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

DNAPLs	
PCE	1.62
Carbon tetrachloride	1.59
Chloroform	1.48
TCE	1.46
1,1,1-TCA	1.34
Methylene chloride	1.33
Coal tar	1.01-1.05

LNAPLs	
Xylene	0.86
Toluene	0.87
Benzene	0.88
Gasoline	0.72-0.76
Jet fuel	0.76
Diesel fuel	0.84-0.85
Fuel oil	0.87-0.95

Laboratory experiments with PCE DNAPL in unsaturated and saturated media

See Figure XI.a in Friedrich Schwille, 1988. *Dense Chlorinated Solvents in Porous and Fractured Media, Model Experiments*. Lewis Publishers, Chelsea, Michigan.

PCE penetration at Borden aquifer field site

See Figure 1 in M.M. Poulsen and B.H. Kueper, 1992.
A Field Experiment to Study the Behavior of Tetrachloroethylene in Unsaturated Porous Media. *Environmental Science & Technology*, Vol. 26, No. 5, Pp. 889-895, May 1992.

Shows structure (even very subtle) of porous medium may affect lateral movement

PCE penetration at Borden aquifer field site

See Figure 2 in M.M. Poulsen and B.H. Kueper, 1992.
A Field Experiment to Study the Behavior of Tetrachloroethylene in Unsaturated Porous Media. *Environmental Science & Technology*, Vol. 26, No. 5, Pp. 889-895, May 1992.

In seemingly uniform sand, subtle structure caused lateral movement
Character of release affected very penetration

Formation of residual and dissolution

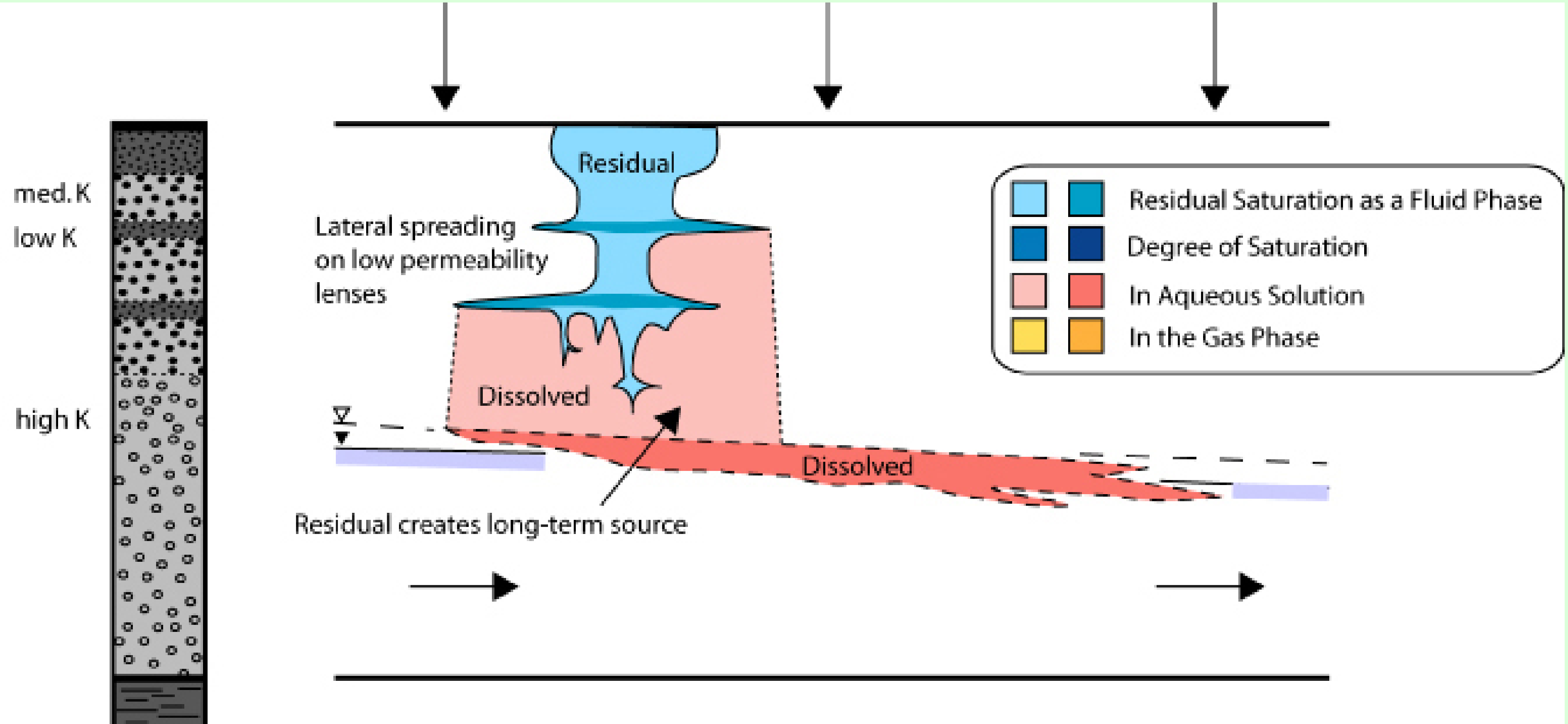


Image adapted from: Friedrich Schwille, 1988. *Dense Chlorinated Solvents in Porous and Fractured Media, Model Experiments.* Lewis Publishers, Chelsea, Michigan.

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

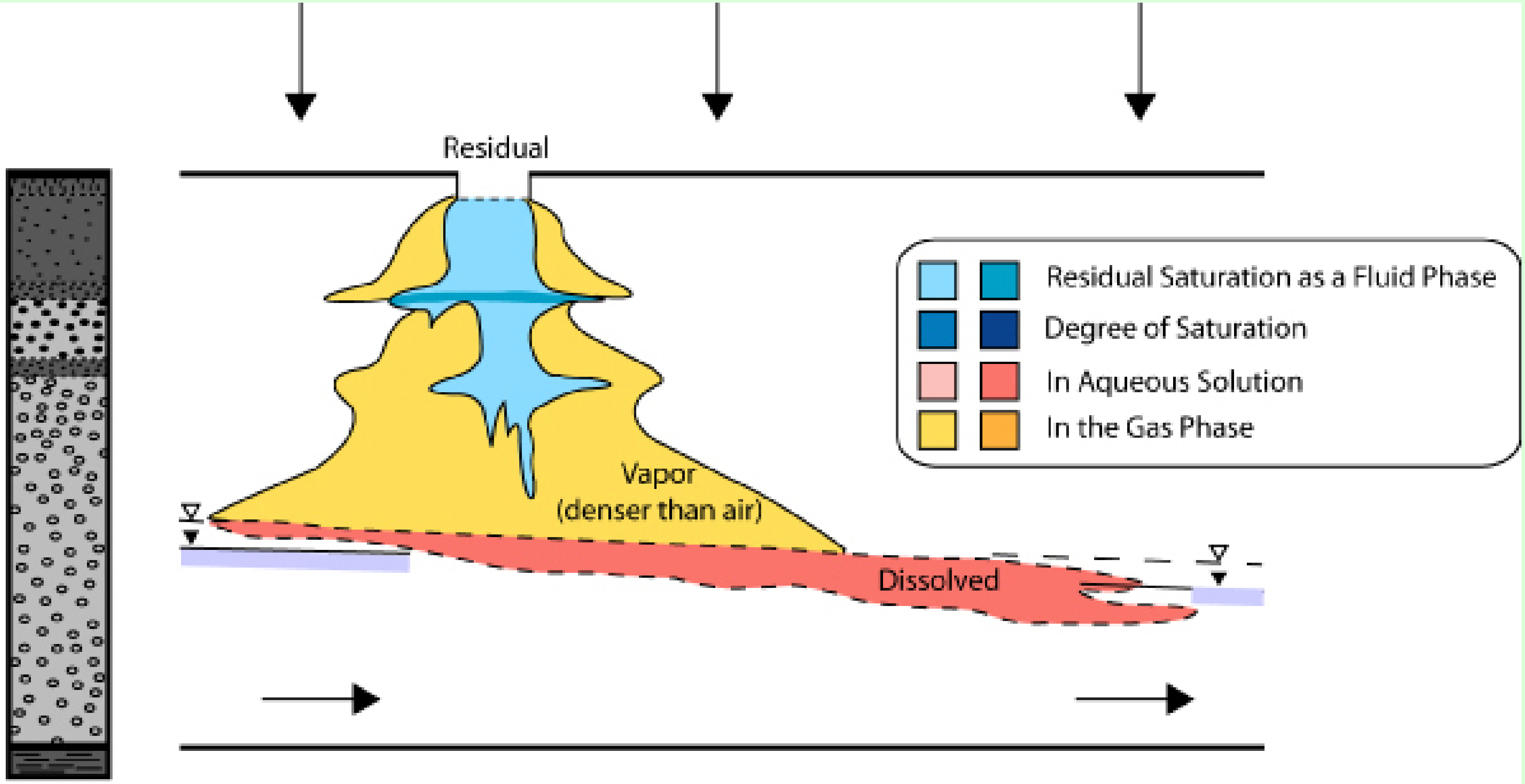


Image adapted from: Friedrich Schwille, 1988. *Dense Chlorinated Solvents in Porous and Fractured Media, Model Experiments.* Lewis Publishers, Chelsea, Michigan.

At 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, $\mathbf{s_r} = \dfrac{\textbf{volume of NAPL}}{\textbf{volume of voids}}$ (dimensionless)

Material	Residual saturation, s_r
TCE	0.15 – 0.2
PCE	0.002 – 0.20
Gasoline	0.12 – 0.60

Source: Cohen, R. M., and J. W. Mercer, 1993. *DNAPL Site Evaluation*. C.K. Smoley, Boca Raton, Florida.

Good rough guess: $s_r = 0.2$

After NAPL passes through soil, fraction remains behind as a residual.

Residual in etched glass “porous medium”

See Plate 1 in S.H. Conrad, J.L. Wilson, W.R. Mason, and W. J. Peplinski, 1992. Visualization of Residual Organic Liquid Trapped in Aquifers. *Water Resources Research.* Vo. 28, No. 2, Pp. 467-478. February 1992.

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).

