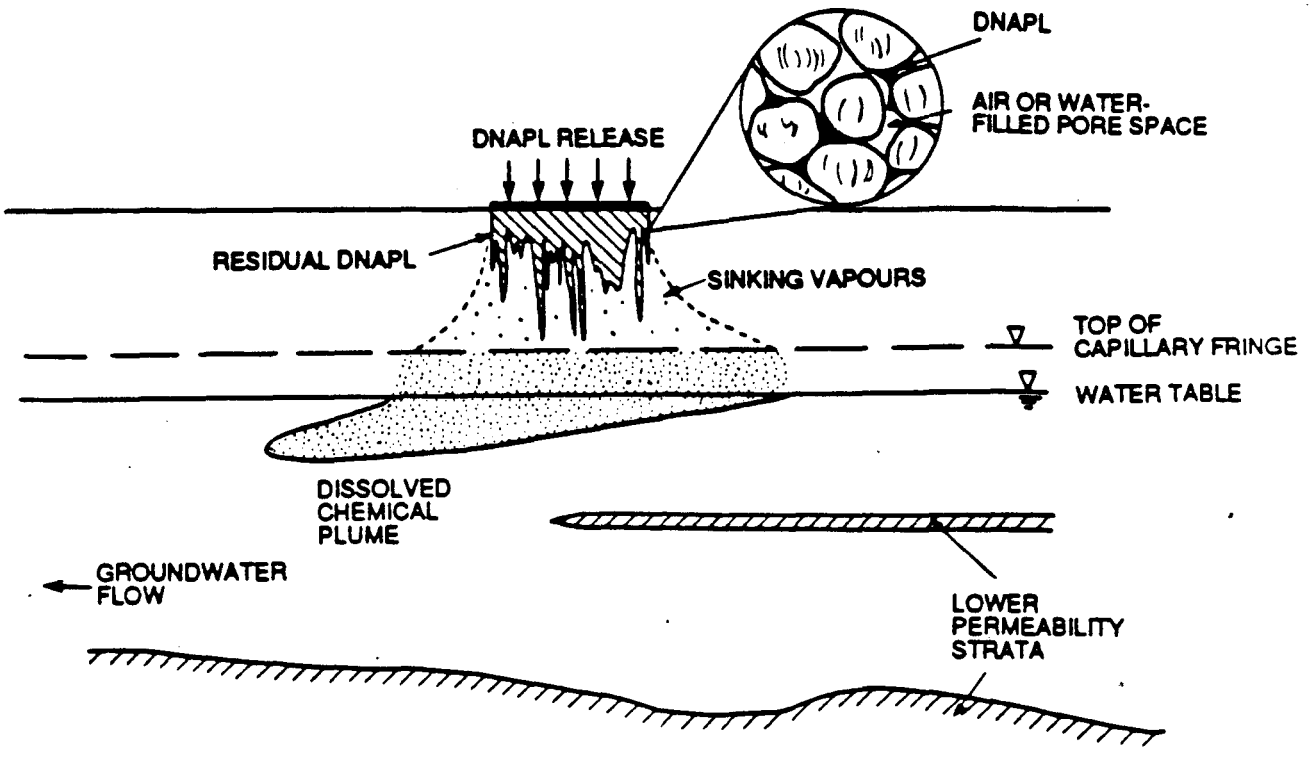
In the following conceptualizations, a quantity of DNAPL chemical is introduced into the subsurface such as might occur due to a release from a waste disposal facility or a chemical spill or leak. In such situations, DNAPL chemicals can penetrate downward through the unsaturated zone and the saturated zone due to its high density. The first three cases consider

introduction of DNAPL into permeable sandy soils. In the first case shown in Figure 1, the quantity of DNAPL chemical is small so that all of the DNAPL forms a residual in the unsaturated (vadose) zone because the input volume does not exceed the retention capacity of the vadose zone. Within this residual zone the DNAPL is present as immobile unconnected and partially connected blobs and filaments (see insert Figure 1). Residual contents for DNAPL chemicals such as trichloroethylene and tetrachloroethylene in unsaturated sandy soils determined by Schwille (1984b) ranged from 3 to 30 L/m^3 (0.6 to 6 gal./cu.yd.), with higher residual contents for finer-grained soils. These residual contents are comparable to those reported for petroleum hydrocarbons by CONCAWE (1979).

Groundwater contamination develops when water that infiltrates through the residual zone carries DNAPL-derived contaminants in dissolved form to the water table. Around and beneath the DNAPL residual in the vadose zone, a halo of lower-level chemical contamination can develop as a result of sinking of vapours through the vadose zone. Due to the vapour pressure and high molecular weight of many DNAPL chemicals, the density of soil air in equilibrium with DNAPL can have densities up to 100 % greater than moist soil air. The downward limit of sinking vapours will be the top of the capillary fringe. As infiltration of precipitation occurs from time to time through the residual zone and the vapour-contaminated zone, a plume of dissolved contaminants develops in the groundwater zone.

The high vapour pressure of many DNAPL chemicals will also result in diffusion of vapours upward through the vadose zone to the atmosphere. This volatilization can occur from the residual DNAPL, the vapour-contaminated zone or from the groundwater zone. Although the potential for loss of DNAPL by volatilization may be significant with respect to the detection

FIGURE 1. Groundwater contamination from a residual DNAPL source in the vadose zone.



of chemical vapours in the soil, the rate of diffusion from depth in the subsurface is relatively slow compared to the residual DNAPL contents and consequently DNAPL can persist in the vadose zone for many years.

