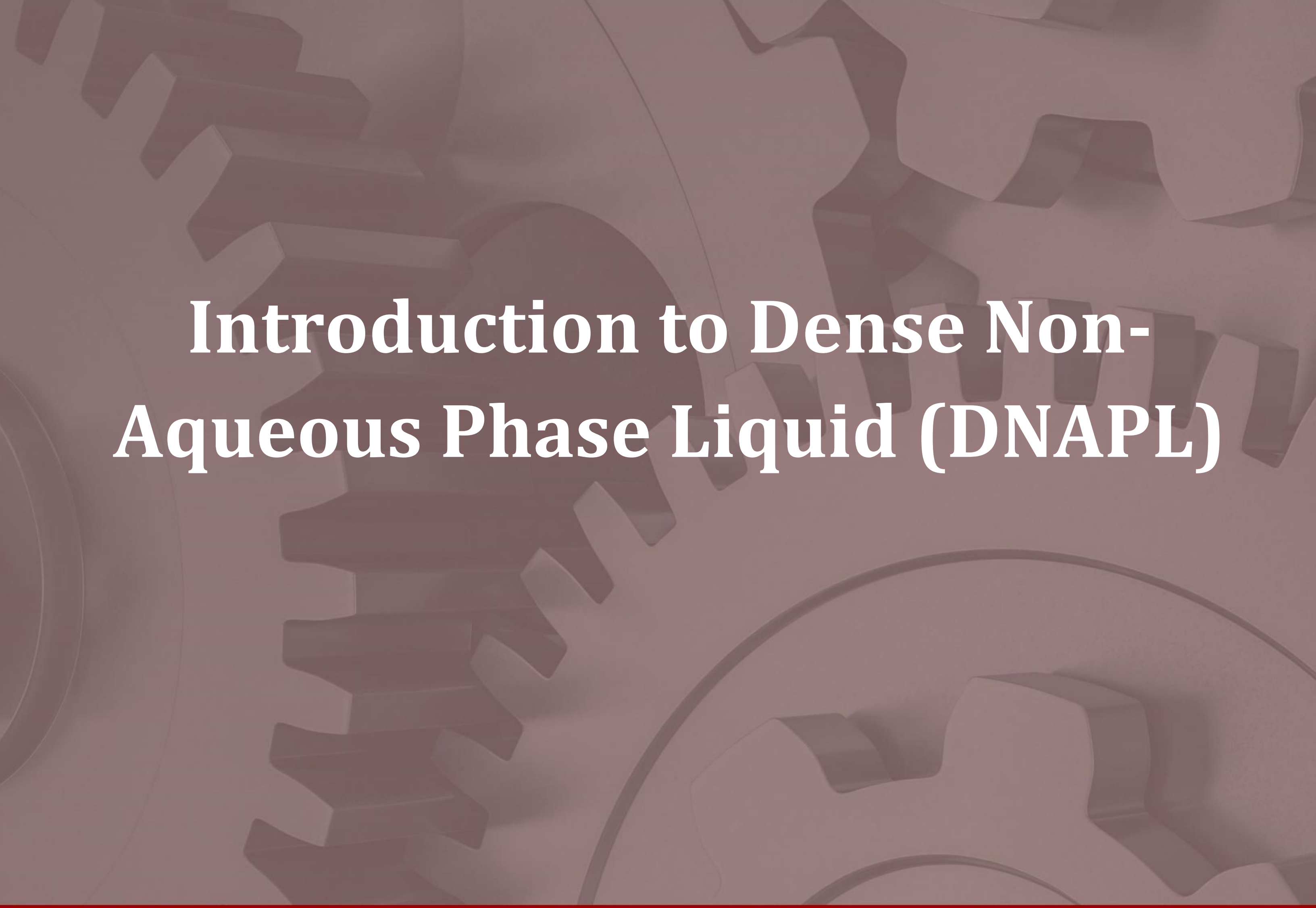

Introduction to Dense Non-Aqueous Phase Liquid (DNAPL)

An Online Continuing Education Course for Engineers

Course Number: EN-2014

Credit: 2 Hours / 2 PDH / 2 CPD

1.0 - Introduction

Groundwater contamination from classes of chemicals such as chlorinated solvents, polychlorinated biphenyls (PCBs), creosote, and coal tar is frequently encountered at hazardous waste sites (40, 43). These types of contaminants have low solubilities in water and have densities greater than that of water. Therefore, they can exist in the subsurface as Dense, Non-Aqueous Phase Liquids (DNAPLs) and have the potential to migrate as a separate liquid phase to significant distances below the water table in both unconsolidated materials and fractured bedrock. Because of the physicochemical properties associated with DNAPLs, they migrate through the subsurface in a very selective and tortuous manner (13, 27, 29). Thus, the majority of DNAPL present in the subsurface may not be found immediately below the entry location and directly encountering DNAPLs with conventional drilling techniques may be difficult.

