

Lecture 5

Non-Aqueous Phase Liquid (NAPL) Fate and Transport

Factors affecting NAPL movement

Fluid properties:

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

Porous medium:

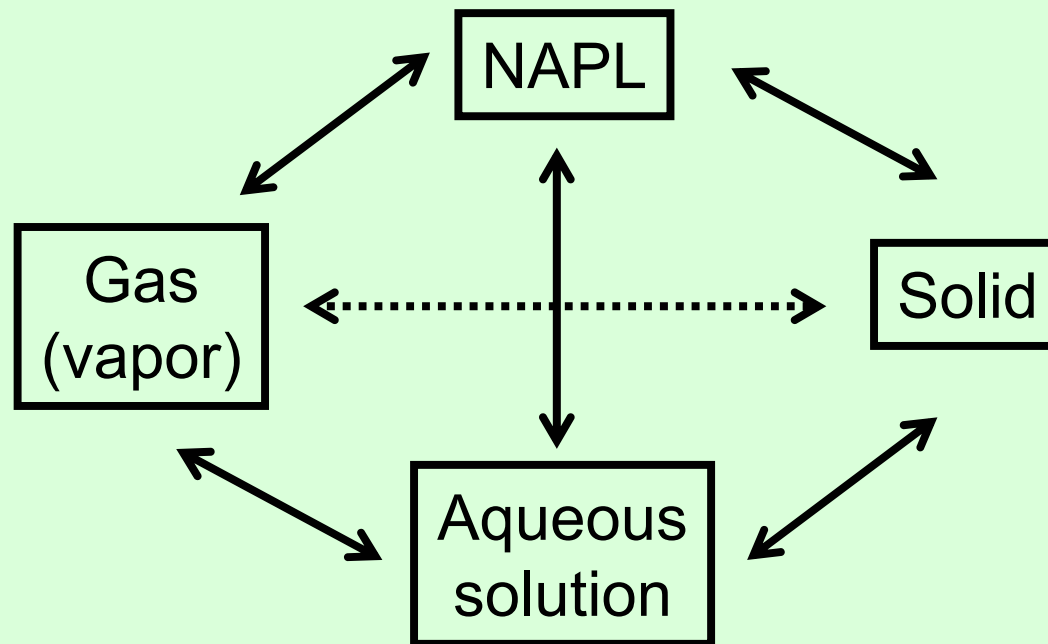
- Permeability
- Pore size
- Structure

Ground water:

- Water content
- ✓ Velocity

Partitioning processes

NAPL can partition between four phases:



Water to gas partitioning (volatilization)

Aqueous \leftrightarrow gaseous

Henry's Law (for dilute solutions)

Dimensionless (C_G , C_W in moles/m³)

$$\frac{C_G}{C_W} = H'$$

Dimensional (P = partial pressure in atm)

$$\frac{P}{C_W} = H$$

Henry's Law Constant

H has dimensions: atm m³ / mol

H' is dimensionless

$$H' = H/RT$$

R = gas constant = 8.20575×10^{-5} atm m³/mol °K

T = temperature in °K

NAPL to gas partitioning (volatilization)

NAPL \leftrightarrow gaseous

Raoult's Law:

$$C_G = X_t (P^\circ/RT)$$

X_t = mole fraction of compound in NAPL [-]

P° = pure compound vapor pressure [atm]

R = universal gas constant [$\text{m}^3\text{-atm/mole/}^\circ\text{K}$]

T = temperature [$^\circ\text{K}$]

Volatility

Vapor pressure P° is measure of volatility

$P^\circ > 1.3 \times 10^{-3} \text{ atm} \rightarrow$ compound is “volatile”

$1.3 \times 10^{-3} > P^\circ > 1.3 \times 10^{-13} \text{ atm} \rightarrow$
compound is “semi-volatile”