For the case shown in Figure 2, the input volume of DNAPL chemical is sufficiently large for excess DNAPL to move into the saturated zone but not large enough for an excess to reach the bottom of the aquifer. The residual contents for DNAPL chemicals such as trichloroethylene and tetrachloroethylene in water-saturated sandy soils determined by Schwille (1984b) are slightly higher than those for unsaturated soil and ranged from 5 to 50 L/m^3 (1 to 10 gal./cu.yd). The rate of DNAPL infiltration into the subsurface may be extremely rapid. For example, in laboratory experiments conducted by Schwille (1984b) in coarse-grained sand, tetrachloroethylene penetrated through a 60 cm (2 ft.) thick unsaturated zone in 10 minutes and a 90 cm (3 ft.) thick saturated zone in 60 minutes.

The presence of lower permeability strata can have a very significant effect on downward movement of DNAPL. The combination of low permeability and capillary pressures can act to prevent downward movement, deflect DNAPL movement laterally and cause the formation of DNAPL layers. Dissolved contaminants derived from the residual DNAPL in the vadose zone and residual DNAPL in the saturated zone cause a groundwater contaminant plume to develop.

If the volume of DNAPL chemical introduced into the subsurface is larger than the retention capacity of the vadose and saturated zones, a portion of the DNAPL will spread out as a layer of free liquid on the bottom of the aquifer as shown in Figure 3, or it will settle out on lower permeability beds in the aquifer. Within these layers, DNAPL fills most of the pore space

FIGURE 2. Groundwater contamination from residual DNAPL sources in the vadose and saturated zones.

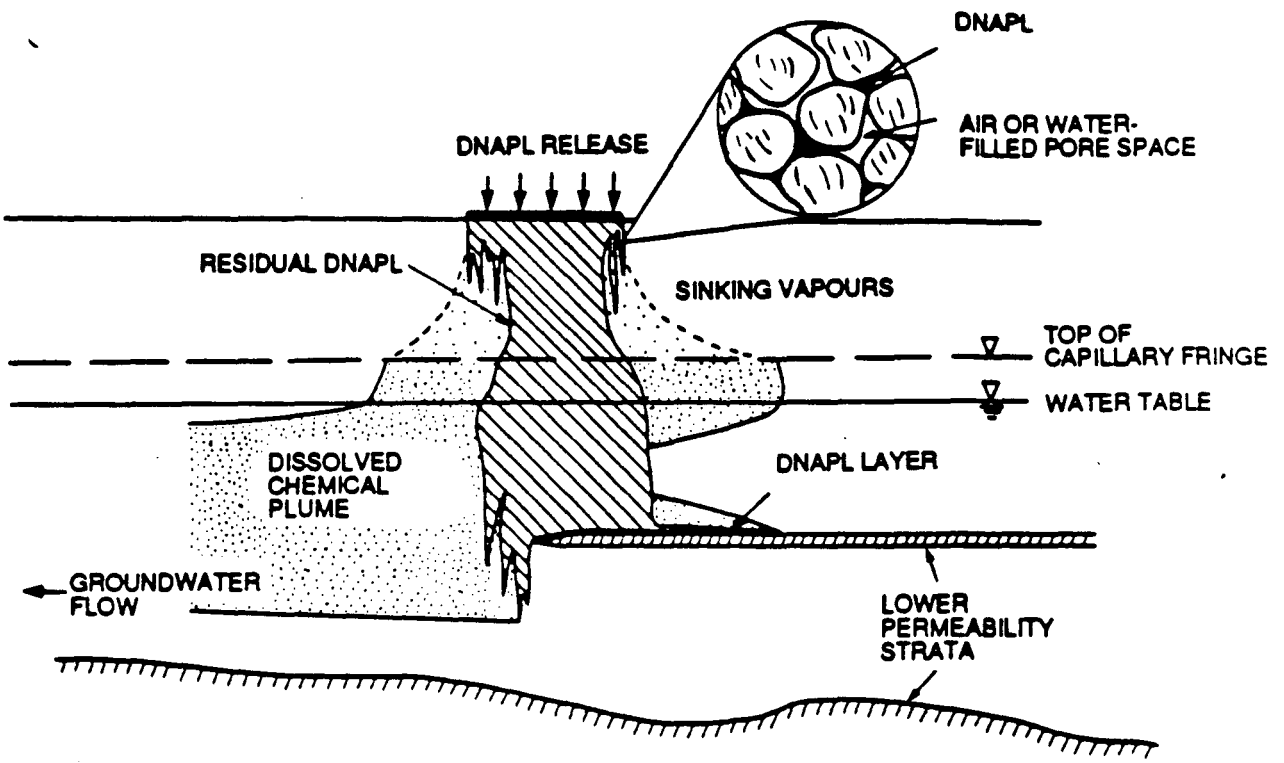
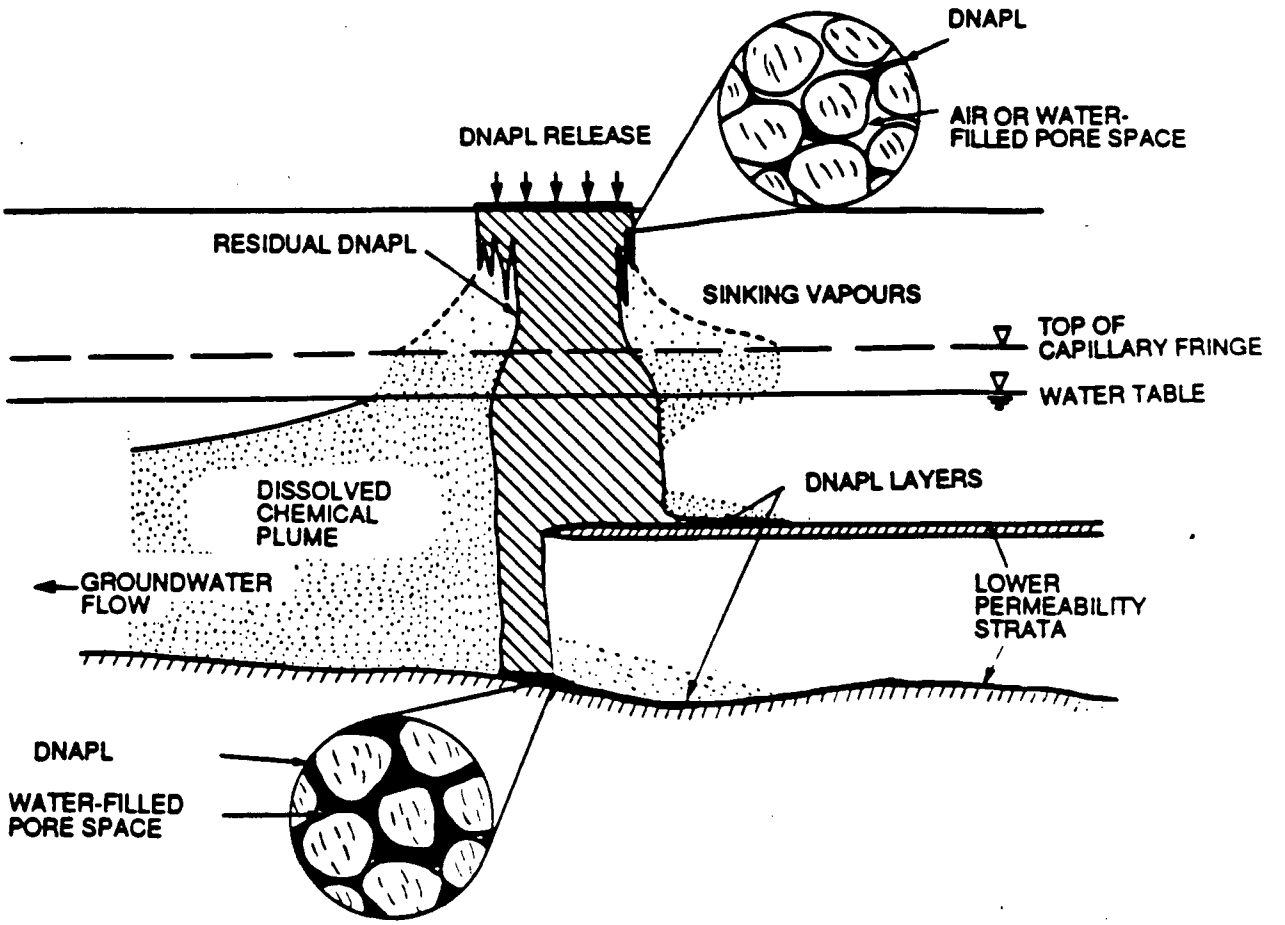