Determining the presence or absence of a DNAPL is an important component of the conceptual site model and is critical to the proper selection of the remediation approach. Subsurface DNAPL acts as a long-term source for dissolved-phase contamination and determines the spatial distribution and persistence of contaminant concentrations within the dissolved-phase plume. Once it has been determined that DNAPL exists within the subsurface, subsequent characterization activities are typically conducted to better delineate the boundaries of the DNAPL source zone. The DNAPL source zone is the overall volume of the subsurface containing residual and/or pooled DNAPL. It should be recognized that there will be uncertainty associated with the delineation of the DNAPL source zone. In addition to the DNAPL, there may be significant amounts of contaminant mass that have diffused into low permeability zones. Back diffusion of contaminant mass from these zones may sustain dissolved-phase plumes for significant periods of time, even after DNAPL has been removed. Establishing the presence and locations of such non-DNAPL sources is beyond the scope of this course.

In recent years there have been advancements in characterization tools, site investigation approaches (14) and knowledge of DNAPL source zone architecture within the subsurface. This course provides a framework for not only assessing the presence of DNAPL, but also for delineating the spatial extent of the DNAPL source zone, a priority at many sites due to the more prevalent use of *in-situ* remediation technologies (38). The strategy described in the course utilizes converging lines of evidence that incorporate the scientific advancements in the the field and expands the applicability of the course to include both unconsolidated deposits and fractured bedrock. An iterative, flexible site investigation approach (7) is encouraged.

2.0 - Nature of the DNAPL Source Zone

Upon release to the subsurface, DNAPL will distribute itself in the form of disconnected blobs and ganglia of organic liquid referred to as residual DNAPL, and in connected distributions referred to as pooled DNAPL (Figure 1). Residual DNAPL is found both above and below the water table within the pathways of DNAPL migration, and typically occupies between 5% and 30% of pore space in porous media (6, 27, 44) and in rock fractures (21). Residual DNAPL is trapped by capillary forces, and typically will not enter an adjacent monitoring well, even under the influence of aggressive groundwater pumping (6, 27).

Pooling of DNAPL can occur above capillary barriers, which are typically layers and lenses of slightly less permeable material (Figure 1). Pooling can therefore occur at any elevation in the subsurface, and not just at the base of permeable zones. Absence of pooling above clay aquitards and bedrock may be due to the presence of dipping fractures, bedding planes, joints and faults which may allow the continued downward migration of the DNAPL. Pools represent a continuous distribution of DNAPL, and typically correspond to DNAPL saturations of between 30% and 80% of pore space in both porous media and fractures. The frequency of pool occurrence and the thickness of pools are increased by the presence of horizontal capillary barriers, lower DNAPL density, higher interfacial tension, and an upward component to groundwater flow (17, 22). The thickness of pools typically ranges from fractions of an inch to a few feet, depending on fluid and media properties (36) as well as the volume released. Because pools represent a connected distribution of DNAPL, the pooled DNAPL is susceptible to mobilization through drilling activities and can short-circuit along existing monitoring wells and piezometers. In addition, pools may also be mobilized in response to changes in hydraulic gradient. The gradient required to mobilize a pool is a function of the DNAPL-water interfacial

