

# Dense non-aqueous phase liquids: Site remediation and redevelopment

## Developing and integrating DNAPL properties, characteristics, and changes through time

### Purpose

This guidance document provides information on dense non-aqueous phase liquid (DNAPL) properties and their characteristics that govern contaminant storage and migration as the DNAPL reacts in the environment. This guidance provides important definitions on DNAPL characteristics and behavior in the subsurface.

### DNAPL Properties and characteristics

#### Types of DNAPL

DNAPL, as defined on the Strategy guidance, is a liquid that is both denser than water and immiscible in water. It is commonly associated with materials used in industrial and commercial processes. Over time, the contaminants that comprise the DNAPL may slowly change by dissolving into groundwater, reducing to simpler compounds, partitioning to soil, or volatilizing within the subsurface environment. Examples include (but are not limited to):

- Chlorinated solvents
- Coal tar
- Heavy petroleum (e.g. No. 6 fuel oil products)
- PCBs
- Pesticides/grain fumigants (consult with the Minnesota Department of Agriculture [MDA], and see <https://www.mda.state.mn.us/pesticide-fertilizer/spills-cleanup> for more info)
- Pentachlorophenol (consult with the MDA, and [visit their website](#))
- Creosote (consult with the MDA, and [visit their website](#))

#### Characteristics of DNAPL

Generally speaking, DNAPL exists in one of three phases at a site (ITRC, 2015 [Figure 2-2](#)):

- **Mobile** – DNAPL is continuous and capillary pressure is high enough to displace groundwater and migrate.
- **Potentially mobile** – DNAPL is continuous, but capillary pressure (described below) is not able to displace groundwater under current conditions. If conditions change, the DNAPL body may begin migrating.
- **Immobile residual phase** – DNAPL “droplets” (ganglia) are present, but not connected to other ganglia. They are unable to exceed capillary pressure and displace groundwater.

In order to determine what phase DNAPL is in and to design an adequate characterization strategy, it is important to understand physical and chemical properties of DNAPL; different types of DNAPL have different physical and chemical properties that govern their behavior in the subsurface. Key properties of DNAPL include:

- **Aqueous solubility:** The maximum concentration of DNAPL that can be dissolved in groundwater. This controls the ability of the DNAPL to produce and sustain a dissolved-phase plume as well as the longevity of the plume.
- **Density/specific gravity:** The buoyancy of DNAPL. Denser DNAPLs have a greater driving force for downward movement while other DNAPLs may be almost neutrally buoyant.
- **Viscosity:** The thickness or resistance to fluid flow. The viscosity affects the rate at which DNAPL can migrate through the subsurface, but not whether or not it will. It comes into play if there are mobile and potentially recoverable volumes of DNAPL that are slow to migrate (e.g. coal tar).
- **Volatility:** The tendency of DNAPL constituents to evaporate into the vapor phase, generally measured by vapor pressure. This directly affects whether or not chemical constituents (in vadose zone) will transfer into the vapor phase.
- **Interfacial tension and wettability:** Interfacial tension represents the force parallel to the interface of one fluid with another fluid (usually air or water), which leads to the development of capillary forces and a pressure difference between different fluids in the subsurface. Wettability affects whether a fluid is wicked into or repelled out of subsurface media, and is a combined property of the media and DNAPL. The wetting process is an interaction between surfaces; if a fluid droplet on a surface has sufficient force to overcome the surface tension, the droplet will stretch out into a thin wetting layer. Typically, water acts as the wicking or wetting fluid and DNAPL is non-wetting, however, DNAPL may be wetting in some aquifer matrices. Where DNAPL behaves as a non-wetting fluid, the interfacial tension between DNAPL and water acts to resist DNAPL spreading.
- **Saturation, relative permeability, and capillary pressure:** Taking a [representative elementary volume](#) (REV) from the subsurface, saturation is the amount of pore space that is occupied by a fluid (DNAPL, air, or water). DNAPL saturation rarely approaches 1.0 because the DNAPL typically shares pore spaces with water or air. Relative permeability is the actual or effective permeability of a fluid in a REV relative to the intrinsic water permeability of a porous medium. Capillary pressure is the pressure difference between two fluids sharing pore space within a REV.
- At low pore saturation, DNAPL mobility is limited because the relative permeability is very small. DNAPL mobility can be increased most often through changes in pressure conditions that affect capillary pressure or chemistry changes that affect interfacial tension. Subsurface geologic materials can also influence DNAPL mobility: materials with smaller pore structures (finer grained or more densely packed) have higher capillary pressure, so DNAPL will tend to follow larger pore hole structures (coarse-grained, unconsolidated material). Note that diffusion, the exchange of ions from high concentration to low concentration, is the primary transport mechanism in low permeability soil.
- **Residual saturation:** This is a fraction of pore space within a REV that is filled by DNAPL at the point it becomes disconnected from an adjacent REV and is no longer mobile. This value represents the fraction of DNAPL potentially remaining in zones that were previously directly exposed to DNAPL migration.
- **Hydrophobicity:** the tendency of a chemical to partition out of aqueous solution and onto aquifer solids or activated carbon. The hydrophobicity of a chemical to soil measured by the octanol-water partitioning coefficient ( $K_{ow}$ ).