FIGURE 3. Groundwater contamination from residual DNAPL and DNAPL layers.



(see insert Figure 3). In situations where the confining stratum is sloped, DNAPL can continue to move downslope and may form puddles or pools in depressions on the confining strata. The lateral movement of DNAPL during formation of these layers will not be controlled by the direction of groundwater flow. In this case, groundwater in the aquifer acquires dissolved chemicals from the DNAPL residual and from the DNAPL layer on the bottom of the aquifer.

3. DNAPL Migration in the Subsurface

The key considerations for DNAPL chemical migration in the subsurface are: the vertical and lateral extent of migration, the rate of migration, and the nature of the residual zones and DNAPL layers which remain in the subsurface. Some of the primary factors which can affect the migration of DNAPL in the subsurface relate to the nature of the chemical source and include: the type of DNAPL chemical, the volume of DNAPL released, the area of infiltration of the DNAPL, and the time period over which the release occurred.

In the case of significant single incident chemical leaks and spills, suitable information on these factors may be available. However, this type of information may not be available for cases where contamination results from slow continual leaks such as may occur from an underground storage tank or line, from numerous intermittant smaller spills such as can occur around chemical loading and off-loading areas, or from the disposal of liquid wastes into landfills.

Different DNAPL chemicals will have different inherent properties such as density, viscosity, interfacial tension and vapour pressure. As will be discussed in the following paragraphs, these properties will influence the relative permeability of DNAPL, the capillary

forces which will act on the DNAPL, and the volatilization of DNAPL from the subsurface.

A key factor in the migration of DNAPL chemical downward into the subsurface will be the magnitude and duration of the density-induced downward pressure gradient created by DNAPL released at the ground surface. The higher the density of the DNAPL, the greater the potential for downward migration into the subsurface. The volume of DNAPL released and the manner in which it was released will have a significant effect of the downward pressure gradient. For a given spill volume, a smaller area of release will result in higher downward gradients and penetration to greater depths than for larger release areas.

