Starting Soon: LNAPLs Training – Part 1 of 3

- Light Non-Aqueous Phase Liquid (LNAPL) Site Management: LCSM Evolution, Decision Process, and Remedial Technologies (LNAPL-3, 2018) - **https://lnapl-3.itrcweb.org/**
- Download PowerPoint file
  - Clu-in training page at **http://www.clu-in.org/conf/itrc/lnapl-3/**
  - Under "Download Training Materials"
- Download information for reference during class
  - **Figure 1.1 (from the LNAPL-3 guidance document)**

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Dial In 301 715 8592
Webinar ID: 841 942 52034#

Welcome – Thanks for Joining this ITRC Training Class

Based on ITRC Guidance Document:
Light Non-Aqueous Phase Liquid (LNAPL) Site Management: LCSM Evolution, Decision Process, and Remedial Technologies (LNAPL-3, 2018)

3-Part Training Series: Connecting the Science to Managing Sites

Part 1: Understanding LNAPL Behavior in the Subsurface

Part 2: LNAPL Conceptual Site Models and the LNAPL Decision Process

Part 3: Using LNAPL Science, the LCSM, and LNAPL Goals to Select an LNAPL Remedial Technology

Sponsored by: Interstate Technology and Regulatory Council (www.itrcweb.org)
Hosted by: USEPA Clean Up Information Network (www.cluin.org)

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- Course time is 2¼ hours
- This event is being recorded
- Trainers control slides
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ITRC (www.itrcweb.org) – Shaping the Future of Regulatory Acceptance

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  - Federal partners

    DOE DOD EPA
  - ITRC Industry Affiliates Program
  - Academia
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  - Technical and regulatory guidance documents
  - Online and classroom training schedule
  - More…

Meet the ITRC LNAPL Trainers – Part 1

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Read trainer bios at https://clu-in.org/conf/itrc/LNAPL-3/

Our Focus is on LNAPL
(Light Non-Aqueous Phase Liquid)

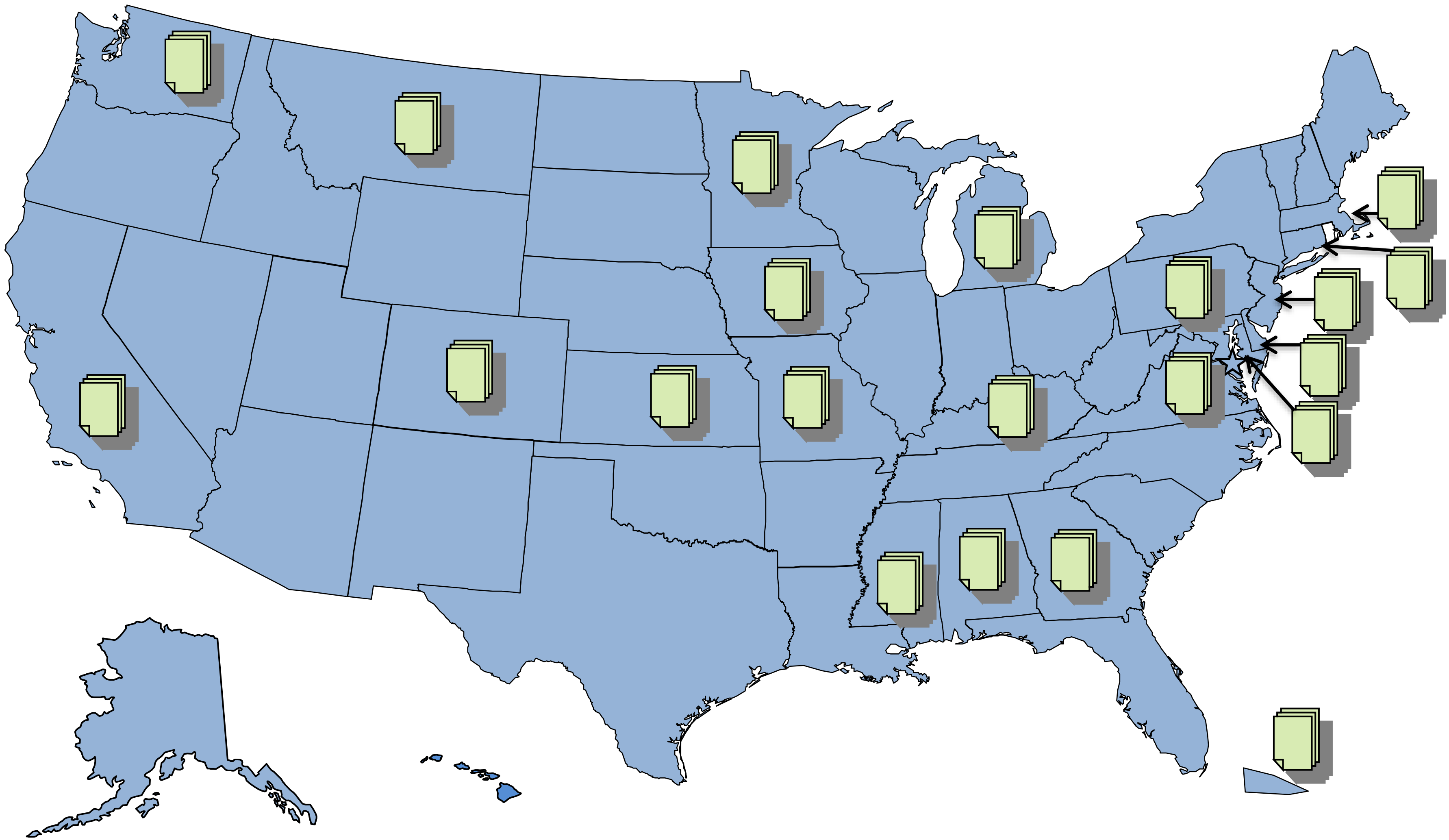
ITRC — Interstate Technology Regulatory Council

- What is LNAPL?
- Why Do We Care About LNAPL?
    - LNAPL Concerns
    - LNAPL can be difficult to accurately assess or recover
- Use LNAPL science to your advantage and apply at your sites

ITRC LNAPL document used or planned use at sites
(reports by all environmental sectors)

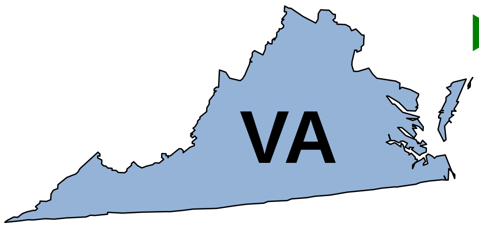
ITRC LNAPLs guidance used or referenced in the development of current or draft state guidance

Connecting LNAPL Science to Regulation

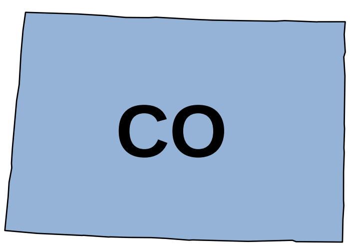


Influencing State Management of LNAPL Sites

Examples: ITRC LNAPLs guidance used or referenced in the development of current or draft state guidance



- Virginia Department of Environmental Quality references ITRC LNAPL guidance documents in its Storage Tank Program's **Closure Evaluation of Sites with Free Product** *(DEQ Guidance Document #LPR-SRR-03-2012, December 28, 2012)*



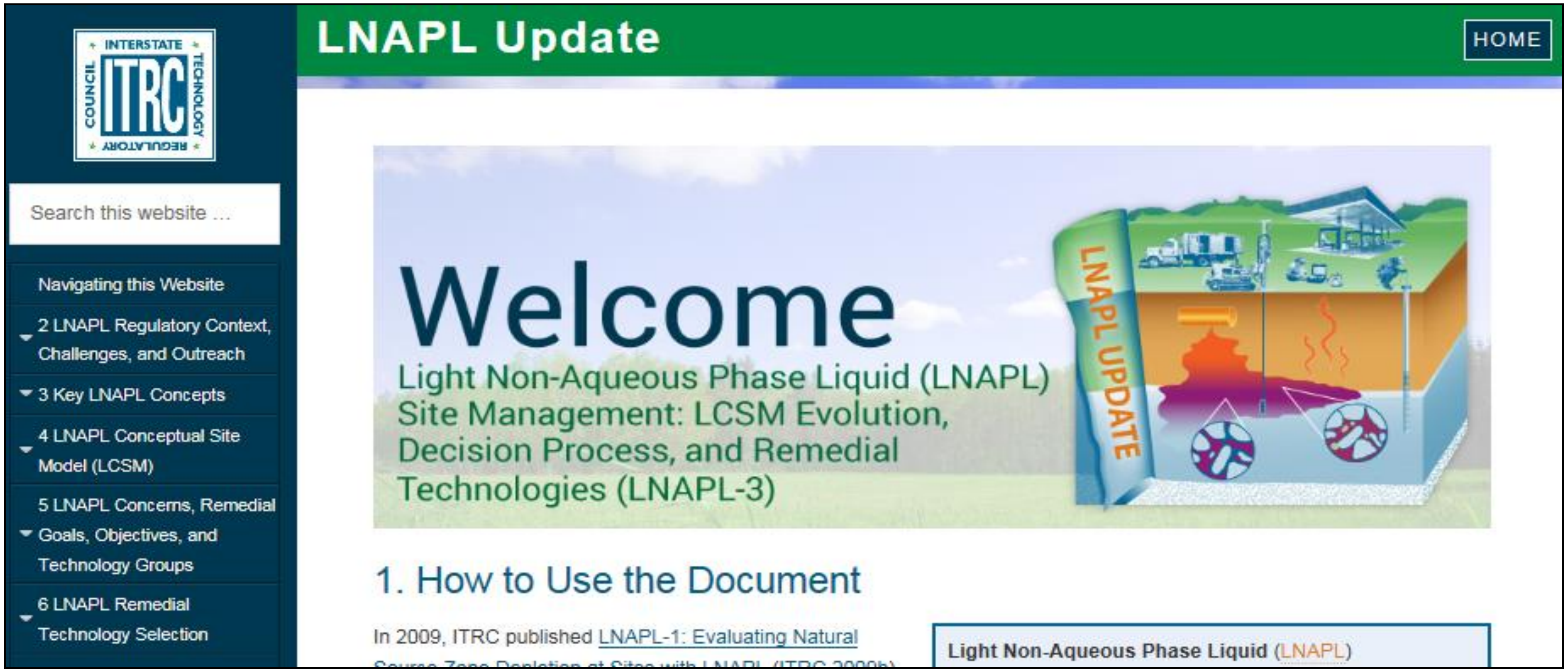
- Colorado Department of Labor and Employment Division of Oil and Public Safety revised its guidance to incorporate concepts from ITRC training courses and guidance documents. **http://www.coworkforce.gov/petroleumguidance/**

ITRC's History as LNAPL Solution Provider

- **2009:** *LNAPL-1 (Natural Source Zone Depletion) and LNAPL-2 (Evaluating LNAPL Remedial Technologies)*
- **2010 - 2017:**
  - LNAPL Online Training (3-parts)
  - LNAPL Classroom Training
  - Over 19,000 Trained
- **2016 - 2018:** ITRC LNAPL Update
- **March 2018:** *LNAPL-3 (LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies)*
- **Spring 2018:** Updated 3-Part LNAPL Online Training

Your Online LNAPL Resource

https://lnapl-3.itrcweb.org/

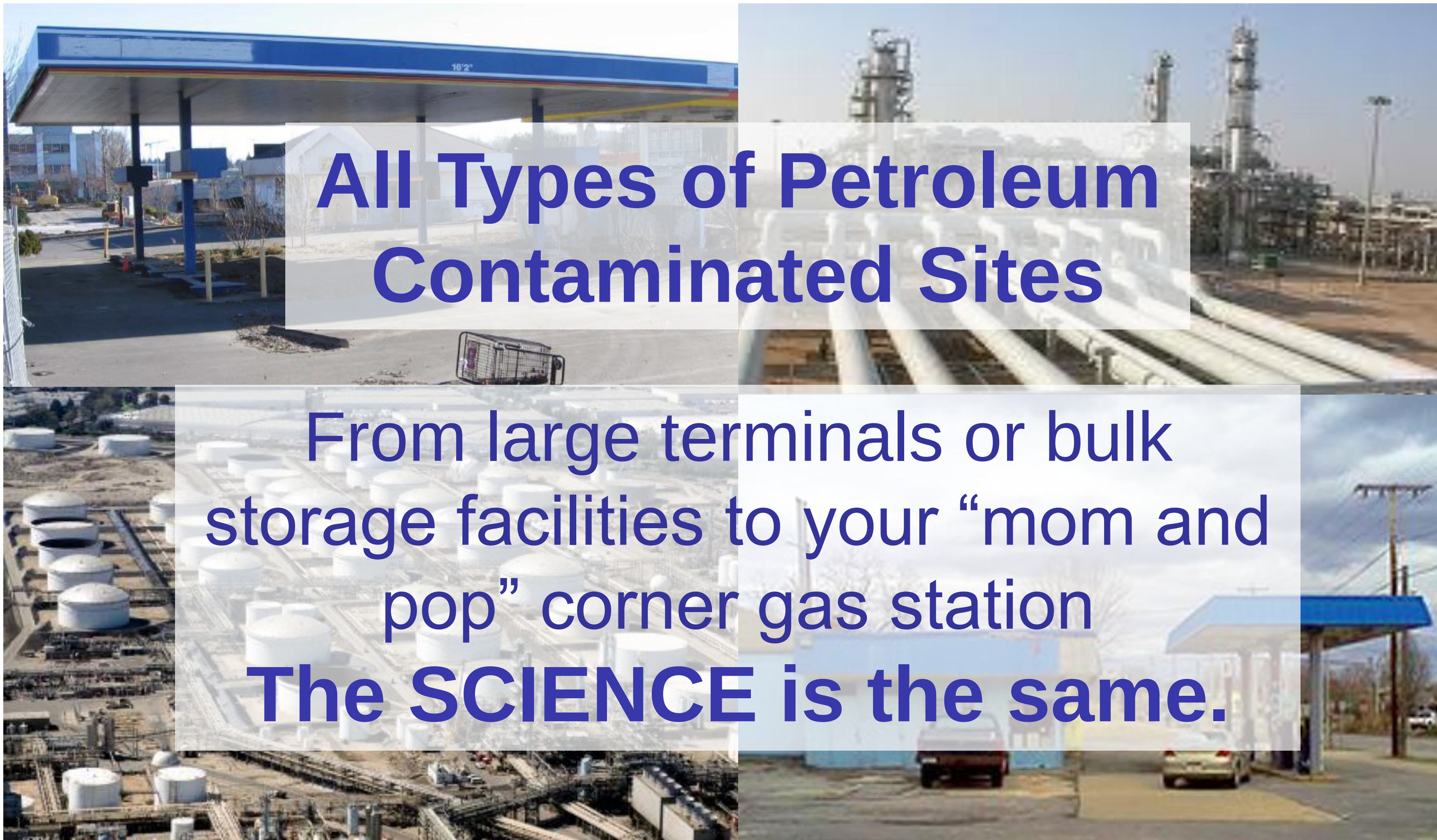


- Expansion of LNAPL Key Concepts
- Development of a LNAPL Conceptual Site Model (LCSM) Section
- Emphasis on identifying SMART objectives
- Expansion of Transmissivity (Tn) and Natural Source Zone Depletion (NSZD) via Appendices

Who Should Use This Document?

- State and federal regulators in CERCLA, RCRA, UST, voluntary programs
- Remediation groups within integrated petroleum and services companies
- Environmental consulting firms, suppliers, and vendors supporting LNAPL site management
- Universities and colleges professors / college students in the environmental field

Where Does This ITRC LNAPL Document Apply?



All Types of Petroleum Contaminated Sites

From large terminals or bulk storage facilities to your “mom and pop” corner gas station

The SCIENCE is the same.

Learning Objectives
3-Part Training Series

Part 1	▶ Use LNAPL science to your advantage and apply at your sites
Part 2	▶ Develop LNAPL Conceptual Site Model (LCSM) for LNAPL concern identification ▶ Inform stakeholders about the decision-making process
Part 3	▶ Select remedial technologies to achieve objectives ▶ Prepare for transition between LNAPL strategies or technologies as the site moves through investigation, cleanup, and beyond ▶ "SMART"-ly measure progress toward an identified technology-specific endpoint

ITRC 3-Part Online Training Leads to YOUR Action

TODAY

Part 1: Connect Science to LNAPL Site Management

(Section 3)

Part 2: Build Your LNAPL Conceptual Site Model

(Sections 4 and 5)

Part 3: Select / Implement LNAPL Remedies

(Section 6)

YOU Apply knowledge at your LNAPL sites

Based on the ITRC LNAPL-3 Document: LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies

LNAPL Remediation Process and Evolution of the LCSM – Related to the Training Courses