Example: equilibrium with benzene

$$P^\circ = 76 \text{ mm Hg at } 20^\circ\text{C} = 0.1 \text{ atm}$$

$$R = 8.205 \times 10^{-5} \text{ m}^3\text{-atm/mol/}^\circ\text{K}$$

$$T = 20^\circ\text{C (assumed)} = 293^\circ\text{K}$$

Assume 100% benzene, mole fraction $X_t = 1$

$$C_G = X_t P^\circ / (RT) = 4.16 \text{ mol/m}^3$$

Molecular weight of benzene, $\text{C}_6\text{H}_6 = 78 \text{ g/mol}$

$$C_G = 4.16 \text{ mol/m}^3 \times 78 \text{ g/mol} = 324 \text{ g/m}^3 = 0.32 \text{ g/L}$$

$$C_G = 0.32 \text{ g/L} \times 24 \text{ L/mol} / (78 \text{ g/mol}) \times 10^6 = 99,000 \text{ ppmv}$$

One mole of ideal gas = 22.4 L at STP (1 atm, 0 C), Corrected to 20 C: $293/273 \times 22.4 = 24.0 \text{ L/mol}$

Gas concentration in equilibrium with pure benzene NAPL

Example: equilibrium with gasoline

Gasoline is complex mixture – mole fraction is difficult to determine and varies

Benzene = 1 to several percent (Cline et al., 1991)

Based on analysis reported by Johnson et al. (1990):

$X_t = 0.0093$ for benzene in gasoline

$$C_G = X_t (P^\circ/RT) = 0.0093 (0.32) = 0.003 \text{ g/L}$$

Concentration in equilibrium with gasoline is 100-fold less than in equilibrium with pure benzene

Gas to solid partitioning

Only a factor in very dry soils

If relative humidity in soil gas $> 90\%$ (almost always the case in soils), then solid grains are coated with water film

Gas to solid partitioning is highly nonlinear, not much studied, and not well understood

Liquid to solid partitioning (adsorption)

Linear adsorption isotherm: $C_S = K_d C_W$

There are also non-linear adsorption isotherm

Example: Freundlich isotherm $C_S = K_f C_W^{1/n}$

Most often, linear isotherm is assumed

Organic soil content and adsorption

Adsorption of organic chemicals is strongly influenced by the organic content of the solid

Measured as f_{OC} = fraction organic carbon (by weight)

If $f_{OC} > 0.001 \rightarrow K_d = K_{OC} f_{OC}$

f_{OC} can be measured by laboratory analysis

K_{OC} is tabulated, or predicted from K_{OW} using empirical formulae (e.g. $K_{OC} = 0.6 K_{OW}$)

K_{OW} = octanol-water partition coefficient

Other adsorption mechanisms

Adsorption also occurs on mineral surfaces, fracture faces, other inorganic solids – but with no similarly simple predictive rule as f_{OC}

Adsorption → retardation (see Lecture 3)

Best to measure retardation in field or laboratory column studies

Retardation affects contaminant movement in both liquid and gas phases

NAPL to liquid partitioning (dissolution)

Aqueous solubility – concentration in water in equilibrium with pure phase chemical

Solubility is function of size and polarity (smaller and more polar molecules are more soluble)

Solubility correlates with $K_{ow} = \frac{\text{conc. in octanol}}{\text{conc. in water}}$

Low K_{ow} → more soluble

Solubility is affected by temperature, salinity, co-solvents

Solubility of mixtures

For compound mixtures, analog of Raoult's Law applies:

$$C_W = X_t C_W^\circ$$

C_W° = concentration in equilibrium with pure phase

Using benzene and gasoline as examples:

$$C_W^\circ = 1800 \text{ mg/L for benzene}$$

$$C_W = 17 \text{ mg/L for benzene in gasoline with } X_t = 0.0093$$

This approximate concentration is found in field measurements by Cline et al. (1991)

Surface effects in dissolution

See Luthy, R., A. Ramaswami, S. Ghoshal, and W. Merkel, 1993. Interfacial Films in Coal Tar Nonaqueous-Phase Liquid-Water Systems. *Environmental Science & Technology*. Vol. 27, No. 13, Pg. 2914-2918. December 1993.