The conductivity of geologic media to the movement of DNAPL chemicals will be a function of the properties of the DNAPL (density, viscosity and interfacial tension), the intrinsic permeability of the medium, and the proportion of the pore space filled by DNAPL, air and water. For conditions where the pore space is filled or nearly filled by DNAPL, the conductivity of the medium to DNAPL, K_n is related to the intrinsic permeability of the medium, k by:

$$K_n = \frac{\rho_n g k}{\mu_n}$$

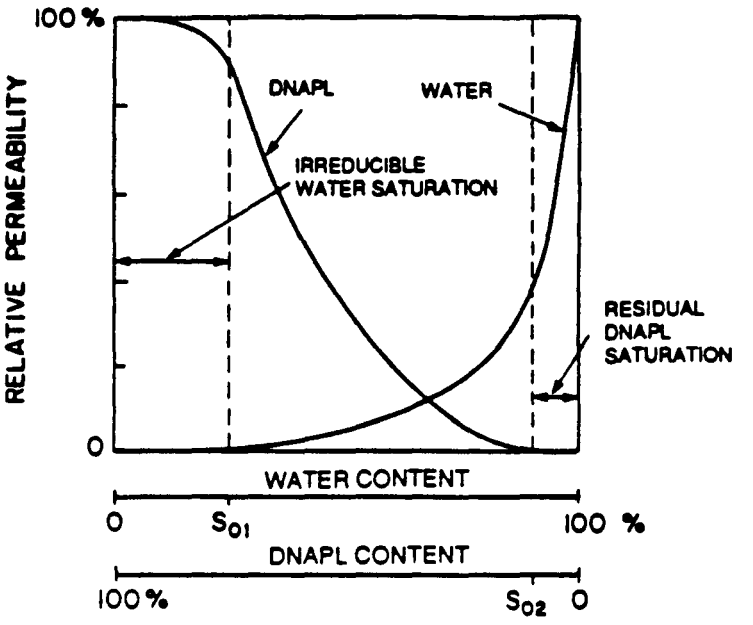
where ρ_n is the density of the DNAPL, g is the gravitational acceleration, and μ_n is the kinematic viscosity of the DNAPL. DNAPL chemicals have densities greater than water and many have viscosities less than water, consequently the conductivity of the medium to DNAPL chemicals will be greater than the hydraulic conductivity.

Under conditions where the pore space of the geologic medium is occupied by DNAPL and water, DNAPL and air, or DNAPL, water and air, the conductivity of the medium to DNAPL will be substantially reduced. The reduced conductivity to DNAPL is commonly refered to as the relative permeability. Figure 4 illustrates a hypothetical relative permeability relationship for a DNAPL-water system. The relative permeability to DNAPL is a maximum when the water content is zero and the permeability to water is a maximum when the DNAPL content is zero. Relative permeability to DNAPL is less reduced by the increasing water content than the permeability to water is reduced by increasing DNAPL content. DNAPL will not be mobile when the DNAPL content is less than the residual saturation (S_{02}). The relative permeability to water can be substantially reduced by the presence of DNAPL, even at DNAPL contents less than the residual DNAPL saturation. Three-phase systems (DNAPL-water-air) can be expressed similarly on triangular diagrams.

Two-phase and three-phase relative permeability relationships have been determined experimentally for petroleum hydrocarbons. Relationships for DNAPL chemicals are expected to be similar in form but DNAPL chemicals can have viscosities and interfacial tensions which can be considerably different from those of petroleum hydrocarbons. Details of the relative permeability relationships such as the residual saturation values may differ for DNAPL chemicals. At present there are no actual test data available on the relative permeability for DNAPL chemicals.

Capillary forces will also have a significant effect on the movement of DNAPL in the subsurface. Capillary forces are responsible for the retention of DNAPL in the residual zones above and below the water table. Capillary forces can also act to restrict the movement of DNAPL into water-saturated porous media. For example, consider a two-phase system

FIGURE 4. Relative permeability relationships for a DNAPL-water system. From Schwille (1984b).



consisting of DNAPL and water. As described by Berg (1975) for petroleum-water system in porous media, the magnitude of the capillary pressure, P_c, is dependent of the interfacial tension between the DNAPL and water, σ, a wettability term expressed by the contact angle between the DNAPL and the water, θ, and the mean effective radius of the pores, r_p, according to:

$$P_c = 2\sigma \cos\theta / r_p$$

For a water-wet porous medium, the contact angle is assumed to be zero and the term $\cos\theta$ then equals one. The capillary pressure increases as the interfacial tension increases and as the radius of the pores decreases. The interfacial tensions for DNAPL-water systems for most chlorinated aliphatic hydrocarbons occur in a very narrow range from approximately 50

to 53 mN/m and are somewhat higher than the 25 to 35 mN/m values for petroleum hydrocarbons. Consequently, DNAPL chemicals may be subjected to higher capillary pressures and may be expected to exhibit residual contents higher than those of petroleum hydrocarbons.Within a given soil there will be a wide range of pore sizes and the distribution of pore size may not be uniform. The penetration of DNAPL chemical as fingers and filaments rather than as a uniform front which was observed by Schwille (1984b) in homogeneous sand may be a result of subtle variations in capillary pressures due to spatial variations in pore size.

