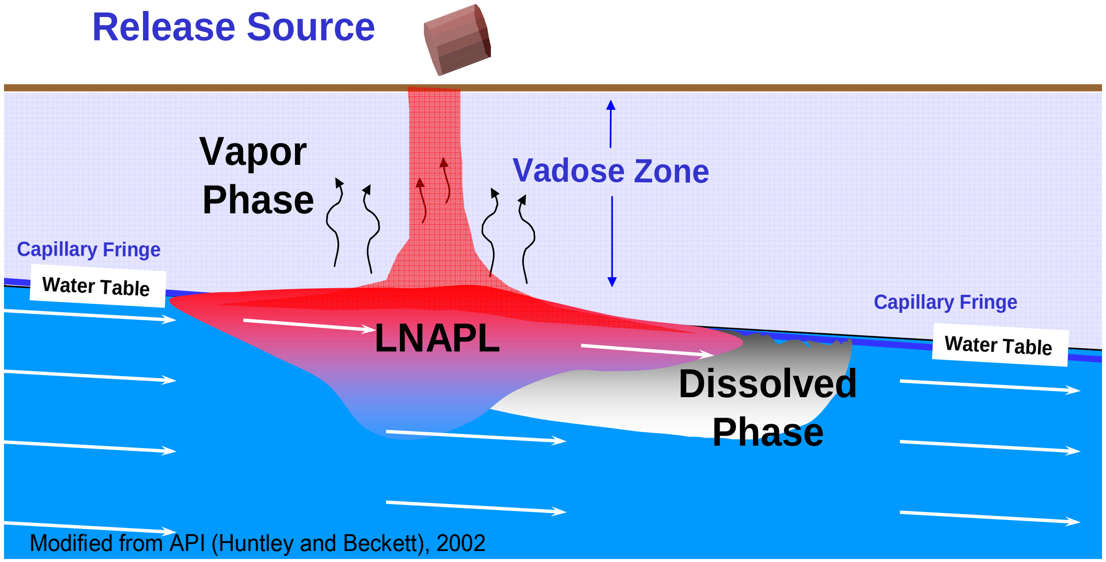
New Approaches and Tools for Evaluating LNAPL Mobility



Modified from API (Huntley and Beckett), 2002

Remtech 2009
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Banff, Alberta

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Golder Associates

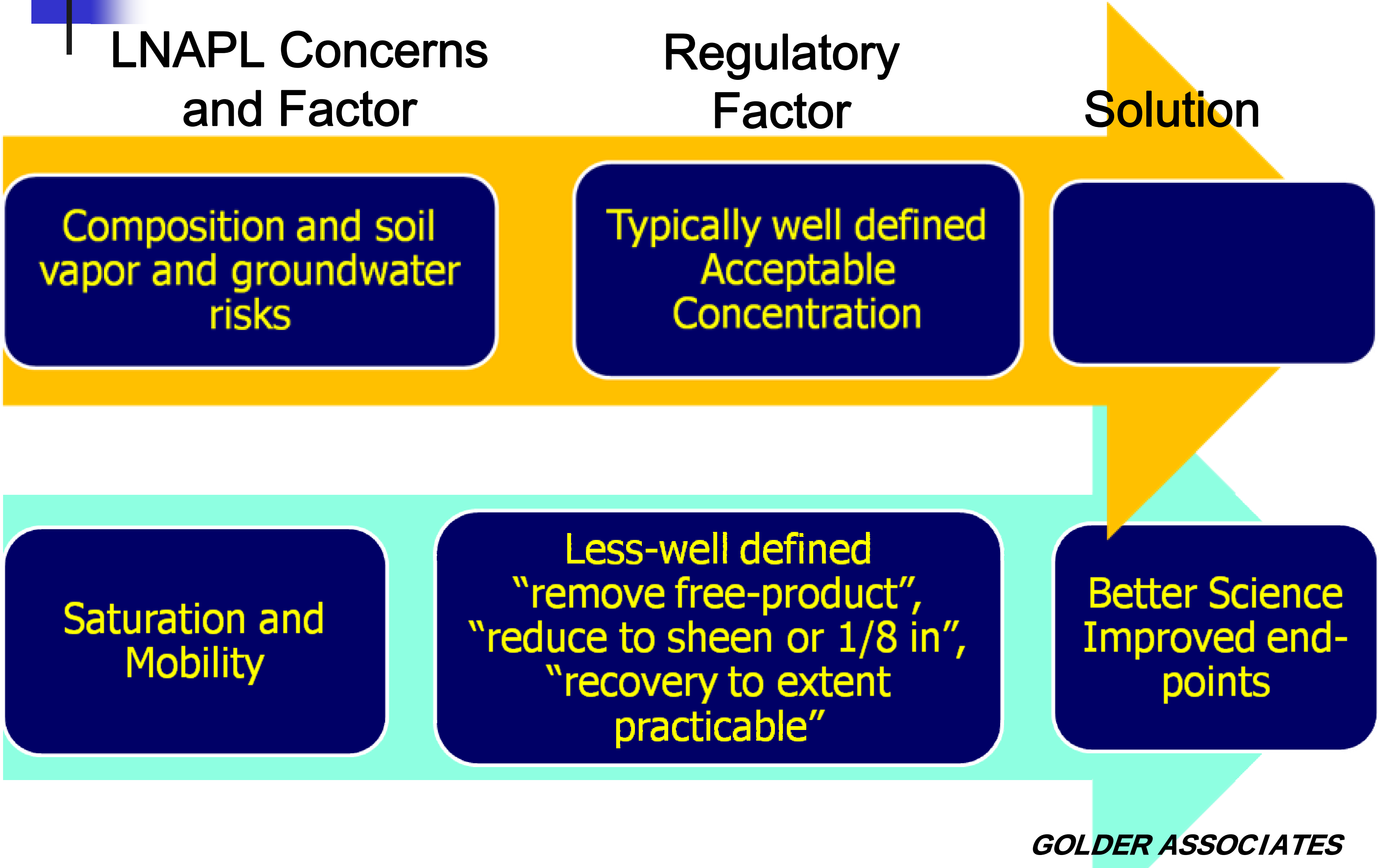
Presentation Outline

- LNAPL Management Paradigm
- LNAPL Basics
- LNAPL Distribution
- LNAPL Movement
- LNAPL Models
- Lines of Evidence Approach for Evaluation of LNAPL Mobility

LNAPL Management Paradigm

LNAPL Concerns	Controlling Factor	Solution
Explosive hazards Dissolved-phase concentration Vapor-phase concentration Direct contact or ingestion	**Composition and Concentration**	Cut-off/treatPathway Change LNAPL Composition Remove mass (?)
Mobility (spreads and creates new or increased risk) Visual aesthetics	**Saturation**	Reduce Saturation (Recovery) Stabilization

LNAPL Management Paradigm



LNAPL Concerns and Factor	Regulatory Factor	Solution
Composition and soil vapor and groundwater risks	Typically well defined Acceptable Concentration	
Saturation and Mobility	Less-well defined “remove free-product”, “reduce to sheen or 1/8 in”, “recovery to extent practicable”	Better Science Improved end-points

Residual Saturation

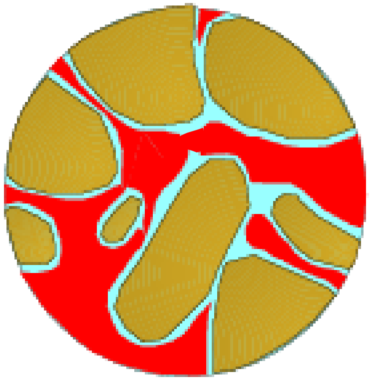
LNAPL Saturation (S_o)

Fraction of pore space occupied by LNAPL

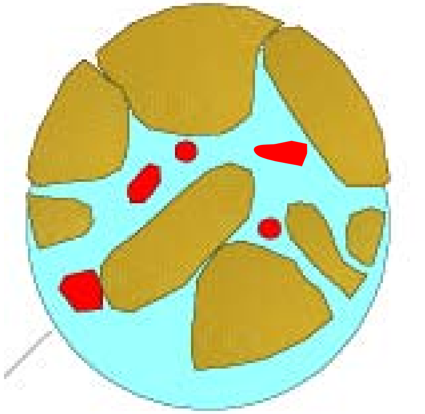
Residual LNAPL Saturation (S_{or})

Saturation at which NAPL becomes discontinuous and is immobilized by capillary forces under ambient groundwater flow conditions” (Mercer and Cohen, 1990).

➡ Key Point: LNAPL only observed in well if $S_o > S_{or}$



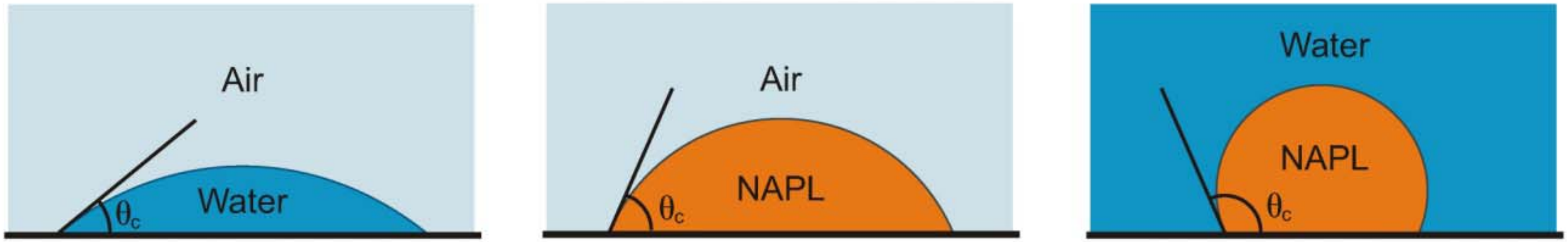
$S_o > S_{or}$



$S_o < S_{or}$

Wetting

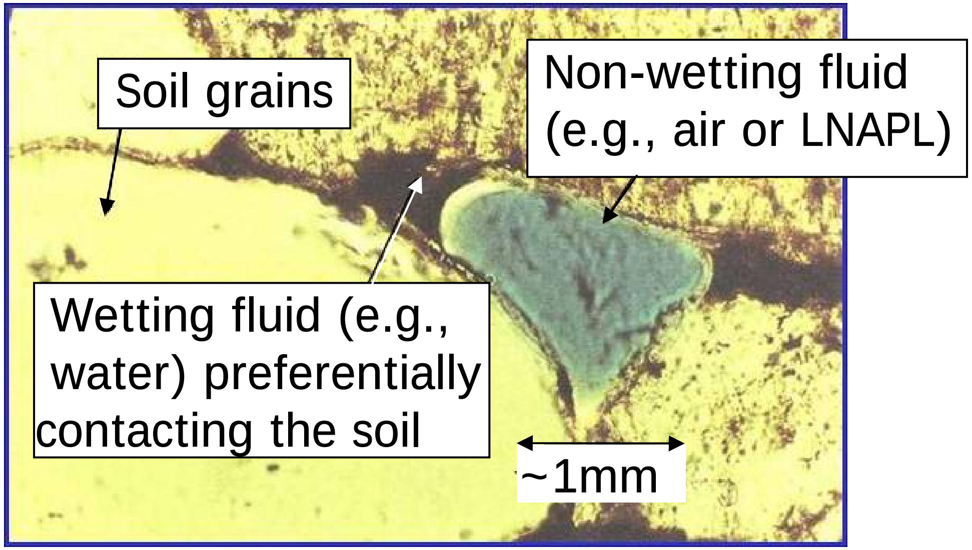
- Phase with smaller contact angle preferentially covers the surface and is called the wetting phase; is a function of the interfacial tension
  - NAPL-water system: Water is wetting, NAPL is non-wetting