Fresh drop of coal tar

**Aged three days, after fluid
withdrawn from inside**

Co-solvent effects in dissolution

Presence of co-solvents may enhance solubility

Example: presence of alcohol increases solubility of organic compounds

MTBE (up to 11% by volume in gasoline) may enhance solubility of BTEX

Vapor density

Vapor density is proportional to molecular weight
(assuming compound is at boiling point)

$$V_d = \frac{P^\circ \text{ MW}}{RT}$$

Want to know vapor density relative to air density to
understand environmental behavior

Density of dry air = 29 g/mol

Relative vapor density

More useful than Vapor Density is Relative Vapor Density (RVD)

RVD = density of vapor-saturated air at 1 atm, 25°C to dry air:

$$\text{RVD} = \frac{\frac{\text{Vapor fraction}}{760} \text{MW} + \frac{\text{Air fraction} (760 - P^\circ)}{760} 29}{29} \quad \text{for } P^\circ \text{ in mm Hg}$$

Example Relative Vapor Densities

Compound	Molecular weight	Vapor density	RVD
Benzene	78	2.7	1.17
TCE	131.5	4.5	1.35
PCE	165.8	5.7	1.12
Gasoline	~100 to 115	~3.3	~1.02

Vapor-phase transport

Diffusion is enhanced in gas phase (D is higher)

Differential pressure in soil gas → advection

Advection in basements of buildings:

Houses are under negative pressure due to advection of hot air out chimneys and furnace flues

Cracks in basement floors and walls provide pathway for gas transport

Vapors tend to travel to and into homes!

Atmospheric pumping

Constant small exchange between atmosphere and soil

Density-driven transport due to relative vapor density

Factors affecting NAPL movement

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Porous medium:

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Ground water:

- Water content
- ✓ Velocity

NAPL movement

NAPL has different viscosity and density from water
Therefore, the aquifer “looks” different to NAPL

Definition of hydraulic conductivity: $K = \frac{k\rho g}{\mu}$

K = hydraulic conductivity (or coefficient of permeability) [L/T]

ρ = fluid density [M/L³] – function of fluid

μ = dynamic viscosity [M/TL] – function of fluid

k = intrinsic permeability [L²] – function of porous medium

g = gravitational acceleration [L/T²]

NAPL movement

$$K = \frac{k\rho g}{\mu}$$

Higher viscosity → lower K → slower flow

Examples: colder ground water, fuel oil

Lower viscosity → higher K → faster flow

Example: TCE vs. water

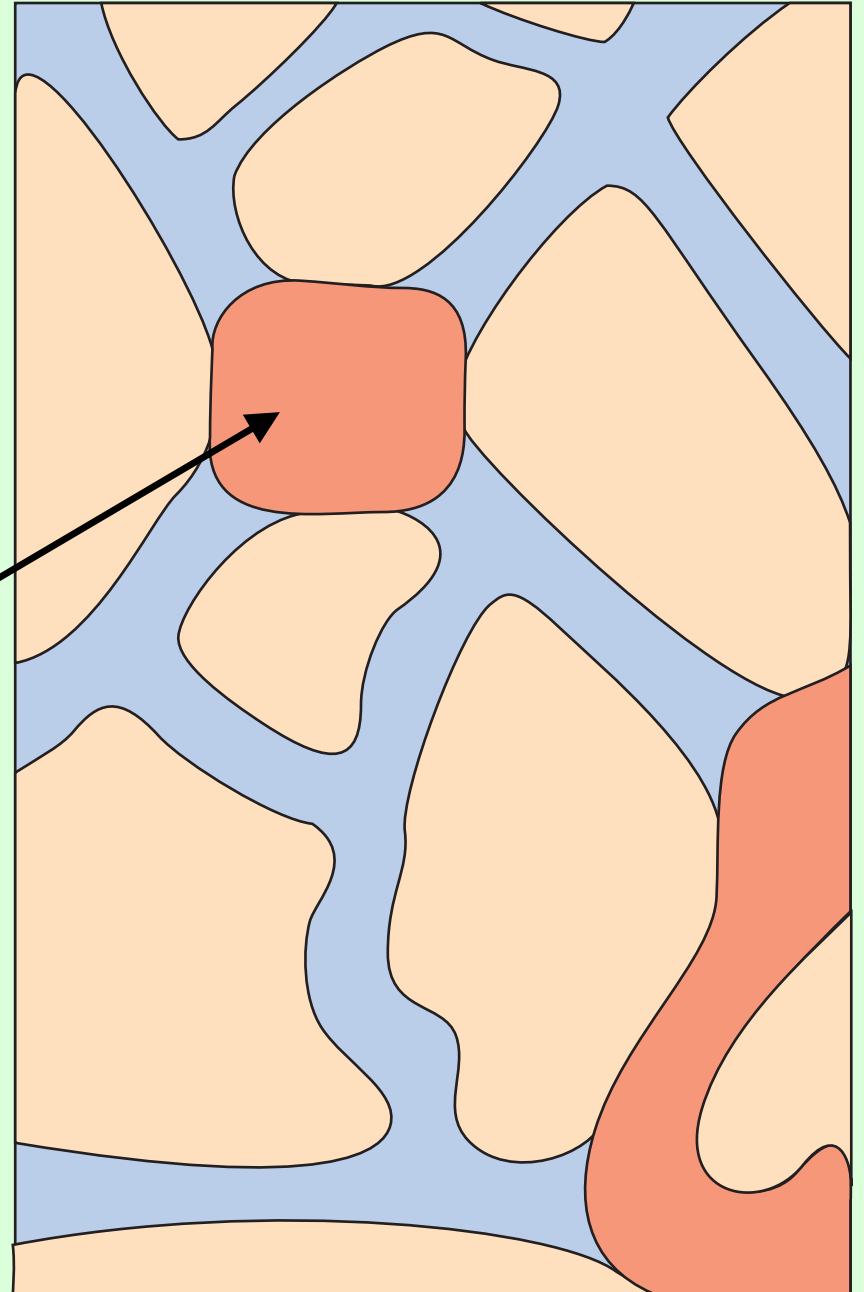
	ρ (g/cm ³)	μ (centipoise)	K
Water	1.0	1.0	K_{WATER}
TCE	1.46	0.56	$2.6 K_{\text{WATER}}$

