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NEWMOA Workshop
DNAPL Investigation and Remediation

Introduction and Part 1
DNAPL Basics
Nathan Hagelin, E&I

Introduction - The problem with Dense Non-Aqueous Phase Liquid (DNAPL) sites

- DNAPLs are a really challenging problem
- Ineffective remedies predominate
- Poor record of site closure
- Lessons learned not adequately transferred
- We can't afford to keep failing
- Good news – we have the technology

Introduction – A (slow) evolution in our thinking

- DNAPLs are complex mixtures that evolve over time
- Physical and chemical properties of DNAPL matter
- Different types of DNAPL require different approaches
- DNAPL sources evolve over time
- Product recovery alone is not effective
- Monitoring wells are not a characterization tool
- Micro-scale hydrostratigraphy is enormously important
- High-resolution source characterization is a good investment
- Flux-based remediation over concentration-based
- Risk-based, exposure-based remedial objectives
- Engineering and institutional controls are effective
- Adaptive, multi-component, multi-stage, long-term remedies
- An evolving notion of "Closure"

Objectives of this course

- Update and refresh our perspective on DNAPL characterization and remediation
- Establish a realistic understanding of DNAPL behavior in the subsurface
- Offer a set of characterization tools and objectives that are effective and realistic in defining the nature and scale of DNAPL source areas
- Provide an understanding of how to set relevant and appropriate remedial objectives, both short and long term
- Review the strengths, limitations, and best application of remedial technologies

- Set a course for a cost-effective and realistic end game vision for your DNAPL sites

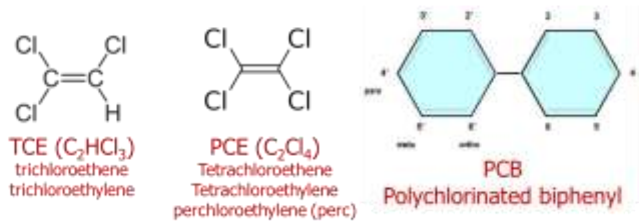
Training overview

- DNAPL types, properties, and behavior in the Subsurface – Hagelin
- DNAPL Site Characterization – Pitkin
- DNAPL Remediation – Ashley

DNAPL types, properties and behavior

Common types of DNAPLs

- ► Chlorinated solvents
- ► Coal tar
- ► Creosote
- ► Heavy petroleum such as some #6/Bunker fuel oil products
- ► Oils containing polychlorinated biphenyls (PCBs)



Poll question

What DNAPLs do you have at your sites? (select all the apply)

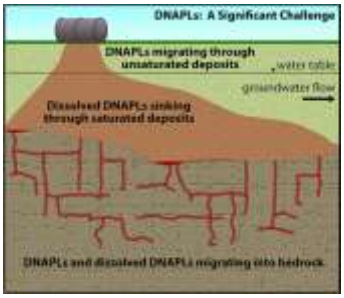
- ► Chlorinated solvents
- ► Coal tar
- ► Creosote
- ► Heavy petroleum hydrocarbons
- ► PCBs
- ► Pesticides
- ► Other? Hg?
- ► None

What is a DNAPL?

- ► Dense – relative to water, they sink!
- ► Non-aqueous phase – aka "neat", "free-product", "immiscible liquid", "separate phase" – existing as a pure chemical in the ground.
- ► Liquid

In fact, all of these properties are a bit sketchy

- ► DNAPL density is a continuum based on composition
- ► DNAPL can exist as a stable separate phase only after its dissolved phase has reached saturation in the surrounding liquid, groundwater
- ► DNAPLs are liquids by definition, but they exist in the presence of other phases, dissolved, vapor, heavy fuels may behave as solids!



DNAPLs pose special problems

- ► DNAPLs, unlike LNAPLs, are not stopped at the water table when released in significant quantities
- ► Once in an aquifer, DNAPLs are generally difficult to find
- ► DNAPLs effect on groundwater is widespread and long term
- ► DNAPLs penetrate porous media and rock, dissolve and diffuse into the matrix where they reside long term and are difficult to reach/remediate
- ► In dissolved phase, contaminants are ubiquitous in groundwater in urban industrial areas, particularly CVOCs
- ► Drinking water limits, and therefore clean up goals, are extremely low

What about phases?