# Physical properties and chemical partitioning of DNAPL

## What constitutes a source zone compared to a dissolved phase zone/plume?

- The **plume** is the downgradient portion of the release outside the source zone. Contaminants in the plume will move through dissolved-phase advective transport and diffusion.
- The **source zone** is any area of contaminant mass storage that contributes to the dissolved phase, and it may include underlying groundwater that is contaminated.

## What are the types of transport?

- **Advective transport:** the component of solute movement attributed to transport in an aquifer from higher to lower equipotential groundwater elevations. This is important because advective flow is an irreversible flux (see mass transfer characteristics on the CSM Development guidance).
- **Diffusive transport:** the movement of ions or molecular constituents under the influence of a concentration gradient. Movement occurs from higher to lower chemical concentrations. This is important because diffusive flow is a reversible flux (see mass transfer characteristics on the CSM Development guidance)

## How does DNAPL move in the subsurface?

As chemical substances react in the environment to form other compounds, their physical properties also change. The fate and transport of each chemical is controlled largely by properties such as specific gravity, solubility, vapor pressure, air-water partitioning coefficient (often referred to as Henry's Law Constant or  $K_H$ ) and hydrophobicity, measured by the octanol water partitioning coefficient ( $K_{OW}$ ), and partitions between air, water and solids in the subsurface. As the pure chemical is released and dissolves in groundwater these physical properties, summarized in the table below (adapted from Cwiertny, 2010) control partitioning between water, vapor and solid in the subsurface. The partitioning relationship is generally explained below and in the corresponding table.

**Table 2-1: Summary of some physical and chemical properties of chlorinated solvents at 25°C.**

	Mass	Specific Gravity	Solubility	Hydrophobicity	Vapor Pressure	$K_H$	Diffusivity
<b>Chlorinated Methanes</b>							
carbon tetrachloride (CT)	153.8	1.59	800	2.64	153.8	28.9	0.90
chloroform (CF)	119.4	1.49	8,200	1.97	196.8	3.8	1.00
dichloromethane (DCM)	84.9	1.33	13,200	1.25	415	1.7	1.15
chloromethane (CM)	50.5	0.92	5,235	0.91	4,275	9.6	1.49
<b>Chlorinated Ethanes</b>							
hexachloroethane (HCA)	236.7	2.09	50	3.93	0.38	-	0.63
pentachloroethane (PCA)	202.3	1.68	500	2.89	4.7	2.5	-
1112-tetrachloroethane (1112-TeCA)	167.9	1.60	2,962	2.39	5.9	0.44	-
1122-tetrachloroethane (1122-TeCA)	167.9	1.54	1,100	-	11.9	2.4	0.86
111-trichloroethane (111-TCA)	133.4	1.44	4,394	2.38	24.2	0.96	0.89
112-trichloroethane (112-TCA)	133.4	1.35	1,495	2.49	123.8	14.5	0.92
12-dichloroethane (12-DCA)	99	1.25	8,606	1.48	79	1.2	1.01
11-dichloroethane (11-DCA)	99	1.17	4,676	1.79	227	6.2	0.98
chloroethane (CA)	64.5	0.90	5,700	1.43	120	1.8	1.07
<b>Chlorinated Ethenes</b>							
tetrachloroethene (PCE)	165.83	1.63	150	2.88	18.1	26.3	0.87
trichloroethene (TCE)	131.39	1.46	1100	2.53	74.2	11.7	0.94
<i>cis</i> 1,2-dichloroethene ( <i>cis</i> DCE)	96.9	1.28	3500	1.86	203	7.4	1.13
vinyl chloride (VC)	65.2	0.91	2763	1.38	2660	79.2	1.34
Units	g/mol		mg/L @ 20°C	log $K_{ow}$	torr	$\times 10^{-3}$ atm·m <sup>3</sup> /mol	10 <sup>5</sup> cm <sup>2</sup> /sec @25°C