Note: 1 poise = g/cm/sec

Two-phase flow

Movement of two phases
causes restrictions relative to
movement of single phase

NAPL blocks path
For water movement

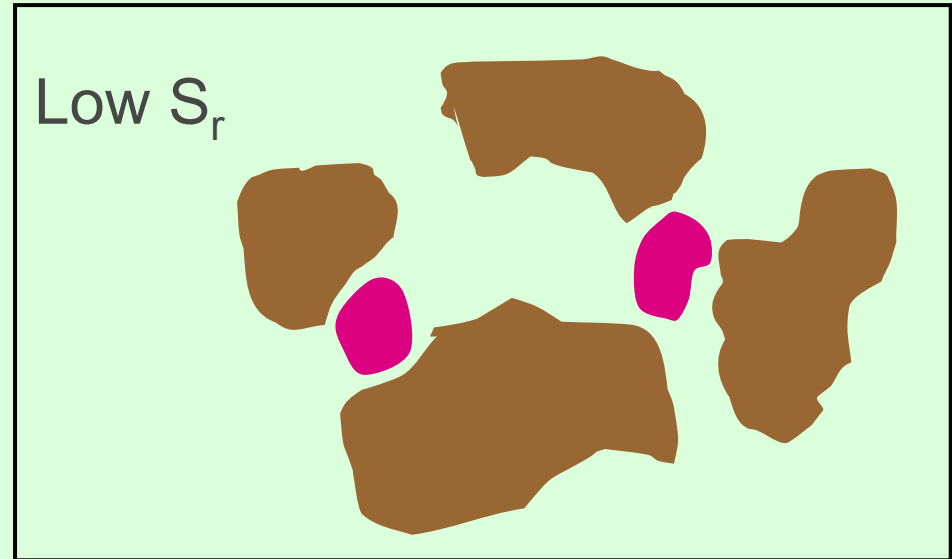


Relative permeability

Relative permeability, K_r

Depends upon relative saturation, S_r :