- Non-aqueous phase
- Aqueous phase
- Gas phase
- Sorbed phase

A dynamic system with multiple phases occurring simultaneously

The predominance of phases changes over time and behavior depends on DNAPL type

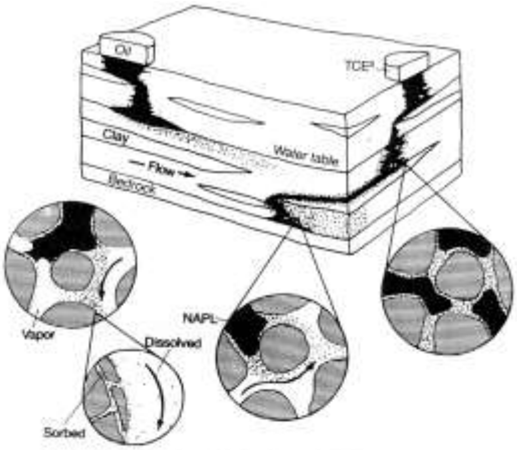


Figure 2.1 Schematic illustration of a DNAPL and a LNAPL in a porous medium, showing geologic and pore scales. A low-permeability clay layer deflects the DNAPL. DNAPL dissolution causes a plume (from Mackay and Cherry, 1989).

Pankow and Cherry, 1996

DNAPL types, properties, and behavior

Properties of contaminant may be significantly different from pure NAPL

- May include other compounds such as grease and oils with chlorinated solvents
- For mixed sources, chlorinated compounds from DNAPL could partition into LNAPL
- NAPL weathering occurs in subsurface
- Industrial grade DNAPLs from manufacturing sites may have impurities

Analysis of site specific NAPL is recommended during a site assessment

(ref – ITRC Integrated DNAPL Site Characterization Guidance, Ch. 2)

DNAPL types, properties, and behavior

- Density
- Solubility
- Volatility
- Sorption
- Viscosity
- Interfacial Tension
- Wettability
- Capillary Pressure
- Saturation
- Residual Saturation

IDSC-1, Chapter 2

NAPL densities

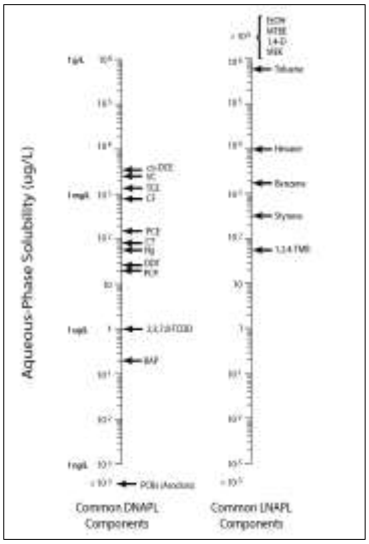
Liquid	Density g/cm³
Water	1.0
Gasoline	0.71 to 0.77
Diesel	0.80 to 0.85
#6 Fuel Oil	1.05
Pure TCE	1.46
Spent degreaser TCE, up to 25% oil and grease	1.38
Pure PCE	1.63
Dry Cleaner PCE recovered from subsurface	1.59
Pure chlorobenzene	1.11
Creosote	1.01 to 1.13
Aged MGP Coal Tar	1.02 to 1.1
PCB	1.0 to 1.6
PCB 1254	1.51
PCB 1260	1.59

Various sources compiled in ITRC IDSC

DNAPL types, properties, and behavior

Aqueous Solubility ($C_{w,sol}$)

- Maximum amount of a pure compound that can be dissolved in water at equilibrium
- Solubility increases with temperature
- Solubility of a pure chemical is different from solubility of typical DNAPLs in the subsurface