See S.H. Conrad, J.L. Wilson, W.R. Mason, and W. J. Peplinski, 1992.
Visualization of Residual Organic Liquid Trapped in Aquifers. *Water Resources Research.*
Vo. 28, No. 2, Pp. 467-478. February 1992.

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

See Fig.5 in S.H. Conrad, J.L. Wilson, W.R. Mason, and W. J. Peplinski, 1992. Visualization of Residual Organic Liquid Trapped in Aquifers. *Water Resources Research.* Vo. 28, No. 2, Pp. 467-478. February 1992.

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.

See Fig.6 in S.H. Conrad, J.L. Wilson, W.R. Mason, and W. J. Peplinski, 1992. Visualization of Residual Organic Liquid Trapped in Aquifers. *Water Resources Research.* Vo. 28, No. 2, Pp. 467-478. February 1992.

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 rain water 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 →

See Figures XVIII.a and b in Friedrich Schwille, 1988. *Dense Chlorinated Solvents in Porous and Fractured Media, Model Experiments*. Lewis Publishers, Chelsea, Michigan.

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

See Friedrich Schwille, 1988. *Dense Chlorinated Solvents in Porous and Fractured Media, Model Experiments*. Lewis Publishers, Chelsea, Michigan.

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.

“The spill question”

Question:	Answer:
“Given a spill on the land surface, how long will it take for the NAPL to penetrate to the water table?” residual saturation.	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.

DNAPL below the water table

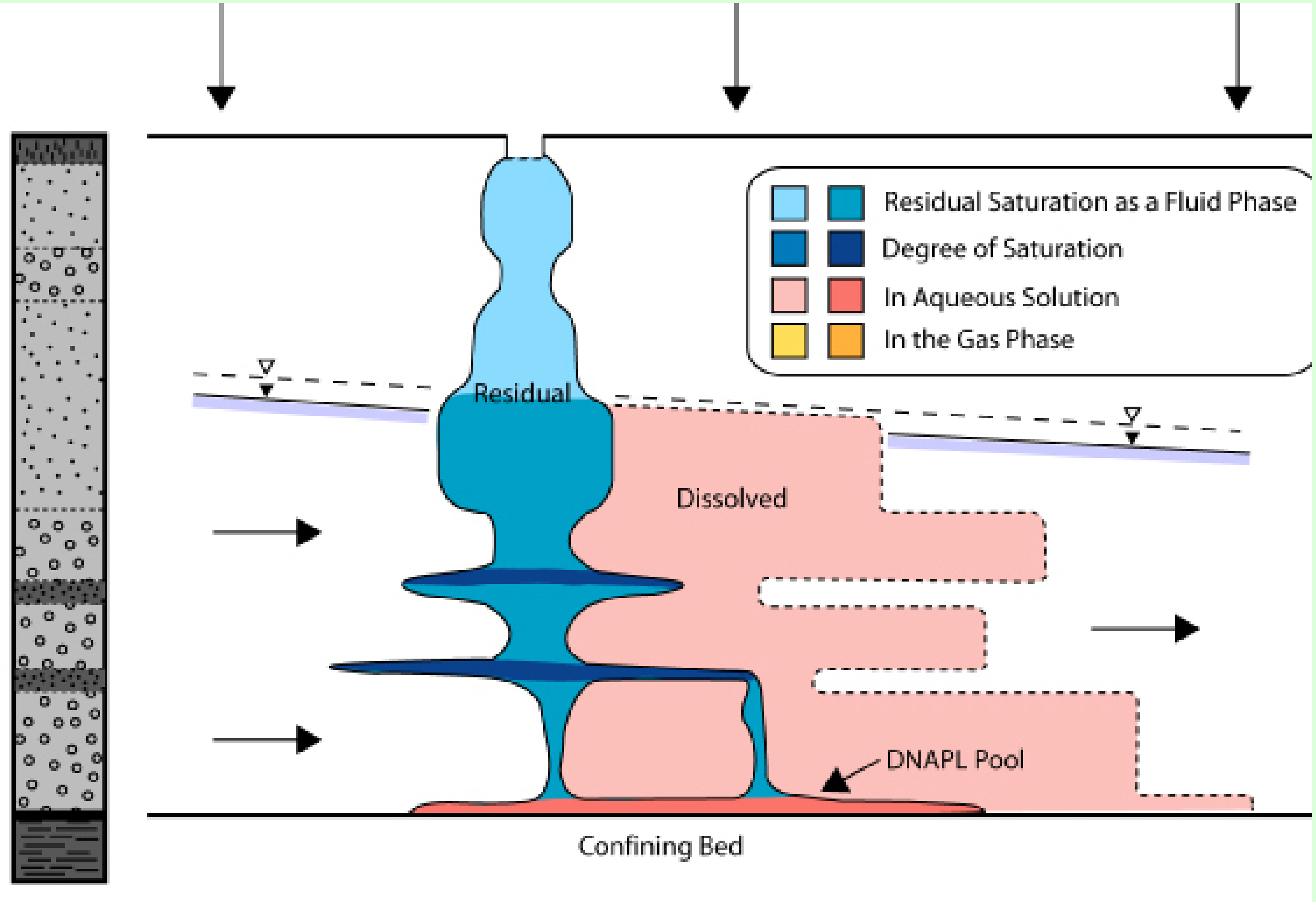


Image adapted from: Friedrich Schwille, 1988. *Dense Chlorinated Solvents in Porous and Fractured Media, Model Experiments.* Lewis Publishers, Chelsea, Michigan.

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.

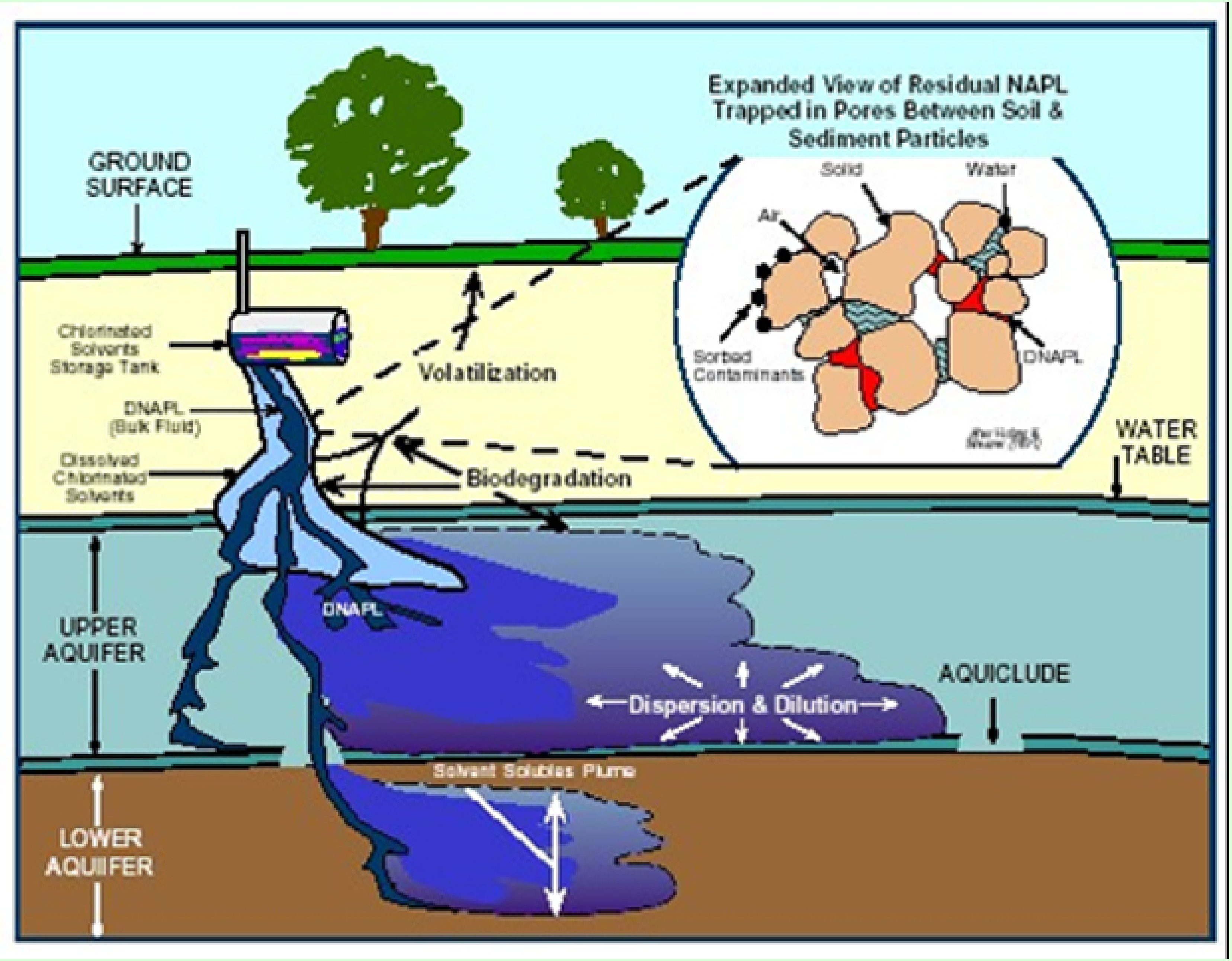
Eventually the DNAPL can reach an “impermeable” (actually, poorly permeable) layer and collect in a pool.

See Figure IX.a in Friedrich Schwille, 1988. *Dense Chlorinated Solvents in Porous and Fractured Media, Model Experiments*. Lewis Publishers, Chelsea, Michigan.

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 ug/L

Superfund guidance (Newell, C. J., and R. R. Ross, 1992. Estimating potential for occurrence of DNAPL at Superfund sites. OSWER Directive 9355.4-07FS. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Ada, Oklahoma. http://www.epa.gov/superfund/resources/gwdocs/estdnapl.pdf. January 1992.) gives:

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



Summary of processes in DNAPL spill. Source: Pope, D. F., and J. N. Jones, 1999. Monitored Natural Attenuation of Chlorinated Solvents. Report Number EPA/600/F-98/022. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. May 1999.