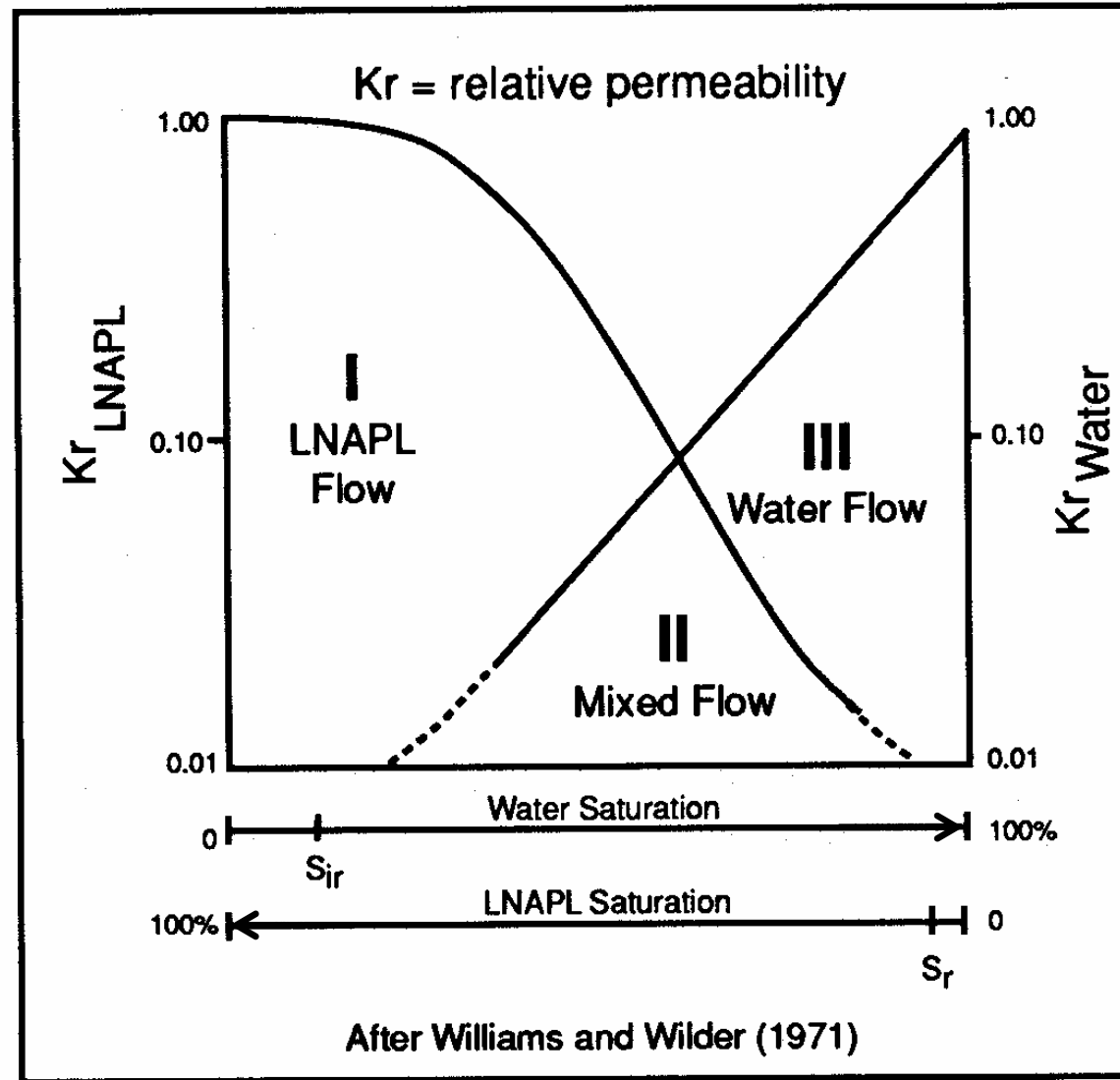
$$S_r = \frac{\text{volume of NAPL}}{\text{volume of voids}}$$



Relative permeability

Three NAPL-water flow regimes:

- I NAPL is continuous phase, K_{WATER} is low
- II Both NAPL and water continuous, K_{WATER} and K_{NAPL} reduced
- III Water is continuous phase, K_{NAPL} is low