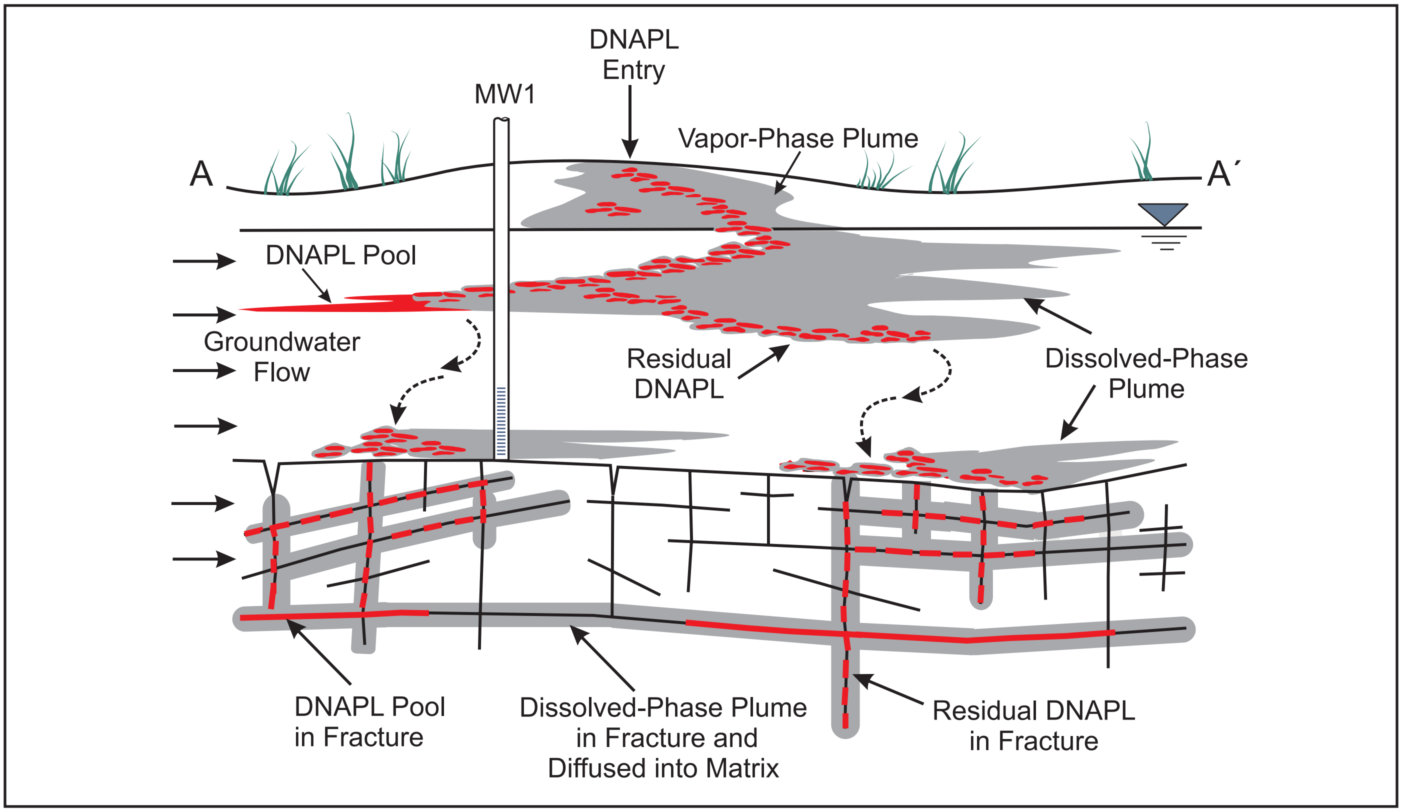

Figure 1 – Schematic illustration of contamination associated with a DNAPL release. Note that DNAPL migrates in three dimensions, and that residual DNAPL accumulated above bedrock is the result of the release at ground surface. The reader is referred to Figure 2 for a depiction of matrix diffusion. Figure is not to scale.

tension, the pool length, and the permeability of the surrounding material (6, 27). Pumping groundwater from beneath DNAPL pools, for example, can lead to an increase in capillary pressure and subsequent downward DNAPL mobilization.

The spatial distribution of residual and pooled DNAPL is strongly influenced by geology, and also by DNAPL properties and release history (frequency, intensity, duration, volume and location). DNAPL migration can occur through lenses and laminations of porous media at the scale of inches or less (17, 29). For DNAPLs that are non-wetting (see wettability in glossary) with respect to water (which is usually the case), migration below the water table is typically through the larger pores (and hence higher permeability regions) in unconsolidated media and larger aperture fractures in bedrock. The orientation of stratigraphic and structural features will largely determine the degree of lateral and vertical DNAPL spreading. DNAPL migration from the release location can occur in any direction, and is typically not greatly influenced by low ambient hydraulic gradients except for creosotes and coal tars which have densities close to that of water.