LNAPL behavior at water table

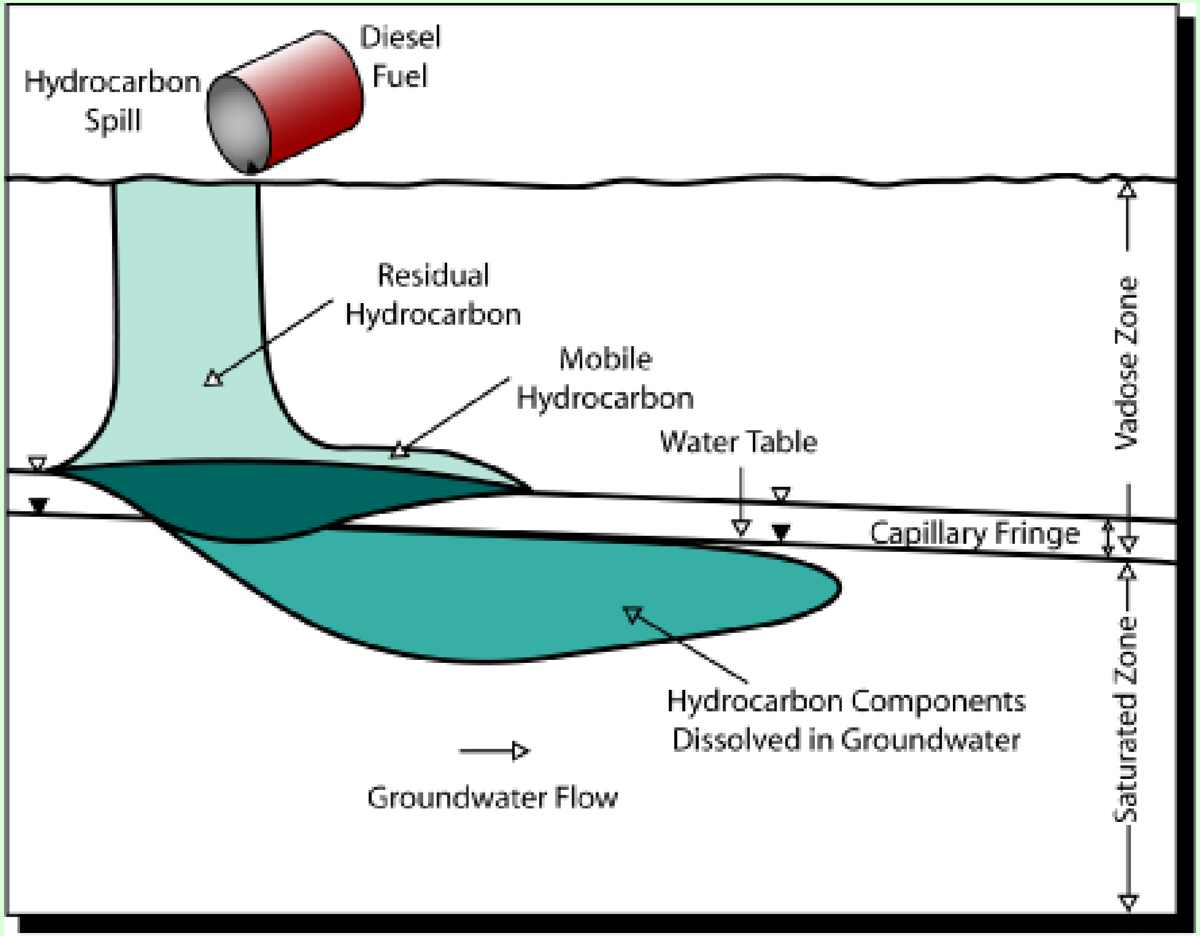


Image adapted from: C.W. Fetter, 1992. *Contaminant Hydrogeology.* Macmillan Publishing Company, New York.

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

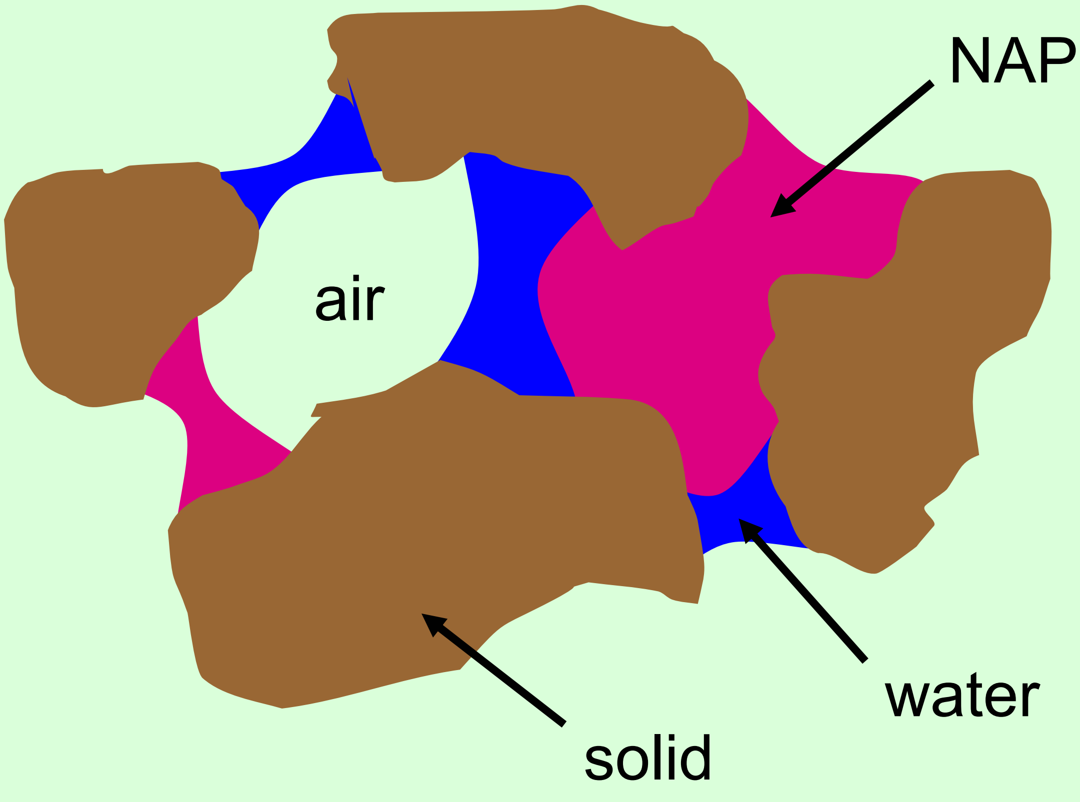
Porous medium:

- Permeability
- Pore size
- Structure

Ground water:

- Water content
- Velocity

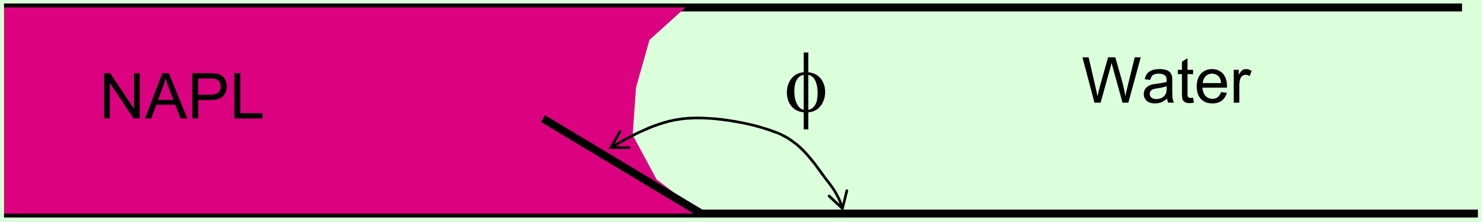
NAPL Movement in Porous Medium



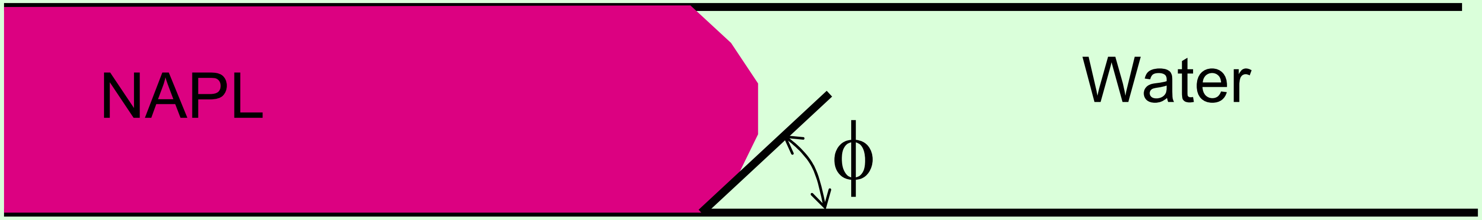
Note: water is drawn as wetting fluid, NAPL as non-wetting relative to water, wetting relative to air

