Lecture 4

Multi-phase Flow in Porous Media
Non-aqueous phase liquids

NAPL = Non-Aqueous Phase Liquid

DNAPL = Dense Non-Aqueous Phase Liquid
  Chlorinated solvents
  Coal tar

LNAPL = Light Non-Aqueous Phase Liquid
  Petroleum fuels
# Typical densities of NAPLs

<table>
<thead>
<tr>
<th>DNAPLs</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>1.62</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>1.59</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.48</td>
</tr>
<tr>
<td>TCE</td>
<td>1.46</td>
</tr>
<tr>
<td>1,1,1-TCA</td>
<td>1.34</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>1.33</td>
</tr>
<tr>
<td>Coal tar</td>
<td>1.01-1.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>LNAPLs</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene</td>
<td>0.86</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.87</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.88</td>
</tr>
<tr>
<td>Gasoline</td>
<td>0.72-0.76</td>
</tr>
<tr>
<td>Jet fuel</td>
<td>0.76</td>
</tr>
<tr>
<td>Diesel fuel</td>
<td>0.84-0.85</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>0.87-0.95</td>
</tr>
</tbody>
</table>
Laboratory experiments with PCE DNAPL in unsaturated and saturated media

PCE penetration at Borden aquifer field site


Shows structure (even very subtle) of porous medium may affect lateral movement
PCE penetration at Borden aquifer field site


In seemingly uniform sand, subtle structure caused lateral movement. Character of release affected very penetration.
Low permeability lenses may soak up NAPL, cause lateral spreading
Residual contamination in unsaturated soil acts as long-term source of contaminants to dissolve into infiltrating recharge
Formation of residual and vapor plume

At the same time, solvent may be vaporizing. Solvent vapor is denser than air, and will sink in unsaturated zone and can contaminate ground water.

Typical residual saturation values

Residual saturation, \( s_r = \frac{\text{volume of NAPL}}{\text{volume of voids}} \) (dimensionless)

<table>
<thead>
<tr>
<th>Material</th>
<th>Residual saturation, ( s_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>0.15 – 0.2</td>
</tr>
<tr>
<td>PCE</td>
<td>0.002 – 0.20</td>
</tr>
<tr>
<td>Gasoline</td>
<td>0.12 – 0.60</td>
</tr>
</tbody>
</table>


Good rough guess: \( s_r = 0.2 \)

After NAPL passes through soil, fraction remains behind as a residual.
Residual in etched glass “porous medium”


Lab studies generally confirm the conceptual model of residual formation. Conrad et al. (1992) conducted two types of experiments. The first is show here. They created a planar porous medium with two plates of etched glass. Filled the pore space with distilled water, then injected red-dyed Soltrol (an oil) from the left (Figure a), and re-flooded with distilled water flowing from the right (in the opposite direction of the injection) (Figure b).

Residual formed different shapes: singlets, doublets, etc. Physical nature of residual depended upon balance between viscous and inertial forces on residual.
Residual in sand porous medium

Second experiment by Conrad et al. (1992) was to construct small water-saturated columns of sand, into which they injected a styrene monomer. The styrene solidified after injection. They then dissolved away the sand with hydrofluoric acid, leaving styrene casts.
NAPL will remain essentially immobile at residual concentration. It dissolves very slowly (for example, TCE has a solubility of 1,100 mg/L) and thus takes a long time to "wash" out. Infiltrating rainwater dissolves out NAPL, becomes itself contaminated, and is likely to carry contaminants to the water table and ground-water system. The residual also acts as a long-term source of vapor in the subsurface.

PCE penetration into unsaturated porous medium

Small amount of PCE released

Later time: more PCE released, Formation of fingers


If small amount of NAPL is spilled to the ground (top figure), it will soak into the soil by capillary action and due to gravity. In the soil, it will reach residual concentration and travel no further as DNAPL. Thus, a small spill will not penetrate to the water table.

If more is spilled on the same spot (bottom figure), NAPL will be displaced downward and the “front” of NAPL residual will advance.
“Fingering” of DNAPL in vadose zone


An areally distributed spill may not infiltrate as a contiguous mass but tends to advance as “fingers.” Fingering is a complex function of the viscosity and density of the fluids and the structure of the porous medium.
Question: “Given a spill on the land surface, how long will it take for the NAPL to penetrate to the water table?” residual saturation.