The overall region of the subsurface containing residual and pooled DNAPL is referred to as the DNAPL source zone. For high density and low viscosity DNAPLs (such as chlorinated solvents), migration in relatively permeable media can cease as soon as a few months to a few years following the time of release (3, 17, 27, 29). Some geological conditions, such as horizontal to sub-horizontal fractures, gently dipping strata and sand seams in low permeability media can give rise to longer time scales for migration of chlorinated solvent DNAPLs, particularly for large volume DNAPL sources. For low density and high viscosity DNAPLs (such as creosote and coal tar), migration has the potential to continue for many decades (12). The overall depth of DNAPL migration is dependent not only on the presence or absence of capillary barriers, but also on the volume released, the interfacial tension, the degree of lateral spreading, and the bulk retention capacity (see glossary) of the medium. Because fractured rock has very low bulk retention capacity, small volumes of DNAPL can migrate greater distances in bedrock in comparison to the same volume released into unconsolidated deposits (18).

Groundwater flowing past residual and pooled DNAPL will result in dissolved-phase plumes of contamination. Complete dissolution of all DNAPL as a result of natural groundwater flow is expected to take from several decades to hundreds of years for most DNAPLs. For multi-component DNAPLs, the presence of more than one component typically suppresses the aqueous solubility of the other components in the DNAPL (6, 27). Exceptions to this can occur, however, when co-solvents such as alcohols are present in the DNAPL. In the absence of co-solvents, the concentration of any particular component dissolving into groundwater can often be approximated using Raoult's Law (2, 6, 27). Early in the dissolution process, the plume chemistry will be dominated by the higher effective solubility components which tend to be those present in the largest mass fraction within the DNAPL, and those with the highest single-component (handbook) solubility values (24). The concentration of any or all components in groundwater downgradient of a multi-component-DNAPL source zone will typically be lower than expected using a single component solubility limit. With time, both the DNAPL composition and the plume composition will change in response to the dissolution process. The dissolved components that comprise the plume will migrate in groundwater subject to advection, dispersion, sorption, volatilization, and degradation processes.

Both residual and pooled DNAPL, and dissolved-phase plumes that are in direct contact with clays, silts, or a porous bedrock matrix, can diffuse into the low permeability media (forward diffusion). If concentrations outside of the low permeability zone become lower than those inside, diffusion will occur back into the higher permeability zone (back diffusion) and can result in plume persistence (5, 33). The forward and back diffusion processes are collectively referred to as matrix diffusion (Figure 2). The persistence of DNAPL in fractures in bedrock, saprolite and clay can be shortened by the matrix diffusion process (19, 28). In addition, the rate of advance of a dissolved-phase plume in fractured rock with a porous matrix can be strongly attenuated by the matrix diffusion process (20, 35). The influence of matrix diffusion on dissolved-phase plume migration in fractured rock and clay relative to other processes such as advection, dispersion, sorption, and possible degradation processes will vary depending on site specific geological conditions and contaminant properties. In general, matrix diffusion has a greater influence on dissolved-phase plume migration in the case of wider fracture spacing, smaller fracture aperture, lower hydraulic gradient, higher matrix porosity, and higher matrix organic carbon.

Above the water table, volatile DNAPL can vaporize into air filled pore spaces (Figure 1). For DNAPLs with significant vapor pressure, this can lead to expanded vapor-phase plumes in the unsaturated zone. The concentration of contaminants in the vapor phase will be governed by the vapor pressure, and for a multi-component DNAPL can often be approximated using Raoult's Law. In relatively warm and dry environments, the persistence of some DNAPLs (e.g., chlorinated solvents) can be relatively short (on the order of months to a few years) in unsaturated media. The absence of residual and pooled DNAPL in the unsaturated zone may not, therefore, be sufficient evidence to conclude that DNAPL has not migrated below the water table at the site of interest.