Wetting vs. non-wetting fluids

Wetting angle ϕ always measured from water



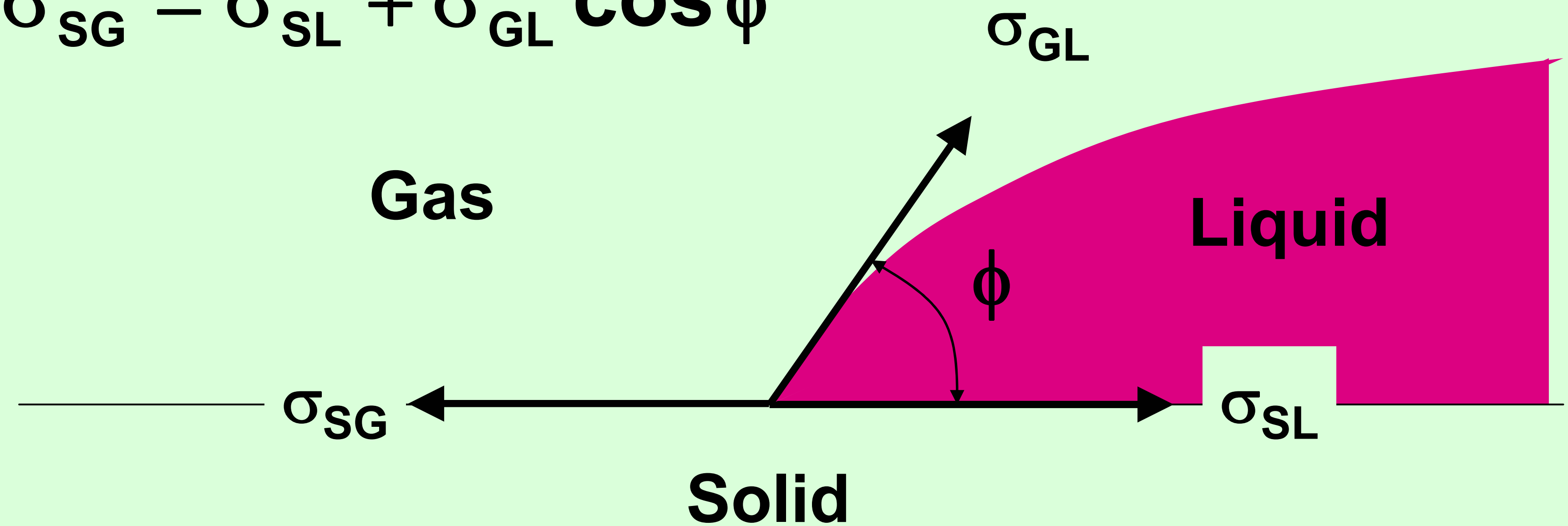
ϕ > 110° → NAPL wets



ϕ < 70° → water wets

Interfacial tension force balance

$$\sigma_{SG} = \sigma_{SL} + \sigma_{GL} \cos\phi$$



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

σ_{SG}, σ_{SL}, σ_{GL} = interfacial tension between solid and gas, solid and liquid, and gas and liquid (dyne/centimeter)

Interfacial tension effects

Wetting angle, ϕ, can be changed by changing surface

Example:

Water wets unwaxed car

Water does not wet (“beads up”) on waxed car

Wax increases σ_{SL}

In soil, coal tar and petroleum products alter soil surfaces, make them oil wet

Interfacial tension values

DNAPL	Interfacial tension with water (dyn/cm)
Tetrachloroethylene	44.4
Trichloroethylene	34.5
1,1-Dichloroethylene	37.0
trans-1,2-Dichloroethylene	30.0
1,1,1-Trichloroethane	45.0
1,2-Dichloroethane	30.0

Values at 20ºC
Source: Cohen, R. M., and J. W. Mercer, 1993. *DNAPL Site Evaluation*. C.K. Smoley, Boca Raton, Florida. Appendix A.

Interfacial tension values (continued)

DNAPL	Interfacial tension with water (dyn/cm)
Carbon Tetrachloride	45.0
Chloroform	32.8
Methylene Chloride	28.3
Chlorobenzene	37.4
1,2-Dichlorobenzene	40.0

Values at 20ºC
Source: Cohen, R. M., and J. W. Mercer, 1993. *DNAPL Site Evaluation*. C.K. Smoley, Boca Raton, Florida. Appendix A.

Force balance on fluid element

Pressure force on top:

$P_{z+\Delta z}\ \Delta x\ \Delta y$

Gravitational force:

$\rho g\ \Delta x\ \Delta y\ \Delta z$

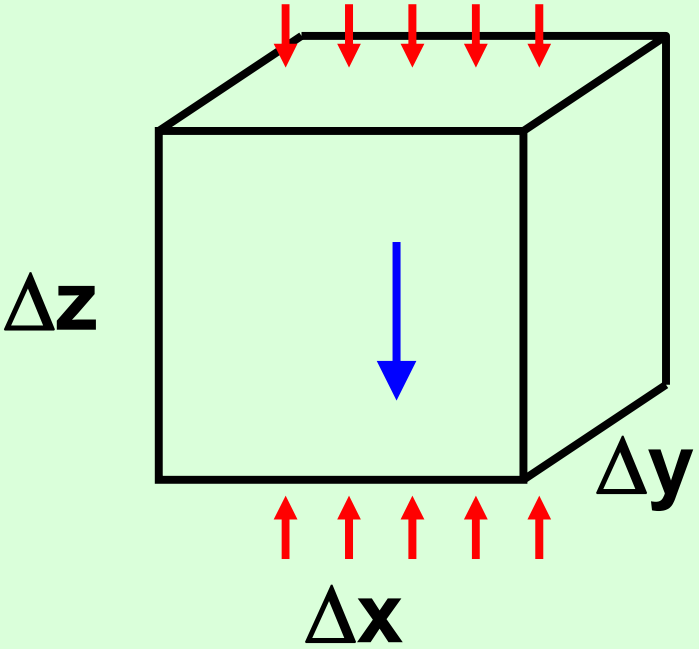
Pressure force on bottom:

$P_z\ \Delta x\ \Delta y$

Σ forces = 0

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

$dP/dz = -\rho g$



Force balance on fluid element

$dP/dz = -\rho g$

Assume constant ρ:

$P = -\rho gz + \text{constant}$

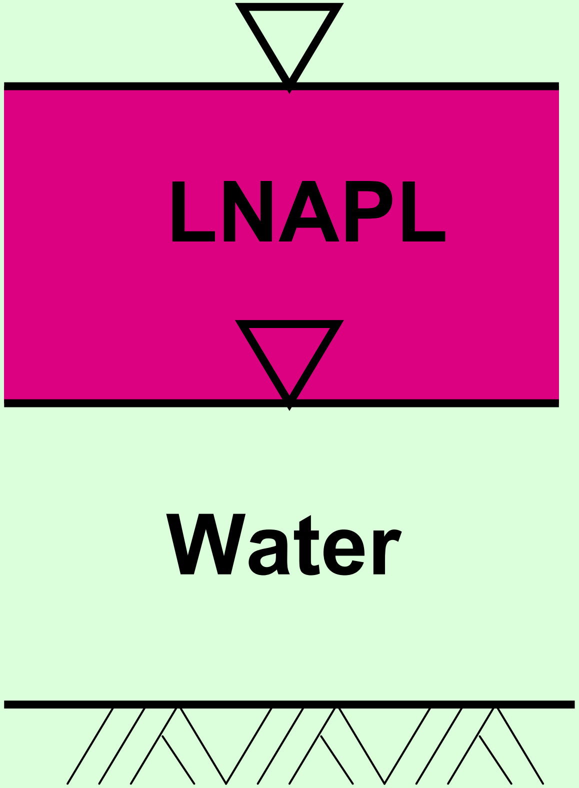
Force balance for water:

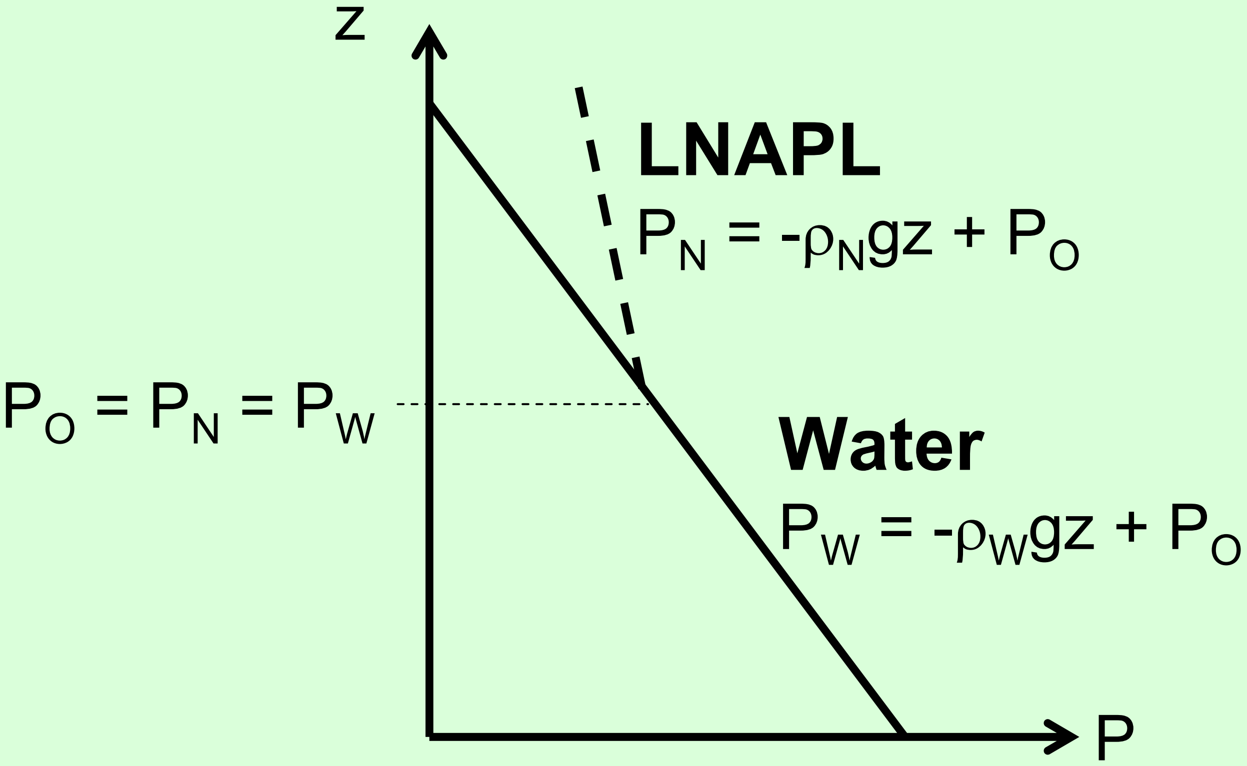
$P_W = -\rho_W gz + C_W$

Force balance for NAPL:

$P_N = -\rho_N gz + C_N$

LNAPL on water





LNAPL

$P_N = -\rho_N g z + P_O$

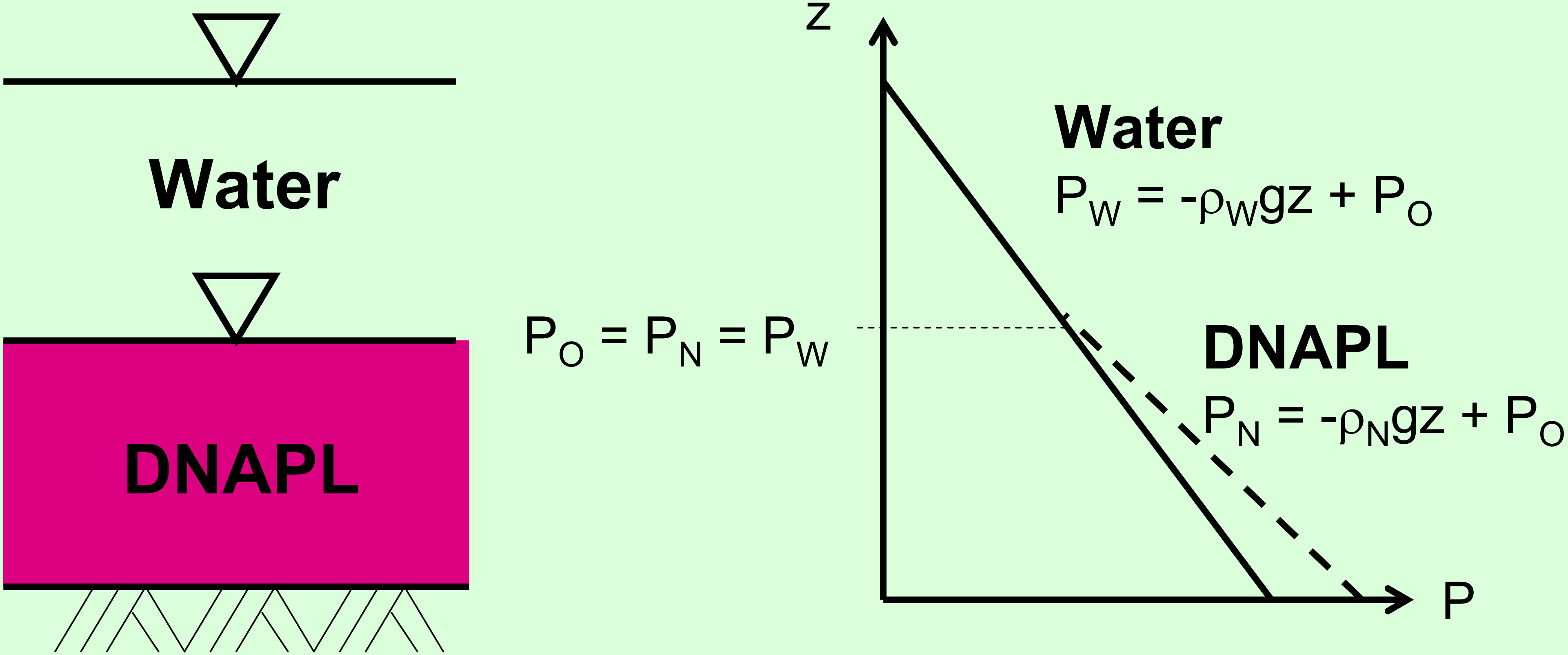
$P_O = P_N = P_W$

Water

$P_W = -\rho_W g z + P_O$

$P_N \geq P_W$

Water on DNAPL



$P_W = -\rho_W g z + P_O$

$P_N = -\rho_N g z + P_O$

$P_O = P_N = P_W$

$P_N \geq P_W$

Capillary pressure

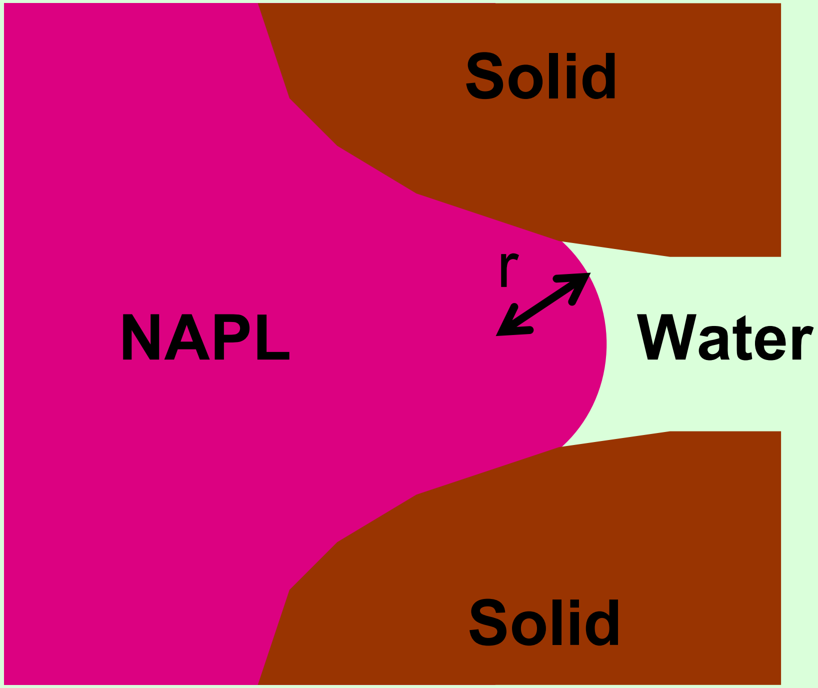
How can NAPL and water exist together in soil at two different pressures?

Difference is interfacial tension

Interfacial tension → capillary pressure

$P_C = P_N - P_W$

Capillary pressure

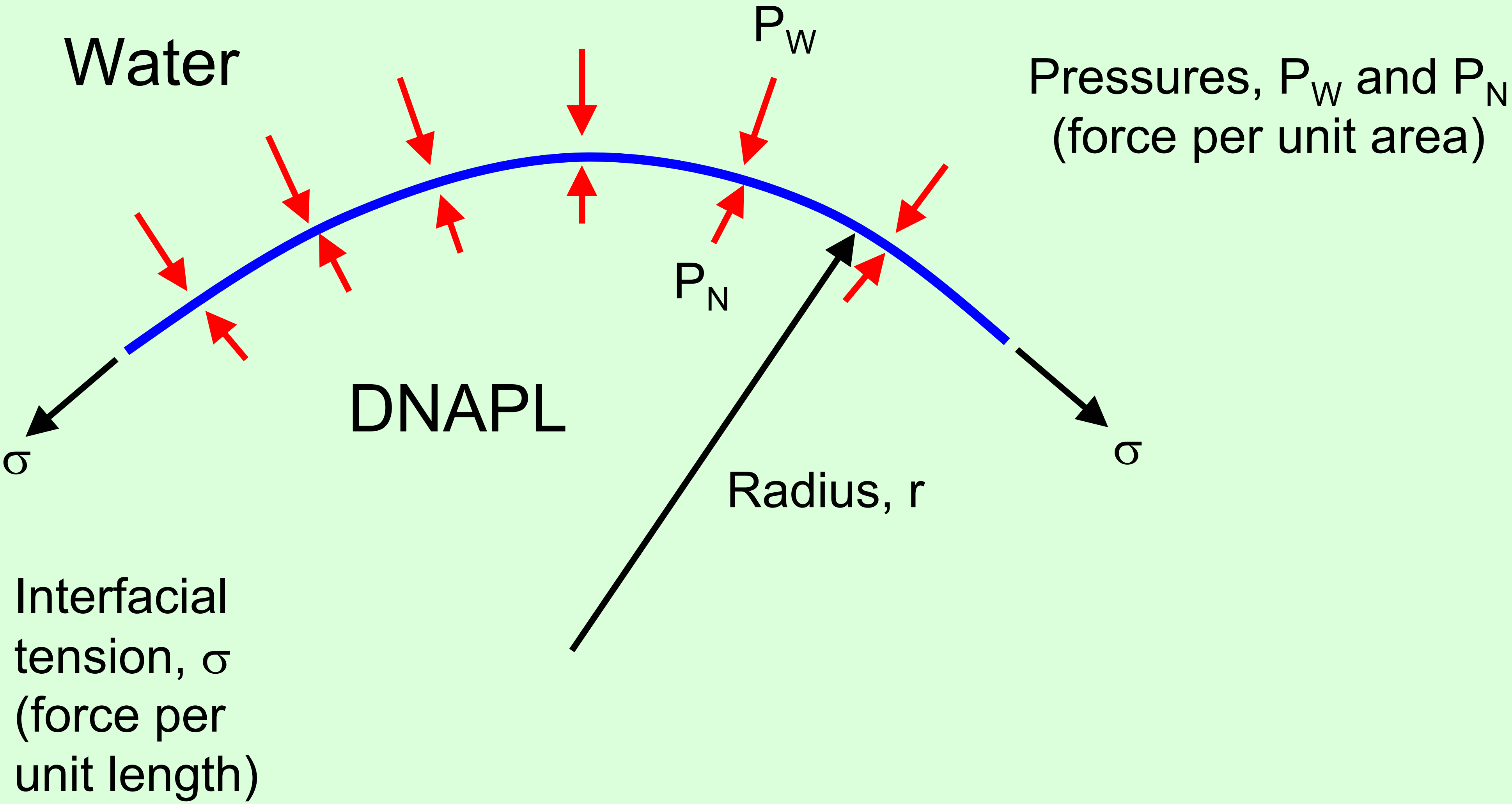


$$P_C = P_N - P_W = -\frac{2\sigma}{r}$$

σ = NAPL-water interfacial tension (dyne/cm)
r = and pore throat radius (cm)