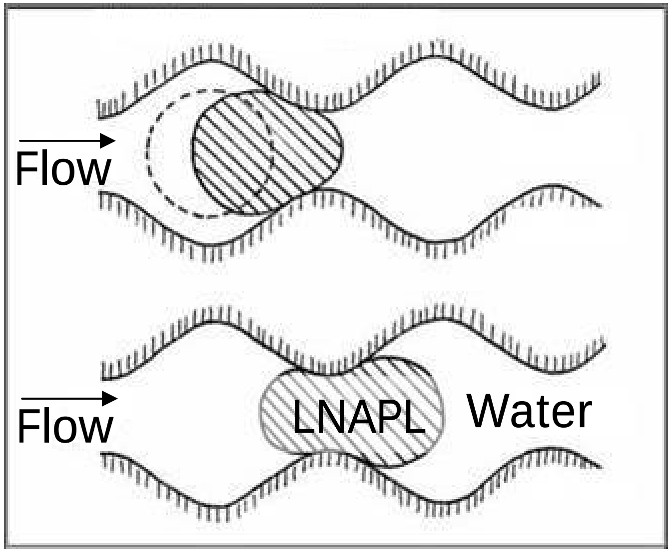
- NAPL-air system: NAPL is wetting, air is non-wetting

LNAPL Movement in Water-wet Soil Pores

From API Bulletin 18



For water wet media



- LNAPL will only move into water-wet pores when entry pressure (resistance) is overcome

LNAPL Movement into Water-wet Soil Pores

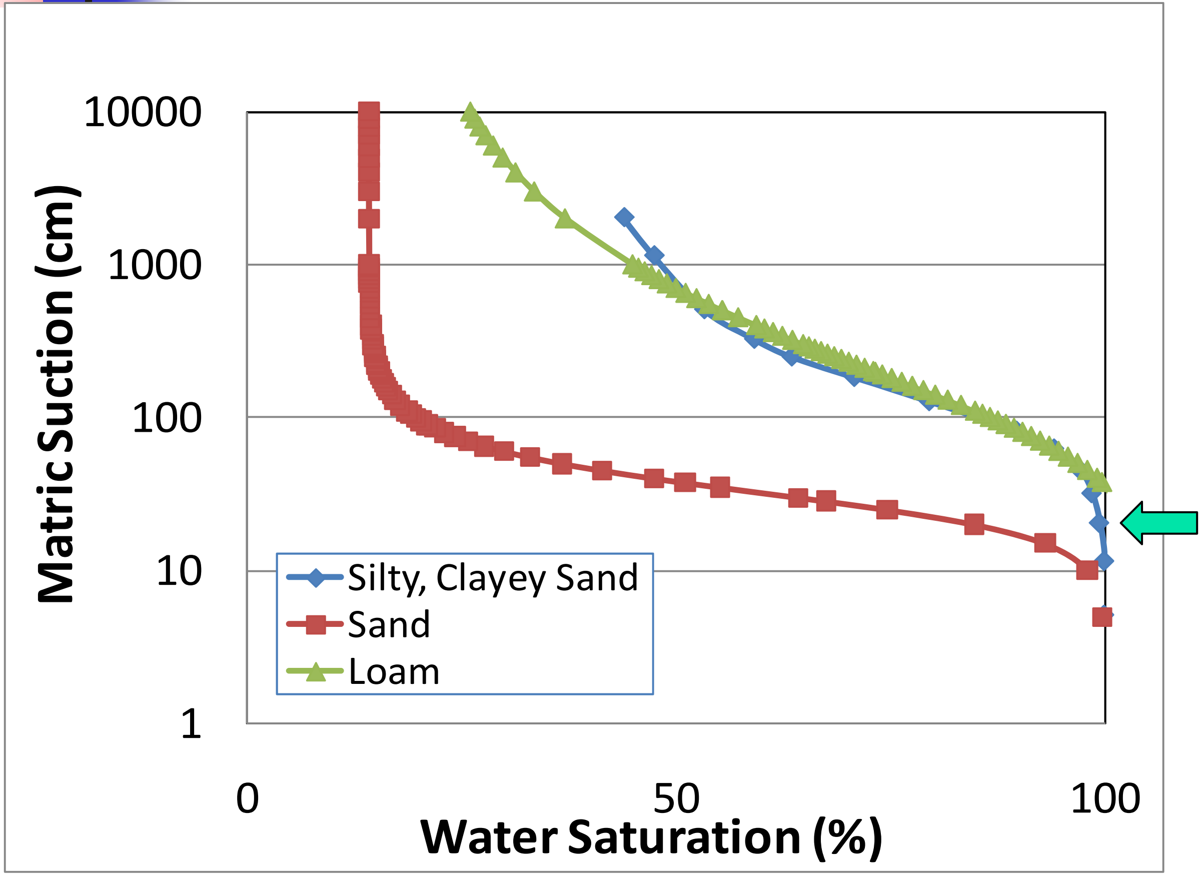
Capillary pressure or head that must be overcome for LNAPL to enter water-wet pores is called **Displacement Head**

$$h_d = \frac{2\sigma\cos\phi}{r(\rho_W - \rho_o)g}$$

- h_d proportional to wetting fluid contact angle, water-LNAPL interfacial tension and LNAPL density
- h_d inversely proportional to pore radius

Key Point: More difficult for LNAPL to move into fine-grained soil (small pore radius)

Water Retention Curves for Different Soil Types



Can be scaled from air-water to LNAPL-water system

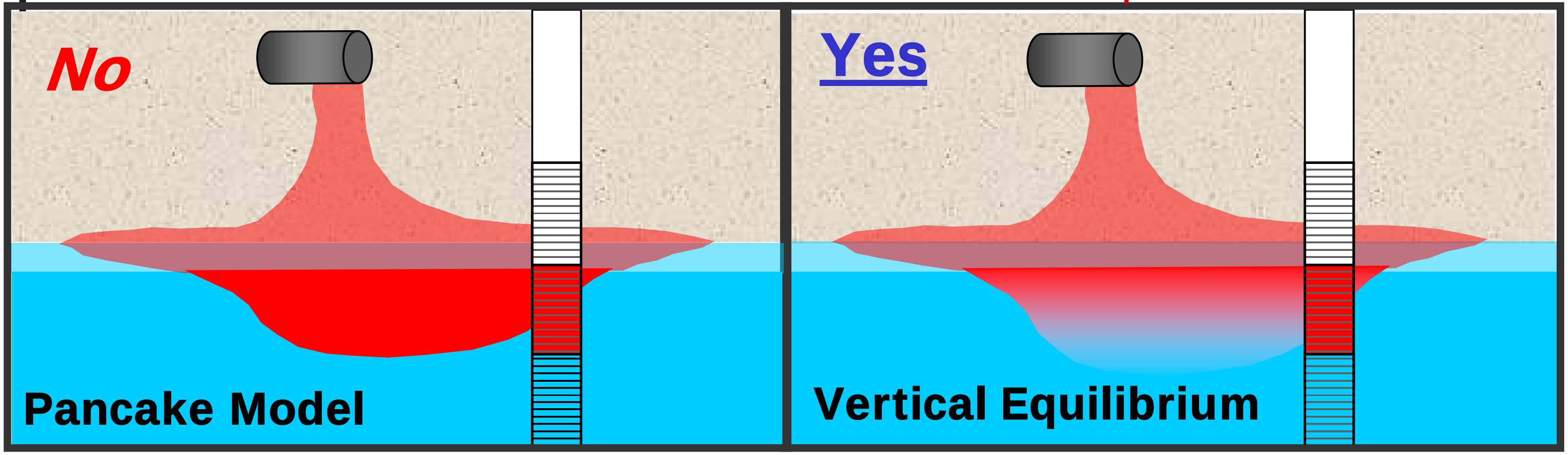
Displacement or air-entry pressure ("bubbling pressure") for air-water system

Key Point: More difficult for water to be displaced from fine-grained soils

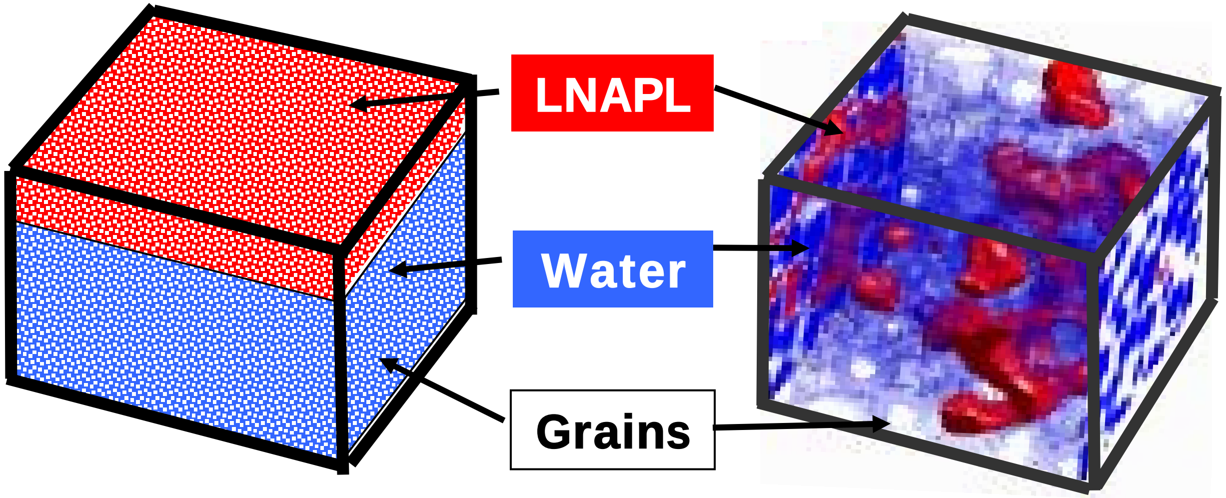
Vertical LNAPL Distribution

From ITRC (2009)