From ITRC IDSC

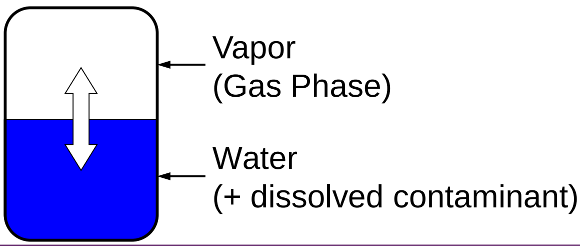
Solubility (S) in the subsurface

- Low S DNAPLs such as coal tar and creosote are persistent
- Risk-drivers in GW are derived from high solubility DNAPLs
- Mixed DNAPLs exhibit very different solubilities (lower) than pure, may be more persistent than pure
- CVOC DNAPLs may partition into petroleum rather than GW, plume may look different from pure CVOC
- Low S DNAPLs may have no detectable plume; components may partition off into groundwater (e.g., naphthalene)
- Aqueous phase treatment (e.g., P&T) drives higher rates of DNAPL dissolution

DNAPL types, properties and behavior

- Volatility – transfer to the vapor phase
- Vapor Pressure – pressure exerted by the vapor phase at equilibrium with pure liquid – strongly temperature dependent
- Henry's Law – ratio of vapor pressure to solubility, on molar basis, mol/vol per mol/vol, dimensionless

(Beware of units, Henry's law is also expressed as pressure in the gas phase (atm-m3/mol) or as a dimensionless concentration ratio)



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Gaseous-Aqueous Partitioning

- Many DNAPLs have high vapor pressures
- High volatility compounds can generate vapor phase plumes
- Vapor plumes can migrate in the subsurface
- Vapor plume can transfer contaminant mass to soil and across the capillary fringe to groundwater
- Vapor plumes become trapped and spread below slabs and pavement
- Vapor Intrusion is an important exposure pathway

Liquid	Henry's Constant d	Vapor Pressure atm
TCFM	3.63	1.06
CTET	1.19	0.12
1,1-DCA	0.23	0.30
1,2-DCA	0.04	0.11
1,1,1-TCA	0.70	0.13
1,1-DCE	1.068	0.80
1,2-DCE, *cis; trans*	0.153; 0.375	0270; .414
TCE	0.39	0.099
PCE	0.72	0.021
1,4-dioxane	0.039	0.0002
Vinyl chloride	1.137	3.44
Chlorobenzene	0.146	0.0116
Benzene	0.228	0.132
PCB	0.08	10^{-5}

Mostly from Pankow and Cherry

Behavior of mixtures

- Raoult's Law: The partial vapor pressure of each component in a mixed solution is equal to the vapor pressure of the pure component multiplied by the mole fraction in the solution.
  - Example: Pure TCE has a saturated vapor concentration of 76,000 ppmV. For a mixture containing 5% TCE in a mineral oil, the saturated TCE concentration would be 3,800 PPMV
- In a mixed component DNAPL, the most soluble component will dissolve first and may dominate in groundwater early but will change over time as the mole fraction of each component changes over time.
- In a DNAPL mixture that contains PCE, 1,1,1-TCA, and 1,4-dioxane, dioxane (miscible) will dissolve first, then TCA, then PCE, in order of decreasing solubility.

These concepts result in complex behavior and changing chemical signatures of releases over time – use caution interpreting your results!

DNAPL types, properties, and behavior

Adsorption – occurs at the surface of a solid

Absorption – uptake into the solid

- Sorption is dependent upon organic content and mineralogy. Generally, clays and organic rich soils have high sorption capacities.
- Desorption, or back-diffusion, from fine grained soils and rock can become the dominant source term in older DNAPL source areas

$$C_s = C_w * f_{oc} * K_{oc}$$

Cs = Soil Concentration, Cw = Water Concentration
foc = fraction of organic carbon and
Koc = soil organic carbon-water partitioning coefficient (high Koc = less mobile)

Partitioning into soil increases with organic content

Chemical with high Koc are harder to remove from soil

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Koc values

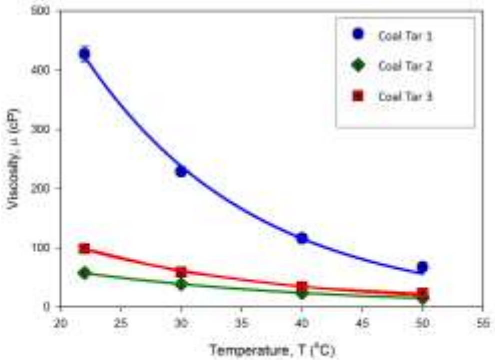
Liquid	Koc ml/g at 25°C
TCFM	159
CTET	439
1,1-DCA	30
1,2-DCA	14
1,1,1-TCA	152
1,1-DCE	65
1,2-DCE, *cis; trans*	86; 59
TCE	126
PCE	364
Vinyl chloride	56
Chlorobenzene	330
Benzene	60
PCB	High, high affinity for soil