With some exceptions, chlorinated compounds have a density greater than water. In the case with chlorinated ethenes the transformation from tetrachloroethene (PCE) to trichloroethene (TCE) to various dichloroethene (DCE) isomers and vinyl chloride (VC) is the result of hydrogen replacing chlorine, under the right conditions, through the process of reductive dechlorination. As the compound becomes less chlorinated, mass, specific gravity and hydrophobicity decrease. A corresponding inverse relationship is observed with solubility, vapor pressure and diffusivity. Higher chlorinated chemicals like PCE and TCE have a greater affinity to partition out of solution and onto soil particles. Whereas less chlorinated chemicals (e.g. VC, *cis* DCE) have a greater solubility and a greater tendency to partition from soil and water to air.

Similar relationships can be drawn from other chlorinated and non-chlorinated chemicals. PAH compounds, for example, tend to have greater specific gravity, larger octanol water partitioning coefficients, low vapor pressure and lower solubility.

### Chlorinated solvent mixtures

Chlorinated solvent mixtures can consist of mixtures of chlorinated solvents and other non-chlorinated solvents like toluene and xylenes. They can also consist of spent solvent saturated with grease, oil and other impurities resulting from the cleaning activities the solvent was used for. These impurities have an effect on the physical properties noted above and other properties such as viscosity, surface tension and capillary pressure.

### DNAPL transformation in the subsurface

Pure chlorinated solvents and chlorinated solvent mixture releases in the subsurface react based on the physical properties that govern partitioning between soil, air and water. DNAPLs will generally penetrate the water table if the soil pore space, viscosity of the DNAPL and capillary pressure between the fluids are sufficient to allow the DNAPL to displace the water. Once in the aqueous environment, the rate of dissolution of the chemical is governed by its solubility and mass diffusion into the soil matrix which is governed by the diffusivity.

### Soil-water partitioning

In the aqueous phase, DNAPL compounds partition out of water onto soil particles. The octanol-water partitioning coefficient ( $K_{ow}$ ) is an indicator of the tendency of an organic compound to sorb onto soil particles. As with chlorinated ethenes, PCE tends to have a relatively low solubility and high soil-water partitioning coefficient as compared to *cis* DCE and VC. As PCE and TCE have greater affinity to soil, *cis* DCE, and in deep aquifers VC, have a greater preference to remain in solution and travel further with groundwater flow.

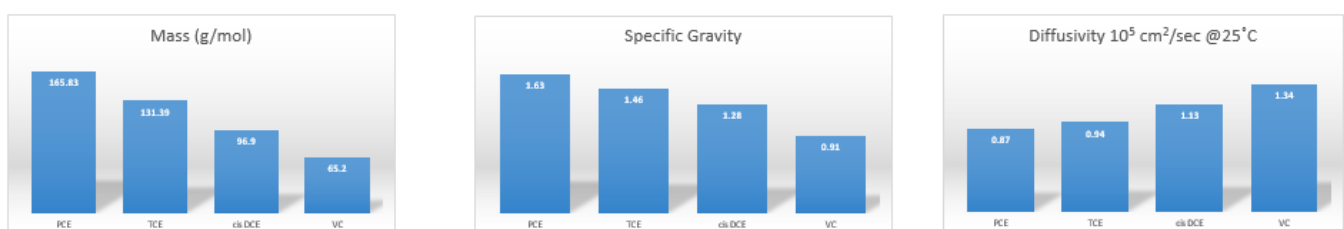
### Water-air partitioning

Air-water partitioning occurs as the DNAPL chemical-water solution comes in contact with air, typically at the water table. The relatively high partitioning coefficient of VC indicates the chemical preference to partition from water to air whereas PCE, TCE and *cis* DCE in solution have lower affinity to partition into air.