3.0 - Types of DNAPLs

Coal Tar is a complex mixture of hydrocarbons produced through the gasification of coal that was produced as a by-product of manufactured gas operations as early as 1816 in the United States. It is still produced as a by-product of blast furnace coke production. Coal tar contains hundreds of hydrocarbons, including light oil fractions, middle oil fractions, heavy oil fractions, anthracene oil, and pitch. The low density (typically 1.01 g/cc to 1.10 g/cc

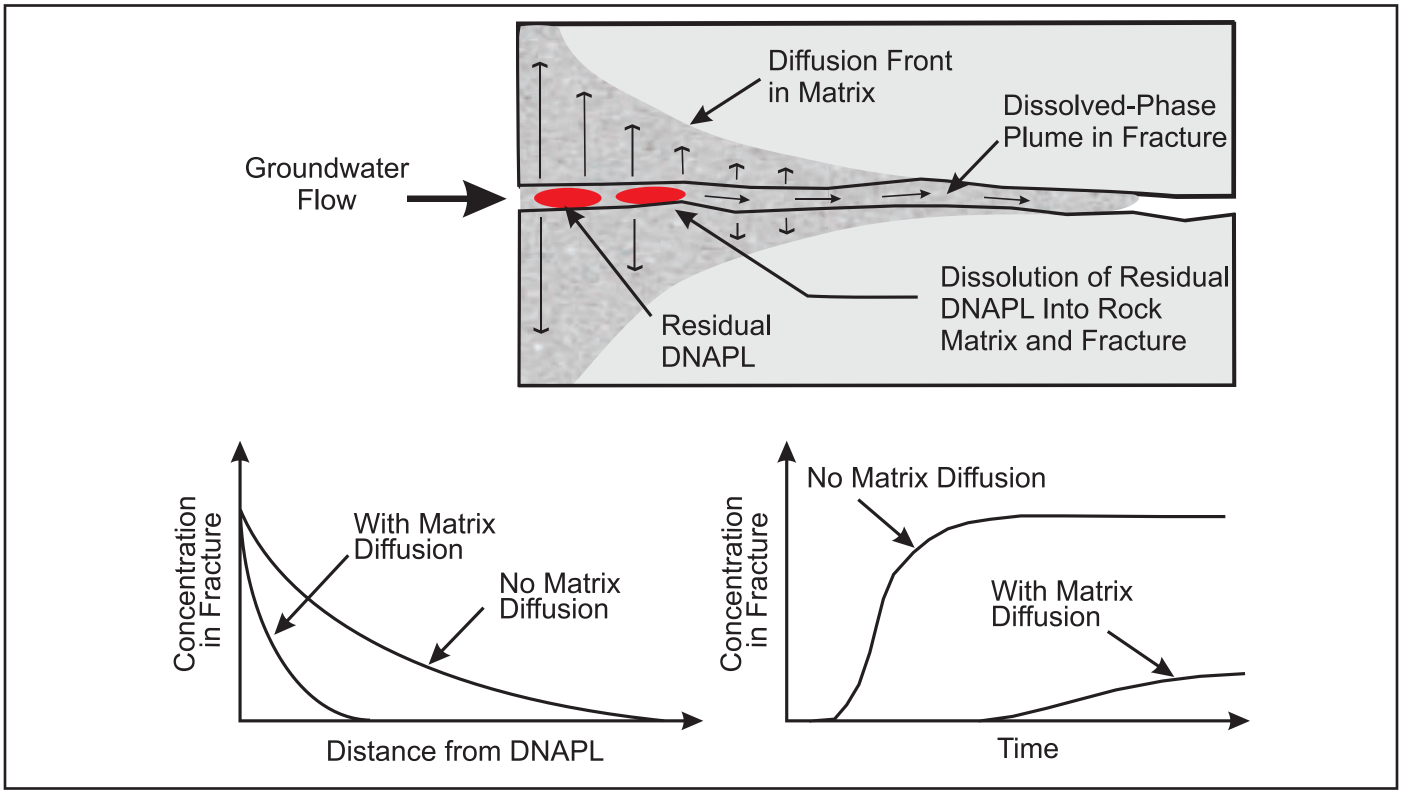

Figure 2 – Matrix diffusion of dissolved-phase contaminants adjacent to DNAPL and along length of plume in fracture. Matrix diffusion can attenuate the rate of plume advance in fractured rock (bottom left concentration vs distance plot), and can result in delayed breakthrough curves (bottom right concentration vs time figure). These factors need to be considered when relying upon groundwater concentration data to assess DNAPL presence.