Handout provided

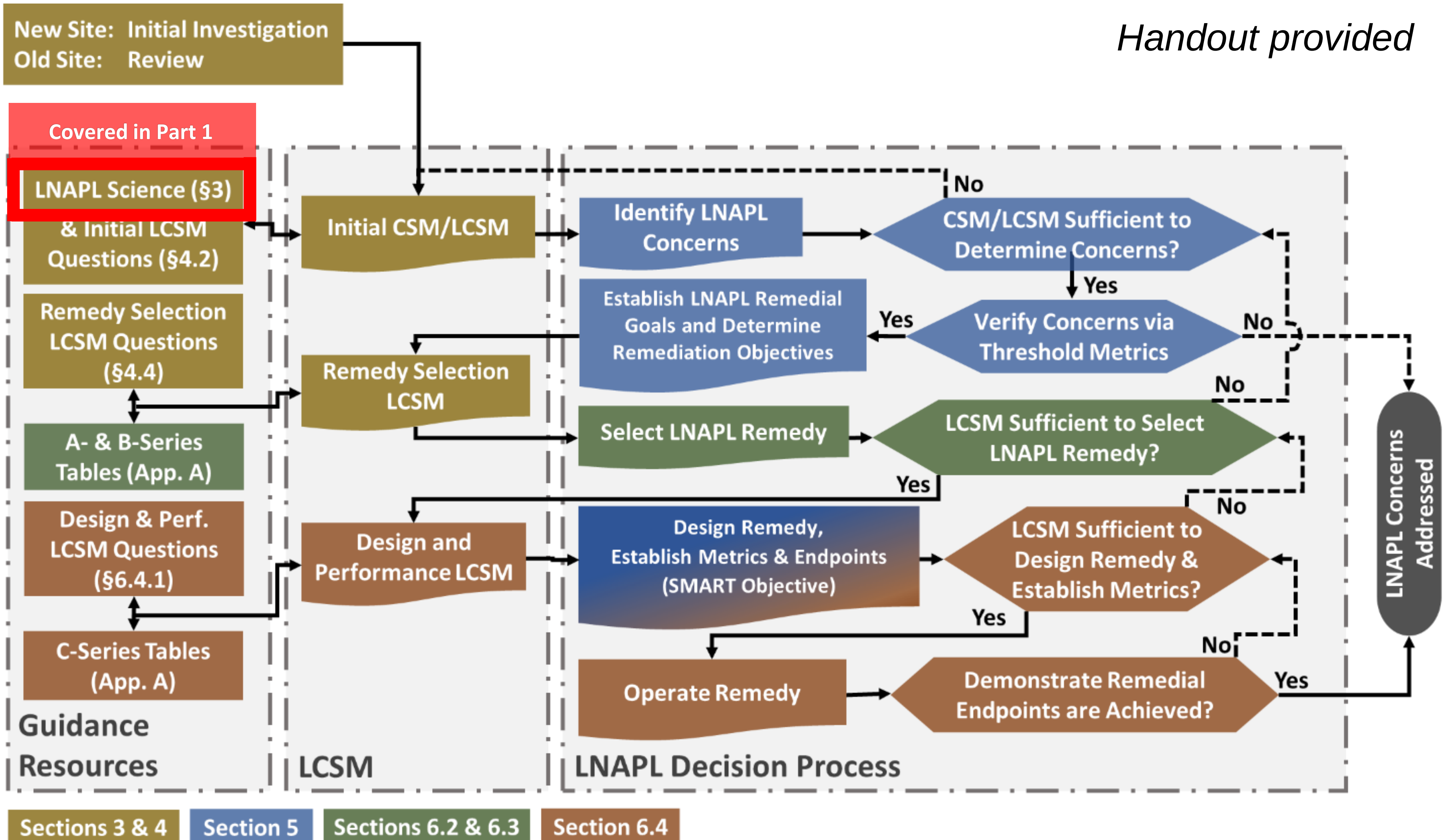


Figure 1-1 – ITRC LNAPL-3

Key Messages

1. LNAPL in wells does not mean 100% LNAPL saturation (dispel “pancake model”)
2. LNAPL can be present in subsurface even if not in wells
    - Indicators
3. LNAPL Composition vs. LNAPL Saturation
    - Raoult’s Law
4. Apparent LNAPL Thickness Challenges in Unconfined Conditions
    - Amount changes with soil type
    - Thickness changes with water table position

Key Messages

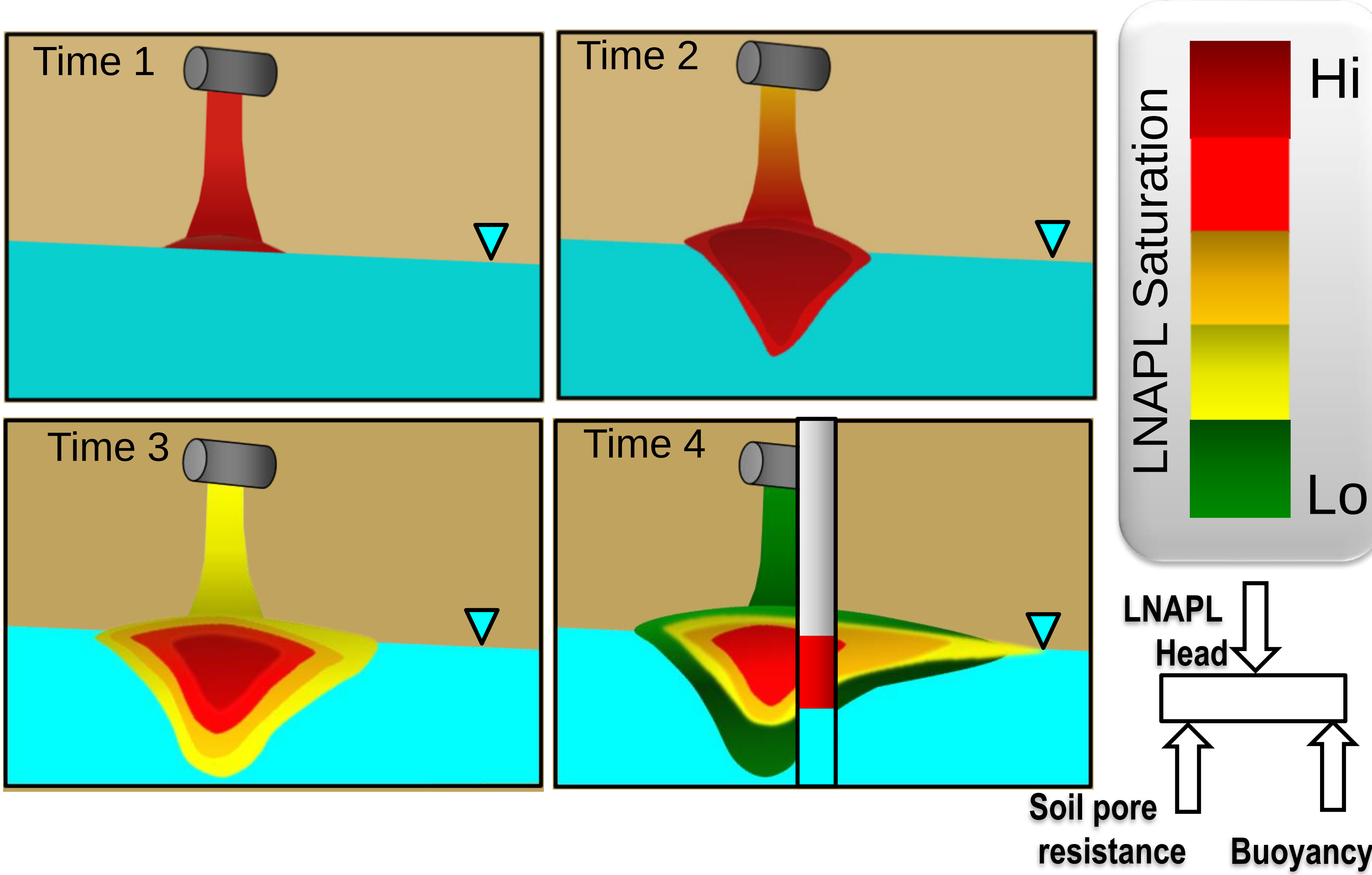
5. Apparent LNAPL Thickness in various hydrogeologic conditions (i.e., perched, confined)
6. LNAPL in well does not mean it is migrating
   - Darcy's Law
   - Limiting processes
7. Transmissivity is a better indicator of recoverability
8. Stable LNAPL bodies can still result in sheens
   - Mechanisms
9. Biological processes are significant in LNAPL depletion

Key Message 1

Groundwater and LNAPL share pore space

LNAPL in MWs $\neq$ 100% LNAPL Saturation in Formation

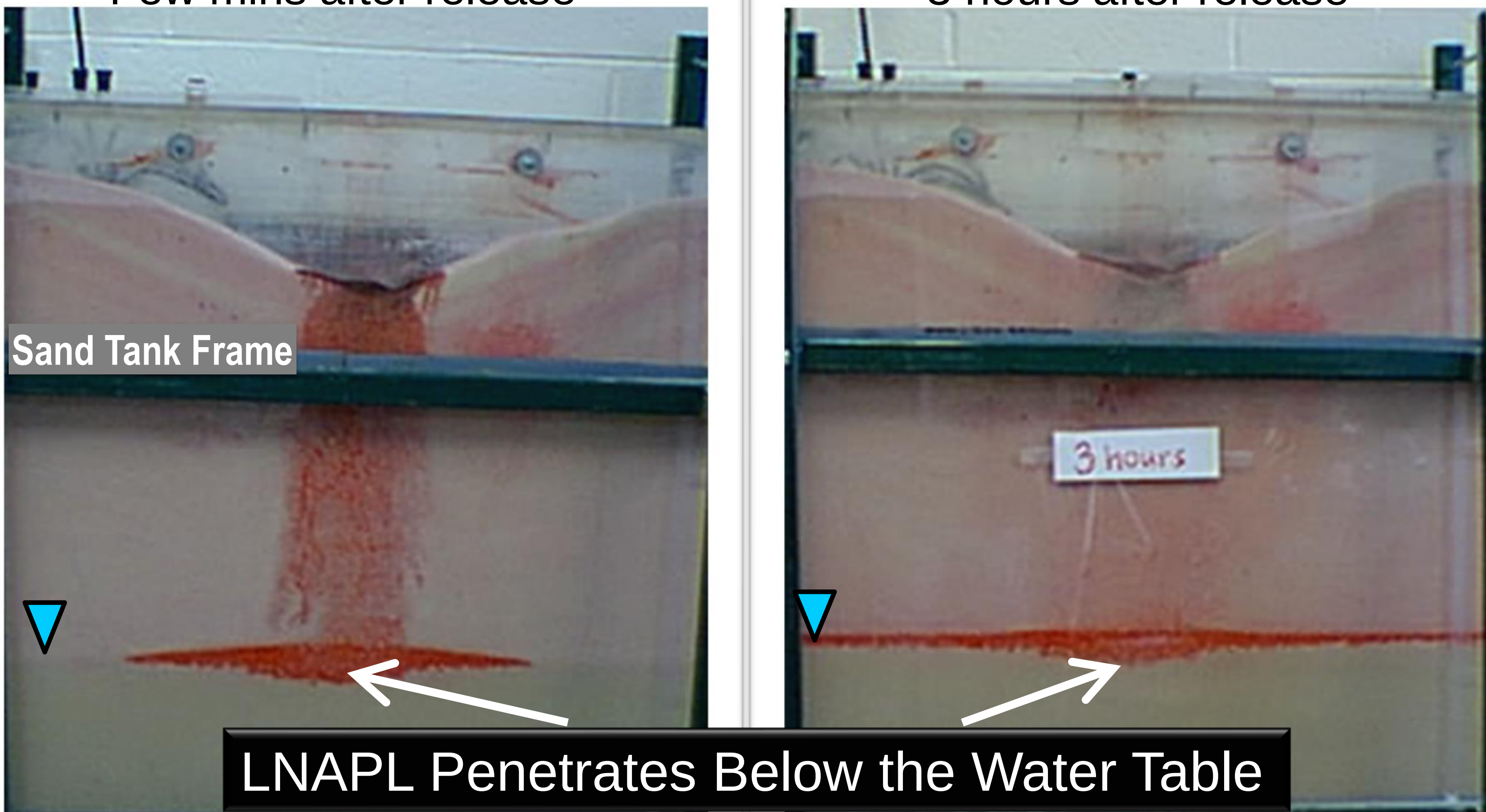
Time Series LNAPL Body Development:
Cross Section View



Lab Tank Experiment
LNAPL Penetrates Below the Water Table

Few mins after release

3 hours after release

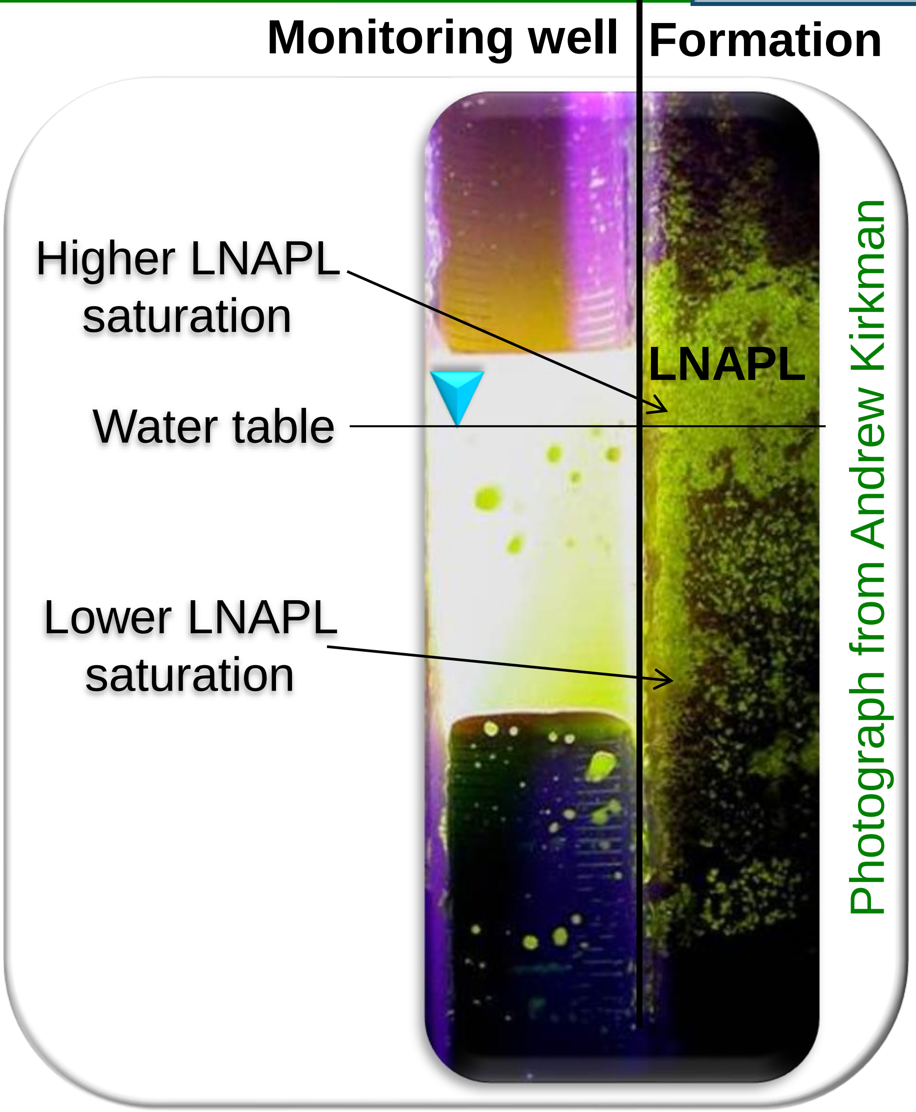


Photographs from Cristin Bruce

Impacts of LNAPL in the Formation: Key Messages

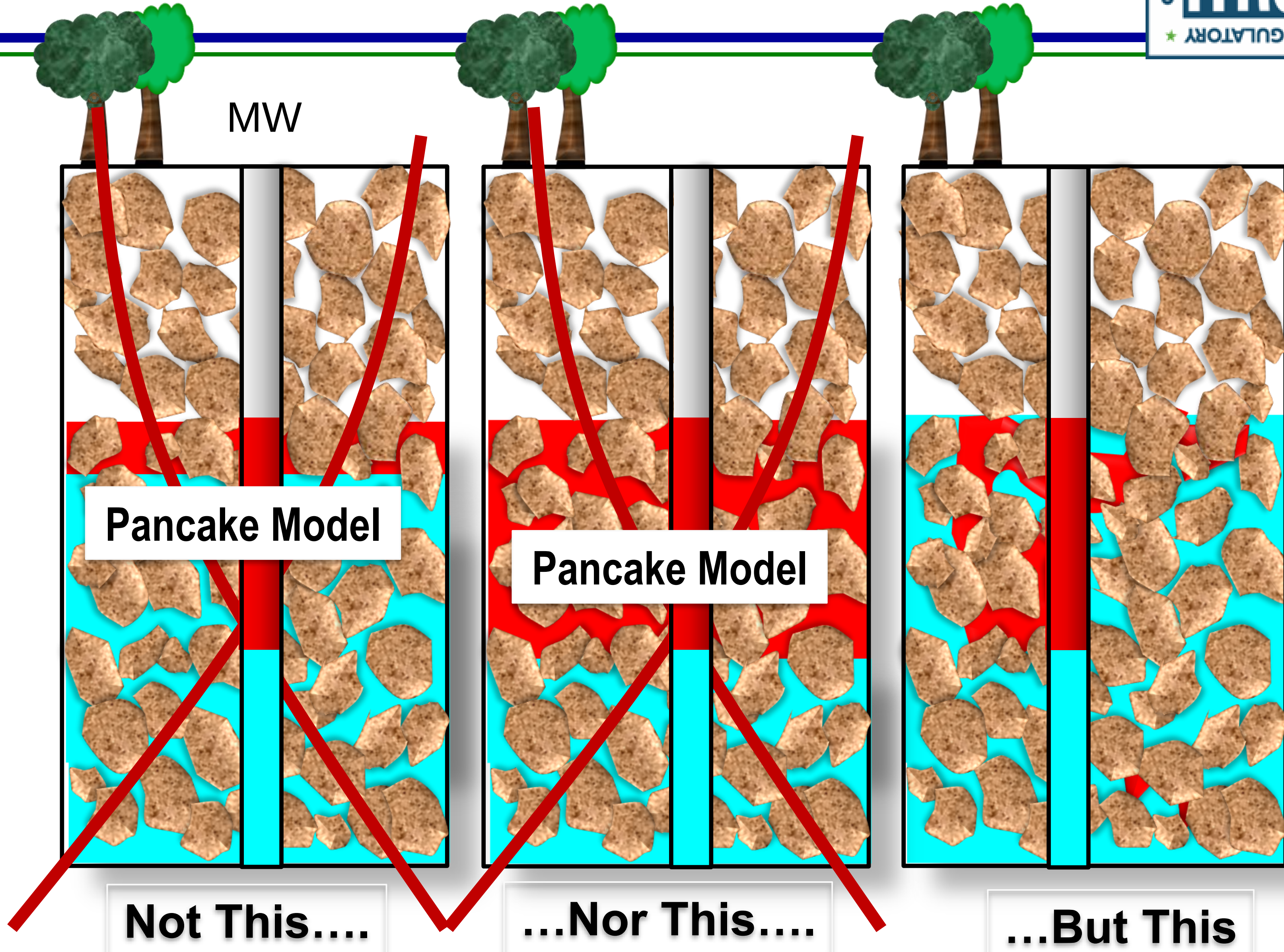
- LNAPL penetrates below the water table
- LNAPL saturation in the formation is not 100% and varies with depth
  - LNAPL shares the pore space with water