Mostly from Pankow and Cherry

DNAPL types, properties, and behavior

Viscosity (dynamic)

- Represents the resistance to shear (flow) of the fluid
- **Sensitive to temp**: μ_w = 0.894 cP 25 °C μ_w = 1.002 cP 20 °C
- Units of measure: Poise (P) = 0.1 Pa·s or g·cm/s



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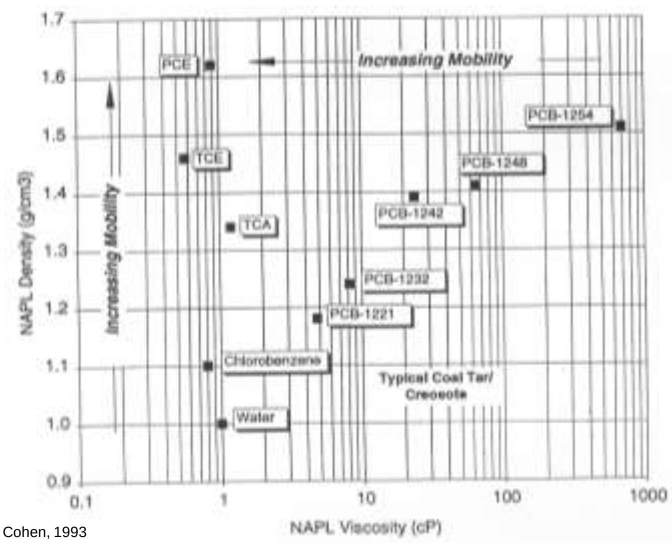
Viscosities

Liquid	centiPoise at 25°C – water = 1.0
1,1-DCA	0.50
1,2-DCA	0.84
1,1,1-TCA	0.84
1,1-DCE	0.36
1,2-DCE, *cis; trans*	0.48; 0.40
TCE	0.57
TCE with oil and grease at 25%	0.78
PCE	0.90
Benzene	0.61
Chlorobenzene	0.80
Creosote	20 to 50
PCB	10 to 50
#6 Fuel Oil	2,300
Coal Tar	20 to 100 and higher

From ITRC IDSC

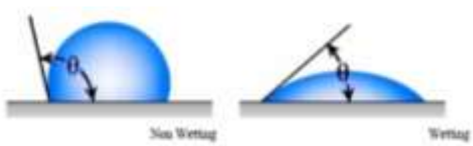
NAPL mobility



Mercer and Cohen, 1993

DNAPL types, properties, and behavior

- DNAPL migration at the macro scale is controlled by gravity
- At the pore scale, other forces come into play that are functions of the fluid properties and the aquifer matrix
- When DNAPL displaces water, the fluids coexist in the matrix, never alone
  - Interfacial Tension – the force parallel to the interface between one fluid with another, the force that keeps two fluids separate
  - Wettability – represents whether a fluid is wicked into or repelled out of a subsurface media, measured by the contact angle between the DNAPL and the matrix in the presence of water



Stone Environmental

- For CVOCs
  - DNAPL occupies the large pore spaces and has a lower affinity for the solid matrix that water – non-wetting fluid
  - Water is usually the wetting fluid and preferentially coats the solid

IDSC-1, Chapter 2

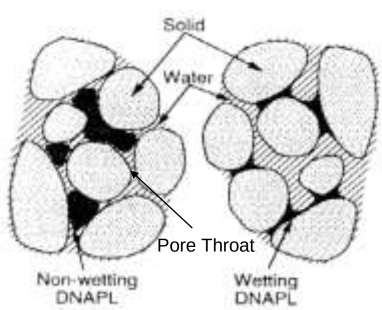
DNAPL types, properties, and behavior

- Capillary Pressure (Pc) is the pressure difference between two fluids sharing pore space within an Representative Elementary Volume (REV).