Answer: Penetration is not a function of time, but of the volume spilled. To penetrate to the water table enough material must be released to saturate the soil column to residual saturation.
Assume a large enough volume of DNAPL is spilled to reach the water table. The DNAPL, being heavier than water, continues to move downward below the water table. The rate of downward movement is slower since the DNAPL must now displace water rather than air (i.e., the DNAPL now has a lower relative density). As it advances, the DNAPL continues to leave behind residual in the soil. Eventually the DNAPL can reach an “impermeable” (actually, poorly permeable) layer and collect in a pool.
DNAPL pools are very hard to find in the field. As a result, other indicators must be used. The concentration of contaminant in the water phase is the most commonly used indicator but has changed over time as experience and knowledge have increased:

Original rule of thumb: $C > 10\%$ solubility
Revised to: $C > 1\%$ solubility
For chlorinated solvents: $C > 10,000 \text{ ug/L}$


1. Concentration in water > 1% solubility
2. Concentration in soil > 10,000 mg/kg
3. Concentration in water > pure phase solubility in equilibrium with water
4. Concentration increases with depth or exhibits anomalous upgradient/cross-gradient patterns
LNAPL floats on water-saturated soil of capillary fringe. Accumulation of LNAPL will depress capillary fringe and eventually penetrate through fringe and into water table. Oil itself has its own capillary fringe.

Rise and fall of water table will create a “smear zone” of residual saturation.
Factors affecting NAPL movement

Fluid properties:
- Density
- Interfacial tension
- Residual saturation
- Partitioning properties
- Solubility
- Volatility and vapor density

Porous medium:
- Permeability
- Pore size
- Structure

Ground water:
- Water content
- Velocity
NAPL Movement in Porous Medium

NAPL = non-aqueous phase liquid

Note: water is drawn as wetting fluid, NAPL as non-wetting relative to water, wetting relative to air
Wetting vs. non-wetting fluids

Wetting angle $\phi$ always measured from water

$\phi > 110^\circ$ → NAPL wets

$\phi < 70^\circ$ → water wets
Interfacial tension force balance

\[ \sigma_{SG} = \sigma_{SL} + \sigma_{GL} \cos \phi \]

\[ \cos \phi = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{GL}} \]

\( \sigma_{SG}, \sigma_{SL}, \sigma_{GL} \) = interfacial tension between solid and gas, solid and liquid, and gas and liquid (dyne/centimeter)
Interfacial tension effects

Wetting angle, $\phi$, can be changed by changing surface

Example:
Water wets unwaxed car
Water does not wet ("beads up") on waxed car
Wax increases $\sigma_{SL}$

In soil, coal tar and petroleum products alter soil surfaces, make them oil wet
### Interfacial tension values

<table>
<thead>
<tr>
<th>DNAPL</th>
<th>Interfacial tension with water (dyn/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrachloroethylene</td>
<td>44.4</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>34.5</td>
</tr>
<tr>
<td>1,1-Dichloroethylene</td>
<td>37.0</td>
</tr>
<tr>
<td>trans-1,2-Dichloroethylene</td>
<td>30.0</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>45.0</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>30.0</td>
</tr>
</tbody>
</table>

Values at 20°C  
### Interfacial tension values (continued)

<table>
<thead>
<tr>
<th>DNAPL</th>
<th>Interfacial tension with water (dyn/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Tetrachloride</td>
<td>45.0</td>
</tr>
<tr>
<td>Chloroform</td>
<td>32.8</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>28.3</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>37.4</td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>40.0</td>
</tr>
</tbody>
</table>

Values at 20°C
Force balance on fluid element

Pressure force on top:
\[ P_{z+\Delta z} \Delta x \Delta y \]

Gravitational force:
\[ \rho g \Delta x \Delta y \Delta z \]

Pressure force on bottom:
\[ P_z \Delta x \Delta y \]

\[ \Sigma \text{ forces} = 0 \]

\[ (P_{z+\Delta z} - P_z) \Delta x \Delta y = -\rho g \Delta x \Delta y \Delta z \]

\[ \frac{dP}{dz} = -\rho g \]
Force balance on fluid element

\[
\frac{dP}{dz} = -\rho g
\]

Assume constant \( \rho \):

\[
P = -\rho g z + \text{constant}
\]

Force balance for water:

\[
P_W = -\rho_W g z + C_W
\]

Force balance for NAPL:

\[
P_N = -\rho_N g z + C_N
\]
LNAPL on water

\[ P_O = P_N = P_W \]

\[ P_N = -\rho_N g z + P_O \]

\[ P_W = -\rho_W g z + P_O \]

\[ P_N \geq P_W \]
Water on DNAPL

\[ P_O = P_N = P_W \]

Water
\[ P_W = -\rho_Wgz + P_O \]

DNAPL
\[ P_N = -\rho_Ngz + P_O \]

\[ P_N \geq P_W \]
Capillary pressure

How can NAPL and water exist together in soil at two different pressures?