Coming Next: How to determine LNAPL is there and how much



LNAPL vertical distribution in a lab tank

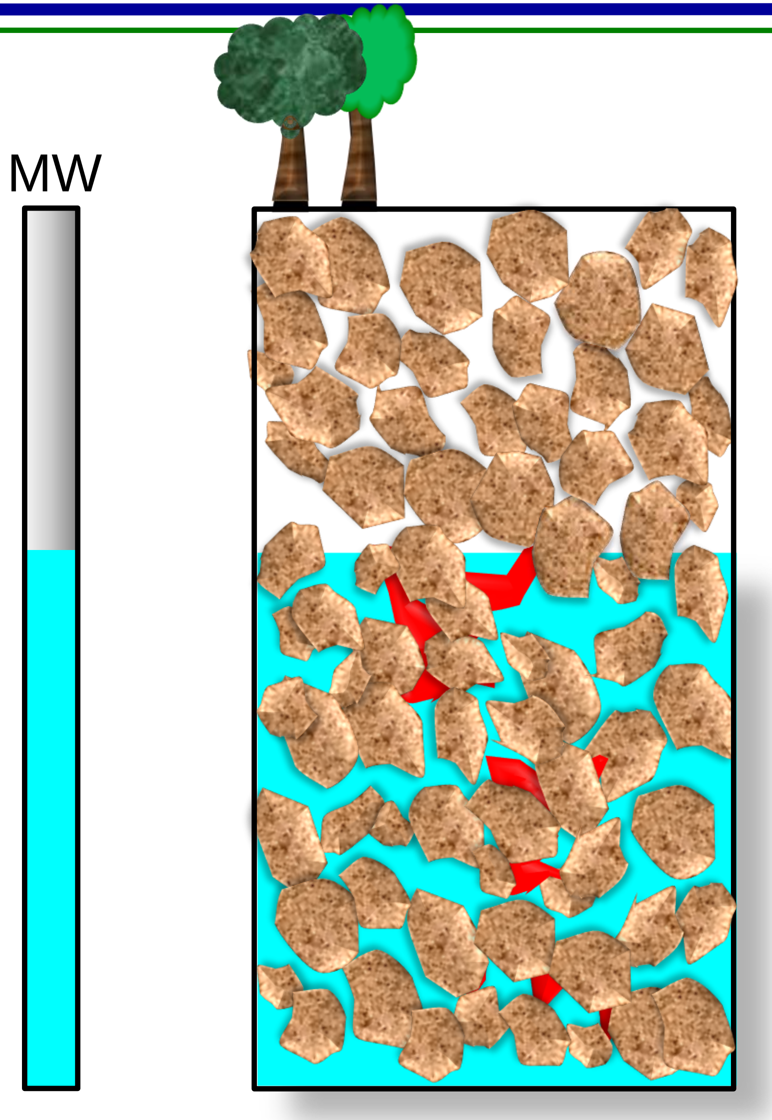
Nature of LNAPL Impacts in the Formation:
Below Water Table And Saturation Varies



Key Message 2

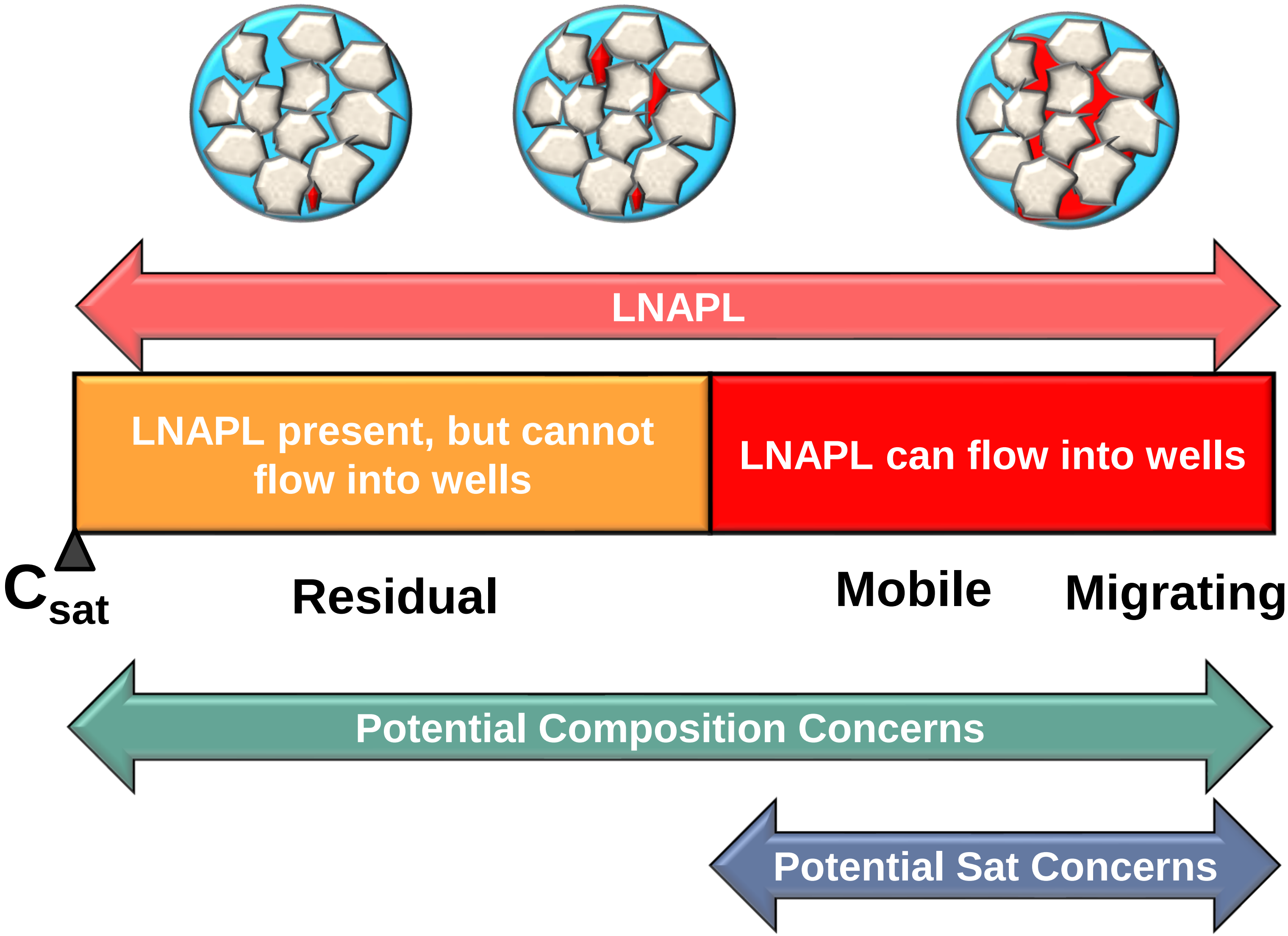
LNAPL can be in the formation even when it is not accumulating in a well

Nature of LNAPL Impacts in the Formation: LNAPL May Not Even Flow Into A Well



- How do you know that LNAPL is present?
- How do you find out where it is?

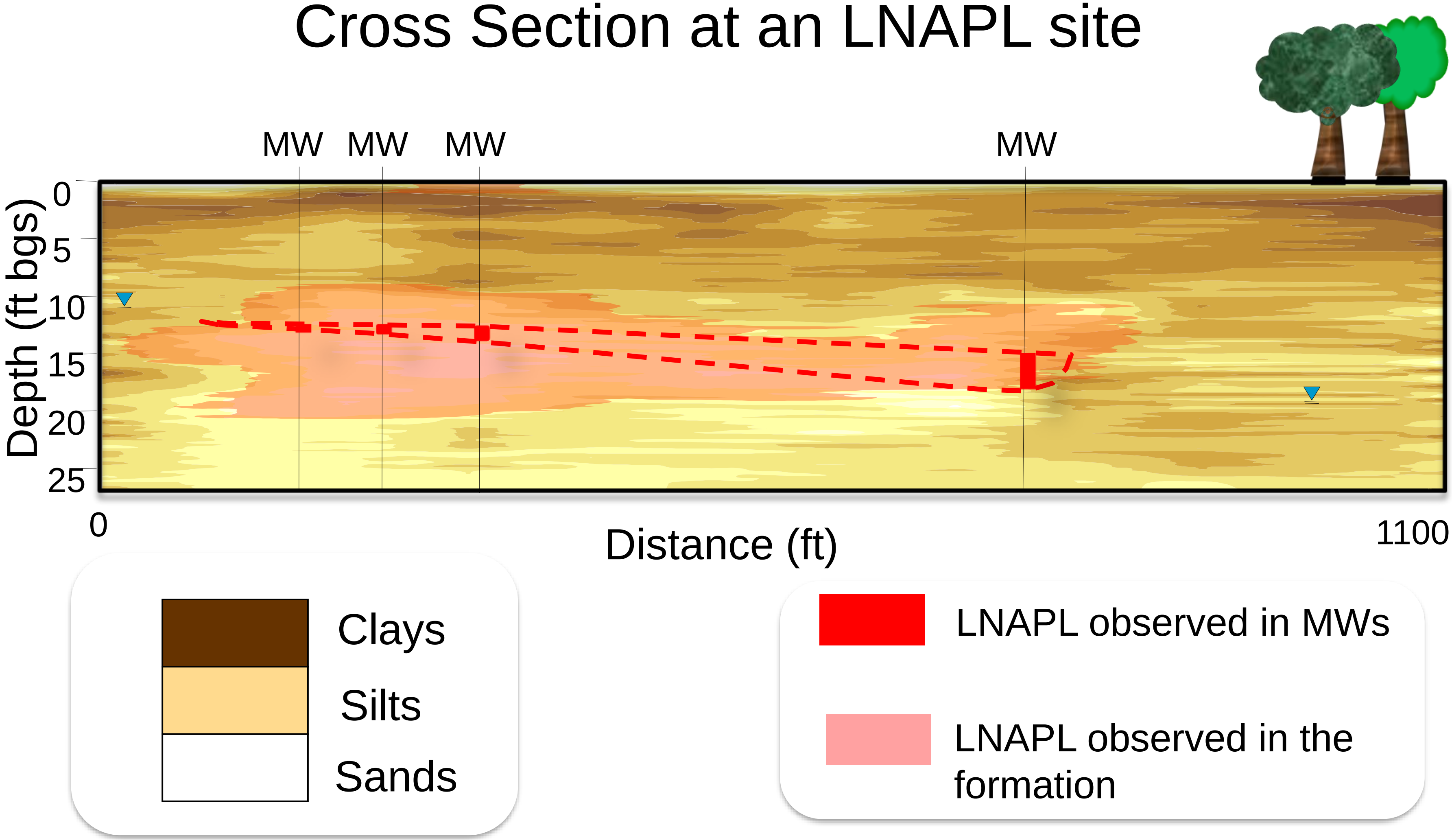
It is All LNAPL!



LNAPL *Vertical* Extent Can Be Greater Than In-Well LNAPL Thickness

Indicator: In-well LNAPL Thickness

Cross Section at an LNAPL site



Dissolved Phase Persistence

If There Is a Persistent Groundwater Plume….

……there is an LNAPL source

……………it may/may not flow into a well

Effective Solubility Of Select Chemicals From Common LNAPL Mixtures

Effective solubility of each chemical in a mixture like gasoline is a function of Raoult's Law

Raoult's Law

$$S_i = x_i S$$

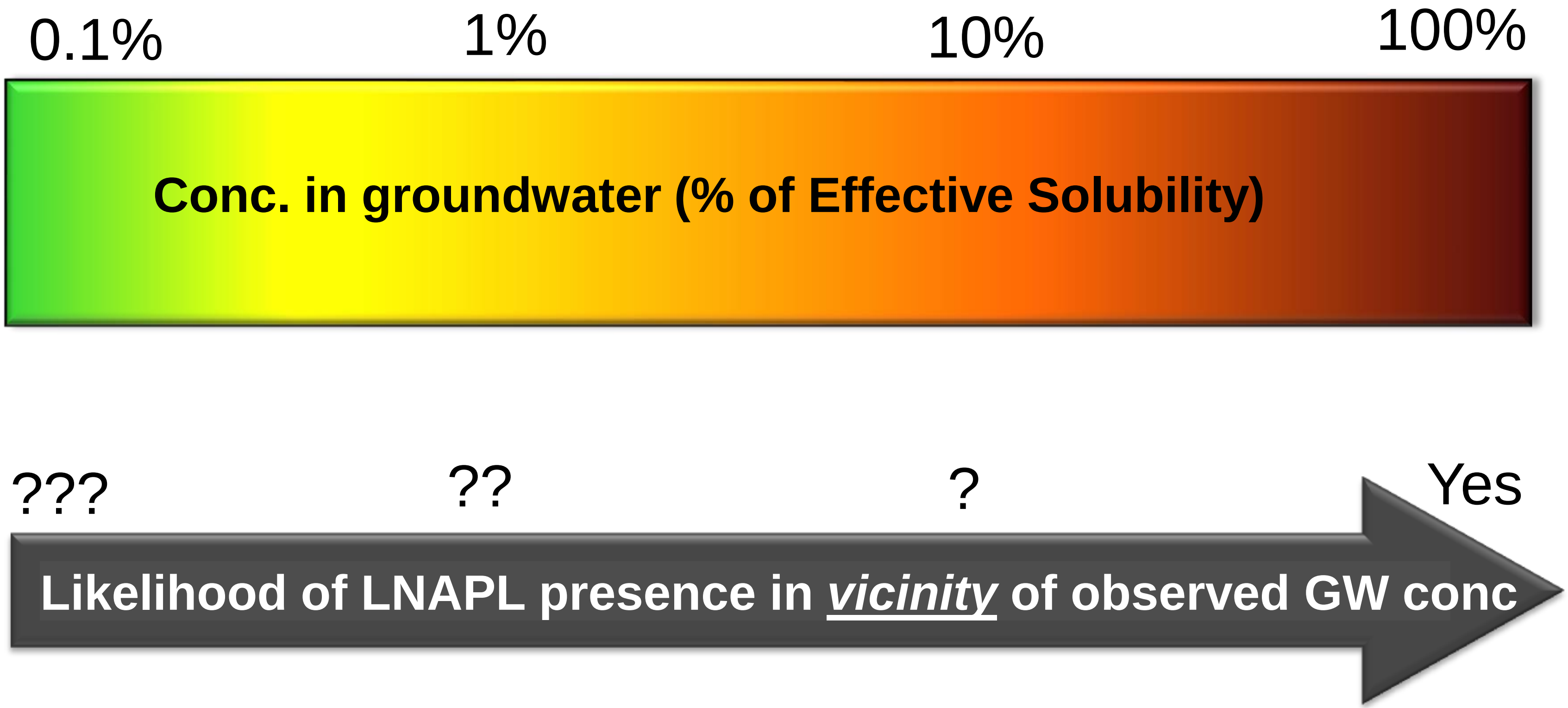
*** (mole fraction in the mixture)**

LNAPL Mixture	Chemical	Sol of Pure Chem. (S) (mg/L)	*Typical* Mole frxn. in Unweathered LNAPL (x_i)	Eff. Sol of Chem. (S_i) (mg/L)
Gasoline	Benzene	1780	0.005 - 0.01	9 -18
Gasoline	Toluene	535	0.05 - 0.10	27 - 54
Gasoline	Xylene	167	0.05 - 0.10	8 - 17
Diesel	Benzene	1780	0.00005	0.22
Diesel	Toluene	535	0.0005	0.67

Calculator at http://www.epa.gov/athens/learn2model/part-two/onsite/es.html

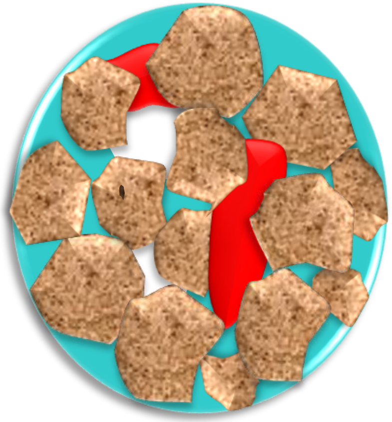
Groundwater Concentrations as an Indicator of LNAPL

Indicator: Dissolved Phase



GW – groundwater, conc - concentration

Calculated C_{sat} Values



- TPH in soil represents hydrocarbon present in soil gas, pore water, sorbed phase, and LNAPL
- C_{sat} indicates the concentration at which soil gas, pore water and sorbed phase are saturated with hydrocarbon

  TPH > C_{sat} → LNAPL

LNAPL	Soil Type	C_{sat} (mg TPH/Kg Soil)
Gasoline	Medium to coarse sand	143
Gasoline	Fine to medium sand	215
Gasoline	Silt to fine sand	387
Middle Distillate*	Fine to medium sand	9
Middle Distillate*	Silt to fine sand	18

* approximate to kerosene/diesel

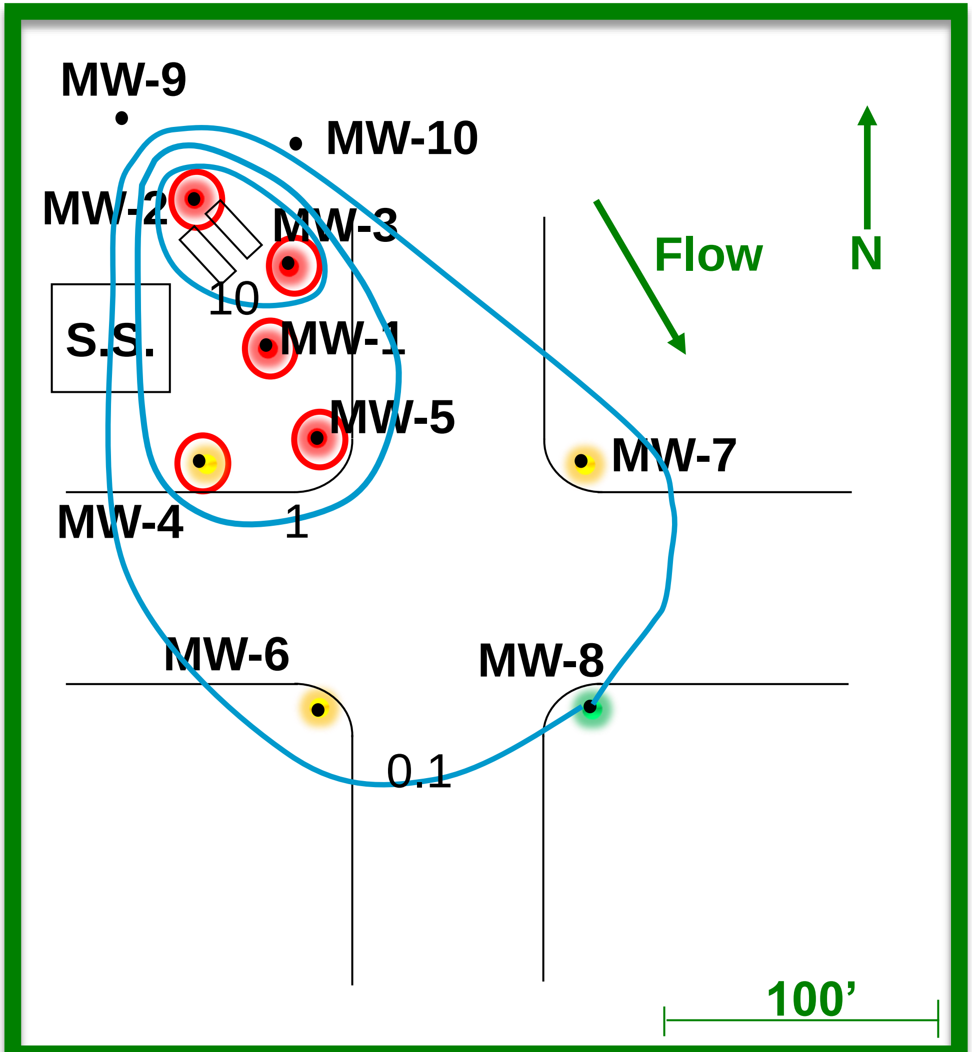
Brost and DeVaull, 2000. API Bulletin 9.