  Pc = Pn - Pw (Bear, 1972)

  Where Pn is the NAPL Pressure and
  Pw is the water pressure

- Pc is a non-linear function of S, with Pc increasing at greater saturation of the non-wetting fluid (Lenhard and Parker, 1987)
- Pc must exceed the threshold value determined by the radius of the pore throat for DNAPL to migrate into / displace water in the neighboring pore



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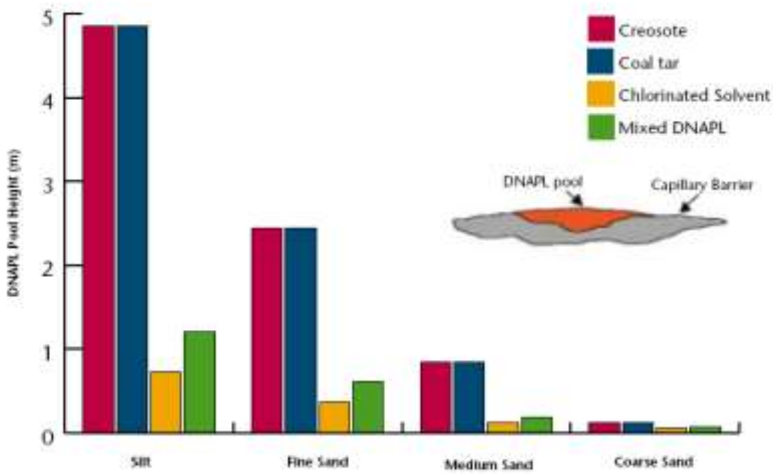
Variability of entry pressures



UK Environment Agency, Publication 133

DNAPL types, properties, and behavior

Saturation (*S*)

- S represents the proportion of the subsurface pore space within a **Representative Elementary Volume** (REV) that is occupied by a fluid (NAPL, air, or water), ranging from 0 to 1.0.

Residual Saturation (S_r)

- S_r is the fraction of pore space within a REV that is filled by the NAPL at the point where it becomes **disconnected from NAPL** in an adjacent REV and is no longer mobile.

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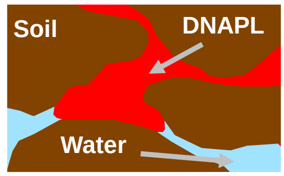
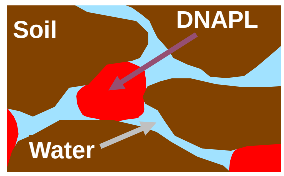
DNAPL types, properties, and behavior

NAPL Saturation and Mobility

- When $S > S_r$, NAPL may be: Potentially Mobile but not migrating under existing conditions, or Mobile and migrating
- When $S < S_r$, NAPL will generally be considered immobile
- Isolated, detached DNAPL is referred to as ganglia





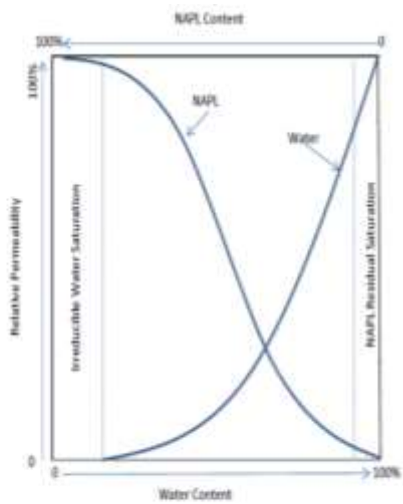
Pennell et al., 1996, ES&T

DNAPL types, properties, and behavior

Relative Permeability (k_r)

- Represents the actual or effective permeability of a fluid in a REV relative to the intrinsic water permeability of a porous medium.
- The value of k_r, ranges from 0 to 1.0 as a non-linear function of saturation (S), where $k_r = 1.0$ at $S = 1.0$ and $k_r = 0$ at $S= 0$

  (Parker and Lenhard, 1987).