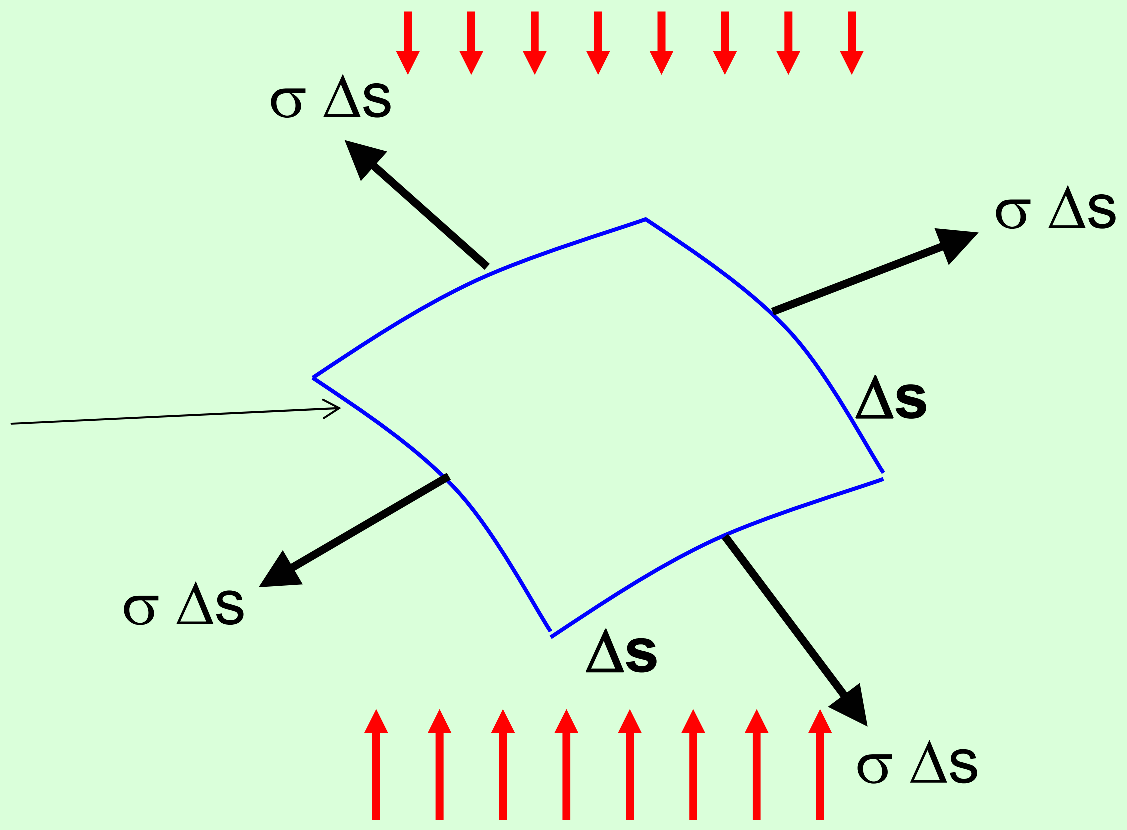
Conclusion: capillary pressure depends on NAPL (σ) and porous medium (r)

Capillary force balance



Relationship between P_C and σ

P_W



LNAPL
above

$\sigma\ \Delta s$

$\sigma\ \Delta s$

Interface

Δs

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

$\sigma\ \Delta s$

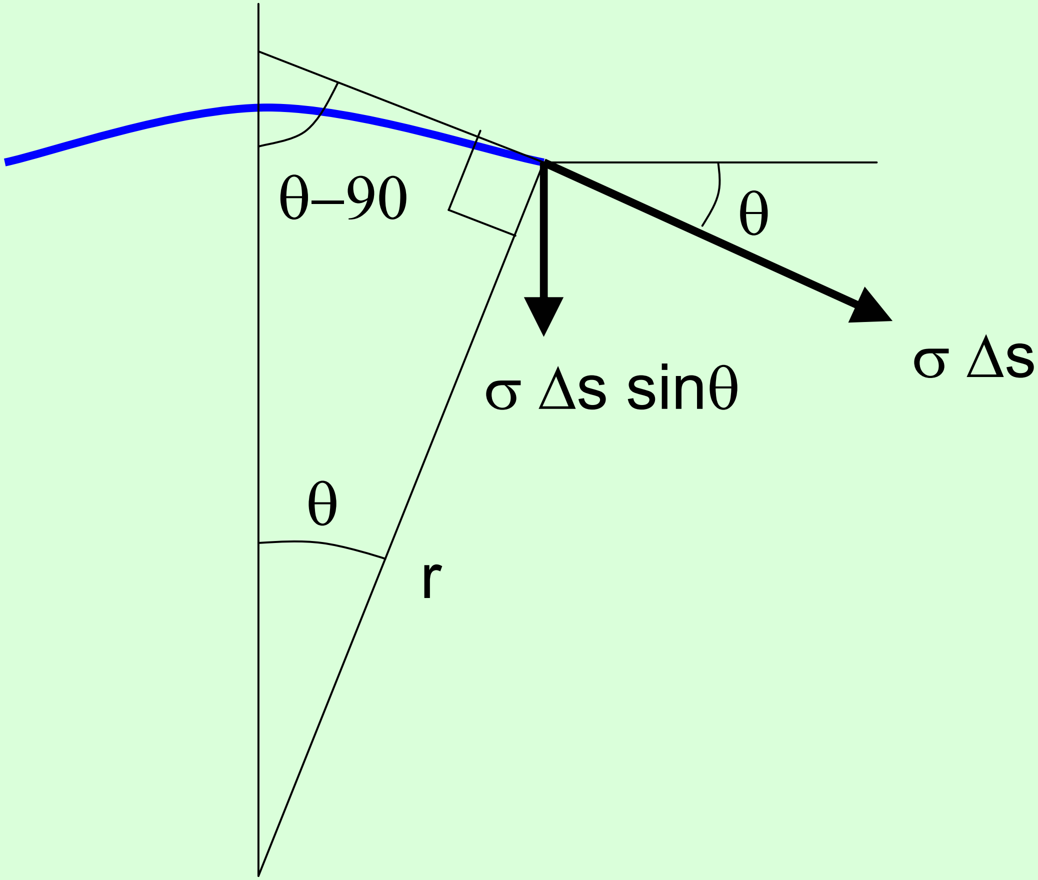
Δs

Water
below

$\sigma\ \Delta s$

$P_N = P_W + P_C$

Relationship between P_C and σ



Force balance:

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

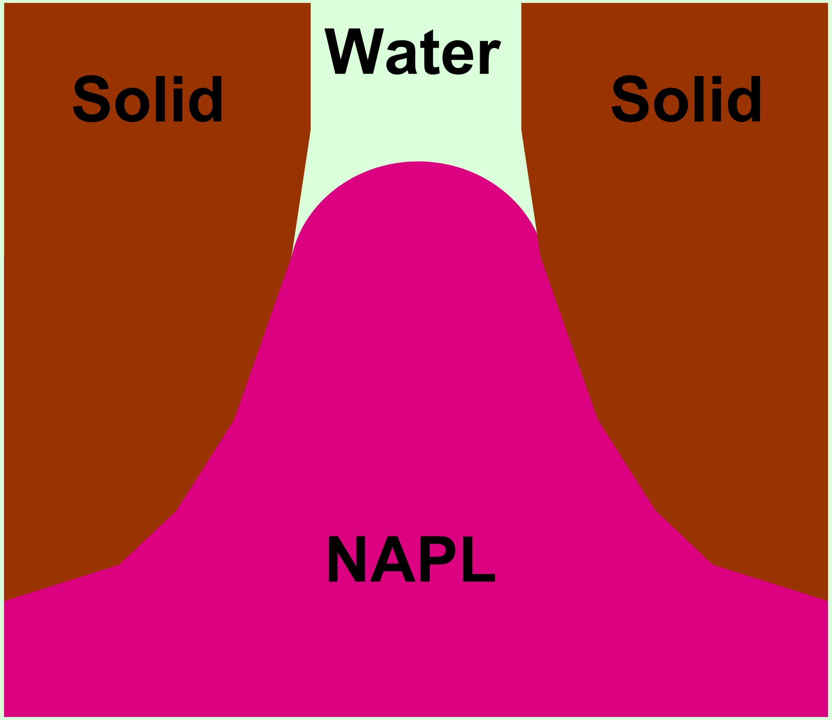
$\sin\theta \approx \theta \approx (\frac{1}{2}\Delta s)/r$

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

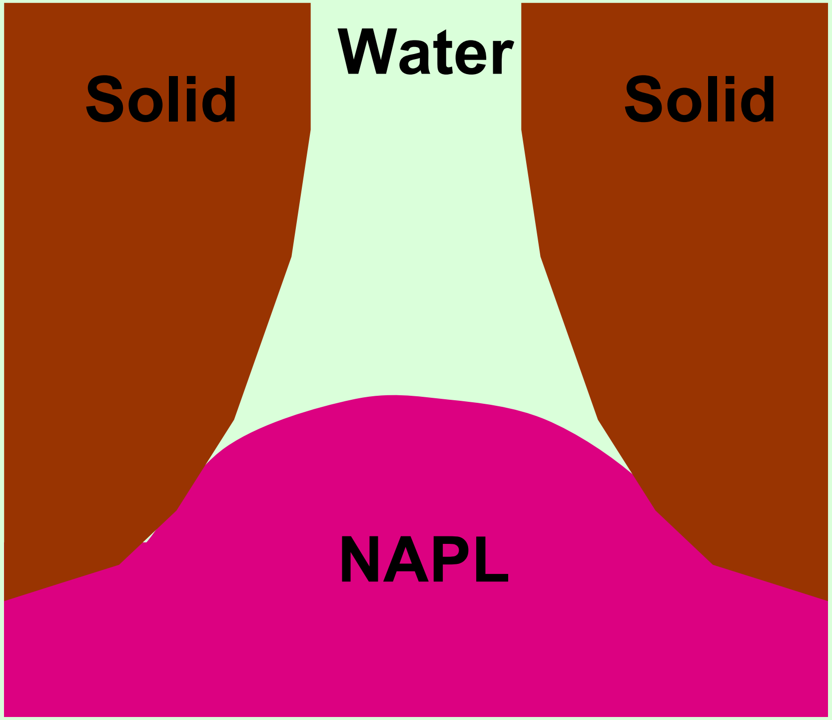
$P_C = -2\sigma / r$

Derivation follows H. Rouse, 1946. *Elementary mechanics of fluids*. Dover Publications, New York.