Pancake Model vs. Vertical Equilibrium Model



- Assumes LNAPL floats on water table
- Uniform LNAPL saturation



- LNAPL penetrates below water table
- LNAPL and water coexist in pores

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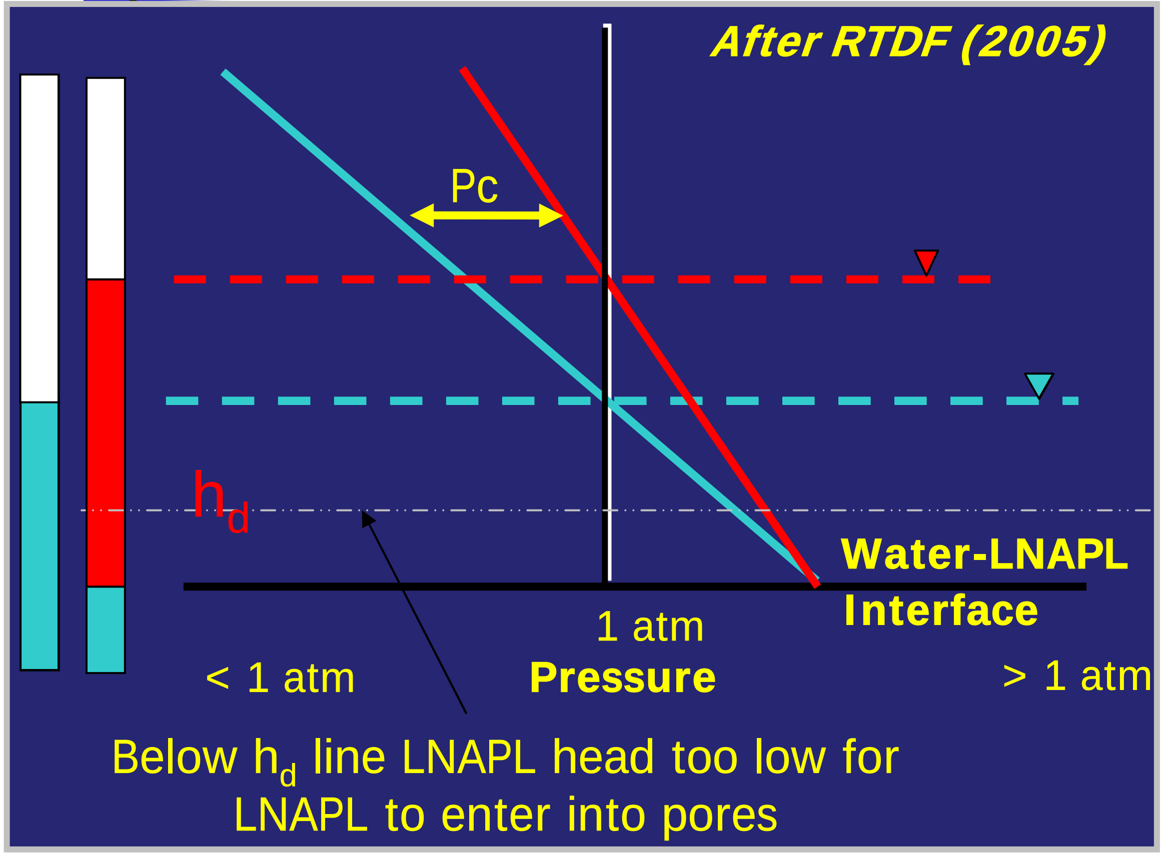
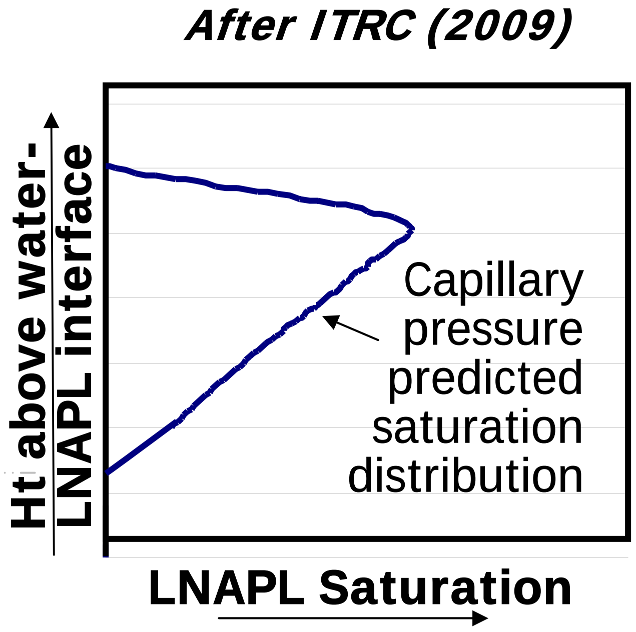
Vertical LNAPL Distribution from Capillary Pressure


After RTDF (2005)

Below h_d line LNAPL head too low for LNAPL to enter into pores

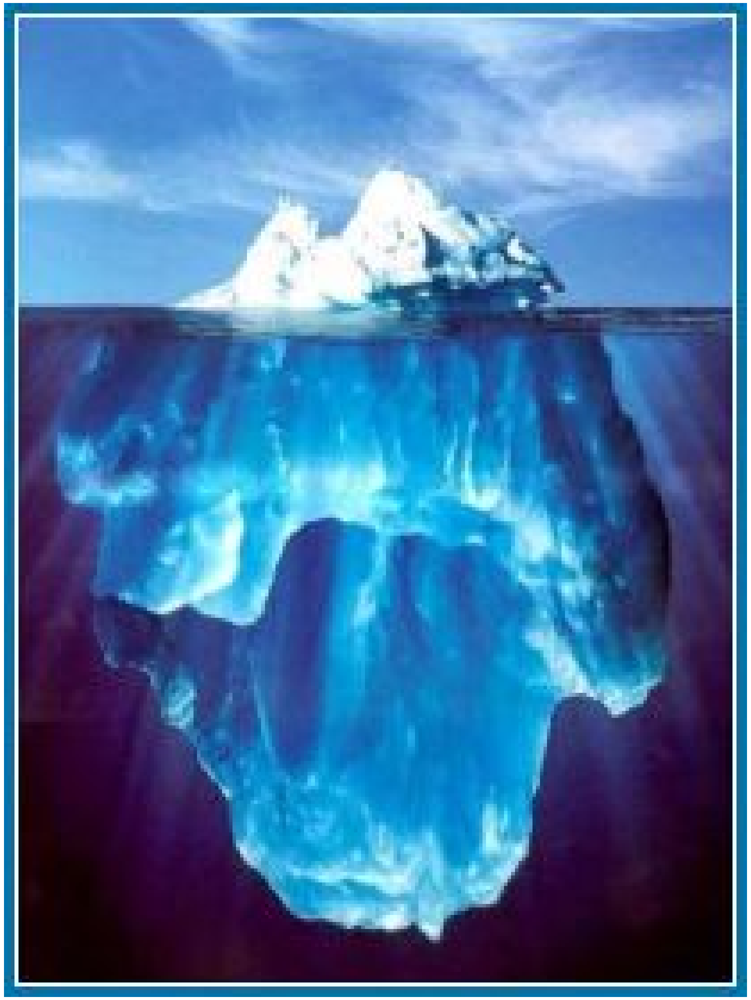

After ITRC (2009)

Capillary pressure predicted saturation distribution

P_C = non wetting pressure – wetting phase pressure

Key Point: Vertical LNAPL saturation is variable, some LNAPL is present below water table

Iceberg Analogy



Note: Picture is not real, digital composite.

http://www.athropolis.com/news/berg-pic.htm

Prediction of Vertical LNAPL Saturation Profile

In-well LNAPL Thickness

Vertical (static) Equilibrium Model (VEQ)

Assumes static water table & homogenous soil

Capillary pressure-saturation relationship
(e.g.,van Genuchten, Brooks-Corey)

Scaling parameters to go from air-water to oil-water system

Vertical LNAPL Saturation Profile

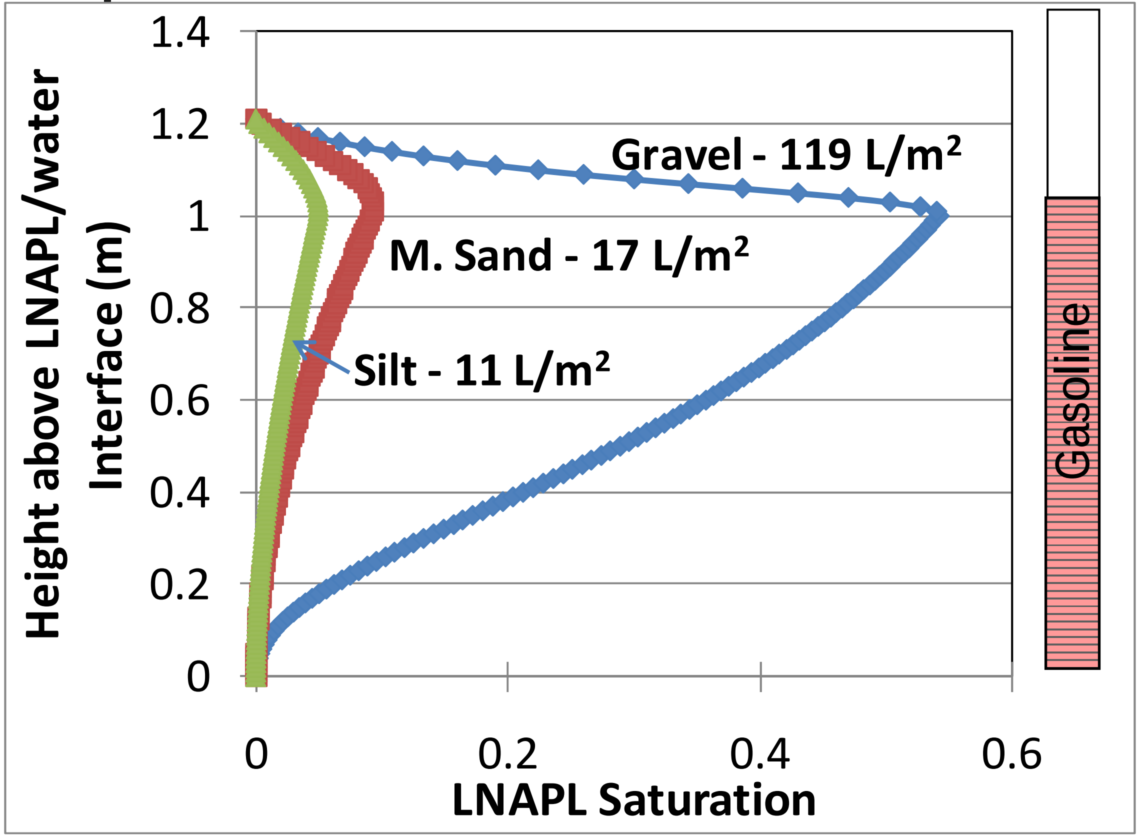
- Available tools include:
  - API LNAPL Distribution and Recovery Model (LDRM) (API 4760)
  - API Interactive LNAPL Guide

Vertical Equilibrium (VEQ) Model

- Uncertainty introduced VEQ model through:
  - Fluctuating water table and LNAPL thickness
  - Geologic heterogeneity
  - Uncertainty in capillary parameters and other soil properties
  - Uncertainty in residual saturation
- Consequently VEQ model is highly approximate and should be used with caution

Vertical LNAPL Saturation Predicted using VEQ Model

Calculated using API Interactive Guide (for 1 m product)



Specific volume, D_n, is LNAPL volume per unit area (L/m²)

$$D_n = A_n \theta (H \bar{S}_o)$$

H = Interval over which S_o calculated

$\bar{S}_o$ = average LNAPL saturation

A_n = unit area

θ = porosity

- Key Point: For given LNAPL thickness, LNAPL saturations greatest for coarse-grained soils – what are the remedial implications?