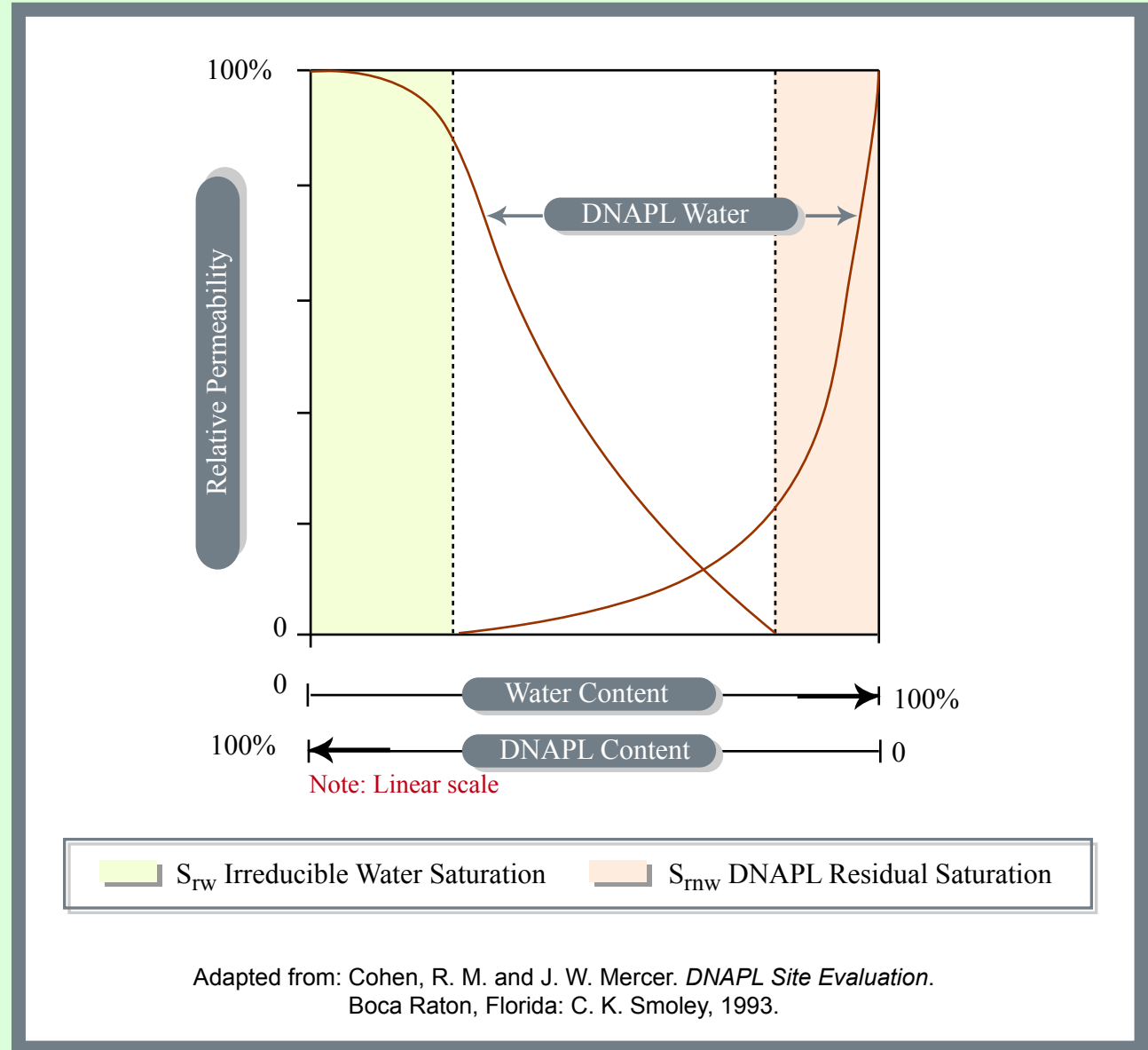


Note: log scale

Figure 4. Hypothetical relative permeability curves for water and an LNAPL in a porous medium.