Before DNAPL can penetrate downward into a water-saturated geologic medium, the DNAPL pressure head must exceed the resistance of the capillary forces. The capillary pressure which must be overcome to allow entry of a DNAPL into a water-saturated media' can be estimated from the laboratory measurement of the threshold or displacement pressure. The measurement of displacement pressure is commonly performed in the field of petroleum reservoir engineering to assess the mobility of oil in the subsurface. Measurements of displacement pressures can be used to the illustrate the potential magnitude of the effect of capillary pressure on the exclusion of DNAPL from water-saturated media. Measurements of displacement pressures in Tertiary Gulf of Mexico sediments (Smith, 1966) suggest capillary pressure of a sand, P_{sand}, with a hydraulic conductivity of 10^{-3} cm/s (2.8 ft./day) would be approximately 1 x 10^4 N/m^2 (1.5 psi). The height of the DNAPL column, Z_n, which can be supported on the sand unit can be calculated using the relationship from Schowalter (1979):

$$Z_n = \frac{P_{sand}}{g(\rho_n - \rho_w)}$$

where g is the gravitational acceleration, ρ_n is the density of the DNAPL and ρ_w is the density of the water. For the DNAPL with a density of 1.3 g/cm^3, this relationship indicates that a DNAPL head of 3.4 m (11 ft.) would be required before the DNAPL would enter the water-saturated sand.

The migration of DNAPL chemicals from coarse-grained media into finer-grained media will also be inhibited by capillary pressures. Due to the contrast in pore size between the two materials, the capillary pressures in finer-grained media will be greater than those in coarse-grained media. The capillary pressure differential must be overcome by the DNAPL pressure head to allow DNAPL to penetrate finer-grained media. Consider, for example, the movement of DNAPL from a sand with a hydraulic conductivity of 10^{-3} cm/s (2.8 ft./day)' into a water-saturated silt layer with a hydraulic conductivity of 10^{-6} cm/s (0.0028 ft./day). Measurements of displacement pressures in analogous Tertiary Gulf of Mexico sediments (Smith, 1966) suggest capillary pressure silt, P_{silt} , could be 7×10^4 N/m^2 (10 psi). The height of the DNAPL column, Z_n ,which can be supported on the silt layer can be calculated using the relationship from Schowalter (1979) similar to that above:

$$Z_n = \frac{P_{silt} - P_{sand}}{g\,(\rho_n - \rho_w)}$$

In this case, 20 metres (66 ft.) of a DNAPL with a density of 1.3 g/cm^3 could be supported by the silt layer. This clearly illustrates that capillary pressures can have a very significant effect on restricting downward DNAPL movement into fine-grained strata.

The vapour pressure of DNAPL chemicals can, in some situations, also affect the migration of DNAPL in the subsurface. DNAPL may be lost from the shallow unsaturated zone by volatilization of high vapour pressure compounds to the atmosphere. Such losses of mass will act to restrict further downward migration if the losses are significant. However, volatilization losses are expected to be significant only in situations where DNAPL chemicals exist close to the ground surface or in dry pervious sandy soil, or where the DNAPL has a very high vapour pressure. In humid climates, losses due to volatilization are not expected to be significant except for very high vapour pressure chemicals.

The potential magnitude of volatilization losses can be illustrated with a simple steady-state diffusive flux calculation based on Fick's Law and an approximation for the effective gaseous diffusion coefficient in soils as described by Marshall and Holmes (1979). Consider, for example, the case in which a DNAPL layer exists in the vadose zone of a sandy soil at a depth of 2 m (6.5 ft.) below the ground surface. The DNAPL layer has an area of 6 m (19.7 ft.) by 6 m (19.7 ft.) a thickness of 0.2 m (0.6 ft.) and contains 2200 L (580 gal.) of chemical. The sandy soil has a porosity of 30 % and is at field capacity with a water content of 10 %. Gaseous diffusion coefficients of DNAPL chemicals can be approximated using a formula from Perry and Chilton (1973) based on molecular weight and atomic diffusion volume. The diffusive flux of chemical, q , from the DNAPL layer to the ground surface can be described by:

$$q = D_o \cdot (n_a/n)^4 \cdot n^{1.5} \cdot (C_{sat} - C_{atm}) / X$$

where D_o is the diffusion coefficient of the DNAPL vapour in wet air, n_a is the air filled porosity, n is the total porosity, C_{sat} is the chemical concentration in the soil air in

equilibrium with the DNAPL, C_{atm} is the chemical concentration in the atmosphere and X is the depth. For the case of a reasonably volatile chemical such as trichloroethylene with a gaseous diffusion coefficient of 8.11 x 10^{-2} cm^2/s and an equilibrium concentration of 0.42 mg/cm^3, approximately 52 years would be required for the mass of chemical in the pool to be removed by volatilization. For the case of 1,1,2,2-tetrachloroethane with a diffusion coefficient of 7.28 x 10^{-2} cm^2/s and an equilibrium concentration 0.046 mg/cm^3, approximately 570 years would be required for the DNAPL layer to be removed by volatilization. These calculations are consistent with observations at chemical spill sites in which DNAPL has remained in the subsurface for many years despite the effect of volatilization.