TPH Cautions

- Do not collect soil samples at predetermined intervals (e.g., not each 5 feet)
- Collect soil samples based on field screening
- Ensure that TPH range is representative of the LNAPL type
  - Do not assess a diesel spill using TPH-G
  - If heavy hydrocarbons (e.g., crude, >C35) then use Oil & Grease method
- Do not stop at the water table!

Inferring LNAPL from Soil TPH Concentrations

Indicator: Conventional Assessment

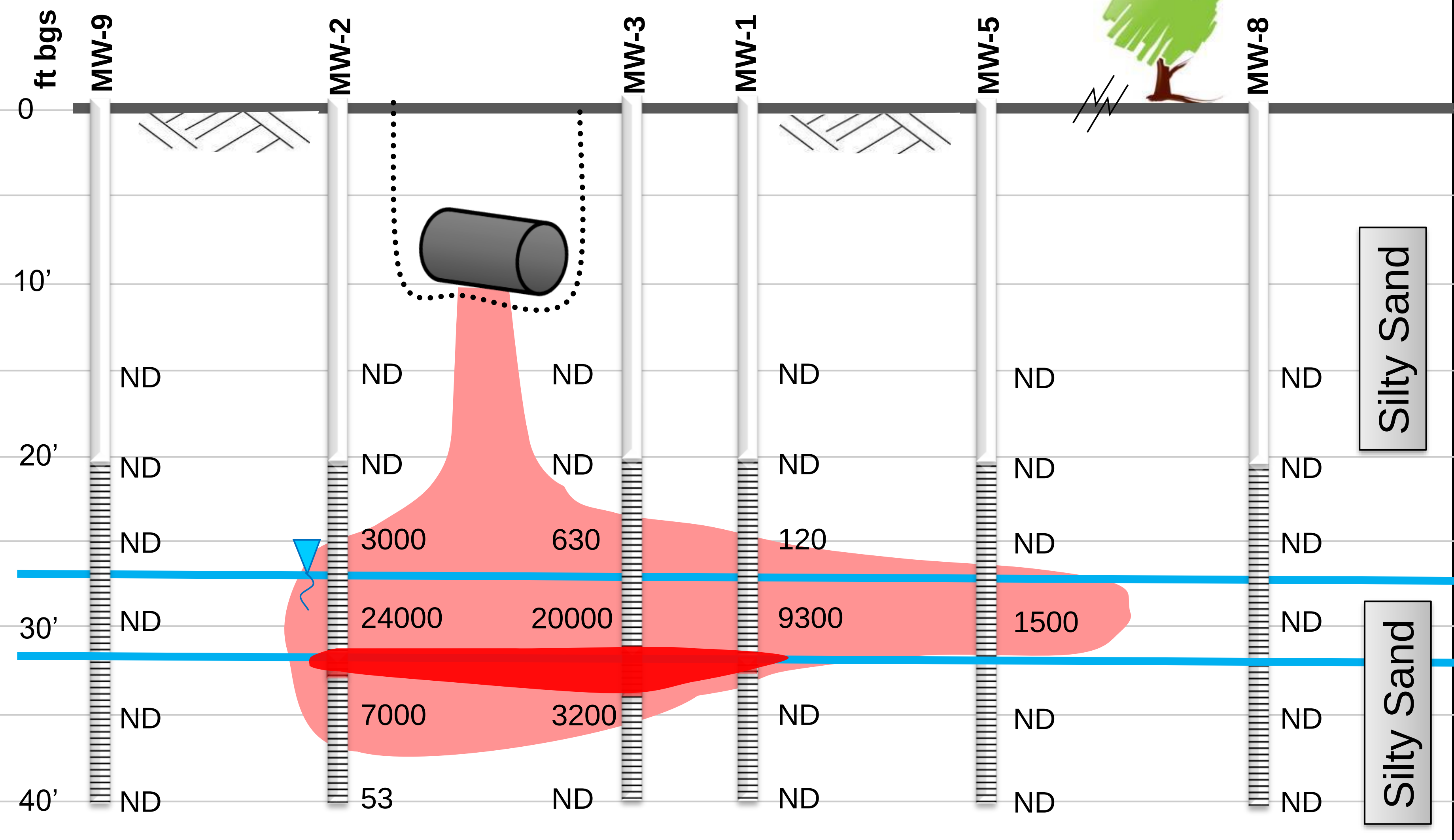


MW	Historical Benzene Concs (mg/L)	*Maximum* Soil TPH Concs (mg/Kg)
1	5	9300
2	13	24000
3	15	20000
4	1.6	1700
5	3.4	1500
6	0.6	12
7	0.35	10
8	0.1	ND<0.005
9	ND<0.001	ND<0.005
10	ND<0.001	ND<0.005

LNAPL present – MW-1, -2, -3, -4, -5

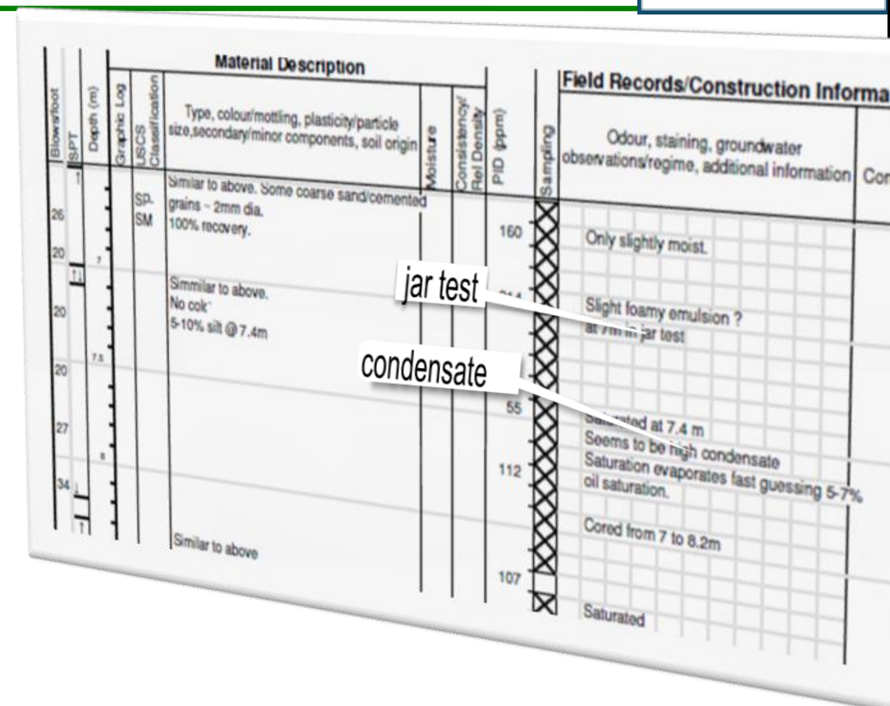
LNAPL Vertical Extent
TPH-G Versus In-Well Thickness

Indicator: Conventional Assessment



OVA and Other Field Observations

- Boring logs to characterize LNAPL source zone geometry
  - Lithology, water content, stain, odor, OVA readings



Picture cheiron-resources.com

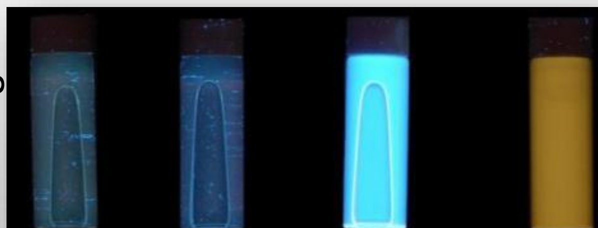
- Shake test
- Oleophyllic dyes for presence of LNAPL
  - Detection +/- 1000 ppm TPH

Fluorescence of LNAPL

White light

Gasoline Jet A Diesel Bunker C

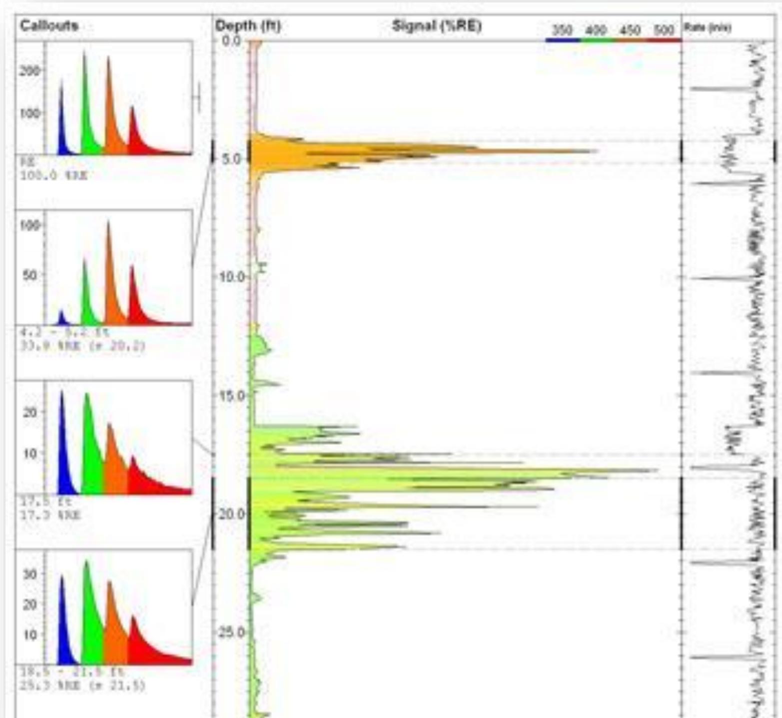
UV light



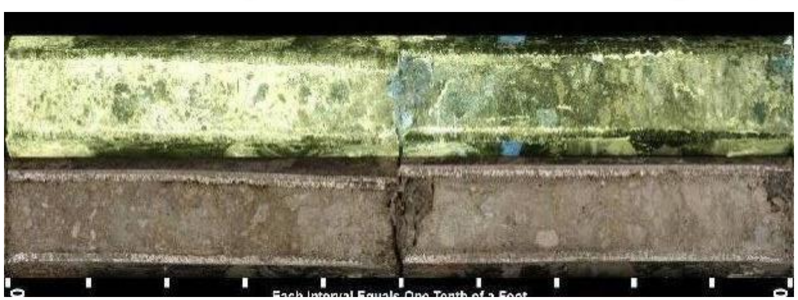
Photographs: Courtesy of PTS Lab

- All that fluoresces may not be LNAPL
  - Minerals, antifreeze, detergents, peat
- All LNAPLs do not fluoresce

Laser Induced Fluorescence

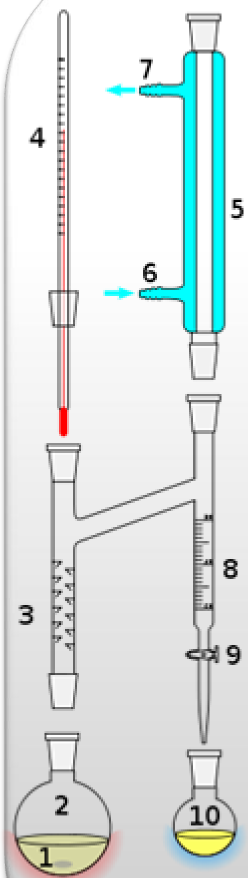


Laboratory Core UV Photograph



10 inches

Pore Fluid Saturation



Dean Stark Extraction

Correlating TPH & Sn

$$S_n = \frac{\rho_b \bullet TPH}{\rho_n n(10^6)}$$

S_n = LNAPL saturation (unitless)
ρ_b = dry soil bulk density (g/cm³)
TPH = total petroleum hydrocarbons (mg/kg)
ρ_n = NAPL density (g/cm³)
n = porosity

(Parker et al., 1994)

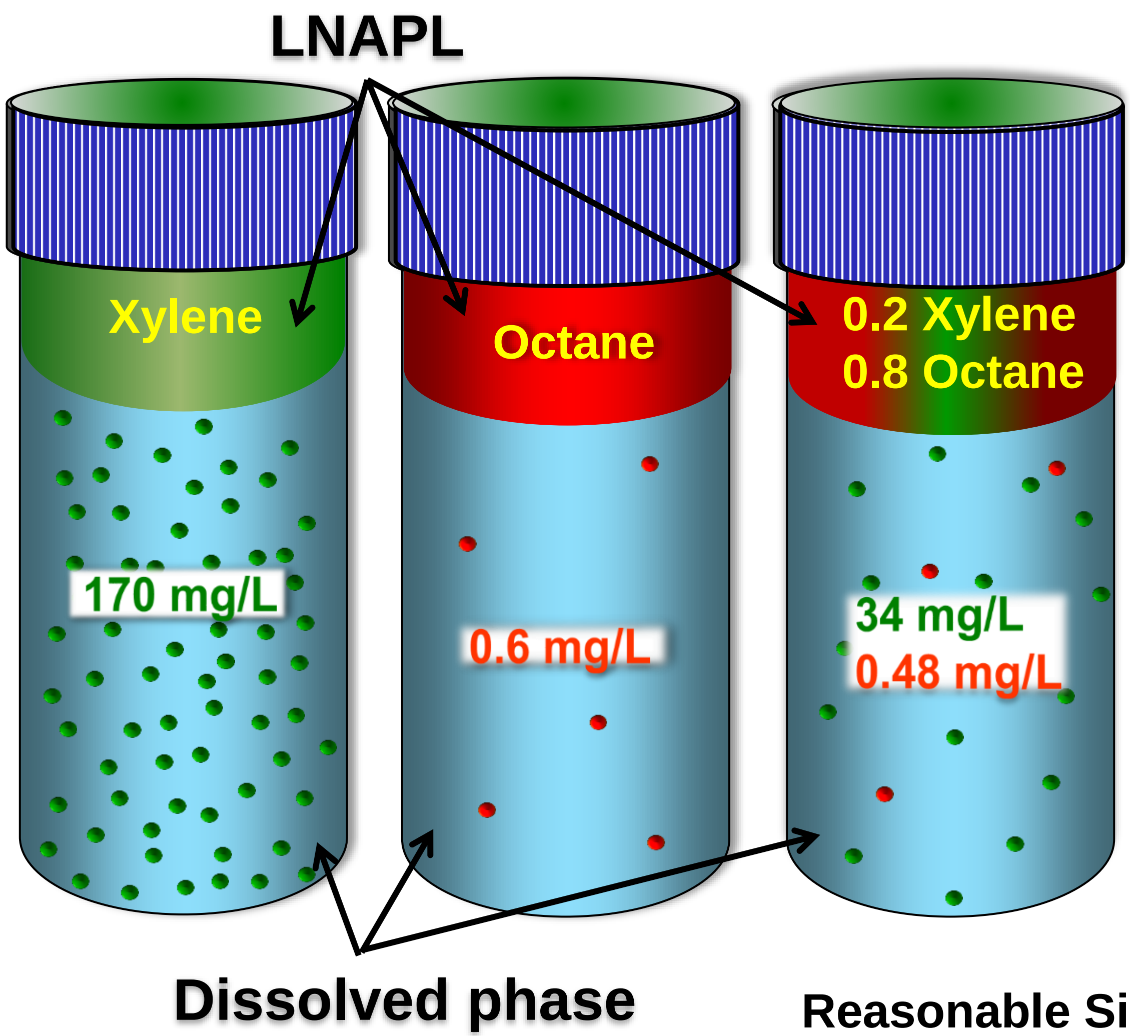
10000 mg/Kg ~4-5%

Key Message 3

LNAPL Saturation vs. Composition

Effective Solubility: Raoult's Law

Indicator: Dissolved Phase



Raoult's Law

$$S_i = x_i S$$

S_i = Effective solubility

S = Sol. of pure chem.

x_i = Mole frxn. of chem.

$$= \text{wt frxn} \times \frac{MW_{NAPL}}{MW_{chem}}$$

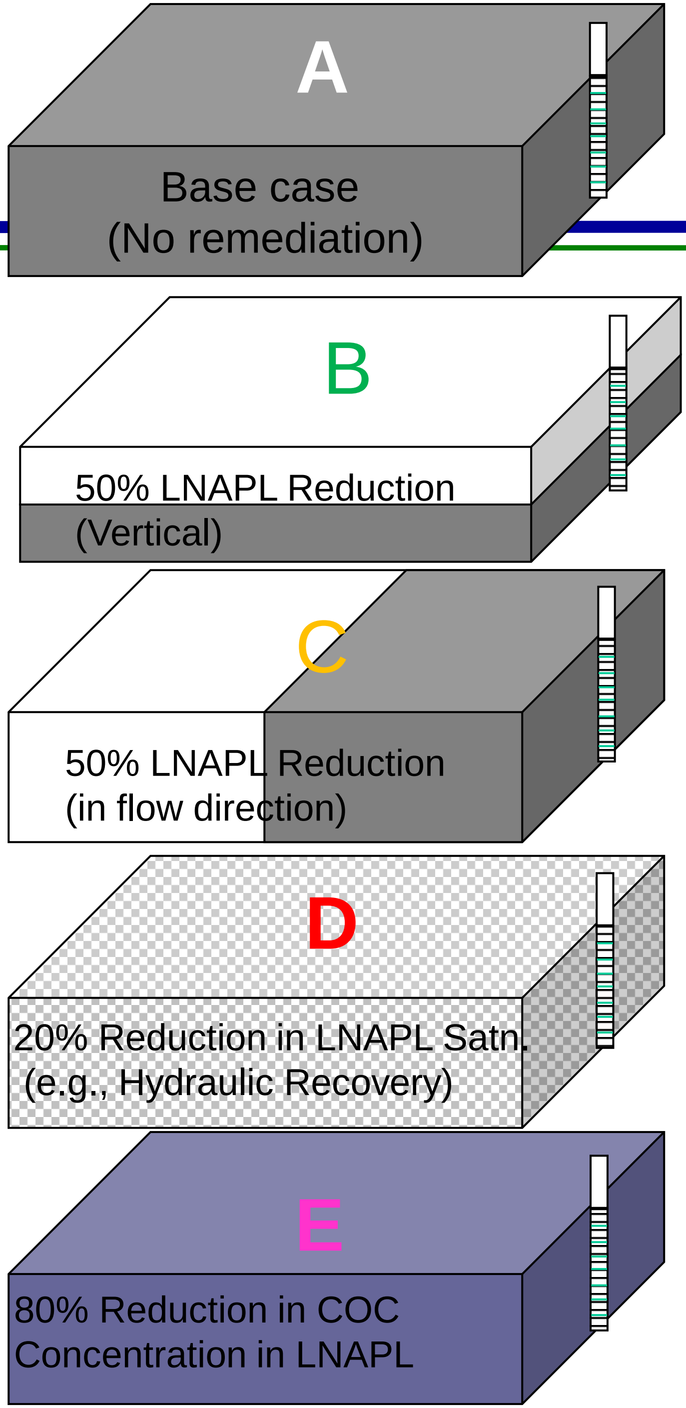
Reasonable Simplification for BTEX:

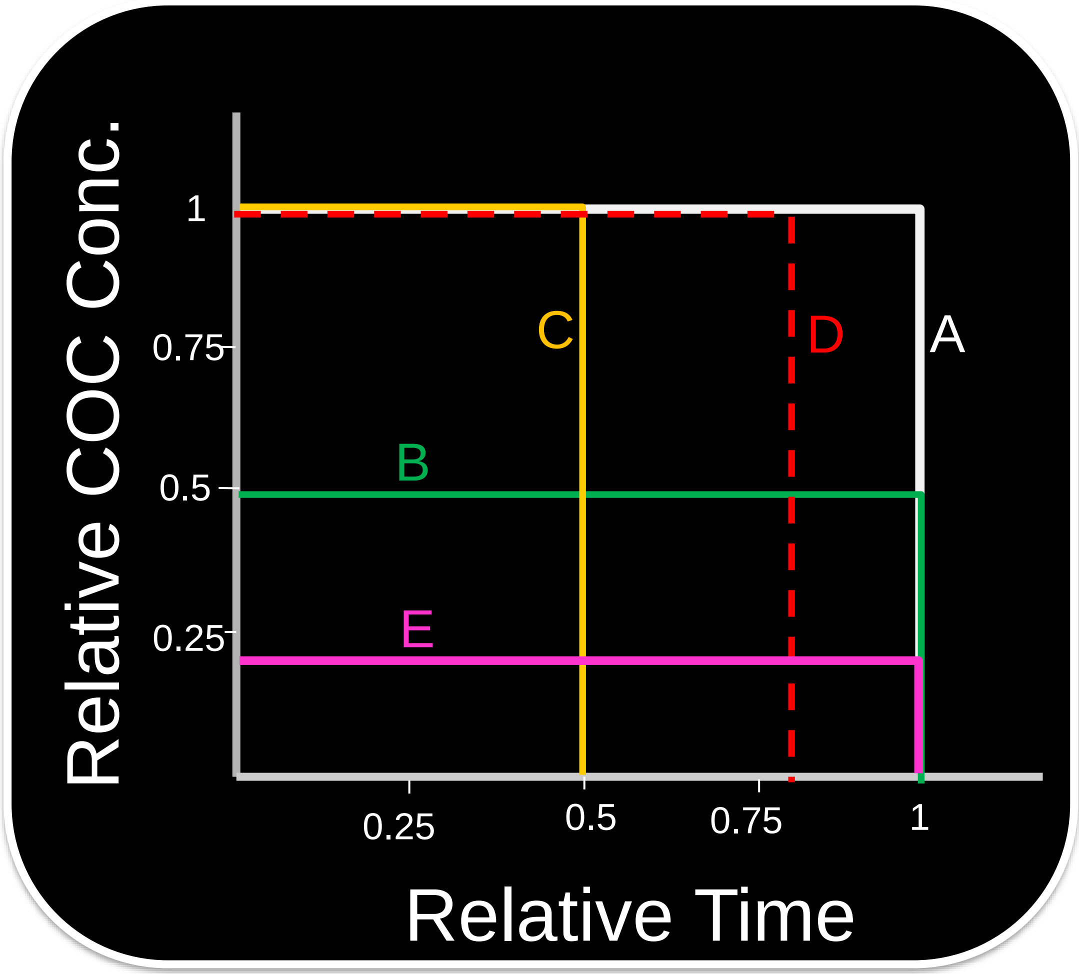
For gasoline: mole frxn. ~ wt. frxn

For diesel: mole frxn ~ 2.5 x wt frxn

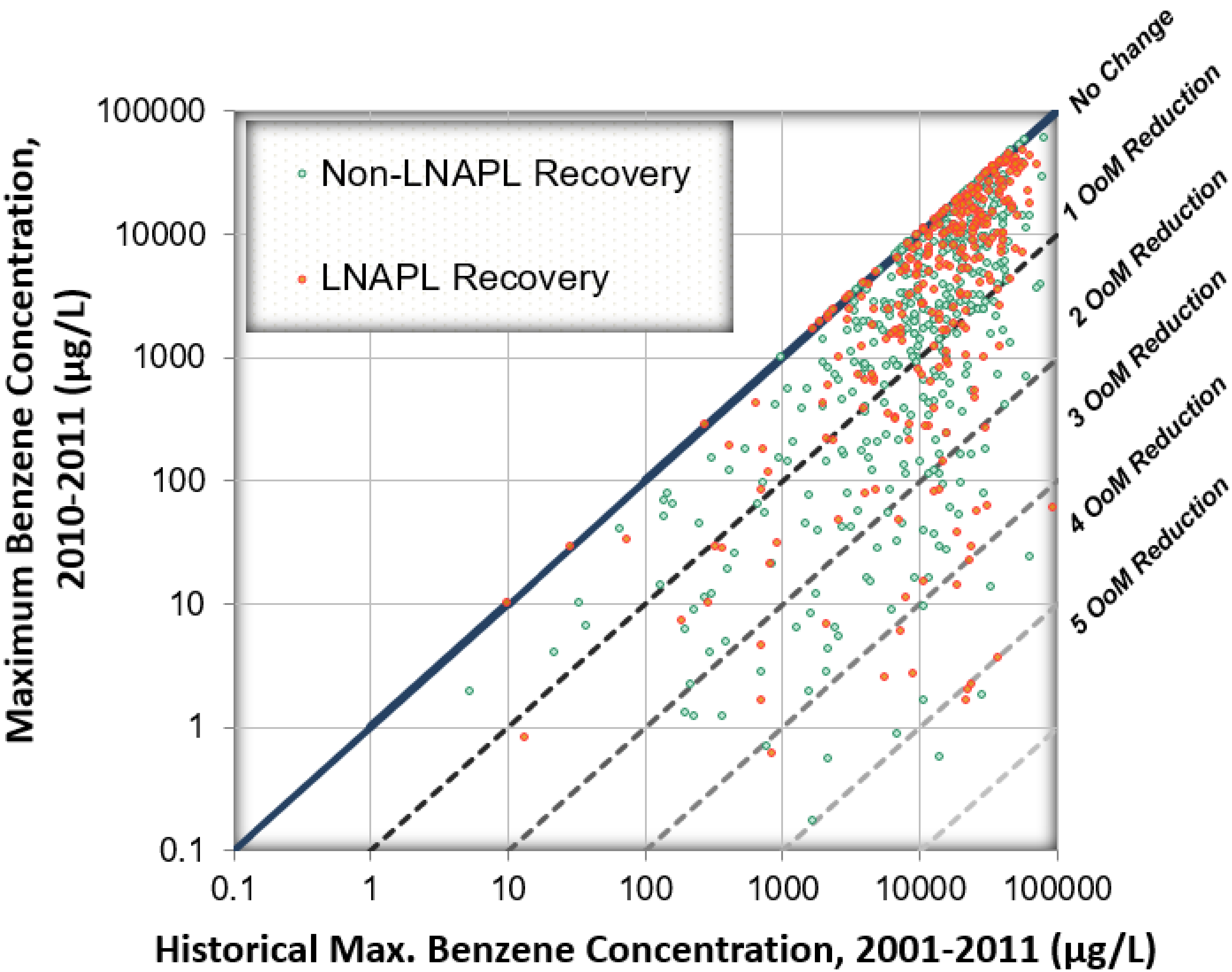
Mass Reduction vs. Composition Change

Strategy





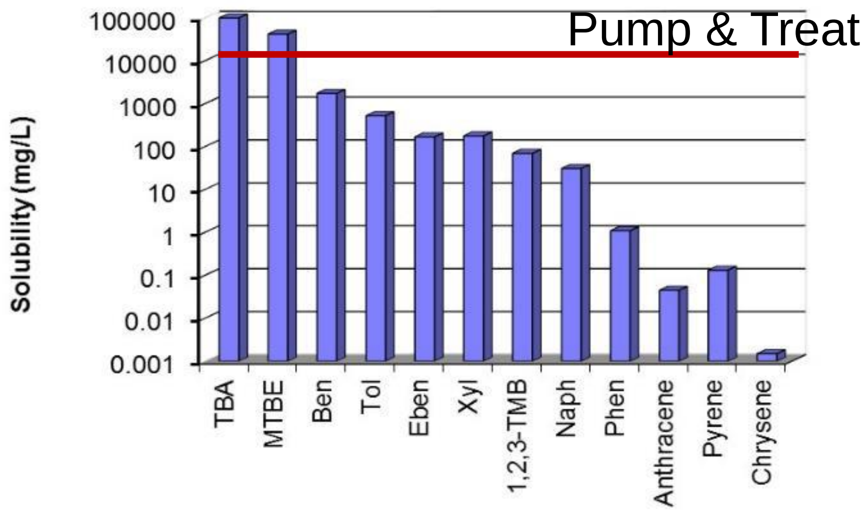
Impact of LNAPL Recovery – Little Benefit In Reducing Dissolved BTEX Concentration



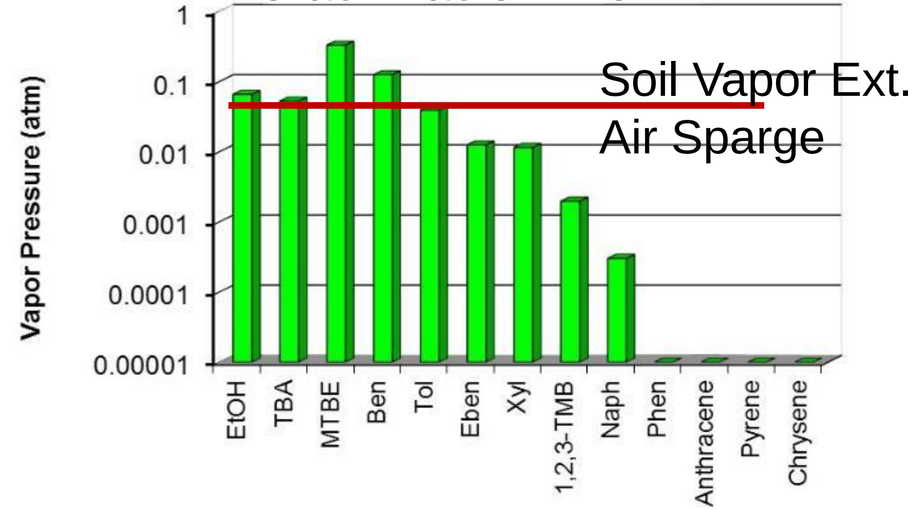
Source: McHugh et al., 2013

How to Change LNAPL Composition

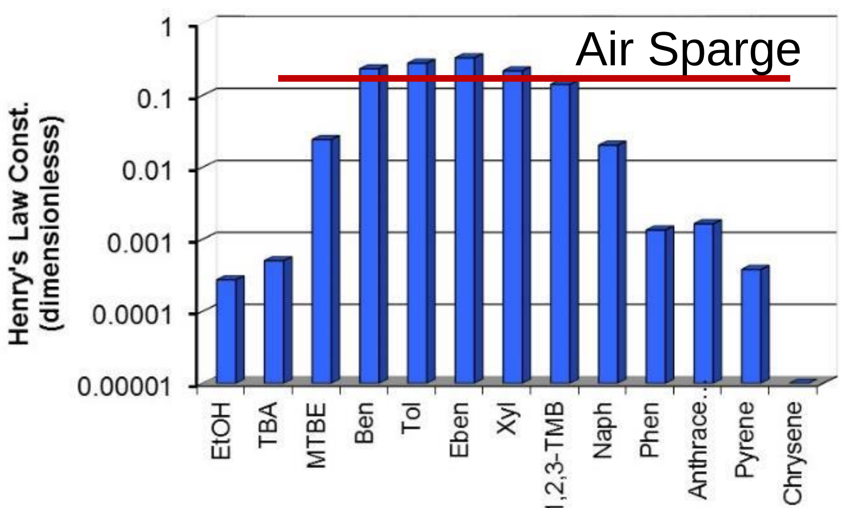
Dissolution



Volatilization from LNAPL



Volatilization from Water



Biodegradation

Compound	Aerobic conditions	Denitrifying conditions	Sulfate-reducing conditions	Iron-reducing conditions
Benzene	++	-	+	-
Toluene	++	++	+	+
m-Xylene	++	++	+	+
p-Xylene	++	+	+	
o-Xylene	++	+/-[1)]	-	-
Ethylbenzene	++	+/-		-
1,2,4-trimethyl-benzene	++			

Knowledge Check

Poll Question

Background: Consider a site with gasoline release:

- LNAPL is observed in onsite MWs
- Goal is to reduce concentrations of Benzene in groundwater in ~2 years

Question: What would be the appropriate remediation approach?

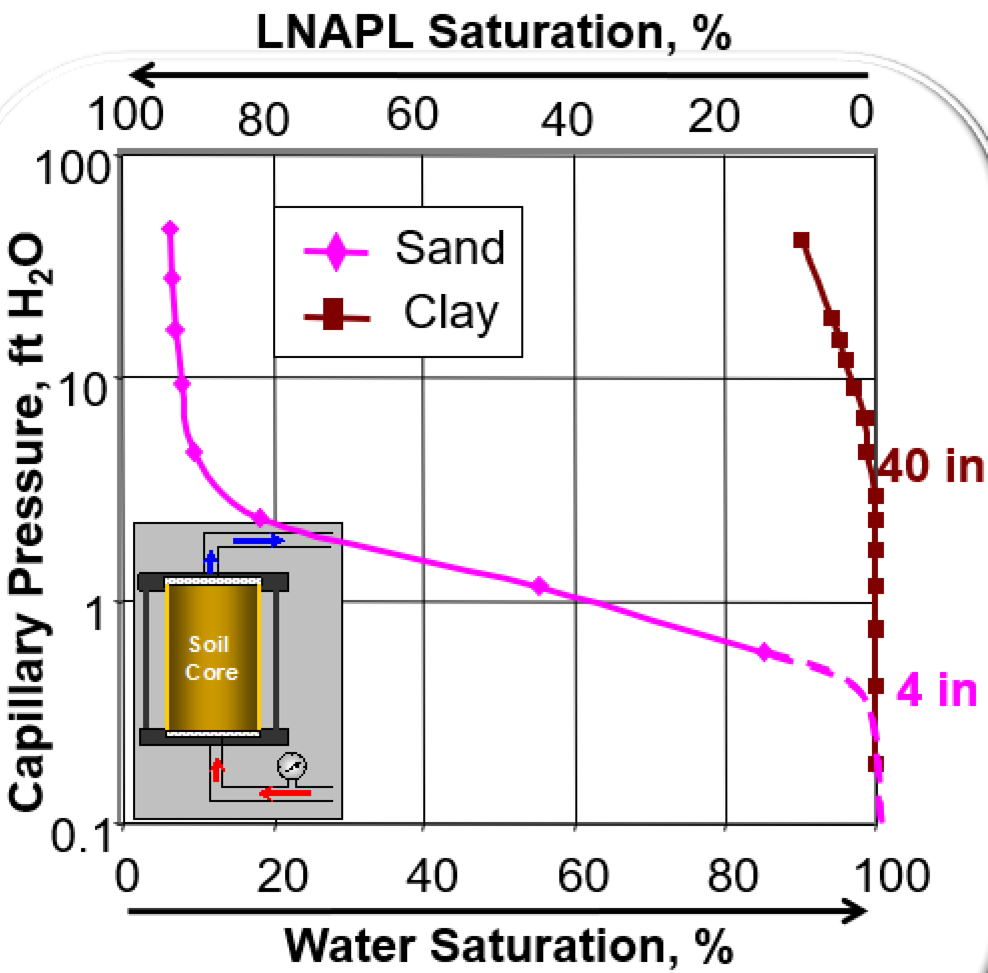
A. Start LNAPL removal by pumping
B. Change LNAPL composition
C. Let Monitored Natural Attenuation take its course

Key Message 4

ALL Apparent LNAPL Thicknesses are not created equal!

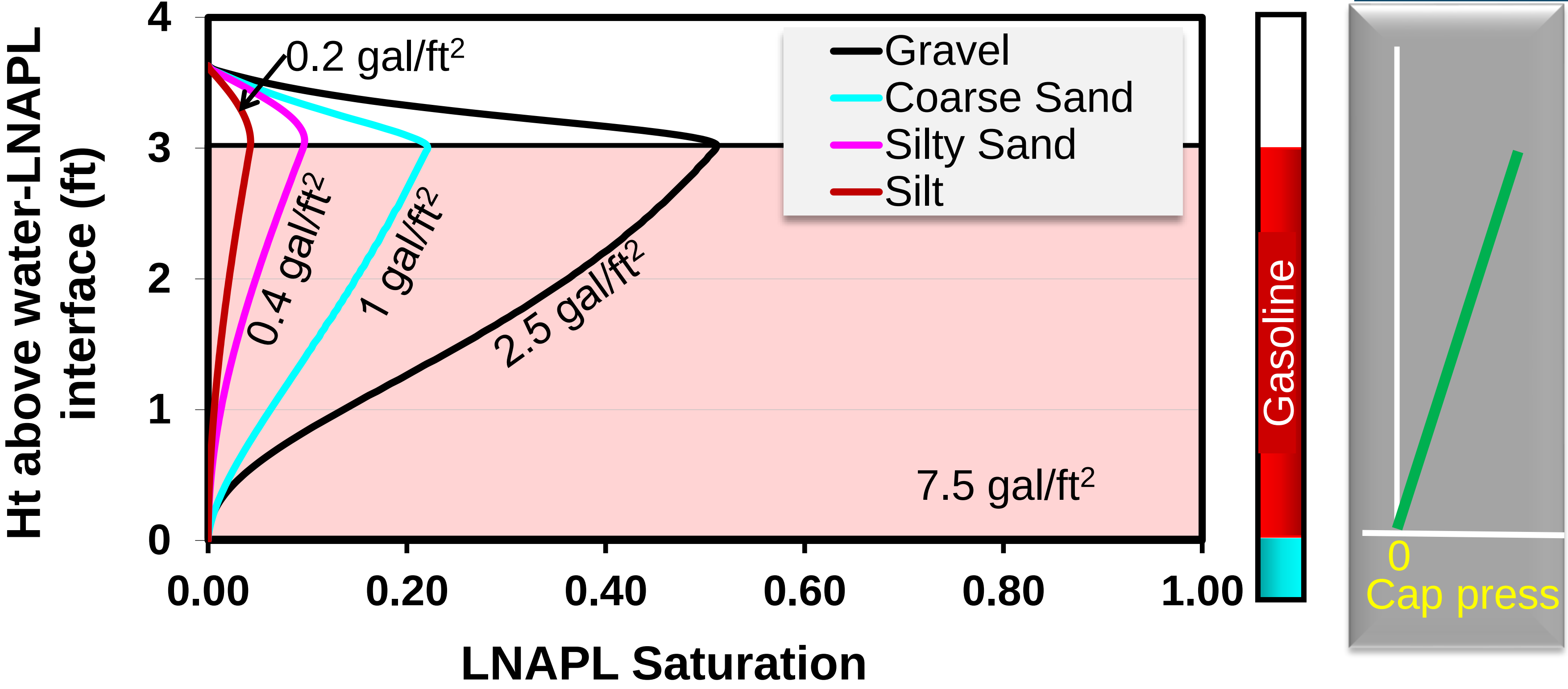
Apparent LNAPL Thicknesses in Unconfined Conditions

