Multiphase Flow

- NAPL enters the subsurface, either as a spill or as a leak
- Travels down some distance in the NAPL (oily) phase until
  - it is spread out too thin
  - it reaches a barrier for flow.

The barrier may be an impermeable layer (e.g. clay or bedrock)
In the case of LNAPL (e.g. most hydrocarbons - gasoline, diesel fuel), the barrier can be the top of the water table
Forms a “pool” which then spreads laterally

DNAPLs (e.g. chlorinated solvents, PCBs, many pesticides) will continue travelling through the aquifer until they find a clay layer or bedrock
If there is still enough DNAPL left, it spreads out horizontally until it either is spread too thin or it finds a new pathway (e.g. fracture in bedrock or clay)
Multiphase Flow

- At the same time NAPL travels downward, it begins to volatilize
- Surrounding vapor phase becomes saturated with organic vapors and these begin to diffuse away from the source
- Soil vapor flow through advection is small unless we actively promote flow.

Once NAPL reaches the capillary fringe and then the water table, it begins to dissolve
- LNAPLs have a relatively small contact area with water and are typically relatively insoluble (except Benzene - a potential carcinogen), so transfer to the water phase is slow
- If the water table rises and falls due to seasonal rainfall and drying, then NAPL is smeared and the contact area increases.

Multiphase Flow

- DNAPLs, which go right through the aquifer, present a greater interfacial contact area and thus the rate of dissolution may be greater
- Rate at which the NAPL disappears depends on solubility of NAPL constituents, as well as groundwater flow velocity

In either case, sorption also occurs. The flowing NAPL phase is separate from the immobile organic fraction associated with the soil.
- Contaminants may sorb from
  - NAPL to soil
  - water to soil
  - vapor to soil.

Groundwater flowing past the NAPL dissolves more and more NAPL
- Forms a “dissolved plume” of contaminants, which moves with the water flow and also disperses out
- Due to mass transfer limitations, the plume is rarely saturated or at equilibrium, so the concentration of pollutant in the water is significantly less than saturation

ANATOMY OF A DNAPL SITE
Complications!

More complications!

Multiphase Flow

Finding the NAPL pools is usually a complex task, because NAPLs will also flow horizontally every time they encounter some resistance in their path.

Clay layers or even just a tighter sand or silt layer can generate significant horizontal movement until the NAPL finds a weak point (fracture or end of layer).

Fractured bedrock is also a pathway for NAPLs.

Multiphase Flow

To enter a new soil layer (and even entry at the surface), the NAPL has to overcome the capillary forces that are holding on to the water or air.

If it's air, the capillary forces actually favor NAPL entry (it is more wetting than air) and it enters quickly into unsaturated and rather dry soil.

Multiphase Flow

NAPL entry into water saturated soil or fractured bedrock, or even into unsaturated soil with a high moisture content, requires the NAPL to form a pool of sufficient height for the gravity forces to be larger than the capillary forces. This allows for lateral spreading.

Multiphase Flow

An additional issue with NAPLs is that as they are travelling down, blobs of NAPL become disconnected from the main flow.

NAPL blobs (called ganglia) are trapped in place by capillary forces, forming a residual saturation of NAPL.

Residual saturation depends on conditions (1-30%).
Multiphase Flow

- Mass transfer occurs from these blobs to the surrounding air or water phase

- This increases extent of vapor phase contamination as well as dissolved plume in the groundwater

We talk about “multiphase” flow because we have two or three phases moving at the same time.

As the NAPL phase moves, it displaces air, water or both air and water (near the water table).

We keep track of the fraction of each phase using saturation, $S_p$

$$S_{tot} = S_n + S_w + S_a = 1$$
Multiphase Flow

- The presence of other phase reduces the area available for NAPL to flow
- The same is true for water flowing past residual NAPL or a NAPL pool, or for air flowing through residual NAPL
- We still use Darcy's law to model the flow, but with a modification

Add a correction factor, called the "relative permeability", \( k_r \), to Darcy's equation

Since there are different fluids flowing, consider \( k \) (permeability) rather than \( K \) (hydraulic conductivity):

\[
Q = \frac{k_r \rho g \Delta h}{\mu_n} A
\]

(modified Darcy's law)

Relative permeability, \( k_r \), varies from 0 to 1
- It is a function of how saturated the material is with a given phase
- Each fluid (air, water and NAPL) has its own relationship between \( k_r \) and \( S \)
  - Usually determined experimentally
  - Some correlations have been developed

How far and how fast can a NAPL travel?
- Depends on
  - Volume of spill
  - Soil permeability
  - Moisture content (relative permeability)
  - Rate of spill (leak vs. massive dumping)
  - Pollutant properties