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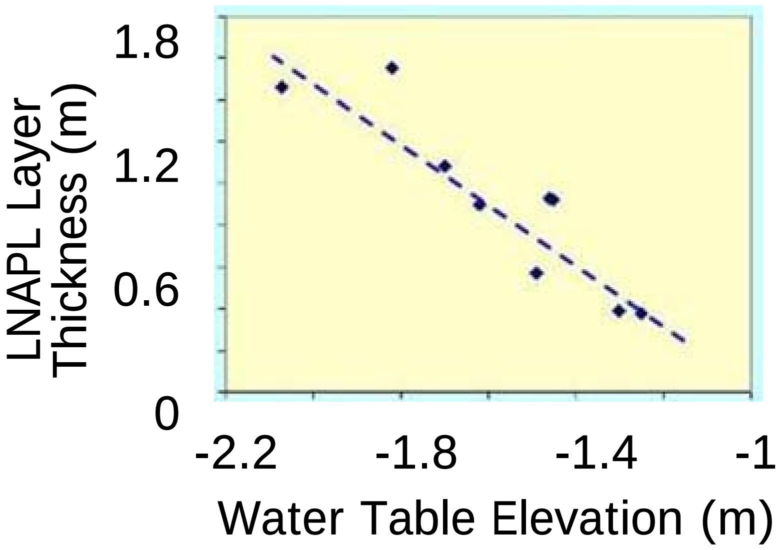
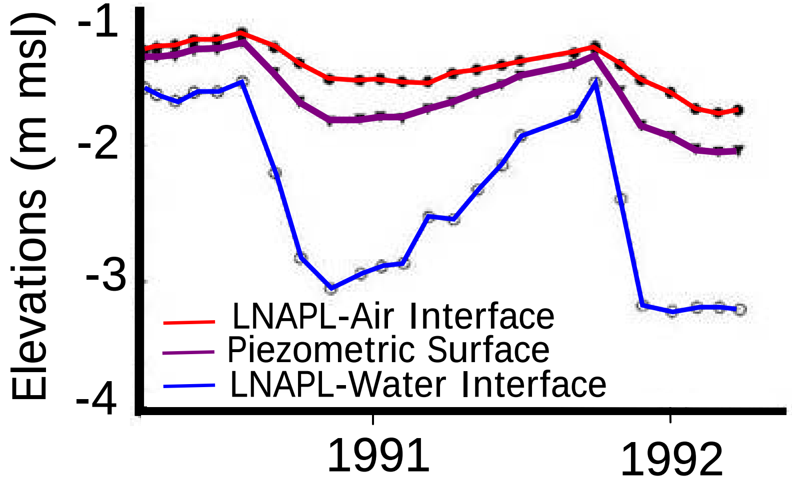
In-well LNAPL Thickness vs. Water Table Height (Unconfined Aquifer)

From Huntley et al. (1994)





Key Point: In-well LNAPL thickness increases with declining water table for unconfined aquifer

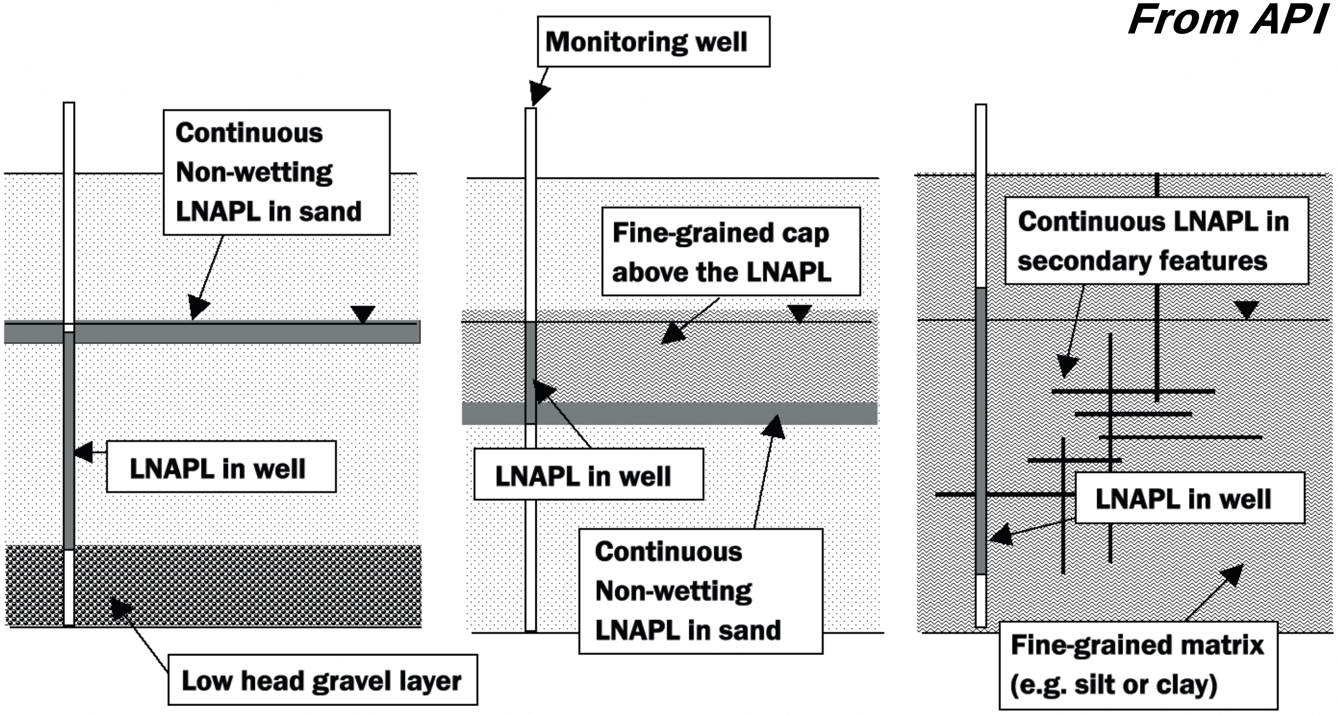
In-Well LNAPL Thickness for Geologically Complex Settings

1) Underlying low head gravel draws LNAPL down the well

2) A fine grained layer above the LNAPL acts as a cap

3) LNAPL is limited to secondary joints and seams

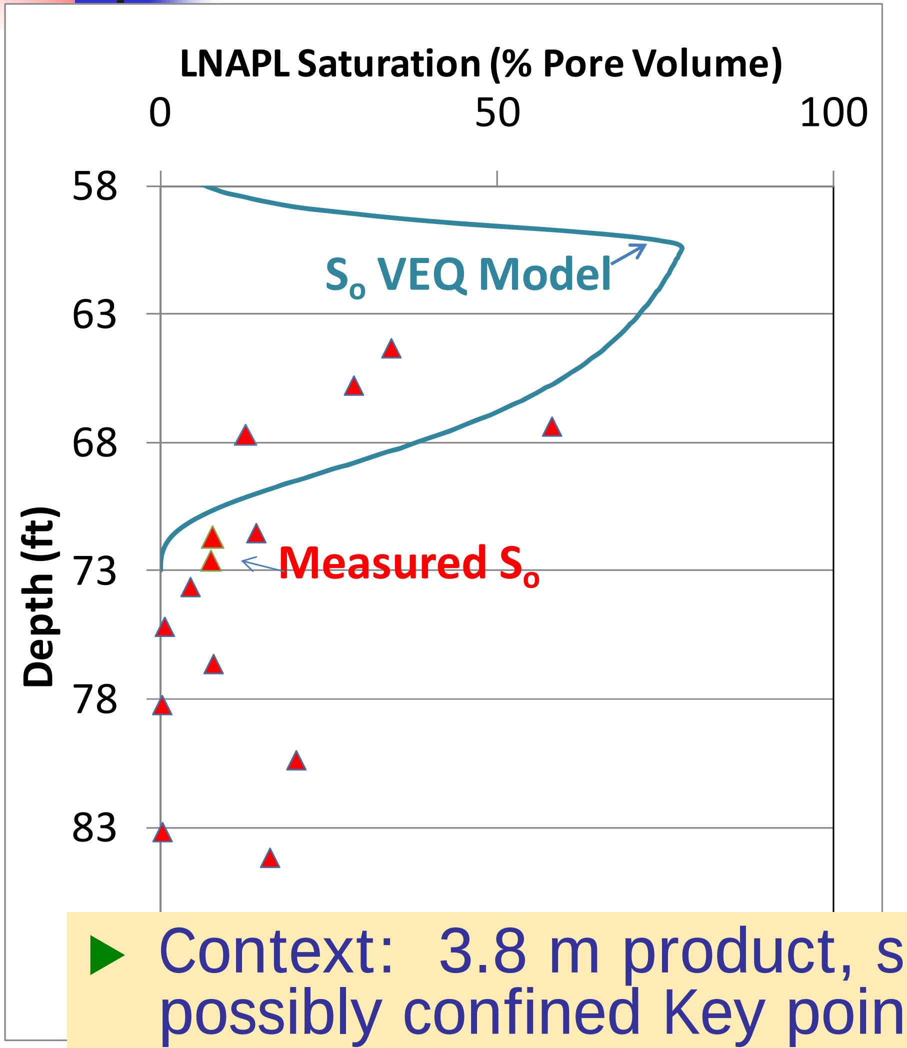
From API Bulletin 18

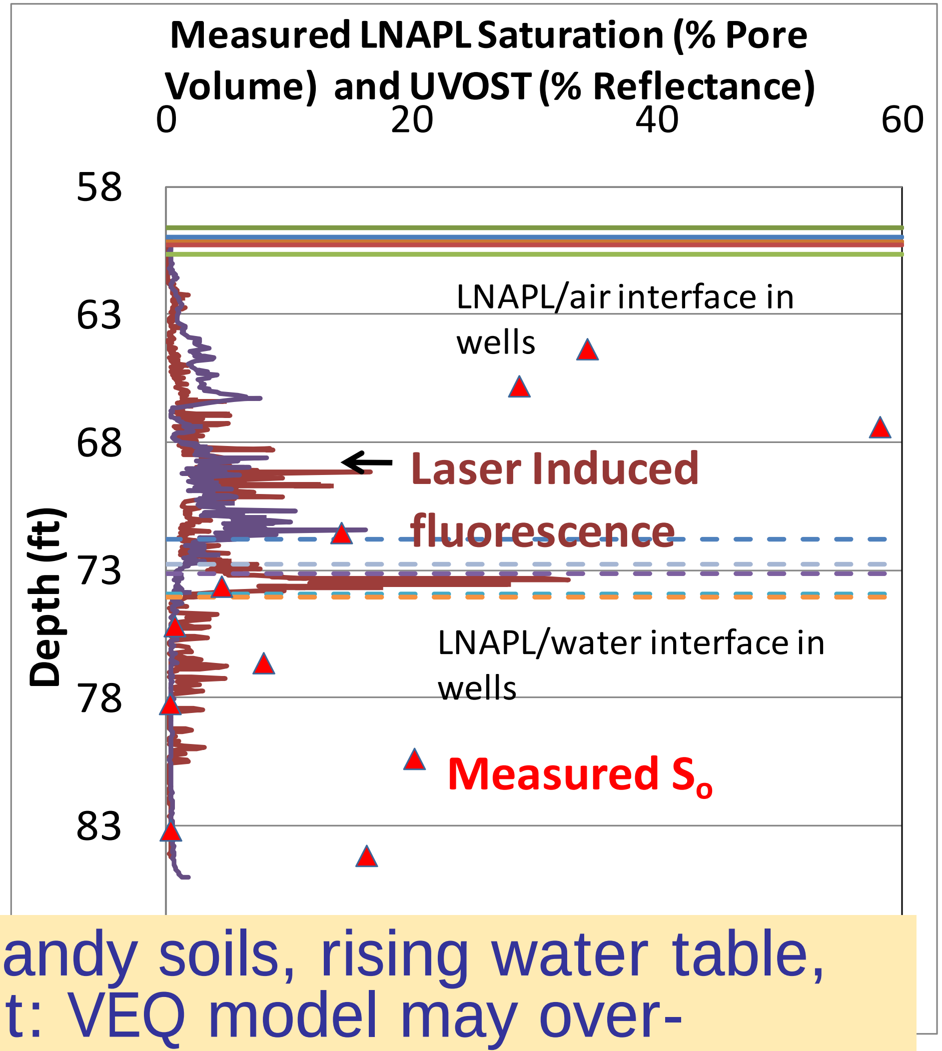


Key Point: Geologic variability can result in exaggerated in-well LNAPL thicknesses