Moisture Retention Curves:
Relate Capillary Pressure & Fluid Saturation



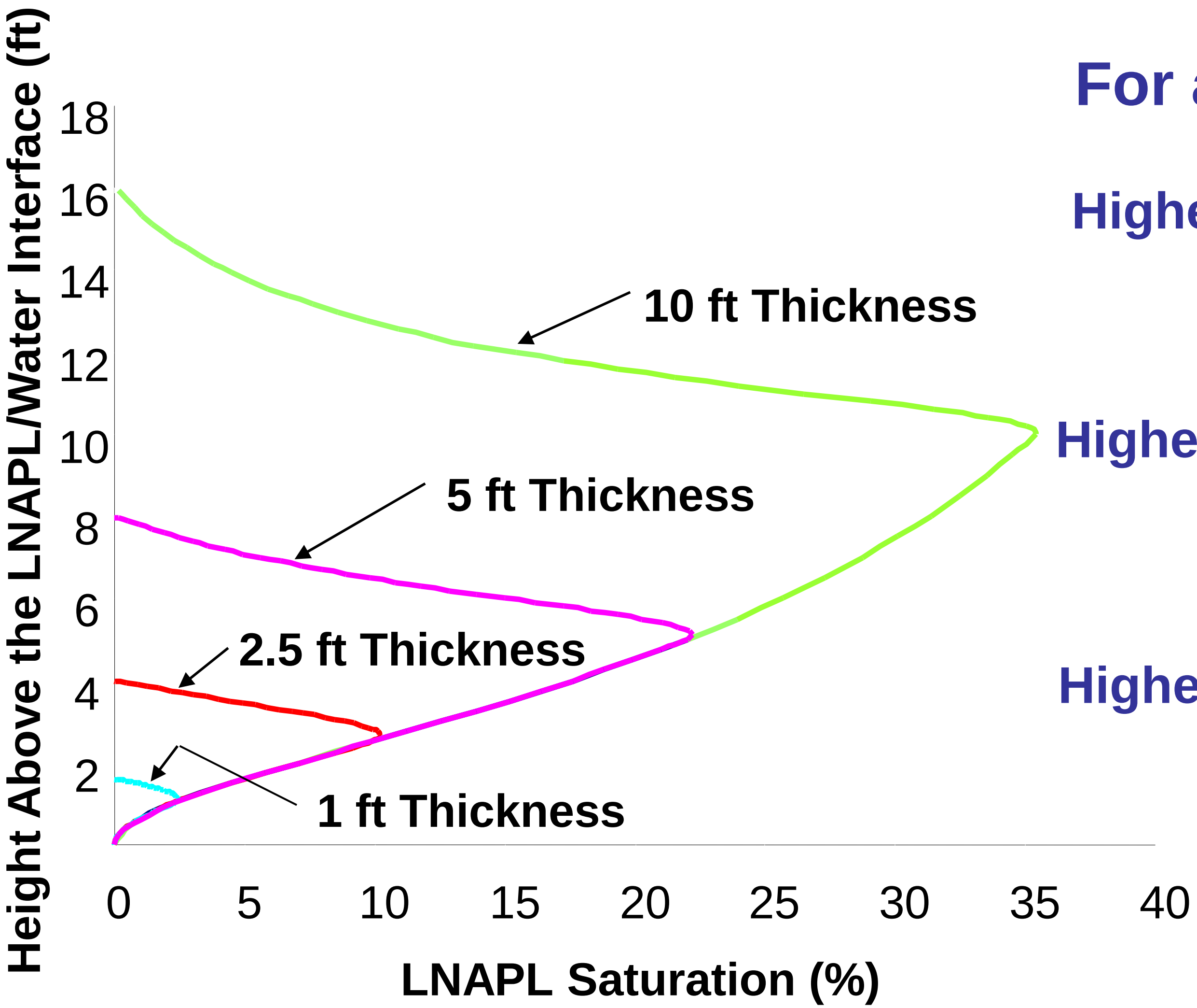
- Relationship between capillary pressure and fluid saturation is established using moisture retention curves
- Unique relationship between capillary pressure and fluid saturations for a given soil type and LNAPL

Grain Size Effects on Vertical LNAPL Distribution (assumed 3 ft of LNAPL in well)



- Volumes based on pancake model (uniform saturations) are over estimated!
- For a given LNAPL thickness, LNAPL saturations and volumes are different for different soil types (greater for coarser-grained soils)

In-Well LNAPL Thickness Inference on Relative Saturation in Silty Sand



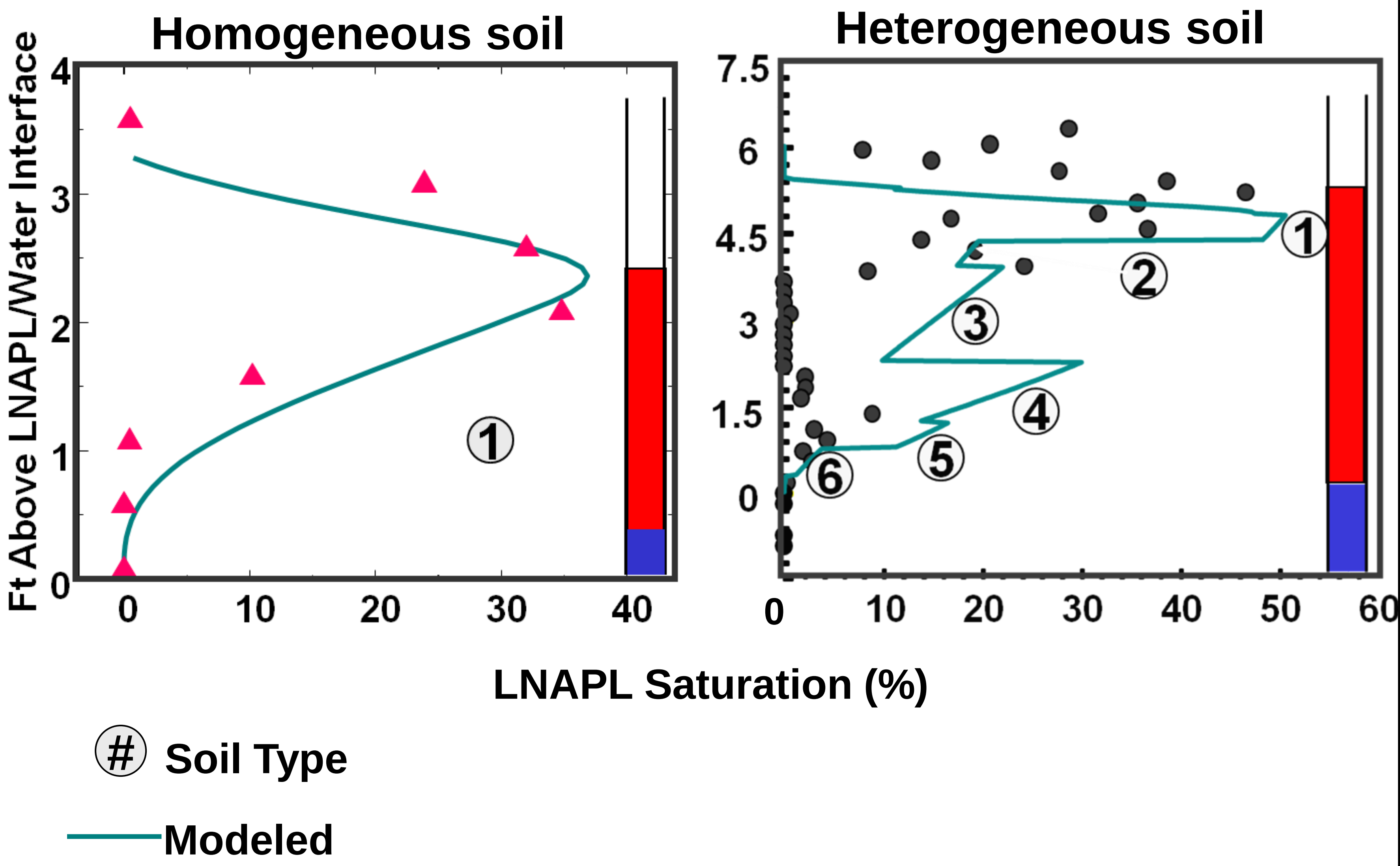
For a *given* soil type

Higher thickness in well

Higher capillary pressure

Higher LNAPL saturation

Measured and Modeled Equilibrium LNAPL Saturations



Beckett and Lundegard (1997) , Huntley et al. (1994)

Key Message 5

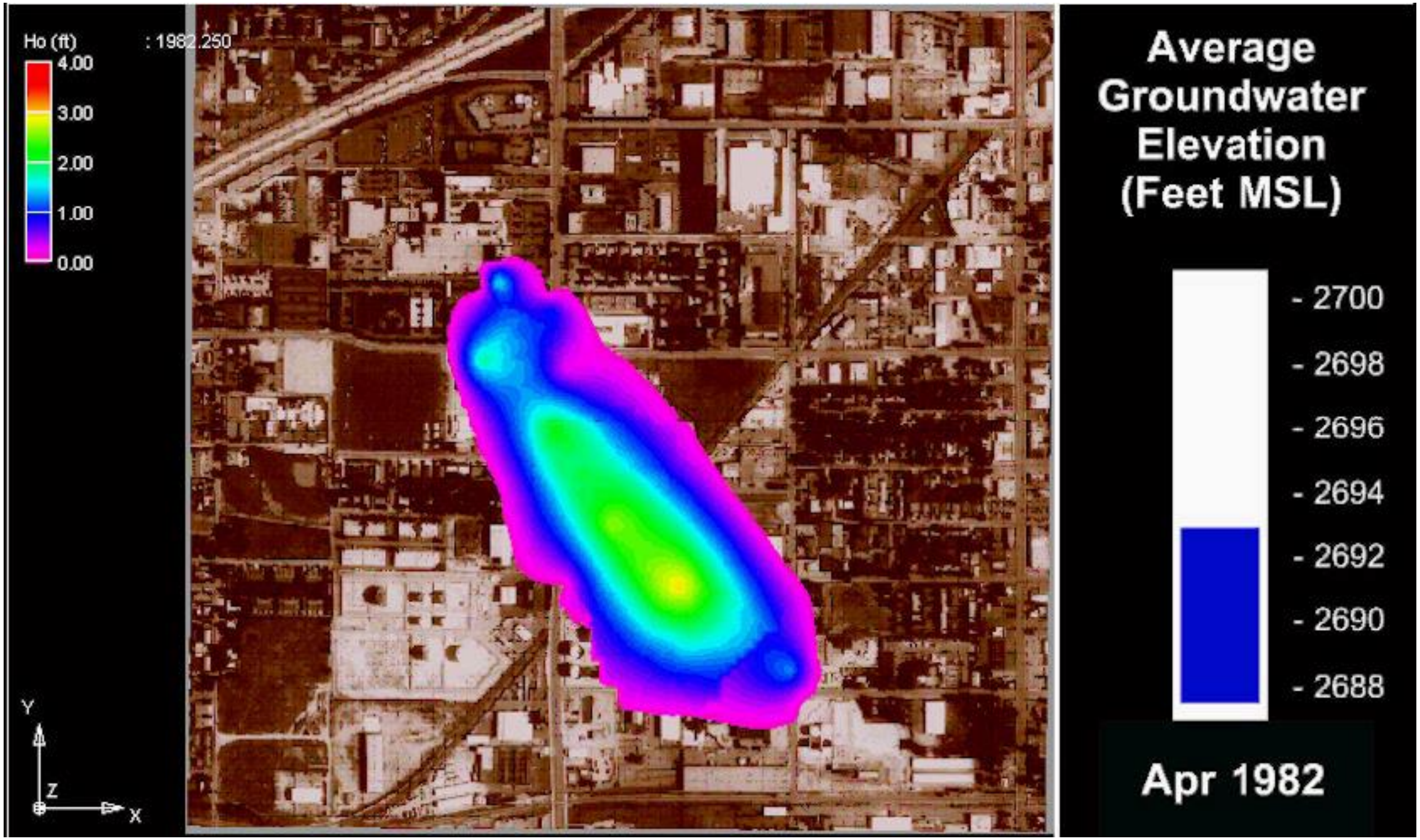
ALL Apparent LNAPL Thicknesses are not created equal!

Apparent LNAPL Thicknesses in Various Hydrogeologic Conditions

Example Seasonal LNAPL Redistribution

Conceptual Challenges – Water Level

LNAPL Monitoring Over Time - Refinery

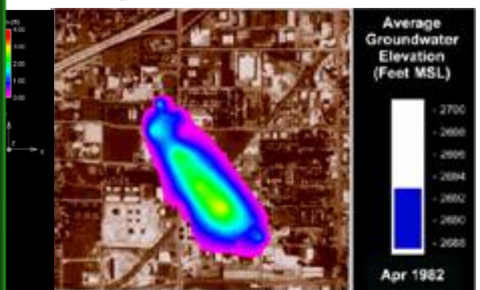


From API Interactive NAPL Guide, 2004

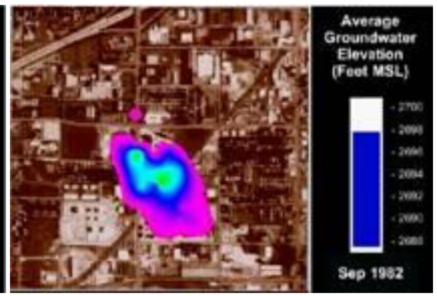
Example Seasonal LNAPL Redistribution

LNAPL Monitoring Over Time - Refinery

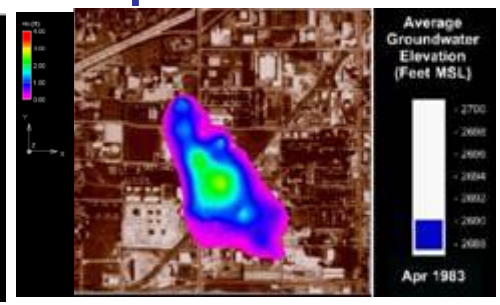
Low Water
April 1982



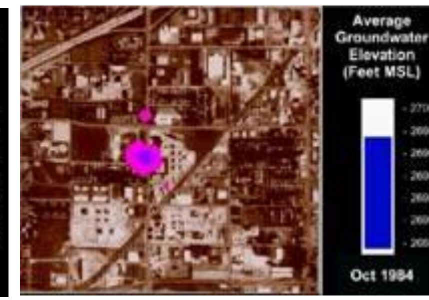
High Water
Sept 1982



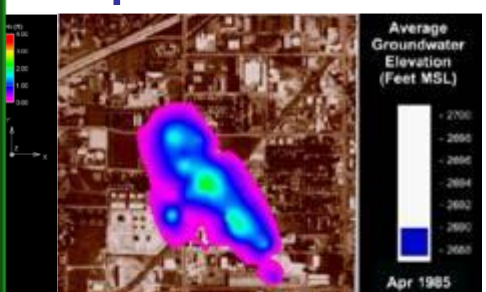
Low Water
April 1983



High Water
Oct 1984

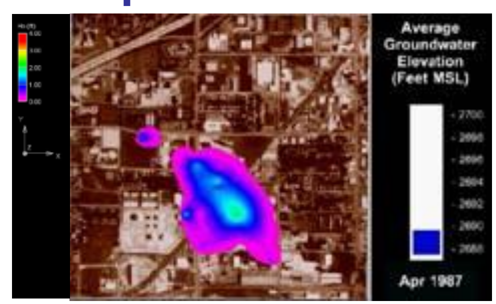


Low Water
April 1985



High Water
Sept 1986

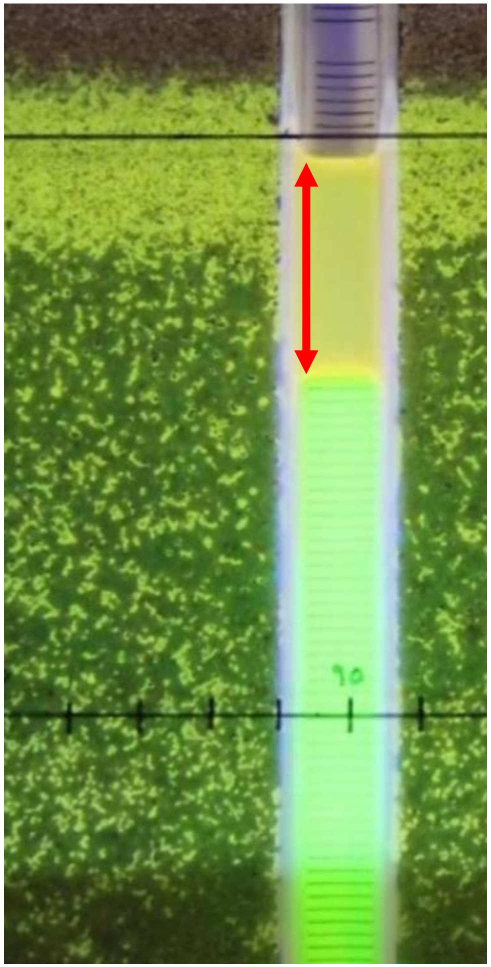
Low Water
April 1987



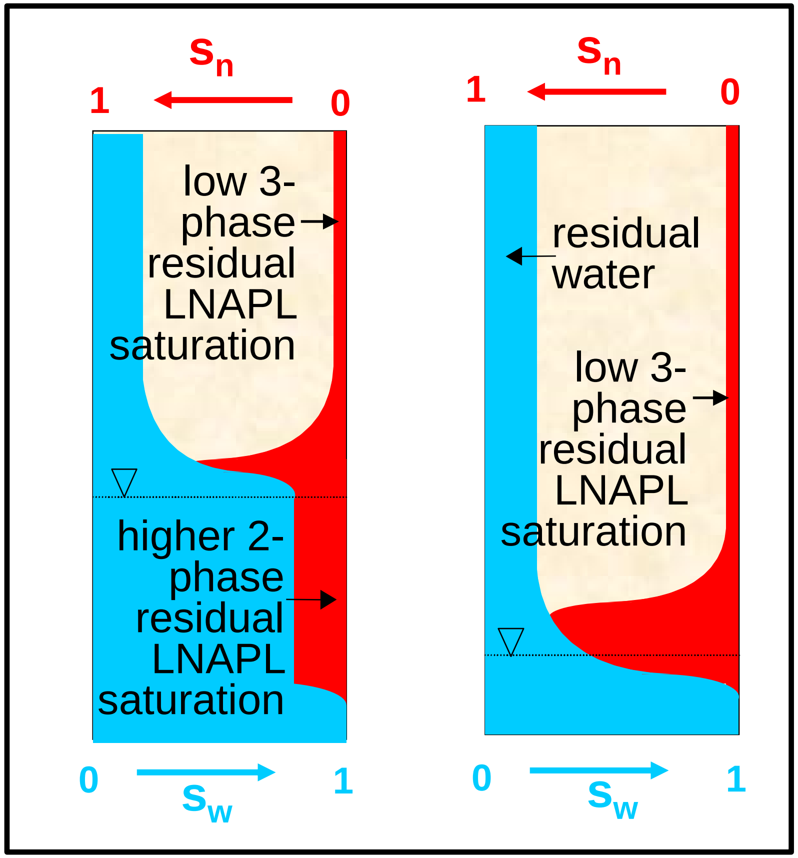
From API Interactive NAPL Guide, 2004

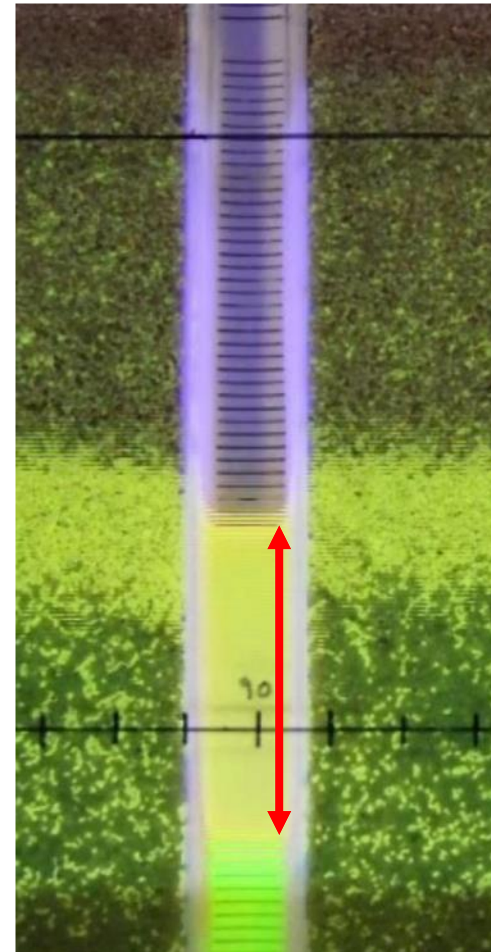
- **Measured LNAPL Depth in Monitoring Wells: 0 to 3 feet**
- **Seasonal Water Table Variation: 8 foot range**