Large, rapid spill
- Tanker accident, pipeline rupture, etc.
- Leak from unlined pits (e.g. oil drilling wastes, disposal lagoons)
- Soil becomes highly saturated with oil (NAPL), \( S_{n_{\text{max}}} \)
- Water and air saturations are near or at residual levels,

\[
S_{W_{\text{res}}}, S_{a_{\text{res}}}
\]
Multiphase Flow

Flow is given by Darcy’s law:
\[ q_n = \frac{k_{r,n}^{\text{max}} \rho_{n} g}{\mu_n} \]

Velocity considers porosity and the decrease in the flow area due to other phases
\[ v_n = \frac{k_{r,n}^{\text{max}} \rho_{n} g}{n \mu_n (1 - S_{w}^{\text{res}} - S_{a}^{\text{res}})} \]

Example: Tanker overturns into a ditch and spills a load of diesel (10 metric tons)
- Soil is a fine sand with \( k = 10^{-10} \text{ m}^2 \), \( n = 0.30 \)
- \( \rho_n = 730 \text{ kg} / \text{ m}^3 \)
- \( \mu_n = 0.45 \text{ kg} / \text{ ms} \)
- \( S_n^{\text{max}} = 0.8 \) (soil and pollutant specific)
- \( k_{r,n}^{\text{max}} = 0.7 \) (soil and pollutant specific)
- \( g = 9.81 \text{ m/s}^2 \)

\[ v_n = 4.6 \times 10^{-6} \text{ m/s} = 0.4 \text{ m/d} \]

If the water table is 5 m below the surface, it will take about 12.5 days to reach it...
How far the spill travels depends on the area of the spill; assume a circular area about 5 m in diameter (should be measured on site)

Diesel will travel through the soil leaving a residual:
\[ S_{n}^{\text{res}} = 0.05 = 5\% \] (estimated)

\[ \text{depth} = d = \frac{V_n}{S_n^{\text{res}} n \pi (D/2)^2} = \frac{10,000 \text{ kg}}{730 \text{ kg} / \text{ m}^3 (0.05)(0.30) \pi (5 \text{ m}/2)^2} = 47 \text{ m} \]

Slow leak into clean soil
- small hole in a UST
- soil will not become fully saturated with NAPL
- there needs to be a minimum NAPL saturation, \( S_{\text{min},n} \) to begin flow
- Since the leak is slow, flow is almost at \( S_{\text{min},n} \), with \( k_{r,n} \) close to zero (problem!)
Approaches:

- Laboratory determination of relationship between \( k_{r,n} \) and \( S_n \)
- Use a correlation (e.g. from oil industry) and soil samples to find \( S_n \):
  \[
  k_{r,n} = k_{r,n}^{\text{max}} \frac{(S_n - S_n^{\text{max}})^2}{(1 - S_w^{\text{res}} - S_a^{\text{res}} - S_n^{\text{res}})^2}
  \]
- Calculate the rate of leakage from mass balance:

\[
2 \text{res} \left( k \right) \left( \frac{	ext{max}}{	ext{res}} \right) S_{SS} S_{SS}(k)
\]

Example: You are the environmental manager of a large industrial operation.

- A storage tank appears to have been leaking PCE at a rate of 0.01 m\(^3\)/day (10 L/day) for the past 60 days.
- Soil samples indicate contamination is spread over 10 m\(^2\), with NAPL saturations of 2% by weight.
- Soil porosity is 0.25

This is a typical way to report soil samples (weight of pollutant/weight of soil):

- A common soil density is around 2,000 kg/m\(^3\)
- PCE has a density of 1,623 kg/m\(^3\)

\[
S_n = \frac{V_n}{V_{\text{pore}}} = \frac{M_n \rho_S}{M_S \rho_n} = \frac{(0.02)(2,000 \text{ kg/m}^3)}{(1,623 \text{ kg/m}^3)(0.25)} = 0.10
\]

The NAPL front is then moving at a velocity of:

\[
V_n \approx \frac{Q_n}{nAS_n^{\text{min}}} = \frac{0.01 \text{ m}^3/\text{day}}{(0.25)(10 \text{ m}^2)(0.10)} = 0.04 \text{ m/day}
\]

These simple calculations must be used only for orders of magnitude.

There are many uncertainties associated with the numbers (parameter values).

Careful with the assumptions!

Fractures or other significant heterogeneities in the soil can really speed things up... or slow them down.

Horizontal movement occurs even in the simplest soil structures (change from one soil layer to another is sufficient to cause lateral flow).
Multiphase Flow

- Numerical models have been developed to study major spills and try to determine what happened to the source.
- Extremely data and CPU (calculation) intensive = $$$$.

Multiphase Flow

- Area of very active research:
  - relative permeabilities vs. saturation
  - two- and three-phase flow
  - effect of soil properties (water wetting vs. oil wetting films) on kr
  - incorporation of multiphase flow into a rate-limited mass transfer framework to account for dissolution, volatilization, sorption (+ reactions...).