P_C depends on NAPL and porous medium

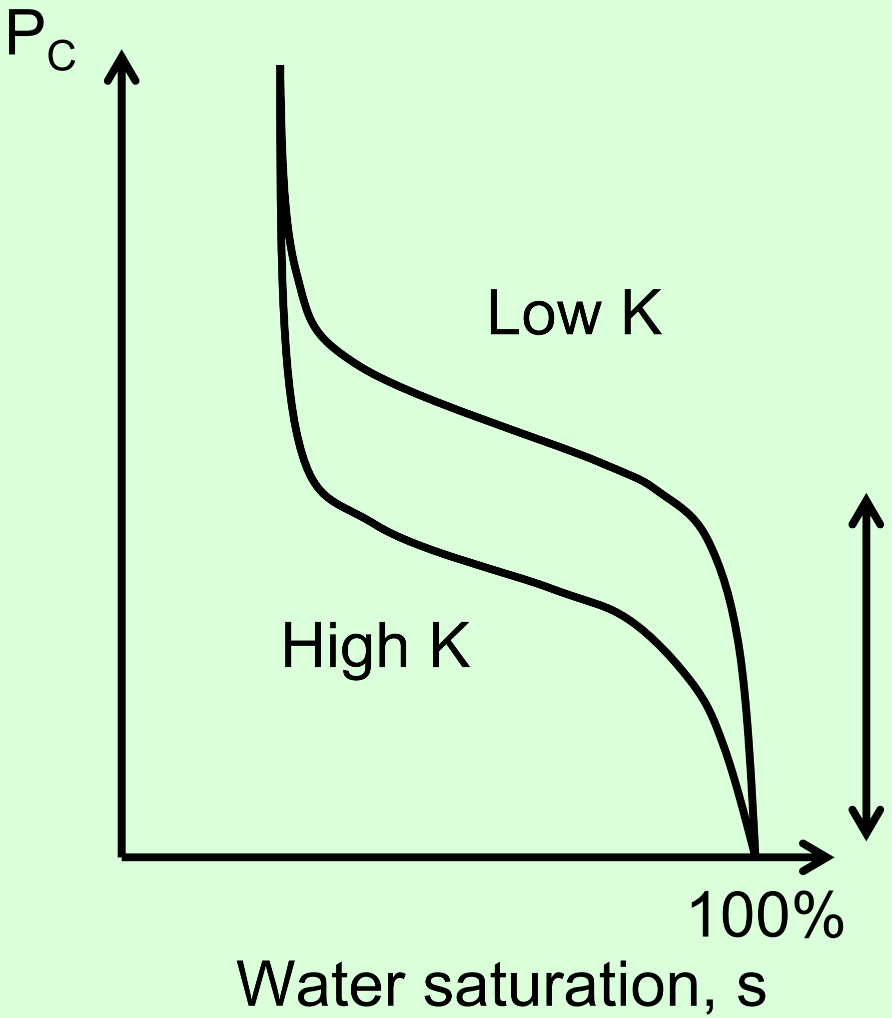


Large P_C (small r or large σ)
→ small water content,
large NAPL residual



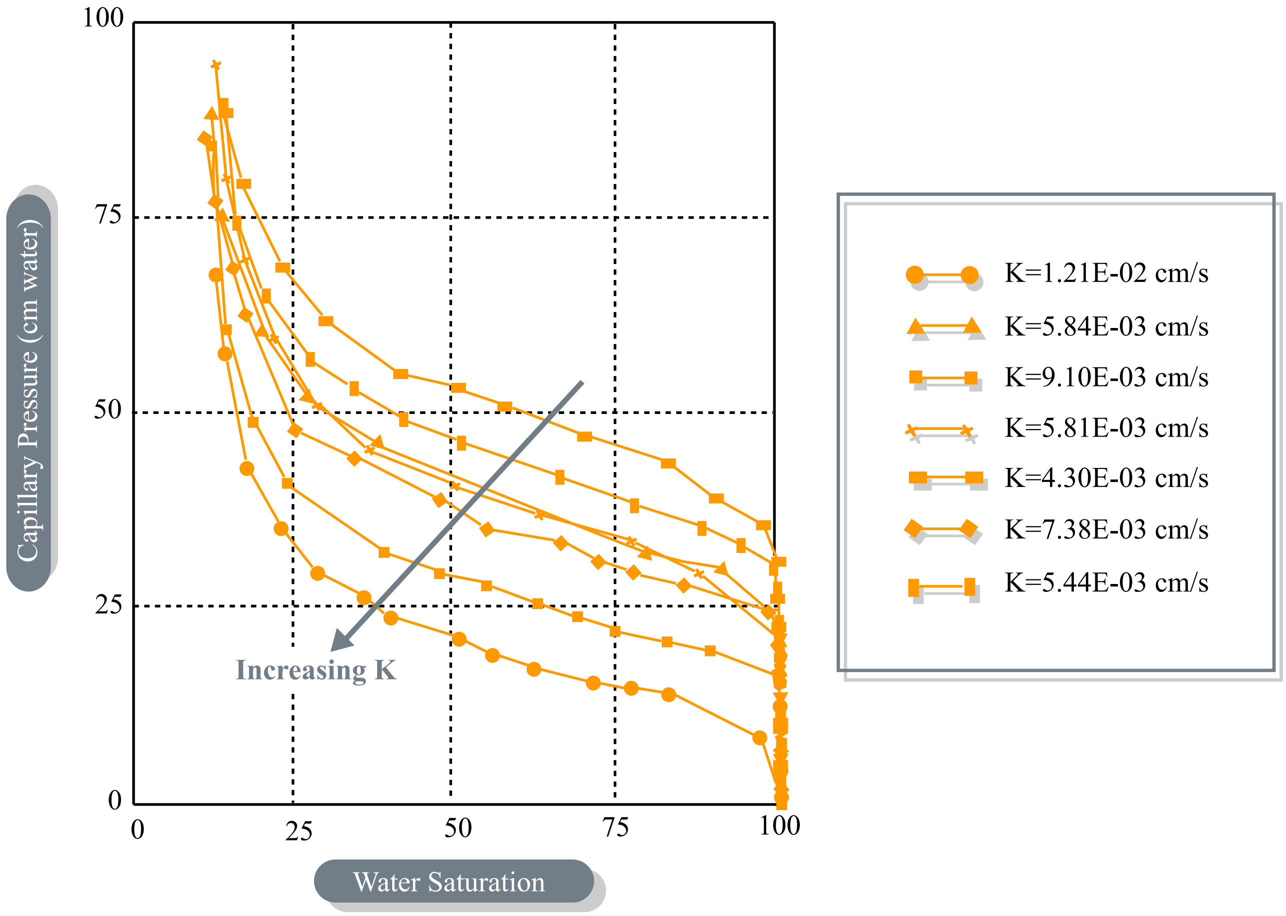
Small P_C (large r or small σ)
→ large water content,
small NAPL residual

P_C vs. water saturation



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

P_C vs. water saturation for PCE



Adapted from: Kueper, B. H. and E. O. Frind. "Two-Phase Flow in Heterogeneous Porous Media. 2. Model Application." *Water Resources Research 27*, no. 6 (June 1991): 1059-1070. Also published in: Cohen, R. M. and J. W. Mercer. *DNAPL Site Evaluation*. Boca Raton, Florida: C. K. Smoley, 1993. Figure 4-6.

Implications of entry pressure

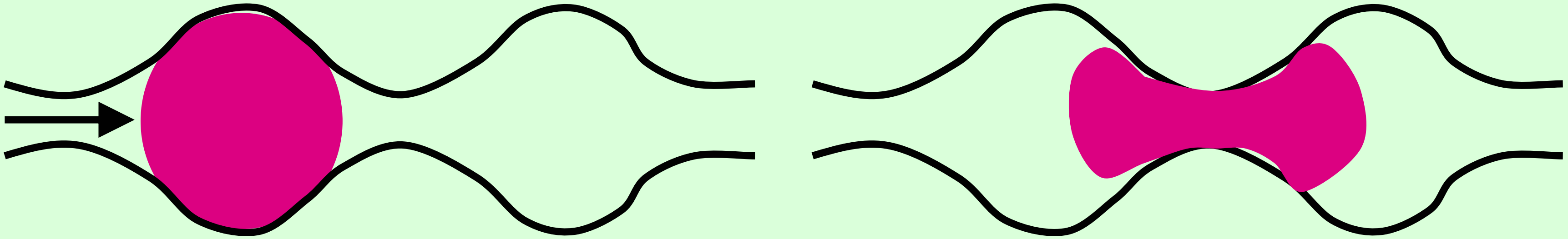
NAPL will pool on low K horizons (such as clay layer) until pool depth creates pressure in excess of entry pressure

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

$$\mathbf{N_C = \frac{\mu_W V_W}{\sigma_{NW}} = \frac{viscous}{capillary}}$$

where:

μ_W = viscosity of water

V_W = velocity of water

σ_{NW} = NAPL-water interfacial tension

Mobilization of entrapped NAPL

Bond number = ratio of gravity to capillary force

$$B_o = \frac{(\rho_{NAPL} - \rho_W)gR^2}{\sigma_{NW}} = \frac{\text{gravity}}{\text{capillary}}$$

where:

ρ_{NAPL} = density of NAPL

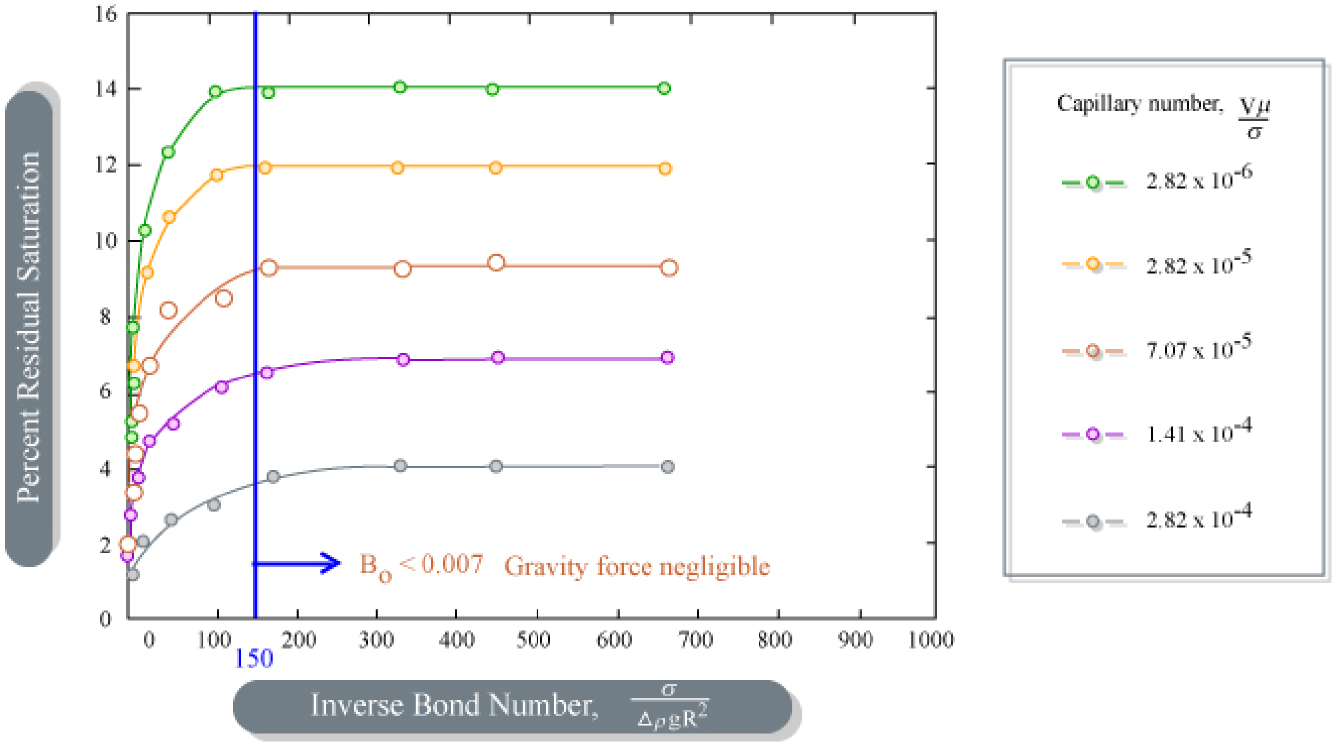
ρ_W = density of water

g = gravitational acceleration

R = grain-size radius

Reference: N.R. Morrow and B. Songkran, 1981. Effect of viscous and buoyancy forces on nonwetting phase trapping in porous media. In: D.O. Shah, Ed. *Surface Phenomena in Enhanced Oil Recovery.* Plenum Press, NY. Pp. 387-411.

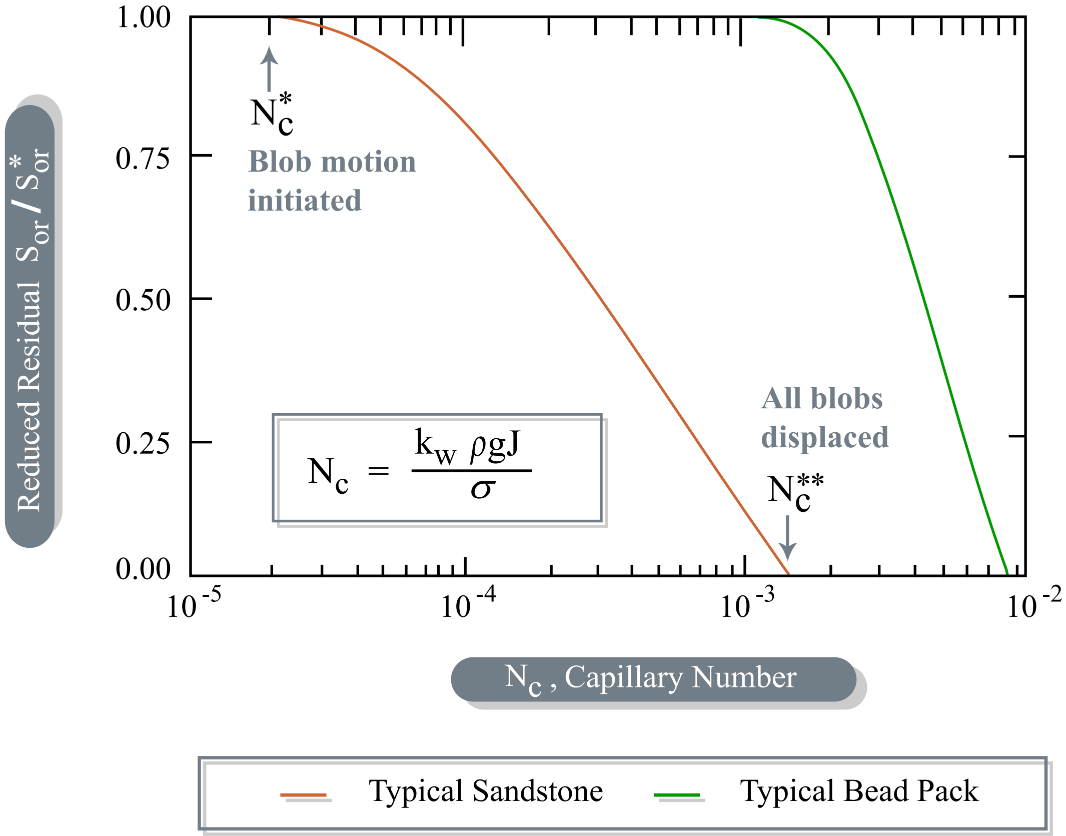
Residual saturation vs. Bond and Capillary Numbers



Adapted from: Morrow, N. R. and B. Songkran. "Effect of Viscous and Buoyancy Forces on Nonwetting Phase Trapping in Porous Media." *Surface Phenomena in Enhanced Oil Recovery*. Edited by D. O. Shah. NY: Plenum Press, 1981, pp. 387-411. Figure 3.

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 007!

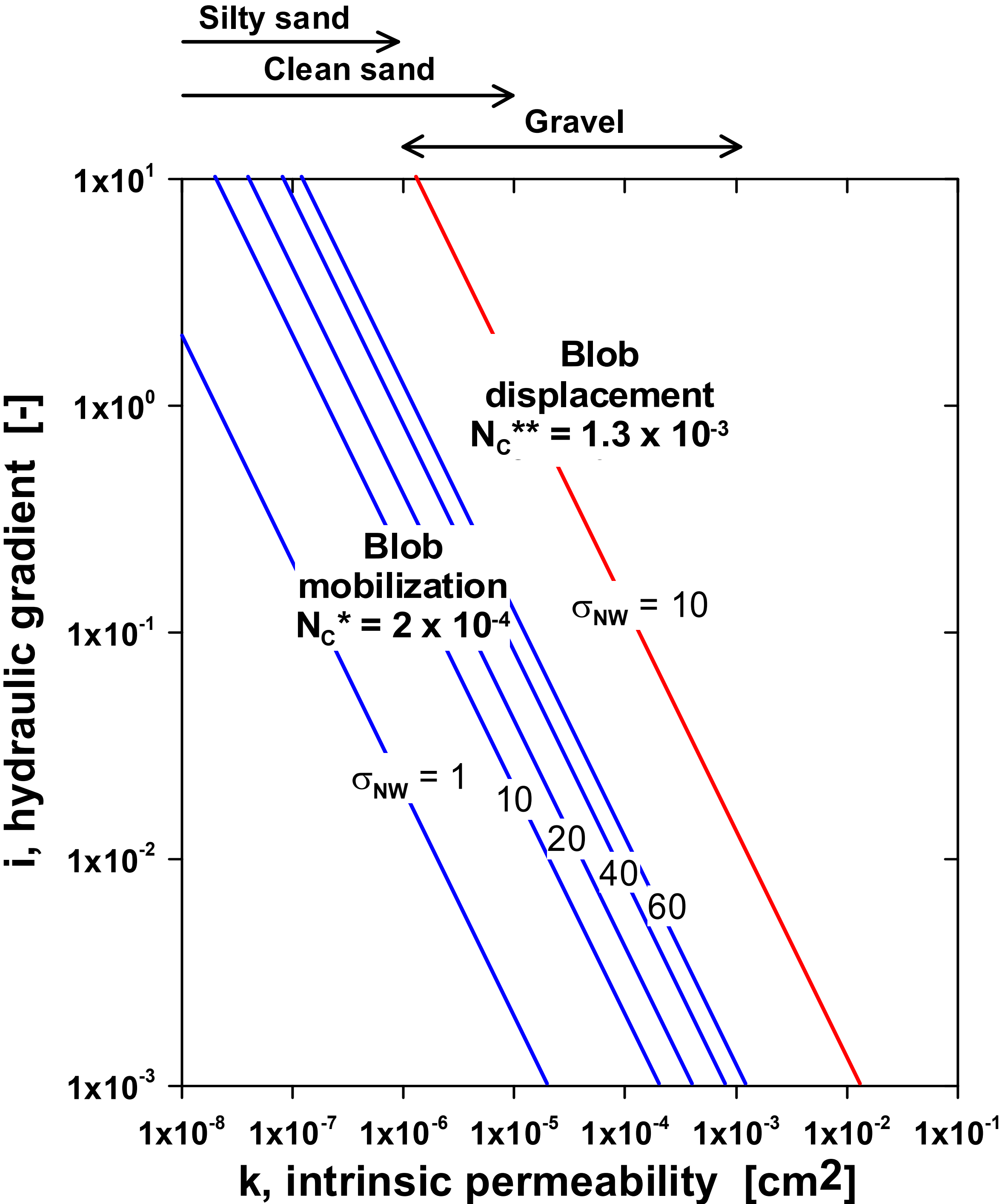
Residual saturation vs. Capillary Number



Adapted from: Wilson, J. L., and S. H. Conrad. "Is Physical Displacement of Residual Hydrocarbons a Realistic Possibility in Aquifer Restoration?" Proceedings of the NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water. Houston, Texas. National Water Well Association. Worthington, OH: Nov, 5-7. 1984.

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



Based on: Wilson, J. L., and S. H. Conrad, 1984. Is physical displacement of residual hydrocarbons a realistic possibility in aquifer restoration? Proceedings of the NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Houston, Texas. National Water Well Association, Worthington, OH. Nov. 5-7. 1984.

Can NAPL be mobilized?

Soil type	Horizontal movement	Vertical movement
Gravel	YES	YES
Sand	NO	YES
Silt or clay	NO	NO

From: Wilson, J. L., and S. H. Conrad, 1984. Is physical displacement of residual hydrocarbons a realistic possibility in aquifer restoration? Proceedings of the NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Houston, Texas. National Water Well Association, Worthington, OH. Nov. 5-7. 1984.

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