Measured and Modeled LNAPL Saturations

From ExxonMobil





- Context: 3.8 m product, sandy soils, rising water table, possibly confined Key point: VEQ model may over-predicted saturation (use with caution)

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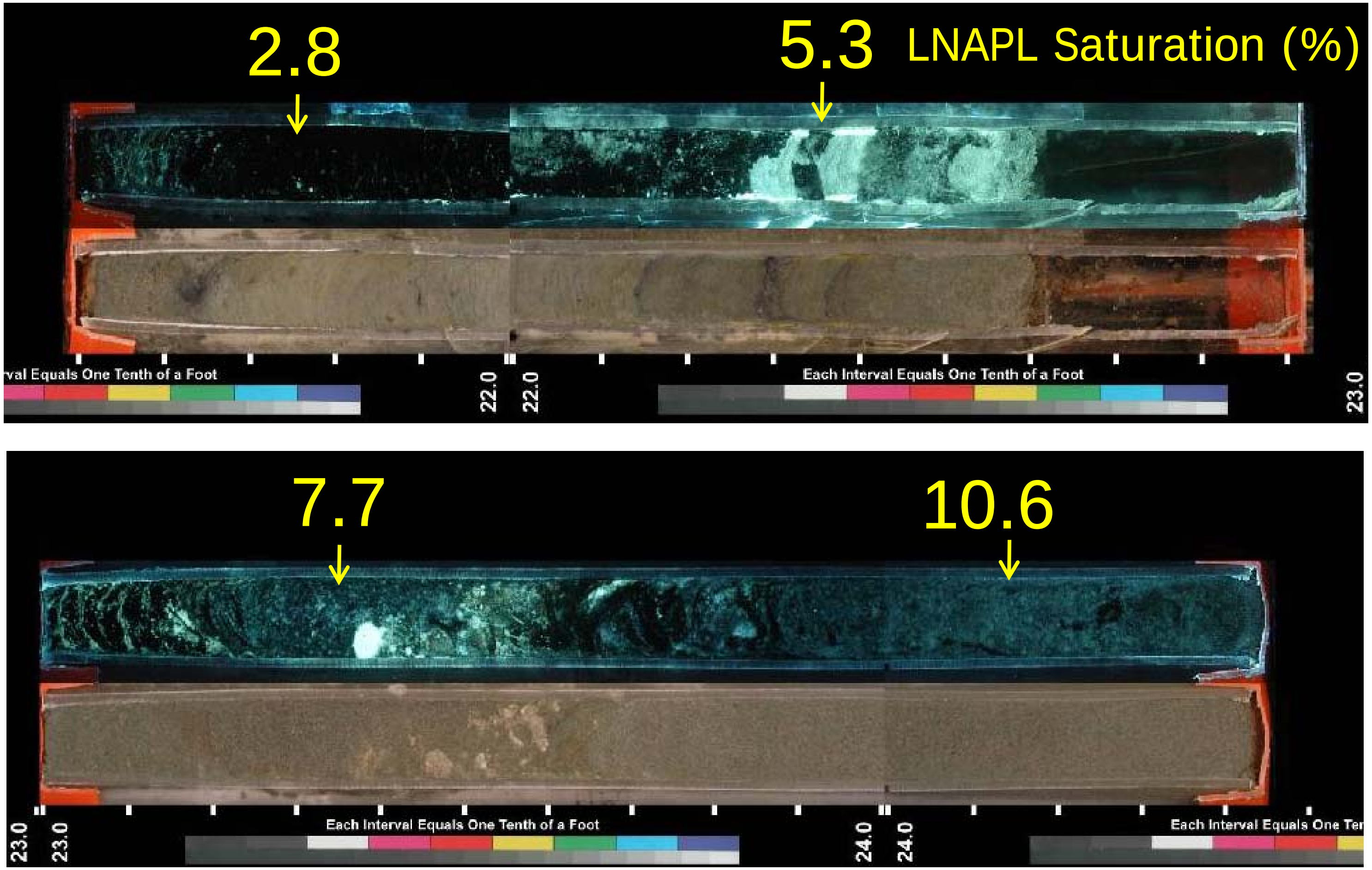
LNAPL Saturations Are Not Uniform

From ExxonMobil

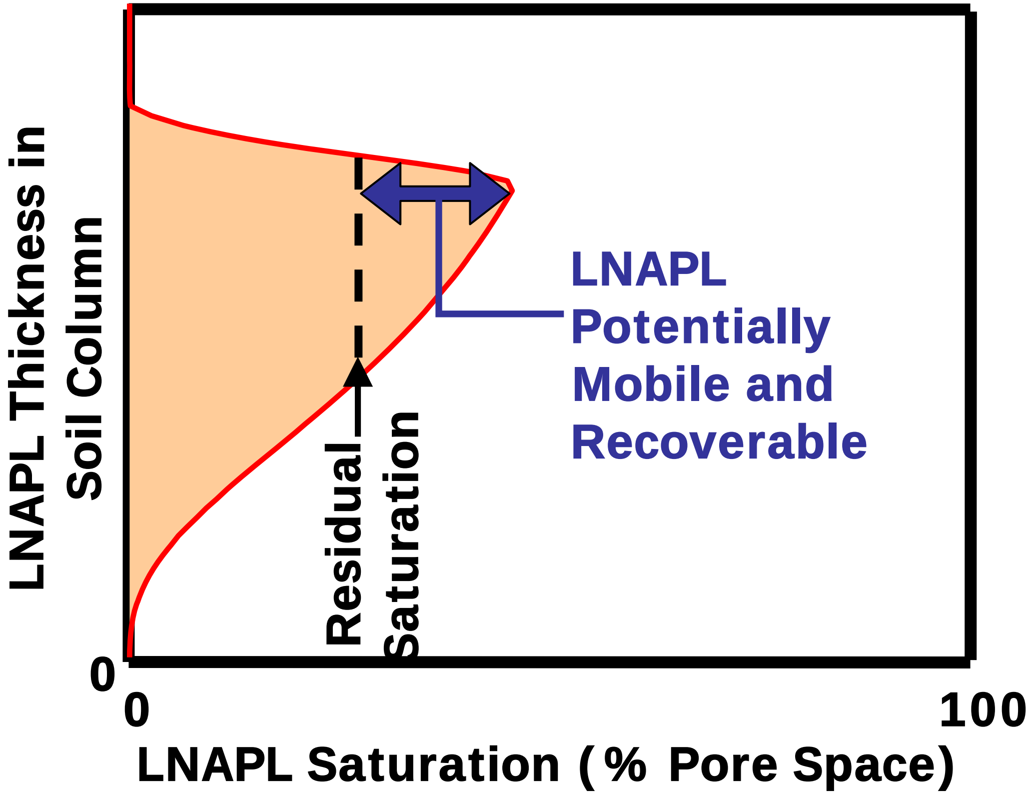


UV Light

Plain light

Potentially Mobile Fraction of the LNAPL Distribution

From Sanjay Garg (Shell)



➡ Key Point: Only LNAPL with saturation > residual saturation is potentially mobile

Darcy's Law for LNAPL

$$V_o = \frac{K_o i_o}{\theta(S_o)}$$

$$K_o = \frac{k_{ro} K_w \rho_o \mu_w}{\rho_W \mu_o}$$

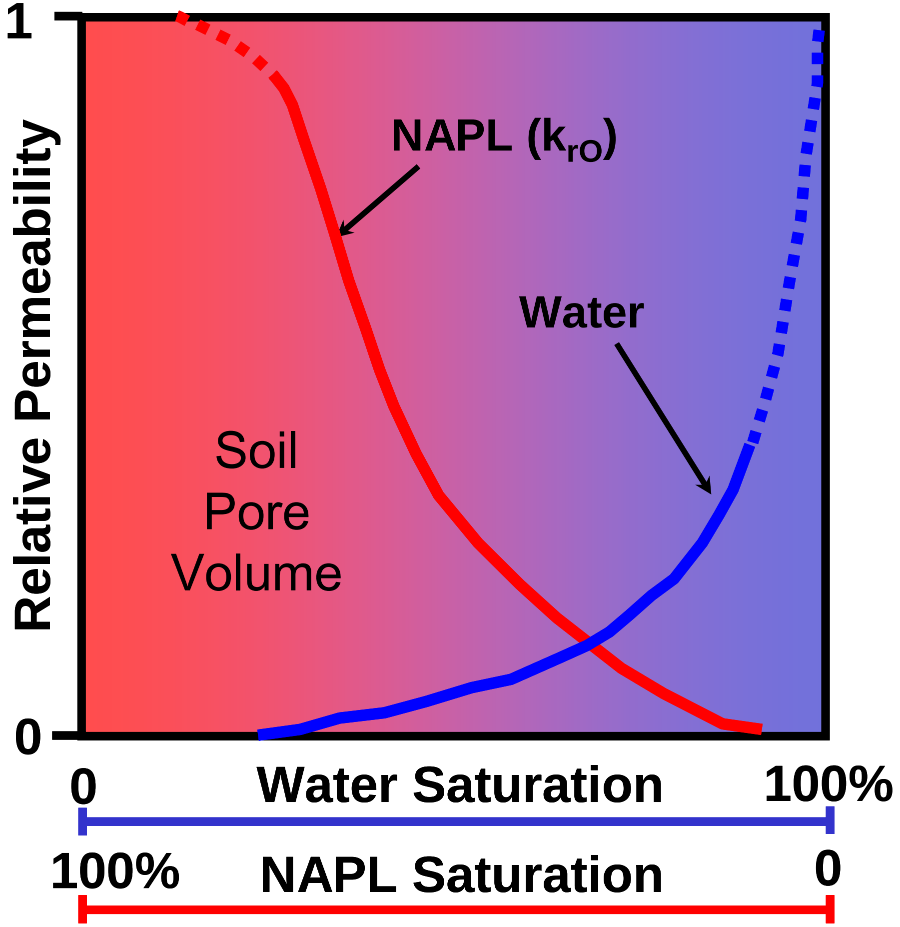
KEY PARAMETERS

Parameter	Parameter Trend	V_o
Relative Permeability of LNAPL (k_{ro})	↑	↑
LNAPL Viscosity (μ_o)	↑	↓