compared to 1.00 g/cc of water [at 4°C]) and high viscosity (up to 200 to 300 times, or more, than that of water) facilitate long time-scales of migration, with the possibility of movement continuing for many decades following initial release. Due to the lengthy list of compounds present in coal tar, many investigators select a sub-set of coal tar compounds based on mobility and toxicity to assess water quality. These compounds may include benzene, toluene, ethylbenzene, xylenes (BTEX), benzo[a]pyrene, naphthalene, and phenanthrene. Depending on the age of the DNAPL and groundwater velocity, some of the lower molecular weight and more soluble compounds of the coal tar may have been leached out of the DNAPL by the time a site investigation is initiated. Naphthalene is often the dominant compound in present day coal tar (9). In addition, the various components in the plume will migrate at different velocities because of varying degrees of sorption and degradation (often aerobic conditions). The lower molecular weight, less sorbing compounds (e.g., BTEX) can migrate significantly further in groundwater than the higher molecular weight, more sorbing compounds (e.g., PAHs).

Creosote is composed of various coal tar fractions and was commonly used to treat wood products. It is still used today in certain wood treating operations and as a component of roofing and road tars. Creosote is a multi-component DNAPL that contains many hydrocarbons, primarily polycyclic aromatic hydrocarbons (PAHs), phenolic compounds, and carrier fluids such as diesel. The low density (typically 1.01 g/cc to 1.13 g/cc) and high viscosity (typically 20 to 50 times that of water) of creosote facilitate long time-scales of migration, with the possibility of movement continuing for many decades following initial release. Most investigators select a sub-set of creosote compounds, based on mobility and toxicity to characterize water quality, such as naphthalene, benzo(a)pyrene, and phenanthrene.

Polychlorinated Biphenyls (PCBs) are a class of 209 chemical compounds referred to as congeners, in which between one and ten chlorine atoms are attached to a biphenyl molecule. The majority of PCBs were manufactured between 1930 and 1977 under the trade-name Aroclor for use in capacitors, transformers, printing inks, paints, pesticides, and other applications. Aroclors differ based on the amount and types of congeners present. PCBs by themselves are DNAPLs, and were often blended with carrier fluids such as chlorobenzenes and mineral oil prior to distribution. The density of most PCB oils ranges from 1.10 g/cc to 1.50 g/cc, while the viscosity ranges from 10 to 50 times that of water. Most congeners are very hydrophobic and their transport can be retarded strongly relative to the rate of groundwater migration. In some cases, however, PCB transport in groundwater can be facilitated through the formation of emulsions or the presence of colloids.

Chlorinated Solvents such as trichloroethene (TCE), tetrachloroethene (PCE) and carbon tetrachloride (CT) have been produced in large quantities since the mid 1900's. Some chlorinated solvents contain trace amounts of stabilizers, preservatives and impurities. Typical uses vary widely and include dry cleaning, metal degreasing, pharmaceutical production, pesticide formulation, and chemical intermediates. Chlorinated solvents can be encountered as single component DNAPLs (e.g., as primarily PCE at a dry cleaning facility, or as primarily TCE at a vapor degreasing facility), or as part of a multi-component DNAPL containing other organic compounds. The relatively high density (typically 1.10 g/cc to 2.20 g/cc) and low viscosity (typically ranging from half to twice that of water) of chlorinated solvents can result in a relatively short time-scale of migration following release compared to coal tar and creosote. In a dissolved-phase plume, most chlorinated solvents are not retarded strongly relative to the rate of groundwater flow.

Mixed DNAPLs A DNAPL that contains two or more compounds is referred to as a multi-component DNAPL (e.g., creosote). A mixed DNAPL is a multi-component DNAPL that contains a wide variety of organic compounds as a result of blending and mixing prior to disposal operations, or as a result of cotemporaneous disposal. Examples include DNAPLs encountered at former solvent recycling facilities and industrial disposal sites. Such DNAPLs can contain aromatic compounds normally associated with LNAPLs (e.g., toluene) along with chlorinated solvents, PCBs, alcohols, ketones, and tetrahydrofuran. The density of mixed DNAPLs typically ranges from 1.01 g/cc to 1.60 g/cc, and the dissolved-phase plumes associated with mixed DNAPLs usually contain a wide variety of compounds with varying mobility.

4.0 – DNAPL Source Zone Investigation Methods

This section presents various site investigation methods and related interpretation techniques that can be useful when characterizing a DNAPL source zone. These methods and techniques will be relied upon in Sections 5 (Assessing DNAPL Presence) and 6 (Delineation of the DNAPL Source Zone). Additional information is provided in (6, 26, 37).