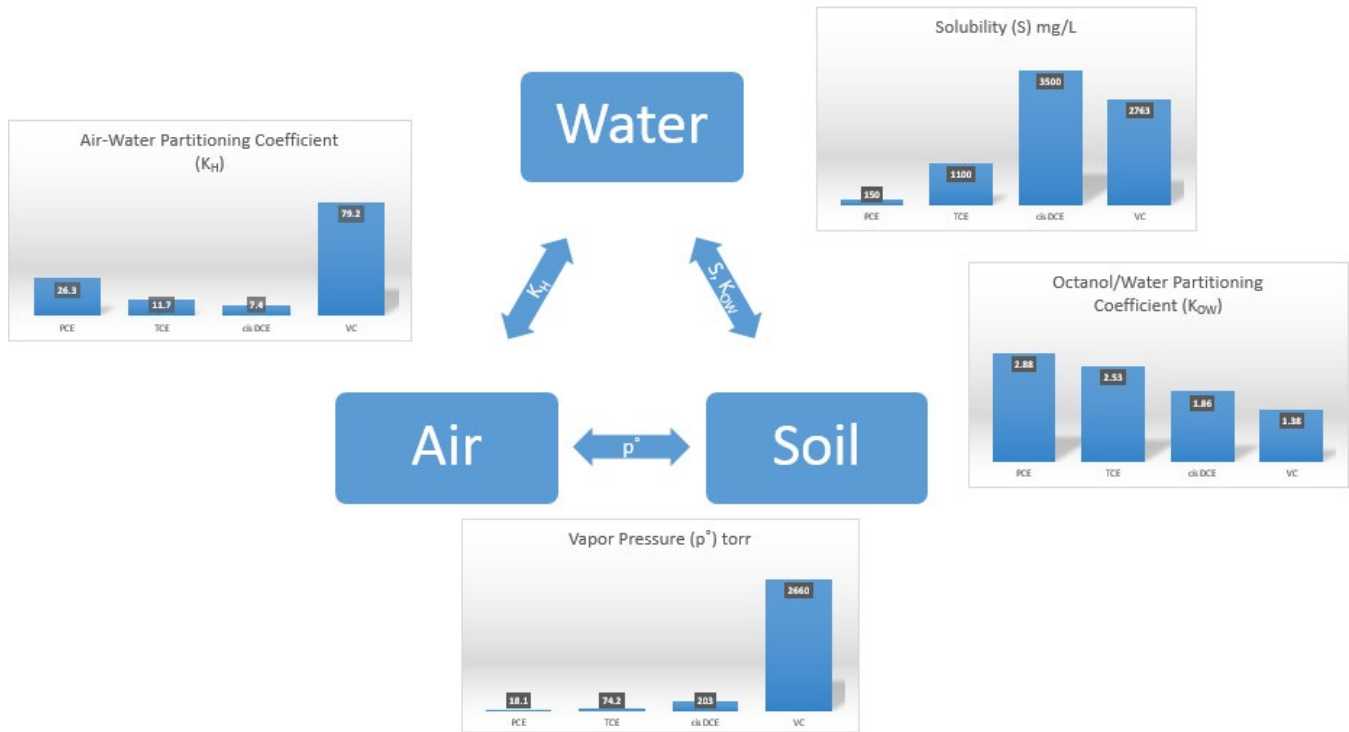
### Soil-air partitioning

In the unsaturated zone, DNAPL chemicals and chemical mixtures travel downward through soil pore space and allowed by the pore space opening and viscosity of the fluid. DNAPL chemicals sorbed onto soil particles will partition to the air as allowed by the vapor pressure of the chemical. PCE, TCE and *cis* DCE, having a relatively low vapor pressure, will tend to remain sorbed onto the soil particle whereas VC, having a relatively higher vapor pressure will readily partition from the solid.

**Figure 2-1: Mass, Specific Gravity and Diffusivity of Chlorinated Ethenes. Values from Table 2-1 above. As chlorinated ethene compounds become less chlorinated mass and specific gravity decrease. A corresponding inverse relationship is observed with diffusivity.**



**Figure 2-2: The three major phases present in the subsurface and the properties of chlorinated solvents that govern the partitioning between these phases (Cwiertny, 2010). Values from Table 2-1.**



Partitioning of Chlorinated Ethenes—released into the subsurface, chlorinated ethenes travel through soil pore space and sorb onto soil particles in the unsaturated zone. Partitioning from soil to air is controlled by vapor pressure ( $p^\circ$ ) of the chemical. Below the water table, the rate of chemical dissolution into groundwater is controlled by solubility ( $S$ ). Once in solution, chlorinated ethenes partition from aqueous solution to soil particles proportional to their octanol/water partitioning coefficient ( $K_{OW}$ ). Chlorinated ethenes in solution at the water table surface partition from aqueous solution to air equal the Henry’s Law constant ( $K_H$ ).