V_o = LNAPL seepage velocity
S_0 = LNAPL saturation
θ = total porosity
k_{ro} = relative permeability of LNAPL
g = gravitational coefficient
ρ_o = LNAPL density

ρ_w = density of water
μ_o = LNAPL viscosity
μ_w = water viscosity
i_o = LNAPL table gradient
K_w = saturated hydraulic conductivity
K_o = LNAPL conductivity

Relative Permeability

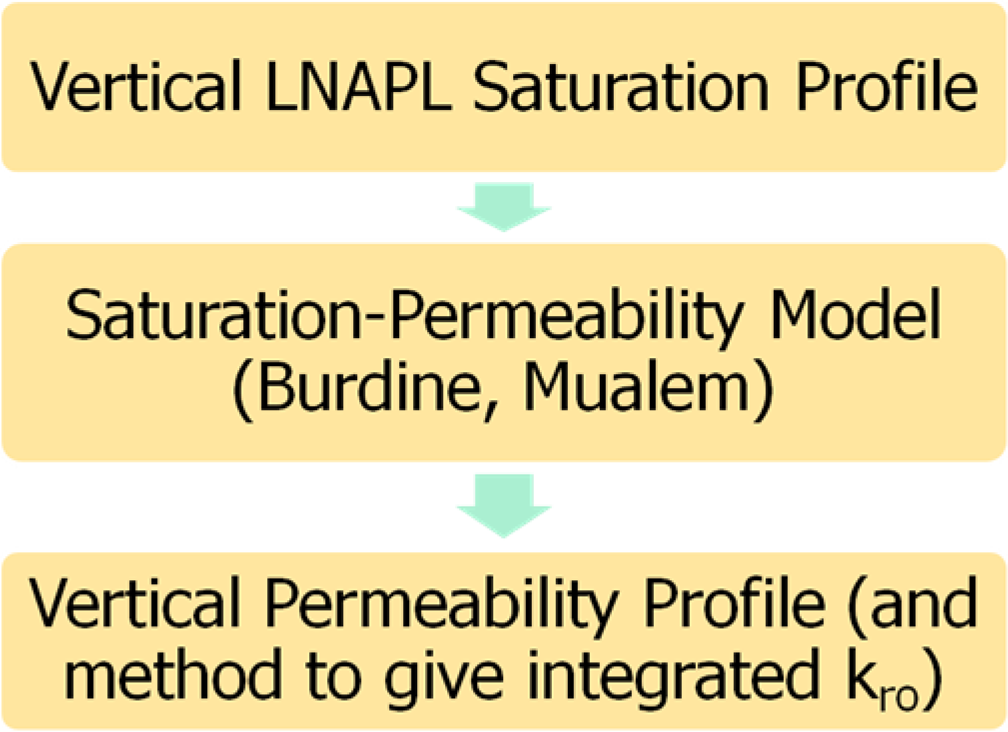


Definition: Porous media ability to allow flow of a fluid when other fluid phases are present

$$k_{ro} = f(So)$$

Key Point: Relative permeability decreases rapidly as LNAPL saturation declines from 100%

Prediction of Relative Permeability to LNAPL



Vertical LNAPL Saturation Profile

Saturation-Permeability Model (Burdine, Mualem)

Vertical Permeability Profile (and method to give integrated k_{ro})

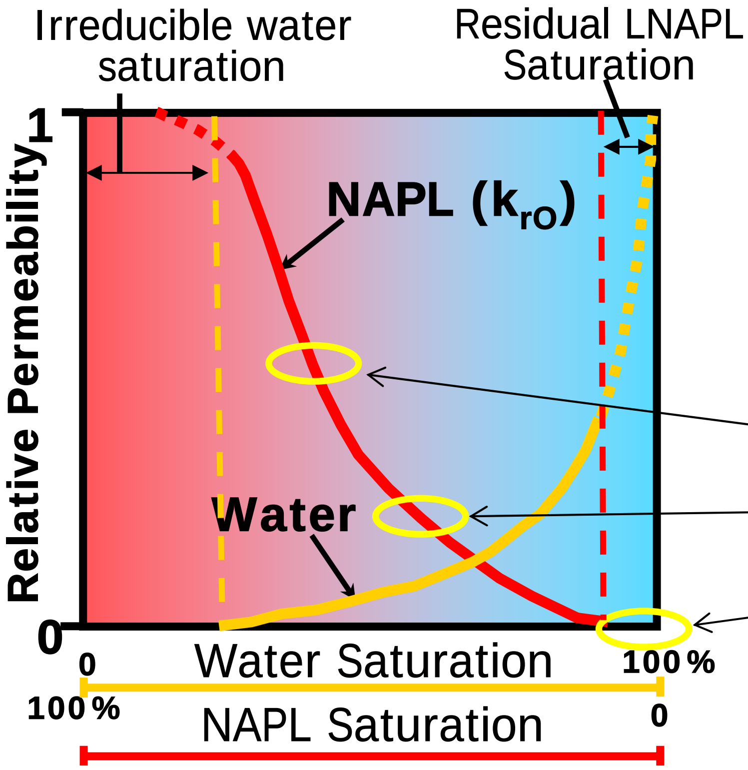
Builds on VEQ model – same cautions apply!

- Available tools include:
  - API LNAPL Distribution and Recovery Model (LDRM) (API 4760)
  - API Interactive LNAPL Guide

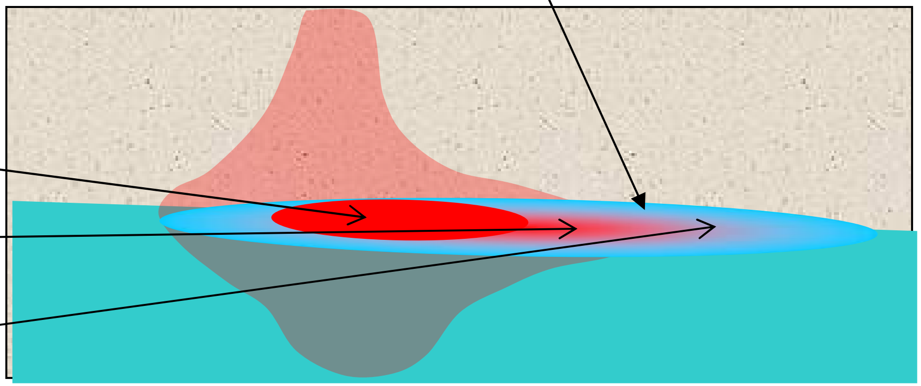
Instead of using model can also estimate K_o from baildown test at wells

Two LNAPL Mobility Concepts

Adapted from ITRC (2009)



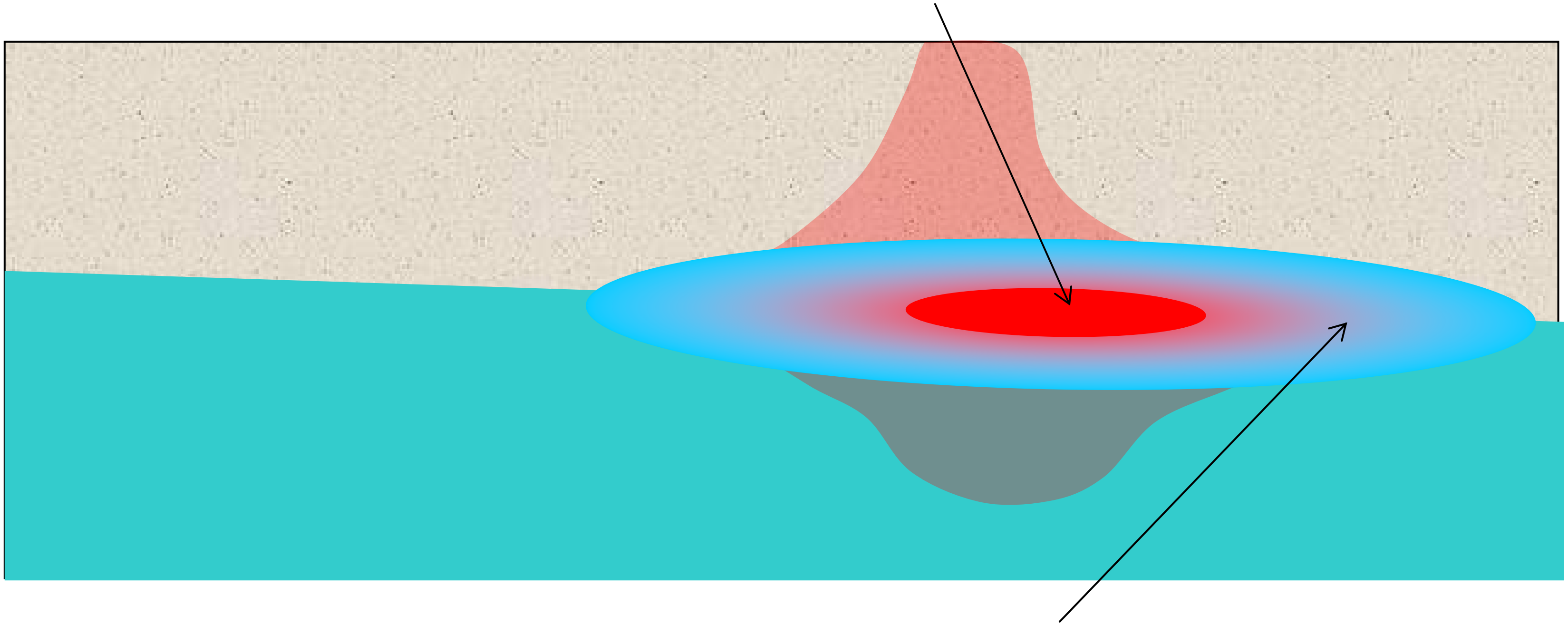
- At plume edge LNAPL saturation & thickness in a well is > 0, but stable if LNAPL Head < Displacement Head



- Saturations/relative permeability decreases away from plume core

Key Point: LNAPL in the plume core may be potentially mobile, but plume footprint often stable

Two LNAPL Mobility Models



Core Plume: LNAPL Seepage Velocity (Darcy’s Law) -

Periphery Plume: Brooks-Corey Displacement Head Model

Lines of Evidence for LNAPL Footprint Stability

1. Site monitoring data
2. Estimated LNAPL Seepage Velocity (Darcy’s Law)
3. Displacement head model for LNAPL movement into water-wet pore (Brooks-Corey model)
4. LNAPL saturation/residual saturation analysis
5. LNAPL mass analysis
6. LNAPL product recovery analysis
7. Age of LNAPL release & weathering analysis
8. Dye tracer test

Precluding Conditions

- Visual evidence NAPL at receptor (e.g., sheens surface water)
- LNAPL presence in wells and:
  - Fractured bedrock
  - Very steep gradients
  - Very large water table fluctuations
  - Preferential pathways
  - LNAPL source very close to receptor