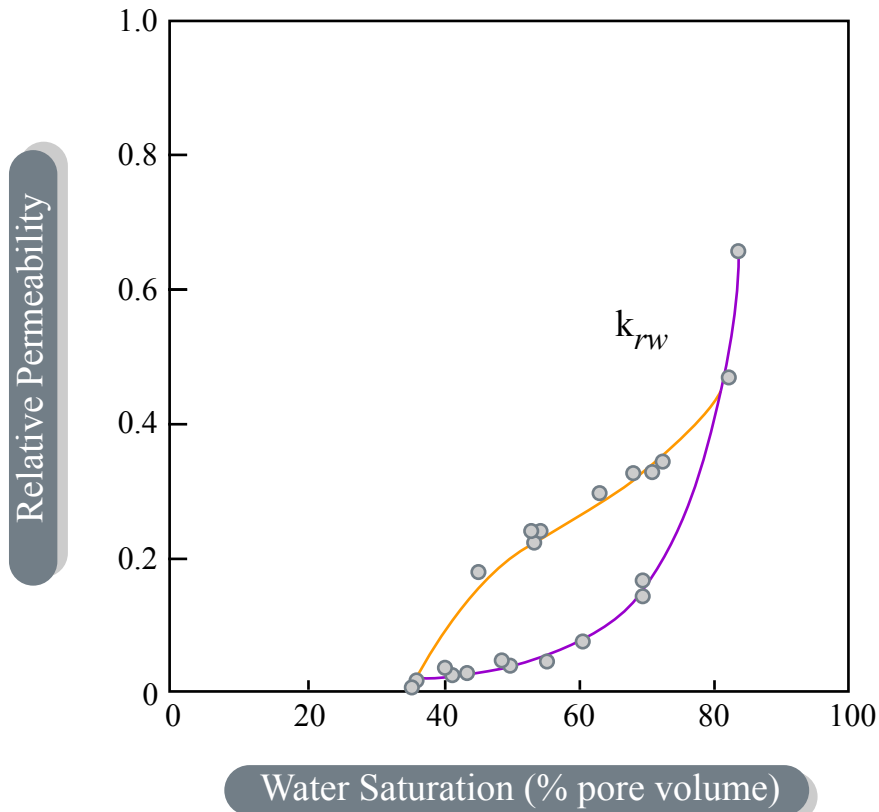
Relative permeability

Note behavior at extremes of water and NAPL saturation: residual water and NAPL exert significant effect on K_r

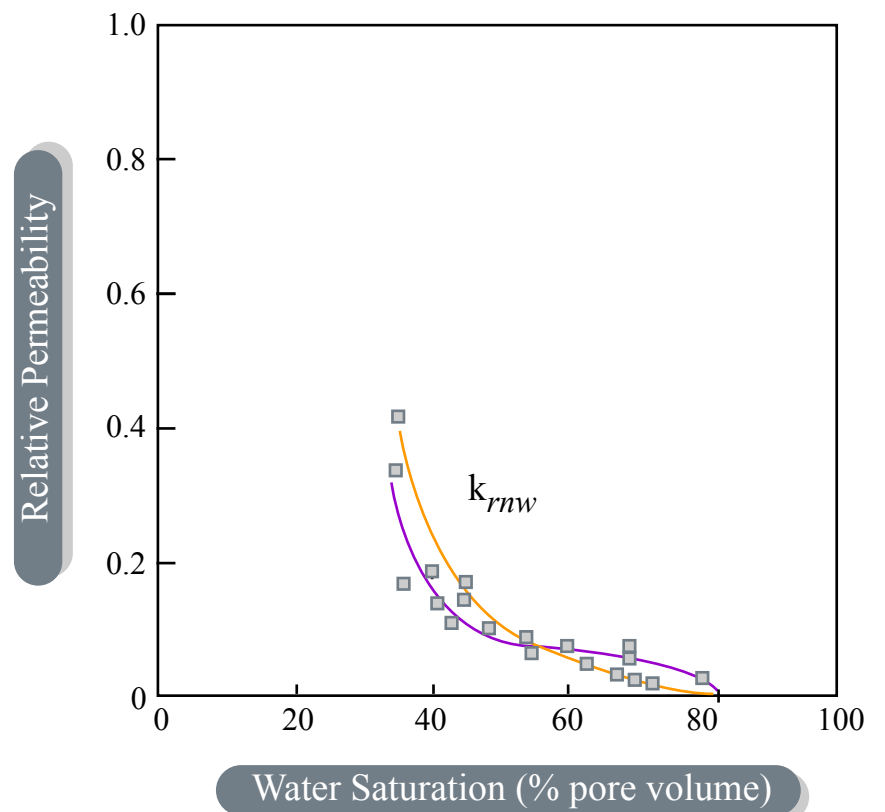


Observation of relative permeability

Relative Permeability for Water



Relative Permeability for TCE



— Injection of water — Injection of TCE