A Visual Observation

DNAPL obtained from the bottom of a monitoring well or as an emulsion from a pumped water sample is conclusive evidence of DNAPL presence (pooled DNAPL). Monitoring wells can be sampled for DNAPL using bottom loading bailers lowered to the bottom of the well or pumping from the bottom of the well. If an interface probe indicates DNAPL presence, then the sample should be retrieved and it should be confirmed (visually, or through laboratory analysis) that the substance is DNAPL. If DNAPL is visually observed in drill cuttings or in a soil sample for the first time, then a sample should be sent to the laboratory for confirmatory evidence. This line of evidence is applicable in both unconsolidated deposits and fractured rock, but it should be noted that visual observation of DNAPL in rock core is rare because of the aggressive flushing nature of the drilling process. Because of the typically sparse and tortuous nature of DNAPL distribution in the subsurface, DNAPL is not encountered and visually observed within many DNAPL source zones.

B Chemical Concentrations in Soil Above Threshold DNAPL Saturation

Chemical concentrations in soil exceeding the value corresponding to a threshold DNAPL saturation are conclusive evidence of DNAPL presence (see Calculation 1). The threshold DNAPL saturation for use in Calculation 1 should be set to be between 5% and 10% of pore space for all DNAPL types. The particular threshold satura-

tion chosen should result in a chemical concentration in soil that is an order of magnitude higher than that determined in line of evidence C. It follows that high organic carbon content soils and highly hydrophobic chemicals may require the use of threshold saturations toward the higher end of the above range. This method is applicable to unconsolidated media both above and below the water table, but is not applicable in fractured rock. The calculation requires knowledge of site-specific parameters and a quantitative chemical analysis of the soil. Care should be taken to sample soil horizons in core exhibiting the highest headspace readings and the
strongest visual indication of DNAPL pr
of fixed depth interva
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C Chemical Concentrat
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D Site Use/Site History

Investigations during the past 30 years have shown that the subsurface occurrence of DNAPL is often associated with the industries, practices, and processes outlined in Table 1. Site Use/Site History can be ascertained using methods such as employee interviews, company purchase and sale records, aerial photographs, and building plans. Former lagoons, underground tanks, floor drains and leach fields are sometimes coincident with the location of DNAPL source areas.

E Vapor Concentrations

The location of a vapor-phase plume may be coincident with the current or former presence of DNAPL in the vadose zone. Mapping the vapor-phase plume may be useful in deciding where to collect additional data.
Be me DNAPLs can completely vaporize in
ort time periods (yet the vapors will persist
), the presence of vapors and the mapping
hase plume should generally not be used in
nclude that DNAPL is present in the vadose
elineate the spatial extent of the DNAPL
should also be taken to avoid mistaking
' from off-gassing of a groundwater plume
erived from DNAPL sources. In-situ
rations can be sampled using invasive
l vapor surveys), and can be monitored
This line of evidence is not applicable
king a significant vapor pressure (e.g.,
, PCBs).

Testing

such as Oil Red O will partition into
g a red color to the organic liquid. Dye
icularly useful when encountering a
Hydrophobic dye techniques include
which a soil or water sample is placed
l amount of dye (6), and down-hole
dye-impregnated absorbent ribbon
borehole wall in either fractured rock or a direct push borehole (30). It should also be noted that the absence of staining on a down-hole ribbon sampler is not evidence of the absence of DNAPL, since only pooled DNAPL can migrate towards the sampler (residual DNAPL may be present in the formation adjacent to the sampling interval, and remain undetected).

Table 1 – Industries and Industrial Processes Historically Associated With DNAPL Presence

Industry	*Industrial Process*
Manufactured gas plant, Wood preservation (creosote), Electronics manufacturing, Solvent production/recycling, Pesticide/Herbicide manufacturing, Dry cleaning, Instrument manufacturing, Metal product manufacturing, Engine manufacturing, Steel industry coking operations (coal tar), Chemical production, Airplane maintenance, Transformer oil production	Storage of solvents in uncontained drum storage areas, Metal cleaning/degreasing, Metal machining, Tool and die operations, Paint stripping, Use of vapor and liquid degreasers, Storage and transfer of solvents in above and below ground tanks and piping, Burning waste liquids, Storage and treatment of waste liquids in lagoons, Use of on-site disposal wells, Loading and unloading of solvents, Transformer reprocessing, Disposal of solvents in unlined pits.