Groundwater flow patterns will have little effect the migration on DNAPL chemicals in the subsurface. In laboratory experiments by Schwille (1984b) the downward penetration of DNAPL chemicals such as trichloroethylene and tetrachloroethylene in coarse and medium sands was not noticably influenced by horizontal groundwater flow rates of as much as 14 m/day (46 ft./day). In some situations, upward groundwater flow may prevent further downward movement of DNAPL through the groundwater zone. The height of a DNAPL column which can be supported by a upward groundwater potential gradient is dependent on the density of the DNAPL and can be described (neglecting capillary forces) by:

$$\frac{\Delta h}{\Delta Z_n} = \frac{(\rho_n - \rho_w)}{\rho_w}$$

where Δh is the difference in hydraulic head across the DNAPL column, ΔZ_n is the height

of the DNAPL column, ρ_n is the DNAPL density and ρ_w is the water density. For the DNAPL with a density of 1.3 g/cm^3, an upward hydraulic gradient of 0.3 would be required to prevent downward migration of the non-aqueous phase. This relationship indicates that only large upward hydraulic gradients could be expected to prevent downward migration of DNAPL chemicals into the subsurface.

Substantial efforts have been directed at the development of computer models for the simulation and ultimate prediction of DNAPL migration through the subsurface. A variety of one- and two-dimensional, two-phase (DNAPL-water or DNAPL-air) and three-phase (DNAPL, air and water) models have been developed by Guswa and Faust (1984), Farquhar and McBean (1985) and Abriola and Pinder (1985) to simulate the penetration of DNAPL chemical into the subsurface from a surface spill. Although these models incorporate the principal controlling parameters into their formulation, they have been based on analogies to petroleum hydrocarbons and they are limited in their application to DNAPL chemicals because of the lack of actual field or laboratory data for key parameters such as relative permeability and displacement capillary pressures.

4. Dissolution of DNAPL into the Groundwater

The disssolution of DNAPL chemicals by groundwater in the subsurface will depend on a variety of factors such as the solubility of the chemicals in water, the area of contact between the DNAPL and the groundwater, the velocity of the groundwater, and the molecular diffusivity of the dissolved chemical in water. At the present time, there are few specific data available regarding dissolution rates or the factors controlling dissolution of DNAPL chemicals in the subsurface. However, the theory of chemical mass transfer developed for

the dissolution of petroleum hydrocarbons in soils and laboratory determinations of petroleum dissolution rates are likely to be applicable to the consideration of DNAPL dissolution.

The solubility of DNAPL chemicals in water range from several tens to several thousand milligrams per litre. Small-scale laboratory experiments (Pfannkuch, 1984; Schwille, 1984b) have shown that the pore water in contact with DNAPL quickly (minutes to hours) acquires dissolved chemicals at concentrations approaching the theoretical solubility of the DNAPL chemical. This condition is observed in field situations only when monitoring wells are situated directly within DNAPL zones. Maximum dissolved concentrations in the groundwater are typically less than ten percent of the theoretical solubility concentration. This phenomenon is likely the result of heterogeneous distribution of DNAPL in the subsurface, the non-uniform pattern of groundwater flow in and around the DNAPL residual zones and layers, and the fact that many DNAPL sources are small in size and difficult to locate for accurate placement of monitoring wells.

A key factor which will control the dissolution of DNAPL chemicals in the subsurface will be the contact area between the DNAPL and the groundwater. The larger the contact area, the greater will be the chemical mass transfer from the DNAPL to the groundwater. The chemical mass transfer rate or dissolution rate is typically expressed as a mass flux (M/T) and is the product of a mass transfer coefficient ($M/L^2/T$) and a measure of the contact area (L^2). The mass transfer coefficient is considered to be a function of the solubility of the DNAPL, the molecular diffusivity of the dissolved chemical in water and the groundwater velocity.

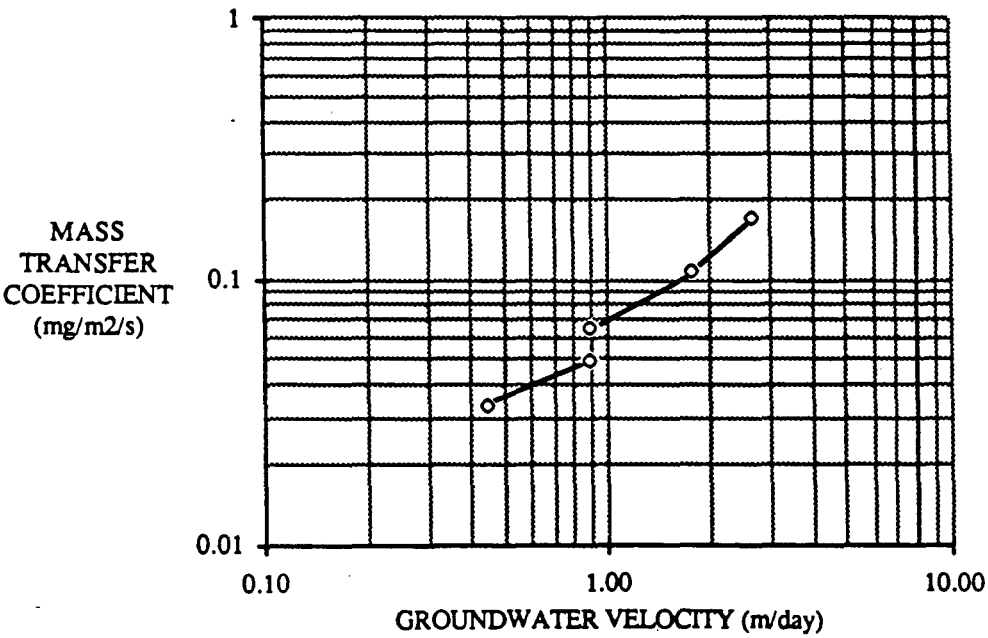
In the case of dissolution of a DNAPL layer in the subsurface, the DNAPL-groundwater contact area is roughly defined by the surface area of the layer. Most of the loss of mass from the pool should be reflected in a decreasing layer thickness rather than shrinking layer surface area. The change in contact area as dissolution proceeds will be minimal unless the layer is very thin.