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DNAPL types, properties, and behavior

Effects of NAPL properties on NAPL Fate and Transport:

Saturation, Relative Permeability, and Capillary Pressure:

- At $\mathbf{S_r}$, NAPL is immobile.
- At very low **S**, approaching the value of $\mathbf{S_r}$, NAPL mobility is very limited because $\mathbf{k_r}$ is very small.
- Increasing NAPL mobility (increasing $\mathbf{k_r}$) can be influenced by
  - changes in pressure conditions affecting $\mathbf{P_c}$,
  - or by changes in chemistry that affect interfacial tension.
- Strongly effected by Geologic Heterogeneity
  - Small changes in k influence migration

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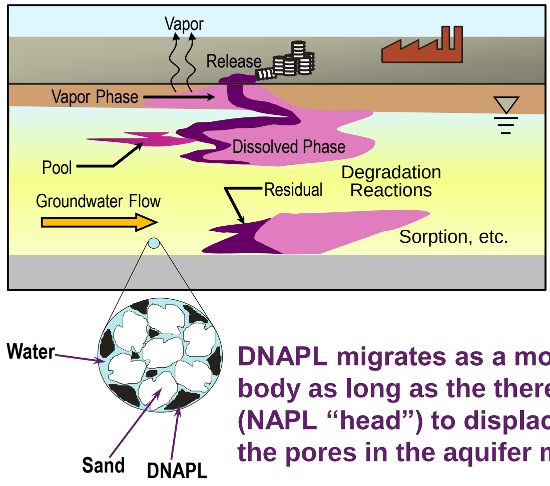
DNAPL types, properties, and behavior



DNAPL migrates as a mobile and "continuous" body as long as the there is enough pressure (NAPL "head") to displace groundwater from the pores in the aquifer matrix.

DNAPL types, properties, and behavior

Geology controls flow!

Lithologic heterogeneity leads to differences in subsurface pore structure and capillary properties.

These can be over very small distances/intervals

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Photo Courtesy of Fred Payne, ARCADIS, Inc

DNAPL types, properties, and behavior

Areas impacted by DNAPL
- DNAPL Source
- Dissolved Phase Plume

Slowly recognized,
- DNAPL phase not always “source”

Low k zones can sustain plume
- Back Diffusion within plume

DNAPL source zones evolve over time, DNAPL may fade away, Source zone migrates downgradient, diffusion become dominant

IDSC-1, Chapter 2

DNAPL types, properties, and behavior

	Source Zone		Plume	
Phase / Zone	Low Permeability ↔	Transmissive →	Transmissive ↔	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

The 14-Compartment Model (Sale and Newell 2011)

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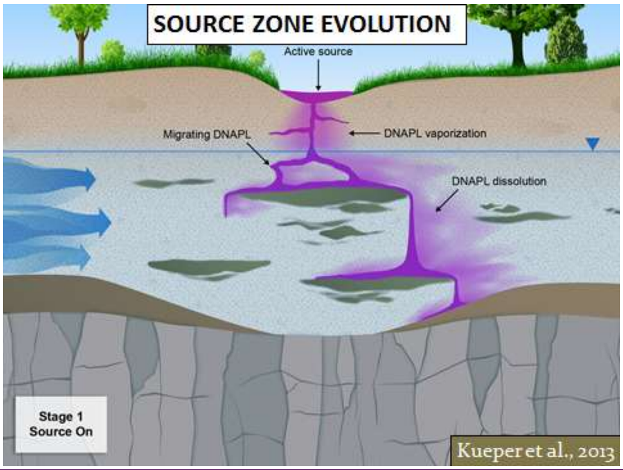
DNAPL types, properties, and behavior

DNAPL Life Cycle Model



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DNAPL types, properties, and behavior

Early Stage

ZONE	SOURCE		PLUME	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	LOW	MODERATE	LOW	LOW
DNAPL	LOW	HIGH		
Aqueous	LOW	MODERATE	MODERATE	LOW
Sorbed	LOW	MODERATE	LOW	LOW

Middle Stage

ZONE	SOURCE		PLUME	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor				
DNAPL				
Aqueous				
Sorbed				