LNAPL Thickness change with water table fluctuation (sand tank study)



High water table



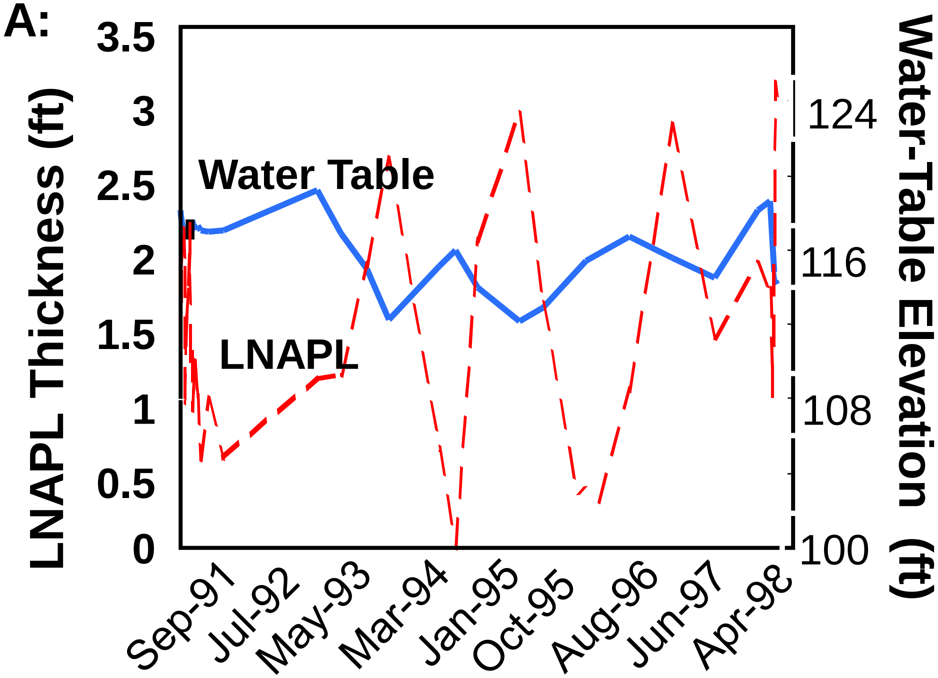


Low water table

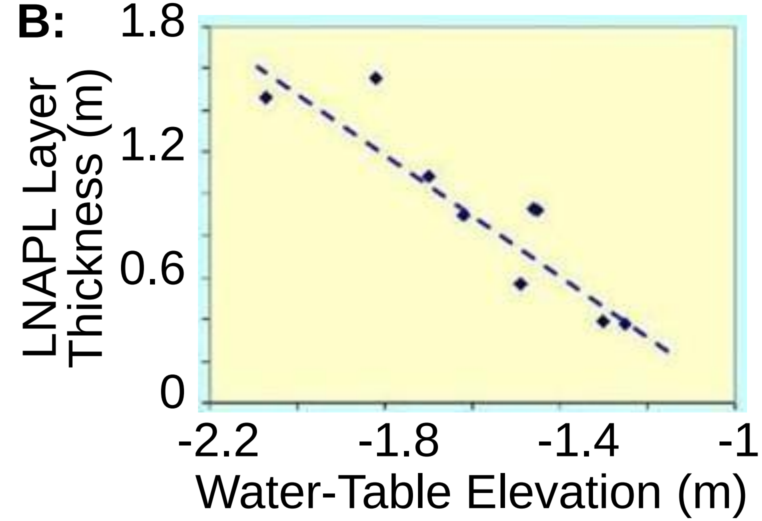
Tank Photo From Alison Hawkins (CSU), graduate student of Dr. Tom Sale

LNAPL Thickness In Well vs. Water Table Elevation (Unconfined)

A:

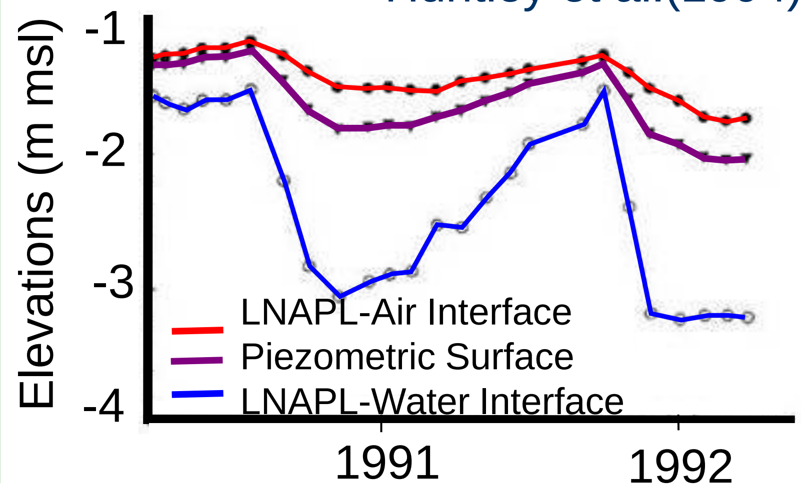


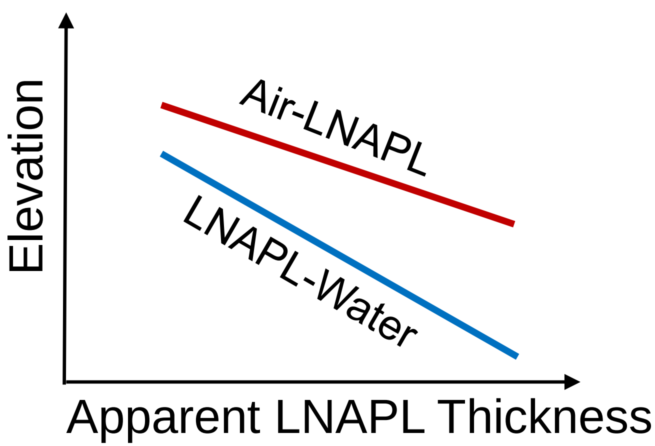
B:



C:

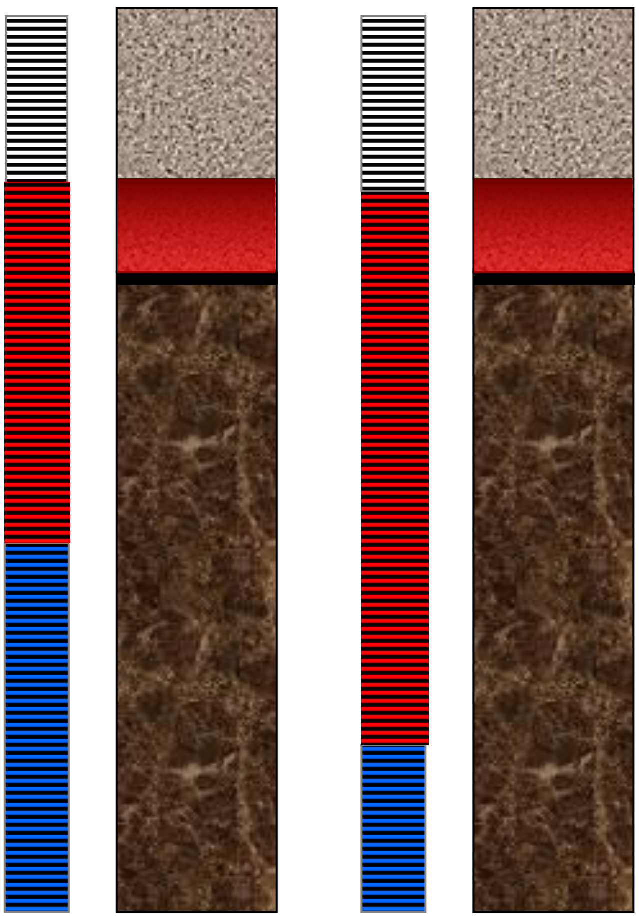
Huntley et al.(1994)

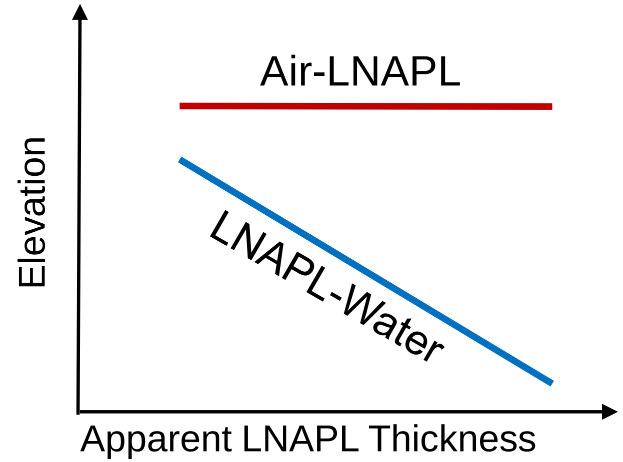


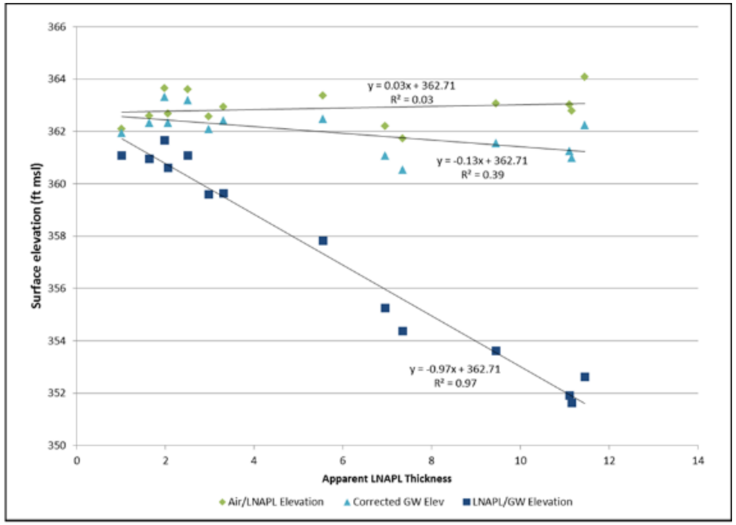


Perched LNAPL Conditions
(Exaggerated Well Thickness)

Conceptual Challenges–Perched

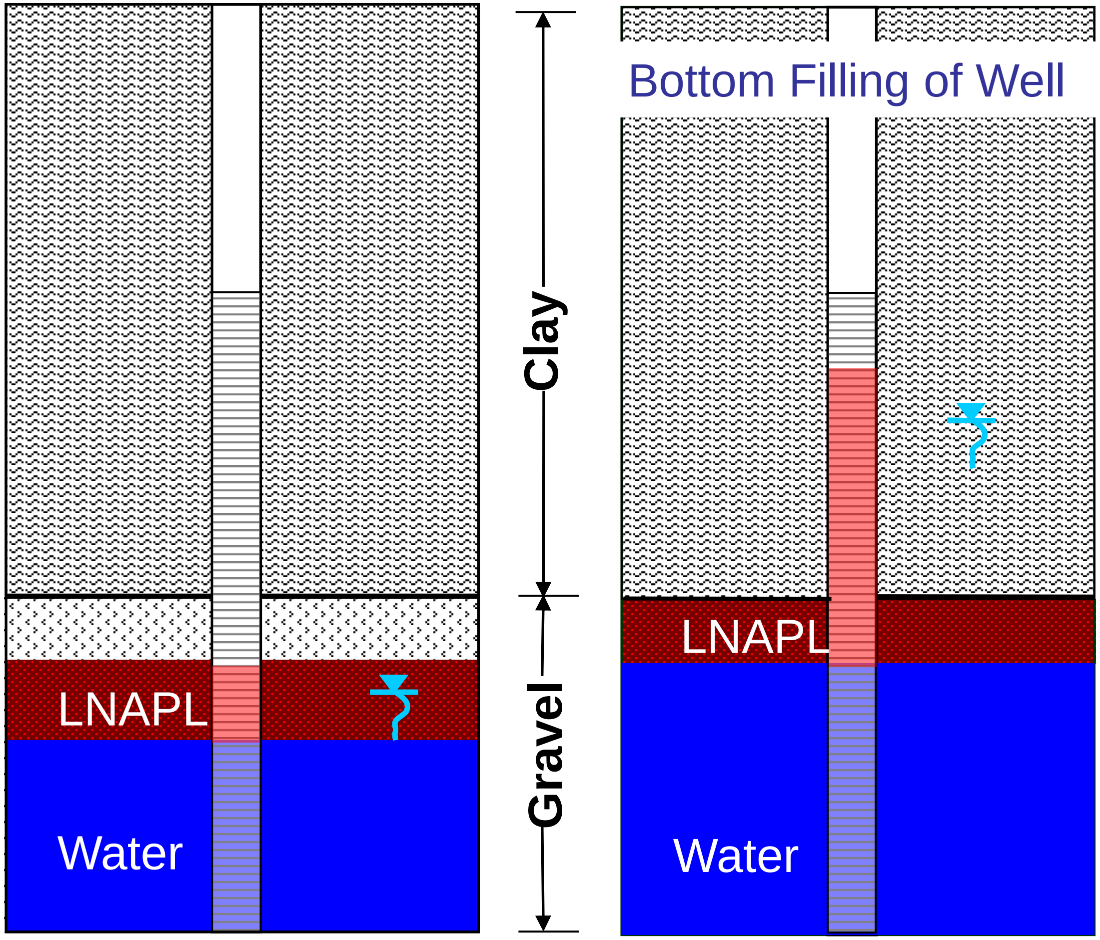


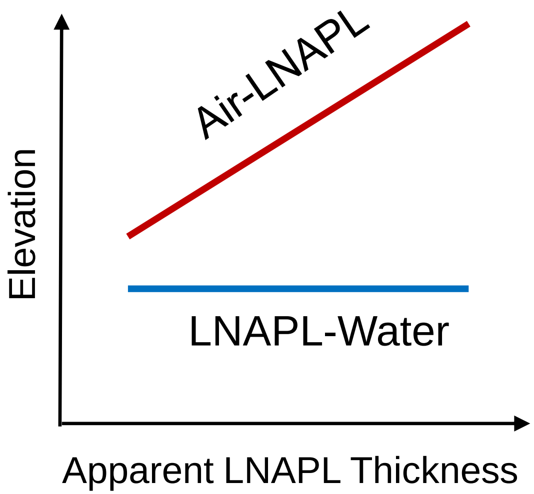




Source: Andrew Kirkman, PE, AECOM

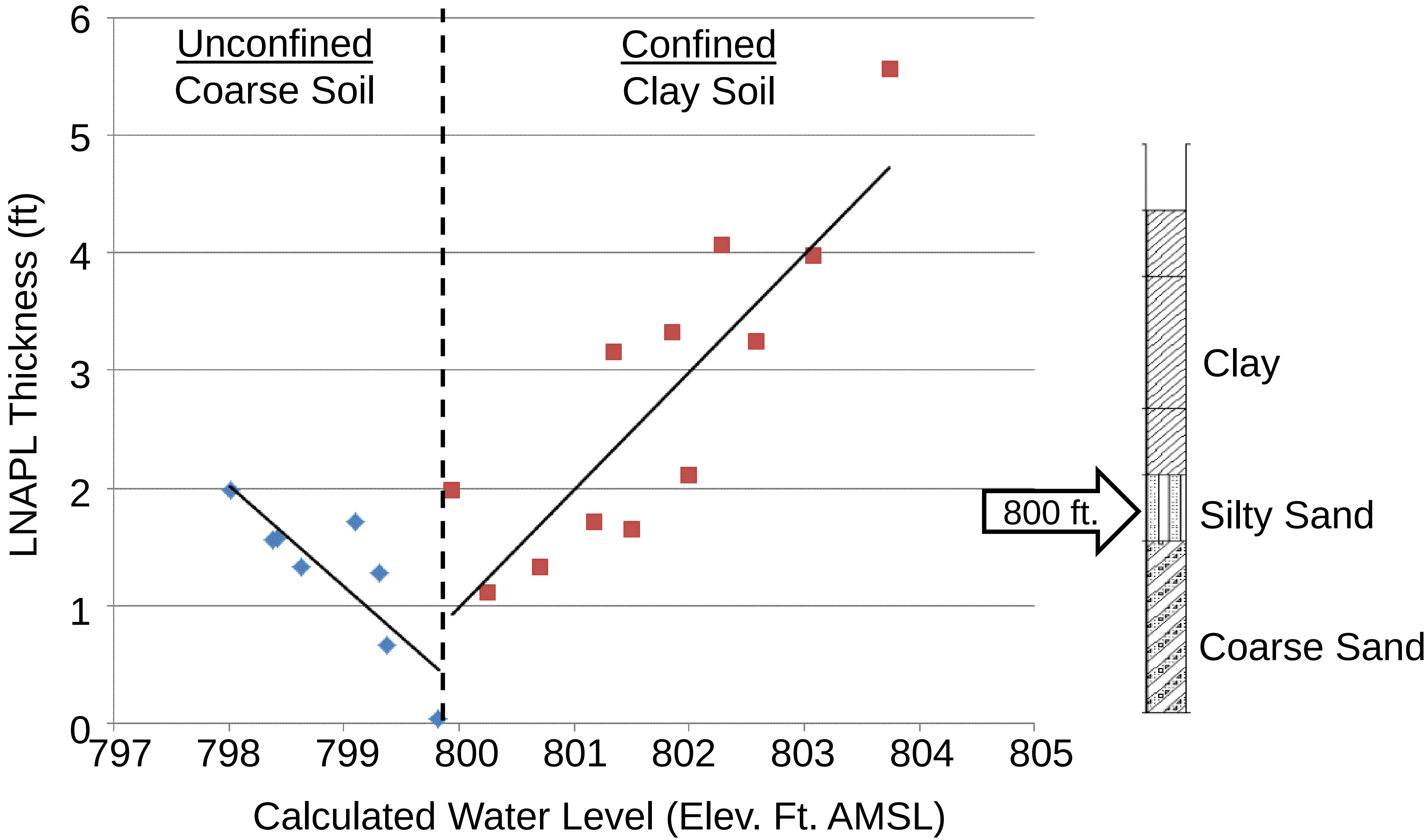
Confined LNAPL Thickness in Well Increases With Water-Level Rise?