At the present time, the only data available on mass transfer coefficients for the dissolution of DNAPL chemicals in groundwater can be derived from 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE) layer dissolution experiments by Schwille (1984b). For these experiments, a DNAPL layer was introduced into the bottom of a tank 1.5 m (5 ft.) in length and 0.5 m (1.6 ft.) in width containing coarse sand having a hydraulic conductivity of 3.5 x 10^{-1} cm/s (1000 ft./day). Water was passed over the layer at varying rates and the concentration of dissolved chemical in the water was measured. By relating the dissolved concentrations to the volume of water flow over the DNAPL layer, the mass transfer coefficient for dissolution of the layer can be calculated. Mass transfer coefficients determined for 1,1,1-trichloroethane ranged from 0.094 mg/m^2/s to 0.46 mg/m^2/s. Mass transfer coefficients determined for trichloroethylene ranged from 0.034 mg/m^2/s to 0.17 mg/m^2/s. These values for the mass transfer coefficients are in the same range as those determined for petroleum fuel oils, kerosene and gasoline (Pfannkuch, 1984). The values of the mass transfer coefficient were found by Schwille to increase with increasing groundwater velocity as shown in Figure 5.

A TCE layer 1.5 m (5 ft.) in length and 0.5 m (1.6 ft.) in width, such as considered in these experiments, and 0.2 m (0.6 ft.) in thickness contains approximately 77 kg (170 lb.) of TCE. For typical natural conditions in a sand aquifer with a hydraulic conductivity of

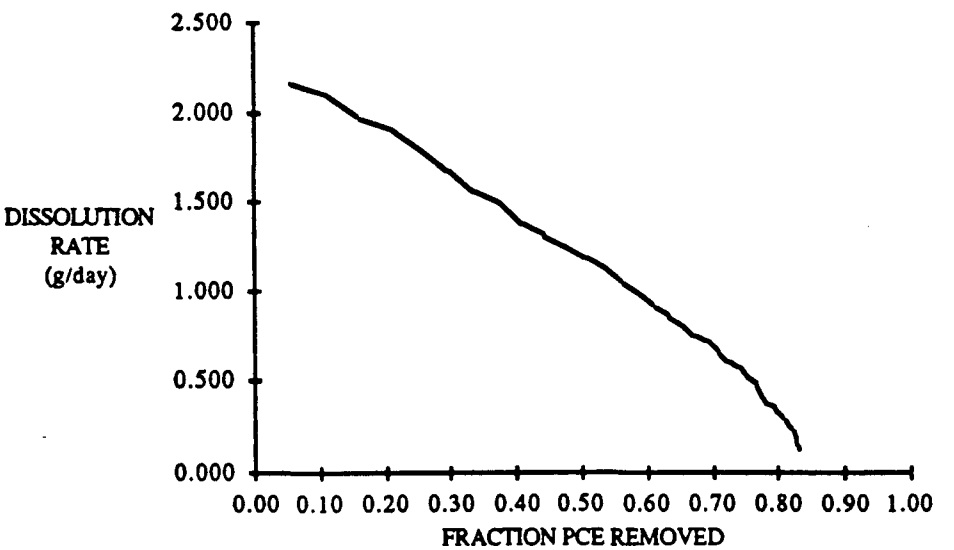
10^{-2} cm/s, porosity of 0.35 and hydraulic gradient of 0.03, the groundwater velocity is 0.75 m/day (2.5 ft.day). From Figure 5, the TCE mass transfer coefficient is 0.05 mg/m^2/s for this groundwater velocity. The contact area for the TCE layer is 0.75 m^2. Therefore the dissolution rate would be 1.2 kg/year (2.6 lb./year) and approximately 70 years would be required for groundwater flow to completely dissolve the TCE layer. This indicates that even small TCE layers can potentially persist for decades or more under natural groundwater flow conditions.

FIGURE 5. Increase in mass transfer coefficient for trichloroethylene (TCE) dissolution with increasing groundwater velocity. Data from Schwille (1984b).



Though it is not possible to quantify, the effective contact area in DNAPL residual zones would be expected to be considerably greater than that provided by a DNAPL layer. If this is the case, the dissolution rate in residual zones may be expected to be greater than that for DNAPL layers, but a valid comparison cannot be made because the contact area will be dependent on the residual DNAPL content and this will decrease as dissolution removes the DNAPL. Small-scale column experiments by Schwille (1984b) to evaluate dissolution of tetrachloroethylene (PCE) residual (residual content 30 L/m^3) indicate a relatively high initial dissolution rate with dissolved tetrachloroethylene concentrations in the water being close to saturation. As the experiments proceeded, the dissolved concentrations and therefore the dissolution rate decreased steadily as tetrachloroethylene was removed from the column (see Figure 6).