Difference is interfacial tension

Interfacial tension $\rightarrow$ capillary pressure

$P_C = P_N - P_W$
Capillary pressure

\[ P_C = P_N - P_W = -\frac{2\sigma}{r} \]

\( \sigma \) = NAPL-water interfacial tension (dyne/cm)

\( r \) = pore throat radius (cm)

Conclusion: capillary pressure depends on NAPL (\( \sigma \)) and porous medium (\( r \))
Capillary force balance

Water

Pressures, $P_W$ and $P_N$ (force per unit area)

Interfacial tension, $\sigma$ (force per unit length)

Radius, $r$
Relationship between $P_C$ and $\sigma$

Net pressure on interface = $P_C (\Delta s)^2$

$P_N = P_W + P_C$
Relationship between $P_C$ and $\sigma$

Force balance:

$$P_C (\Delta s)^2 = -4\sigma \Delta s \sin \theta$$

$$\sin \theta \approx \theta \approx (\frac{1}{2} \Delta s)/r$$

$$P_C (\Delta s)^2 = -4\sigma \Delta s \Delta s/2r$$

$$P_C = -2\sigma / r$$

$P_c$ depends on NAPL and porous medium

Large $P_c$ (small $r$ or large $\sigma$) → small water content, large NAPL residual

Small $P_c$ (large $r$ or small $\sigma$) → large water content, small NAPL residual
$P_C$ vs. water saturation

Entry pressure (or threshold pressure) – pressure needed to penetrate into soil

Water saturation, $s$

Low $K$

High $K$
$P_C$ vs. water saturation for PCE

Implications of entry pressure

NAPL will pool on low K horizons (such as clay layer) until pool depth creates pressure in excess of entry pressure

Residual NAPL will remain entrapped unless displacement pressure exceeds entry pressure
NAPL mobilization

Capillary forces “trap” NAPL and resist mobilization

Mobilization occurs when blob in pore is pushed through pore throat:
Mobilization of entrapped NAPL

Capillary force may be overcome by viscous force (i.e., from flow) or gravity force

Capillary number = ratio of viscous to capillary force

\[ N_c = \frac{\mu_w V_w}{\sigma_{NW}} = \frac{\text{viscous}}{\text{capillary}} \]

where:

\( \mu_w \) = viscosity of water
\( V_w \) = velocity of water
\( \sigma_{NW} \) = NAPL-water interfacial tension
Mobilization of entrapped NAPL

Bond number = ratio of gravity to capillary force

\[ B_o = \frac{(\rho_{\text{NAPL}} - \rho_W) g R^2}{\sigma_{NW}} = \frac{\text{gravity}}{\text{capillary}} \]

where:
\[ \rho_{\text{NAPL}} = \text{density of NAPL} \]
\[ \rho_W = \text{density of water} \]
\[ g = \text{gravitational acceleration} \]
\[ R = \text{grain-size radius} \]

Residual saturation vs. Bond and Capillary Numbers

Above an inverse Bond number value of 150 (Bond number < 0.007) gravity forces are negligible. Note the cosmic symmetry in having the limiting Bond Number be 0.007!

Wilson and Conrad (1984) define NC* as the critical Capillary number at which blob motion is initiated. They define NC** as the Capillary number necessary to displace all of the blobs.
Hydraulic gradient to mobilize NAPL

Can NAPL be mobilized?

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Horizontal movement</th>
<th>Vertical movement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravel</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>Sand</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td>Silt or clay</td>
<td>NO</td>
<td>NO</td>
</tr>
</tbody>
</table>

Can NAPL be mobilized?

Very difficult:
need steep gradient in coarse gravel
need impossibly steep gradient in finer soils

Other technologies seek to reduce capillary force by adding surfactants to enhance mobilization