Late Stage

ZONE	SOURCE		PLUME	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor				
DNAPL				
Aqueous				
Sorbed				

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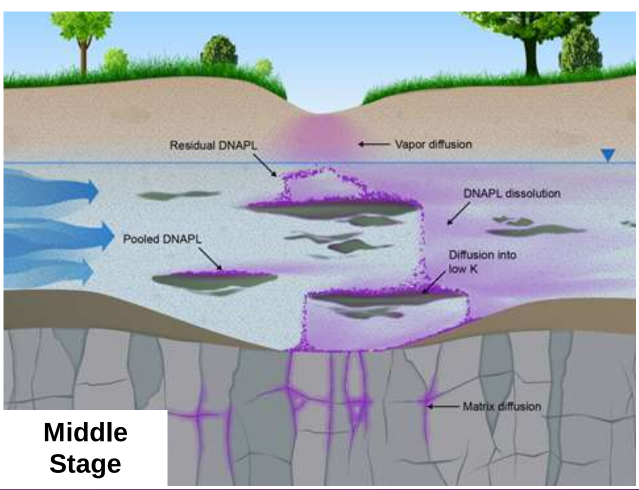
DNAPL types, properties, and behavior

DNAPL Life Cycle Model



Middle Stage

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Kueper et al., 2013

DNAPL types, properties, and behavior

Early Stage

ZONE	SOURCE		PLUME	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	LOW	MODERATE	LOW	LOW
DNAPL	LOW	HIGH		
Aqueous	LOW	MODERATE	MODERATE	LOW
Sorbed	LOW	MODERATE	LOW	LOW

Middle Stage

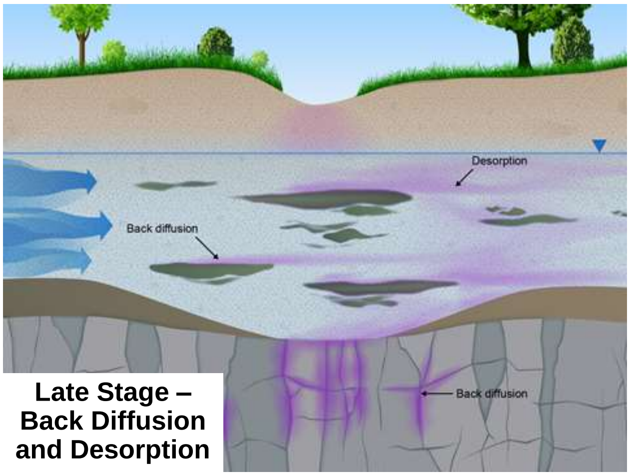
ZONE	SOURCE		PLUME	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	MODERATE	MODERATE	MODERATE	MODERATE
DNAPL	MODERATE	MODERATE		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE

Late Stage

ZONE	SOURCE		PLUME	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor				
DNAPL				
Aqueous				
Sorbed				

DNAPL types, properties, and behavior

DNAPL Life Cycle Model



Late Stage – Back Diffusion and Desorption

IDSC-1

Kueper et al., 2013

DNAPL types, properties, and behavior

Early Stage

ZONE	SOURCE		PLUME	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	LOW	MODERATE	LOW	LOW
DNAPL	LOW	HIGH		
Aqueous	LOW	MODERATE	MODERATE	LOW
Sorbed	LOW	MODERATE	LOW	LOW

Middle Stage

ZONE	SOURCE		PLUME	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	MODERATE	MODERATE	MODERATE	MODERATE
DNAPL	MODERATE	MODERATE		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE

Late Stage

ZONE	SOURCE		PLUME	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	LOW	LOW	LOW	LOW
DNAPL	LOW	LOW		
Aqueous	MODERATE	LOW	LOW	MODERATE
Sorbed	MODERATE	LOW	LOW	MODERATE

Paradigm shift in the DNAPL behavior model

Heterogeneity replaces homogeneity

Anisotropy replaces isotropy

Diffusion replaces dispersion

Back Diffusion may be a significant source of contamination and plume growth

Lognormal replaces Gaussian

Transient replaces steady state conditions

Non-linear replaces linear sorption

Non-ideal replaces ideal sorption