FIGURE 6. Decrease in tetrachloroethylene (PCE) dissolution rate with the fraction of PCE removed in soil column tests. Data from Schwille (1984b).



By the time 90 % of the tetrachloroethylene had been removed, the dissolution rate had decreased to 10 % of the initial rate. This decrease in dissolution rate may simply reflect a decrease in contact area as DNAPL is removed. Such a decrease in dissolution rate in the residual zones will decrease the dissolved chemical concentrations released from the source and will lengthen the time required for removal of DNAPL by dissolution in the groundwater.

5. Significance of Subsurface DNAPL Chemical Sources

The presence of DNAPL chemicals in the subsurface has significant implications regarding the interpretation of groundwater contamination patterns and the design of remedial measures at waste disposal facilities and chemical spill sites. The penetration of DNAPL into the subsurface extends the source of groundwater contamination from at or close to the ground surface to a potentially far greater depth. This means that groundwater contamination patterns resulting from a DNAPL source may be significantly different than those which might develop from a near-surface source.

The presence of a DNAPL source may result in the highest concentrations of dissolved chemicals occurring at the base of an aquifer rather than near the top as would be typical of a near-surface contamination source. Therefore, the possible presence of a deeper DNAPL source must be considered in the planning of borehole and monitoring well locations and depths for hydrogeologic investigations.

The potential importance of a subsurface DNAPL chemical source cannot be overstated. For example, consider a idealized case of trichloroethylene in sandy soil (porosity of 30 %) in a residual zone below the water table measuring 3 m (9.8 ft.) by 3 m (9.8 ft.) in area and 5 m

(16.4 ft.) in depth with a residual content of 30 L/m^3 (6 gal./cu.yd.). Such a residual zone could contain approximately 1350 L or 1985 kg (360 gal. or 4365 lb.) of trichloroethylene. Similarly a small pool measuring 6 m (9.8 ft.) by 6 m (9.8 ft.) in area and 0.2 m (0.6 ft.) in thickness in a sandy soil could contain approximately 2200 L or 3235 kg (580 gal. or 7115 lb.) of trichloroethylene. Such quantities are relatively small with respect to the quantities of chemicals handled by many industries and the quantities of waste chemicals disposed of in many older disposal sites, but they are very large in relation to target concentrations for drinking water for trichloroethylene of 0.005 mg/L.

The presence of DNAPL chemicals in the subsurface will have very significant implications with regard to remedial measures to control groundwater contamination at chemical spill sites and waste disposal facilities. DNAPL chemicals can potentially penetrate downward into the subsurface to beyond the depth of feasible removal by excavation. Similarly, DNAPL chemicals can also migrate into areas which are otherwise inaccessible to excavation such as beneath buildings or process areas, rivers, lakes and into bedrock formations. These zones of residual DNAPL and DNAPL pools can comprise very significant sources of long-term groundwater contamination. Purging and treating contaminated groundwater from the dissolved plume, although effective at controlling the migration of the dissolved chemicals, will not generally be effective in remediating the contaminant source because the DNAPL residual zones and DNAPL layers can represent such a large mass of chemical.

Conventional methods for the removal of contaminated groundwater or floating non-aqueous phase liquids (ie. petroleum) such as purge wells and collector trenches may not be effective for the removal of DNAPL because the movement of DNAPL is not controlled by the groundwater flow pattern. DNAPL layers cannot be reliably recovered by hydraulic means.

Recovery wells installed directly within a DNAPL layers can be used to recover some quantity of pure chemical but the radius of influence of such wells is generally small and the DNAPL layers can be difficult to locate precisely. Even if recovery of part of the layer of possible, a residual DNAPL will remain. The DNAPL in the residual zone is, by its very nature, immobile under the ambient potentiometric conditions.

In areas where DNAPL chemicals have penetrated beyond the depth of feasible removal by excavation or exist in otherwise inaccessible locations, the removal of the residual zones and layers may only be possible by novel in situ removal techniques. However, the ability to remove DNAPL chemicals from the subsurface, particularly from bedrock formations, has not been demonstrated at the present time. Methods such as induced volatilization, hydraulic removal and chemically-enhanced hydraulic removal have been evaluated for the removal of lighter-than-water petroleum hydrocarbons from the subsurface. The principles of such methods may be applicable to the removal of DNAPL chemicals from the subsurface. Accelerated dissolution and chemically-enhanced dissolution methods are other options which may be potentially applicable for removal of DNAPL chemicals from the subsurface.

Before methods for the in situ removal of DNAPL from the subsurface can be successfully implemented, the location and nature of the DNAPL must be known. The depth and areal extent of DNAPL residual zones and DNAPL layers must be sufficiently well known to allow adequate borehole access for inducing air or water flow through the contaminated zones. In many situations, hydrogeologic investigation techniques and our current level of understanding of the behaviour of DNAPL chemicals in the subsurface are not sufficiently developed to allow accurate definition of DNAPL location. In addition, factors such as the effect of the presence of DNAPL on the groundwater flow rates and the DNAPL dissolution

rates must also be known sufficiently to allow prior prediction of the removal effectiveness. This is not possible at the present time. Further research is required to develop appropriate investigative techniques and a sufficient understanding of DNAPL behaviour in order to evaluate and demonstrate the effectiveness of in situ methods for the removal of DNAPL chemicals from the subsurface.

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