1. Site Monitoring
Line of Evidence

- LNAPL may be mobile when temporal sampling indicates:
  - increasing thickness of LNAPL in monitoring wells
  - advancement of LNAPL across a monitoring well network
  - Advancing dissolving plume from NAPL source zone (dissolved plume halo)

2. LNAPL Seepage Velocity Model Inputs

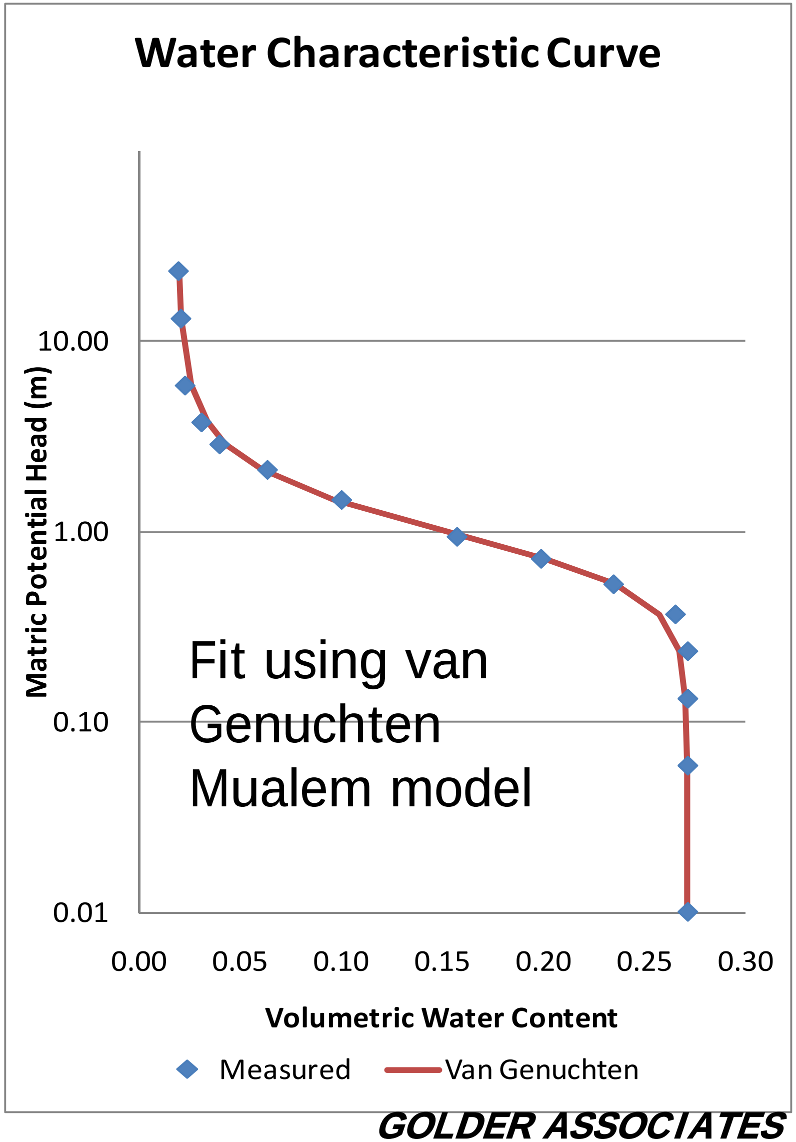
Parameter	Tier 1	Tier 2
LNAPL thickness	Measure	Measure
LNAPL gradient	Measure	Measure
LNAPL properties	Default or measure if mixture or weathered LNAPL	Measure
Capillary parameters (VG N, α), porosity	Default for soil type, requires grain size (e.g., API Interactive model, database)	Measure
Residual saturation	Default for soil type	Measure
Water saturation	Default for soil type	Measure

2. Van Genuchten Capillary Parameters

Preserving core using Liquid Nitrogen

Collect soil cores

Centrifuge Capillary Test



Fit using van Genuchten Mualem model

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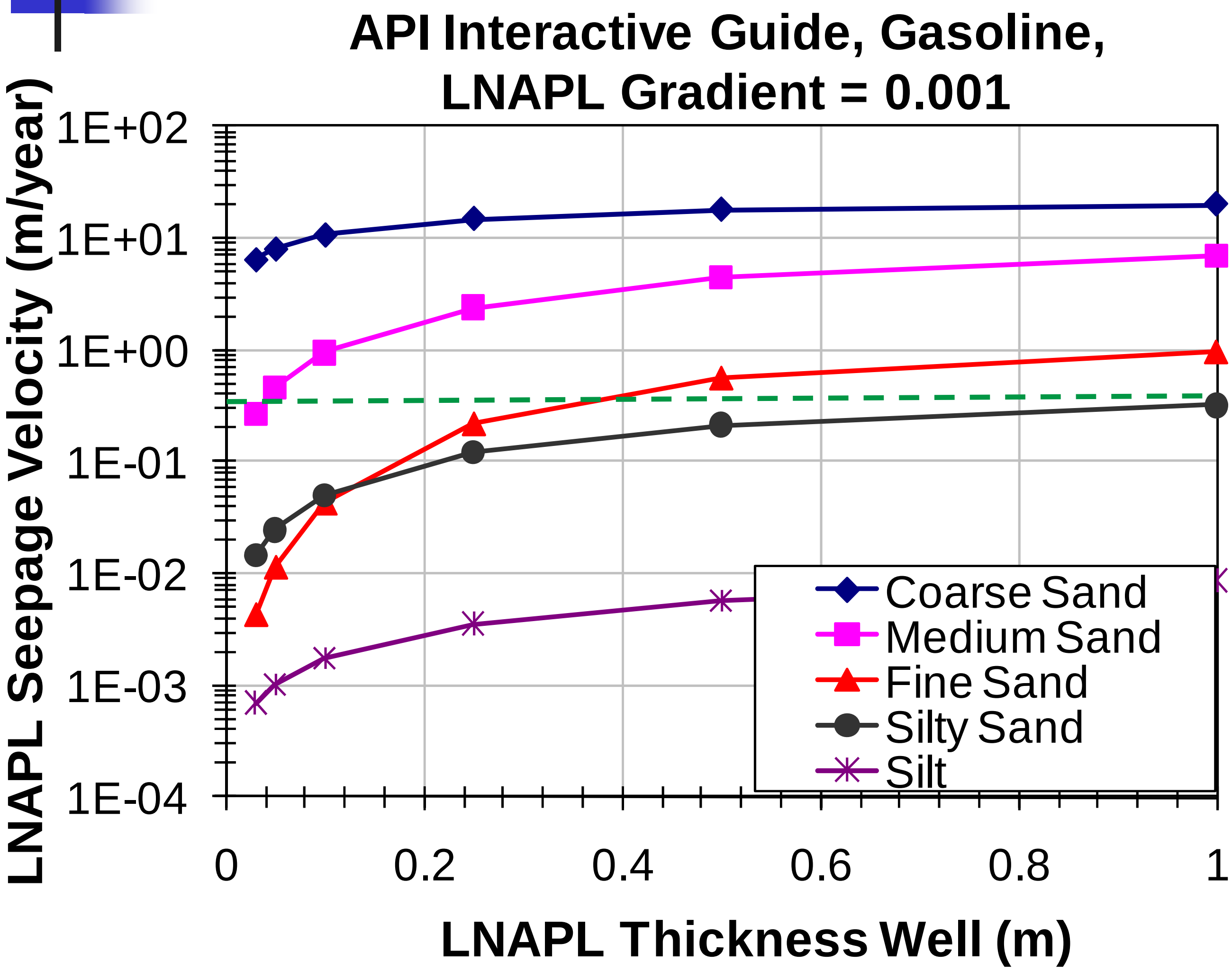
2. LNAPL Seepage Velocity



ASTM suggests de-minimus velocity of 0.3 m/year below which would not need to be concerned with LNAPL mobility

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3. Brooks-Corey Displacement Head Model

Displacement head

$$\Delta\Psi = \Psi_{bow} - \Psi_{boa}$$

$$\Psi_{bow} = \frac{\Psi_{baw}\sigma_{ow}}{(1-\rho_r)\sigma_{aw}}$$

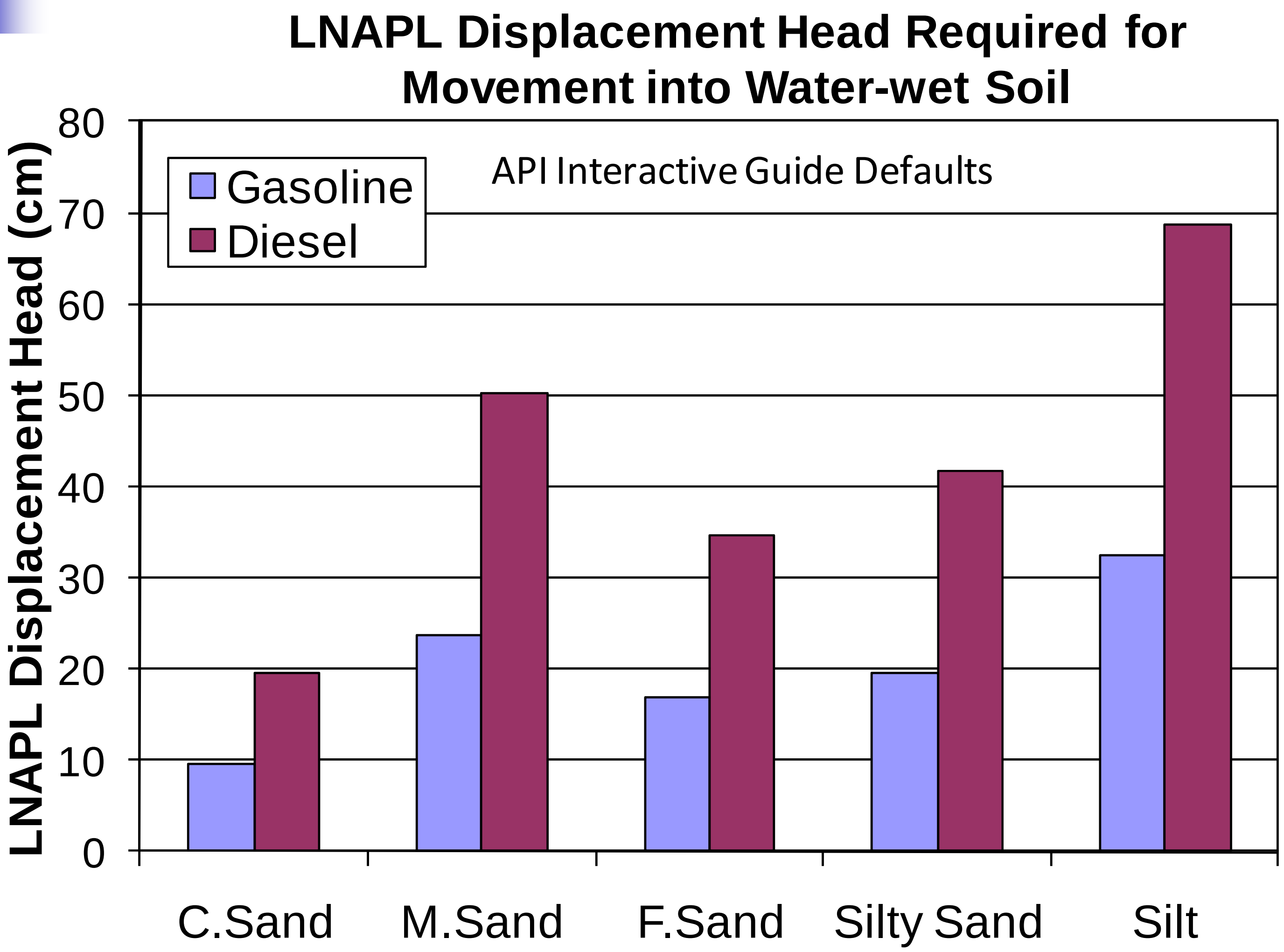
$$\Psi_{boa} = \frac{\Psi_{baw}\sigma_{ao}}{\rho_r\sigma_{aw}}$$