**How do characteristics change as solvent composition changes (i.e. virgin vs. used solvent)?**

DNAPL found at a site may not have the same composition as the original chemical purchased from a manufacturer because the original chemical becomes contaminated with impurities as it is used. These impurities can change the physical and chemical characteristics of the original chemical. To account for this, collect samples of the DNAPL (if possible), and analyze for parameters that could affect the subsurface behavior (ex: viscosity, specific gravity, effective solubility, chemical composition, wetting characteristics, etc.). However, be aware that determining chlorinated solvent DNAPL properties by sampling is rare because of the small release volumes, limited and complex preferential flow paths resulting in complex DNAPL distributions, low-resolution characterization, and solvent loss due to volatilization, dissolution, and diffusion. The result is a DNAPL that will likely change in composition as it degrades and undergoes these physical processes over time.

**DNAPL evolution in the subsurface**

When DNAPL is discharged to the subsurface, it primarily flows downward by gravity. This flow (downward density flow) is controlled by chemical and physical differences and the interactions between the DNAPL and the soil-gas, soil moisture, soil matrix, gravity, and the head (pressure) in the DNAPL. Some of the DNAPL is retained in the available pore space in the unsaturated zone as ganglia or, if it is the wetting fluid, as a soil matrix coating. This DNAPL is trapped by capillary forces and acts as a source of dissolved phase contamination when recharging water above the water table comes into contact with the DNAPL-contaminated pore space.

The DNAPL generally migrates downward until it encounters materials with pore sizes too small to penetrate (capillary entry pressure is the key property governing DNAPL penetration into a subsurface media). At this point, it spreads laterally and potentially accumulates until enough pressure is created to allow the DNAPL to penetrate the pore throat. Once the DNAPL reaches the top of the water table, the interfacial tension may prevent the DNAPL from moving through the capillary fringe into the water table (this is because DNAPLs are generally nonwetting and hydrophobic). Once enough DNAPL accumulates on top of the capillary fringe, the

column reaches a sufficient height where gravity provides enough pressure for the DNAPL to overcome the groundwater capillary pressure to displace water in the pore spaces and cause flow into the saturated zone.

Two important considerations for downward migration include the following:

1. Matrix heterogeneity causes subtle differences to pore structure and capillary properties (i.e. porosity, permeability, grain size, etc.). Consequently, the downward DNAPL migration leads to variable “isolated fingers” of preferential migration.
2. After cessation of the release, the DNAPL leaves a residual trail that is essentially immobile unless pore pressure changes (such as matrix disturbance). There may also be higher than residual saturation zones of DNAPL not actively migrating (ex: thin DNAPL lenses perched above low-permeability zones). This residual DNAPL in the vadose zone can act as an ongoing source of dissolved-phase groundwater contamination and soil-gas/vapor intrusion source.

Once DNAPL reaches the saturated zone, its flow is influenced by the interfacial tension between the DNAPL and groundwater. Given enough DNAPL mass, and depending on the characteristics of the DNAPL and the matrix (i.e. viscosity, wettability, etc.), interfacial tension typically prevents DNAPL from spreading evenly and forces the DNAPL to follow preferential pathways caused by subtle matrix changes.

### ***Multi-component waste DNAPLs***

Coal tars, creosotes, and heavy oils are especially viscous and do not tend to form small ganglia and globules like ganglia and globules formed with chlorinated solvents. Coal tars and creosotes move in the subsurface and in doing so separate into lighter, more soluble components from the heavier components. The lighter components typically consist of BTEX, naphthalene, and alkylated naphthalenes, and are generally degradable under aerobic and anaerobic conditions. The compounds remaining in the mass are much less soluble as aging occurs.

Degradation of the soluble components from the NAPL source zone results in depletion of the dissolved oxygen in the zone immediately downgradient from the NAPL source and an anaerobic zone results from the source area. With distance from the source area, this anaerobic zone gradually dissipates.

### ***DNAPL and LNAPL mixtures***

If chlorinated DNAPL mixes with LNAPL, the DNAPL can preferentially partition into the LNAPL rather than the groundwater. This changes what would be expected if it were a chlorinated only DNAPL plume as greater concentrations of the DNAPL are entrained in the LNAPL.

## **How can the DNAPL phases move counter to groundwater flow?**

As noted above, the primary factors that cause DNAPL to potentially move upgradient are gravity, chemical diffusion, and chemical characteristics such as density/specific gravity. DNAPL could also move downward and pool on top of a lower permeability bed causing it to flow in a down-slope direction that may be counter to groundwater flow.

DNAPL vapor phase movement is driven by changes in atmospheric pressure and temperature independent of groundwater flow. It can also diffuse outward along preferential pathways from the source in any direction (including upgradient). It can condense into droplets (through pressure and temperature change) that either adsorb to soil or infiltrate with precipitation to groundwater.