- Key Point: If in-well LNAPL thickness is less than displacement head, LNAPL body may be stable (but potentially somewhat non-conservative model based on estimation of bubbling pressure)

For more information see Golder report for BC Ministry of Environment
http://www.env.gov.bc.ca/epd/remediation/reports/index.htm

- API 4760

3. Brooks-Corey Displacement Head Model



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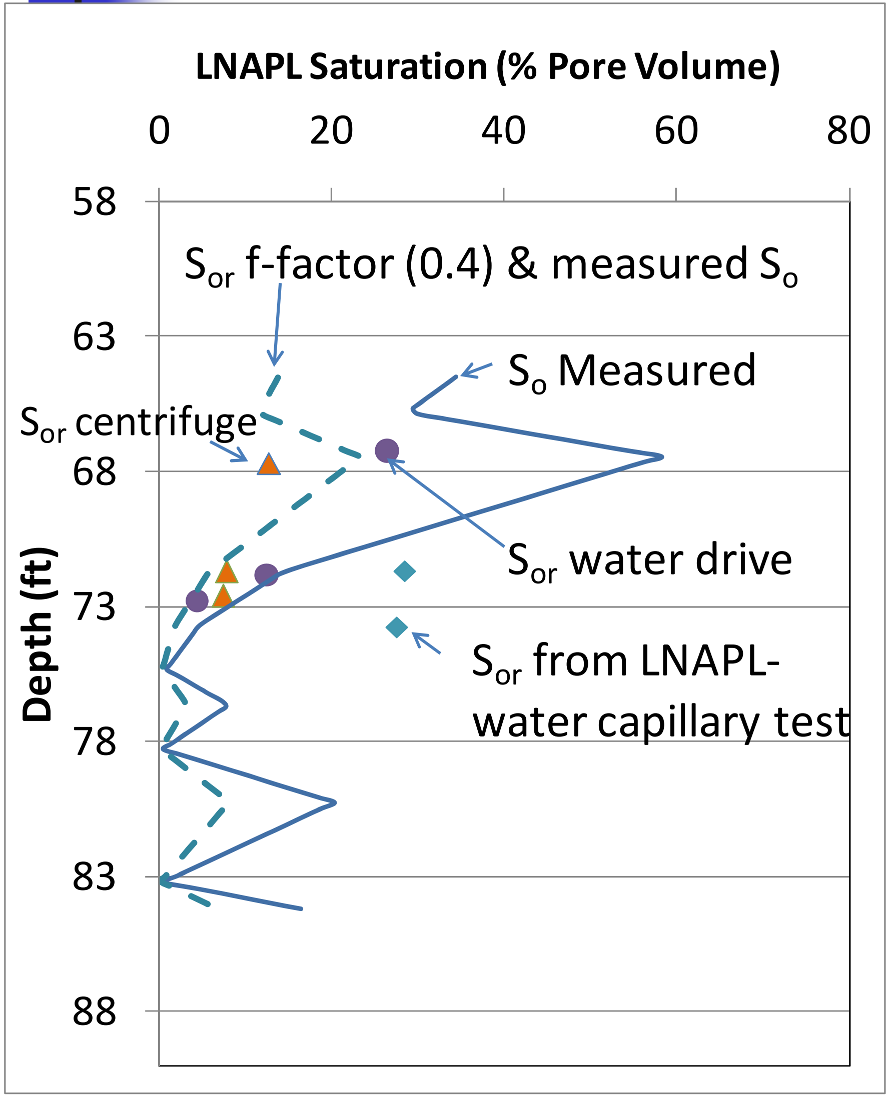
4. LNAPL Saturation Analysis

- Is $S_o > S_{or}$?
- S_{or} is dependent on initial LNAPL saturation, soil water content at time of LNAPL release and soil pore size distribution
- One approach is to measure total and residual saturation in soil cores
  - Centrifuge test (1000g)
  - Water drive
- Another is estimate using f-factor where $S_{or} = f\ S_o$ (assumes no lower limit to S_{or})

4. LNAPL Saturation Analysis

From ExxonMobil



- Key Points: So > Sor, water drive and centrifuge tests produced LNAPL indicating potential mobility, difficult to say which is best test.
- There are some sites where Sor > So, where no product produced

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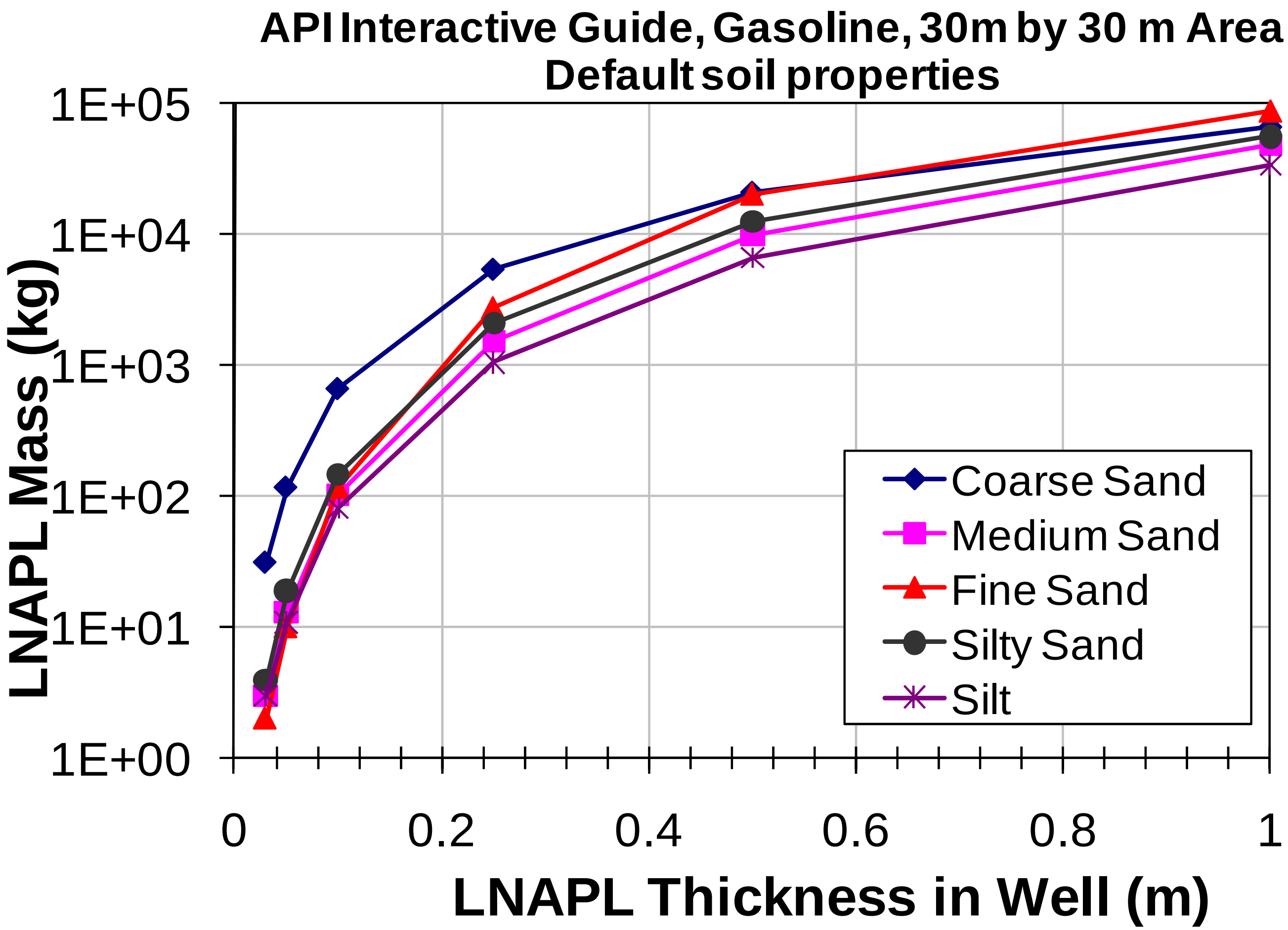
5. LNAPL Mass Analysis



Key Point: For small thicknesses, LNAPL mass or volume may be relatively small

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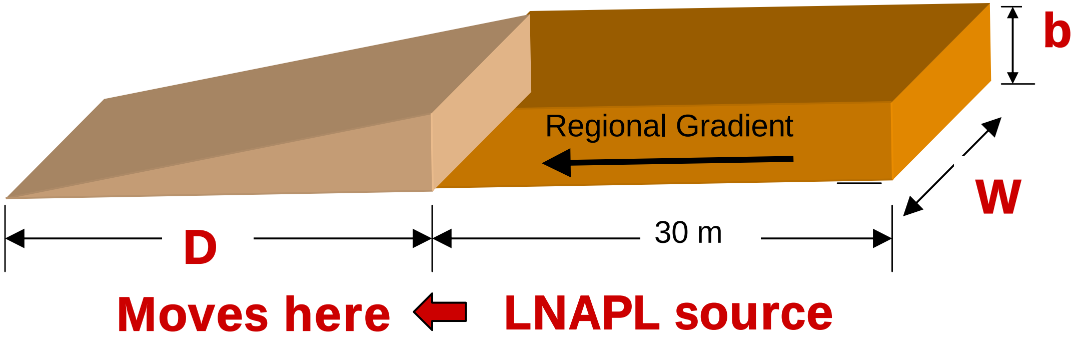
5. LNAPL Mass Analysis – How far could LNAPL move?

Assume all LNAPL above residual saturation within impact-ed zone is potentially mobile, how far could it move?



$$V_o = Abn(S_o - S_{or})$$

$$A = \frac{V_o}{\frac{1}{2} bnS_{or}}$$

$$D = \frac{A}{W}$$

Medium Sand
A = 30 m by 30 m impacted area
b= thickness above S_{or} = 0.7 m
V_o = Potentially mobile LNAPL volume = 9.6 m^3
S_{or} = Residual LNAPL saturation = 0.15
n = total Porosity = 0.38

D = Distance = 16 m

- Key Question: What are implications of LNAPL moving relatively small distances?

Conclusions

- Opportunity for improved LNAPL management based on good science and new tools
- LNAPL saturations are not uniform, but are controlled by soil heterogeneity (greater LNAPL volume in coarse-grained soil)
- As the LNAPL saturation increases, the relative permeability and potential LNAPL velocity also increases
- There is need to move beyond conservative in-well LNAPL thickness thresholds to lines-of-evidence approach that takes advantages of new approaches and tools