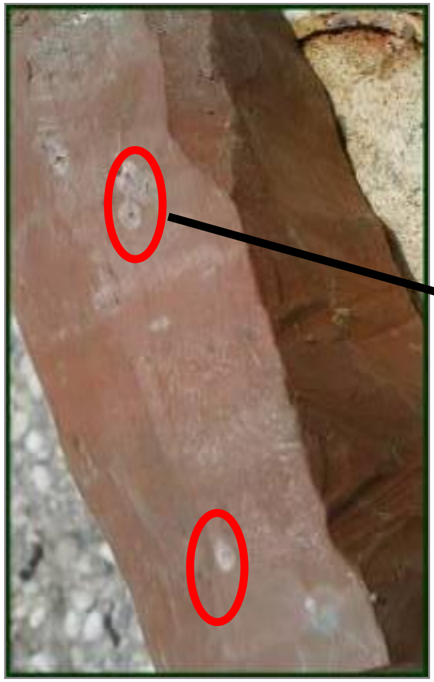
Monitoring well is a giant pore!

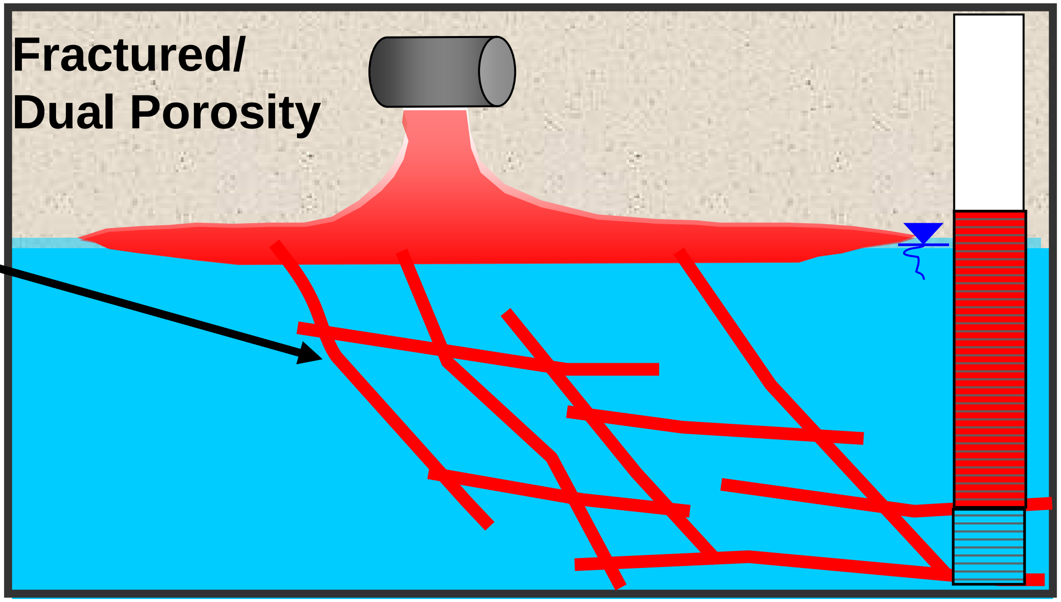
LNAPL Thickness vs. Potentiometric Surface Elevation (Confined)



Fractured and Preferential Pathway Conditions

- LNAPL that is confined in a large pore network that is defined by capillary pressure contrast
  - e.g., open fractures, sand surrounded by clay, macropores





Why Identifying Hydrogeologic Condition of LNAPL Occurrence Important

- Minimizes or exaggerates LNAPL thickness in wells relative to LNAPL thickness in formation
- Volume estimates – modeling and recovery system implications
- Recovery can decrease – while LNAPL thickness is constant
- Understanding LNAPL migration pathways
- Development of effective LNAPL remedial strategy
  - Identify zones to target for LNAPL remediation
  - Critical for identifying appropriate LNAPL remediation technology
- Recovery rate constant for perched – controlled by rate draining off the perching layer (lowering water table won't help)

Knowledge Check

Poll Question

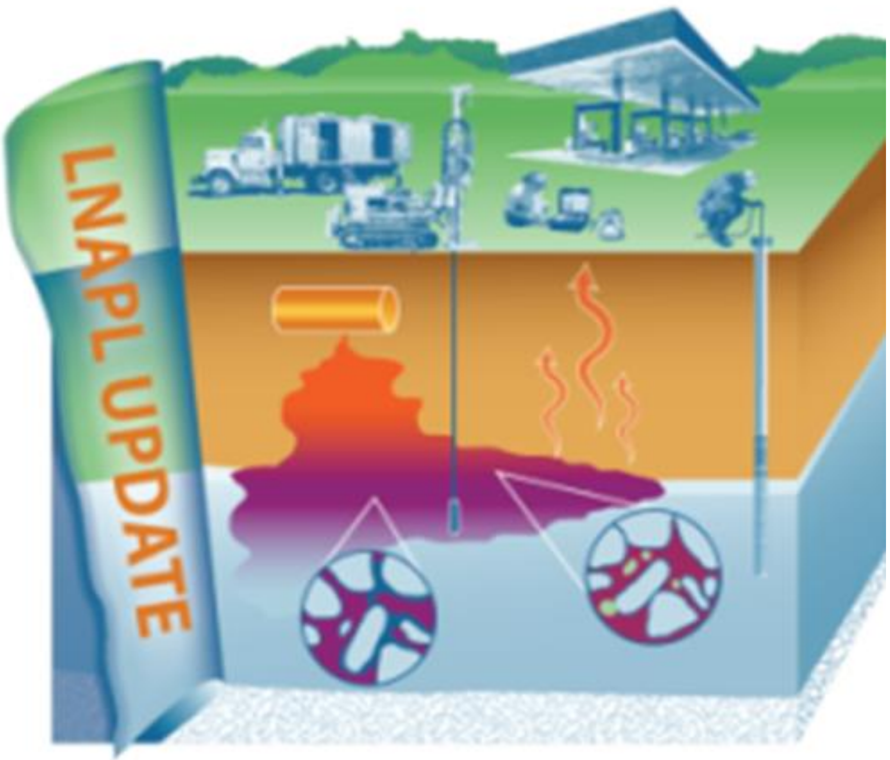
Background: A site has 7 ft. of LNAPL in a well. After a heavy rainfall season, the LNAPL thickness increases to 9 ft.

Question: Which of these is likely to be correct?

A. LNAPL is unconfined
B. LNAPL is perched
C. LNAPL is confined
D. LNAPL is moving / migrating

Q&A Break

Follow ITRC

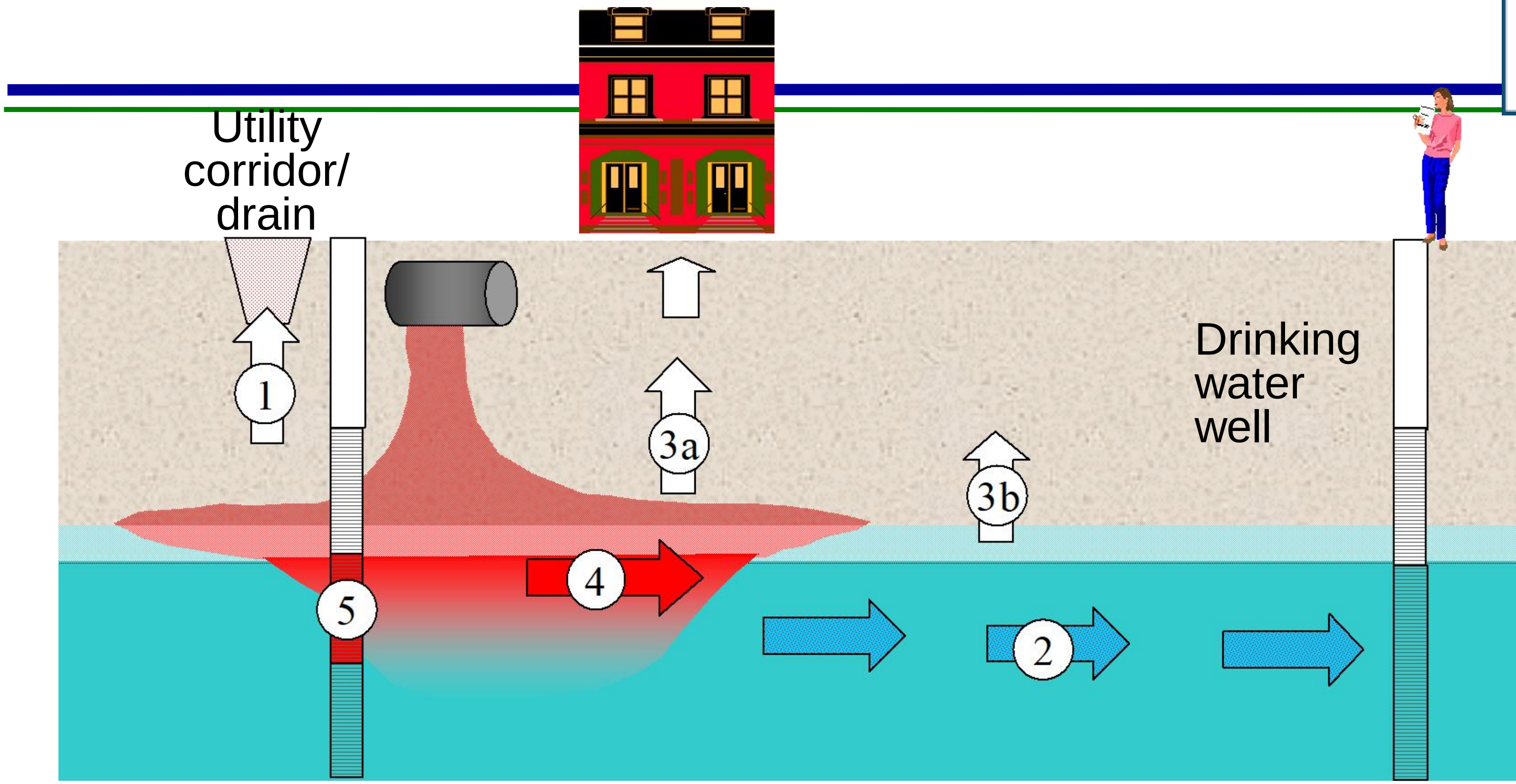


- 1st Question and Answer Break

Key Message 6

Mobile LNAPL does not necessarily mean that the LNAPL is migrating

LNAPL Management Considerations



Source: Garg

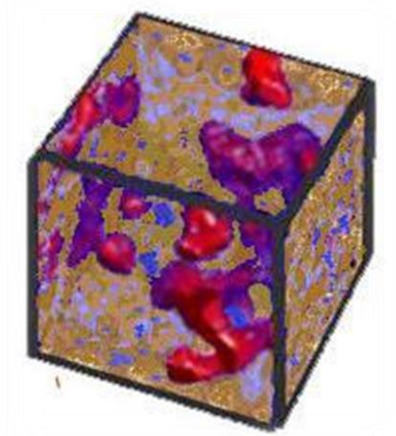
Emergency concerns when LNAPL in the ground (typically addressed by regulations)	Concerns when LNAPL in the ground (typically addressed by regulations)	Potential concerns when LNAPL in wells (not typically addressed by regulations)
(1) Vapor accumulation in confined spaces causing explosive conditions ***Not shown*** - Direct LNAPL migration to surface water ***Not shown*** - Direct LNAPL migration to underground spaces	(2) Groundwater (dissolved phase) (3a) LNAPL to vapor (3b) Groundwater to vapor ***Not shown -*** Direct skin contact	(4) LNAPL potential migration (5) LNAPL in well (aesthetic, reputation, regulatory)

Darcy's Law for LNAPL

- Darcy's Law governs fluid flow in a porous media
    - $q = K\,i$
- In a water / LNAPL system, not just dealing with a single fluid (groundwater or LNAPL)
- Darcy's Law applicable to each fluid (water / LNAPL) independently

Darcy's Law for water flow: $q_w = K_w\, i_w$

Darcy's Law for LNAPL flow: $q_n = K_n\, i_n$



q = Darcy flux (L/T)

K = fluid conductivity (L/T)

i = gradient

$_w$ = water

$_n$ = LNAPL

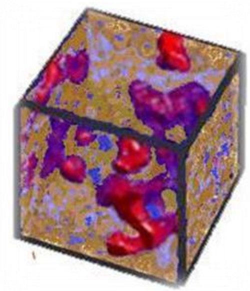
Will next look at LNAPL conductivity (K_n) and LNAPL gradient (i_n)

LNAPL Conductivity

Darcy's Law: Applicable to LNAPL

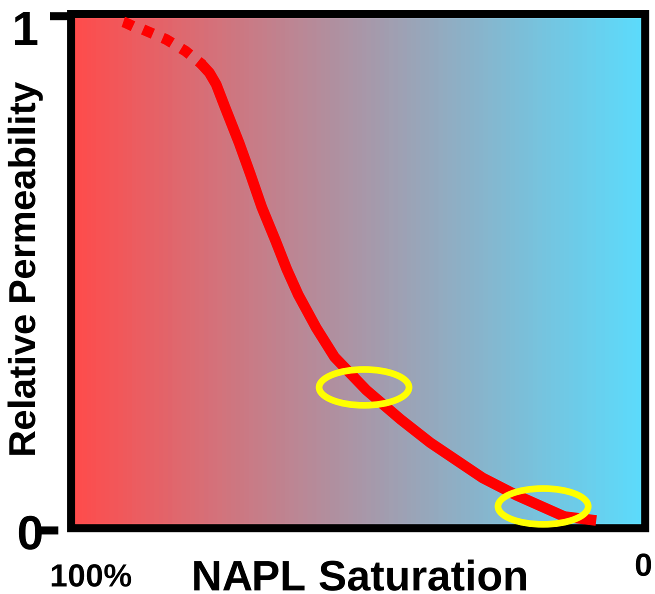
LNAPL conductivity:

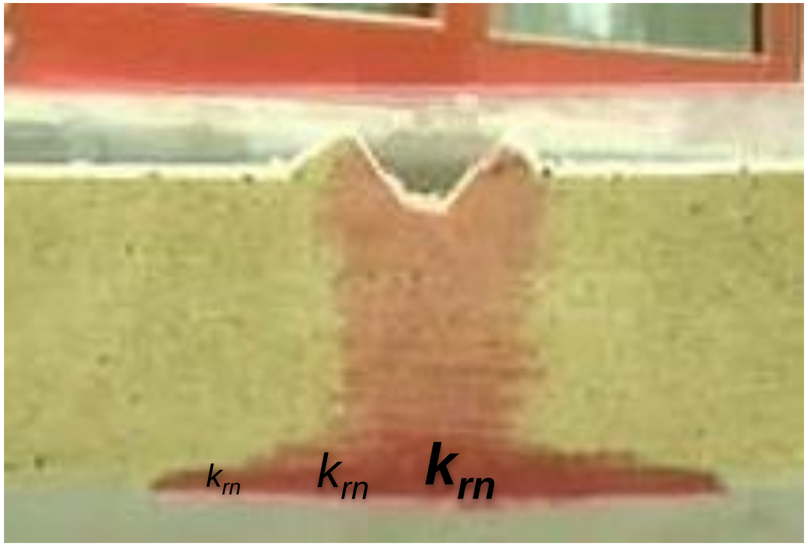
$$K_n = \frac{\rho_n \cdot g \cdot k}{\mu_n} k_{rn}$$



$$K_n = K_{w,sat} \frac{\rho_n}{\rho_w} \frac{\mu_w}{\mu_n} k_{rn}$$

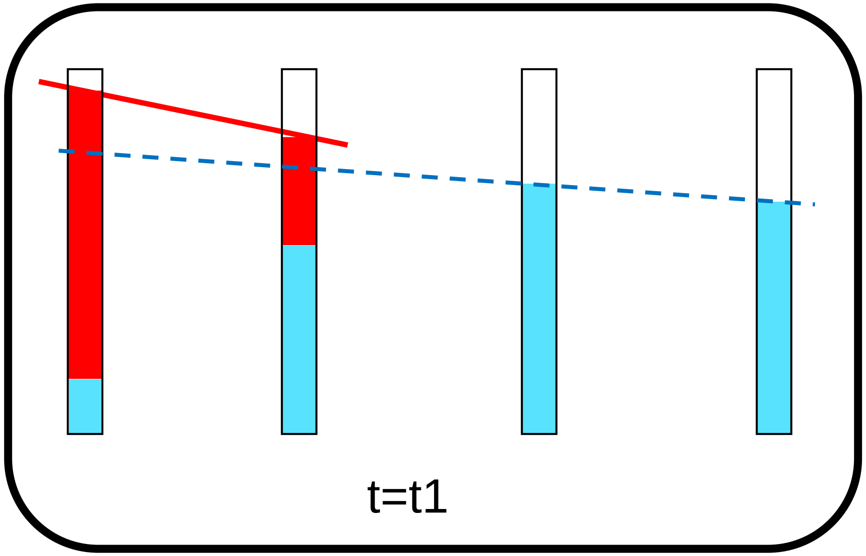
K = conductivity
k = intrinsic permeability
k_r = relative permeability
ρ = density μ = viscosity
$_n$ = LNAPL $_w$ = water
g = acceleration due to gravity

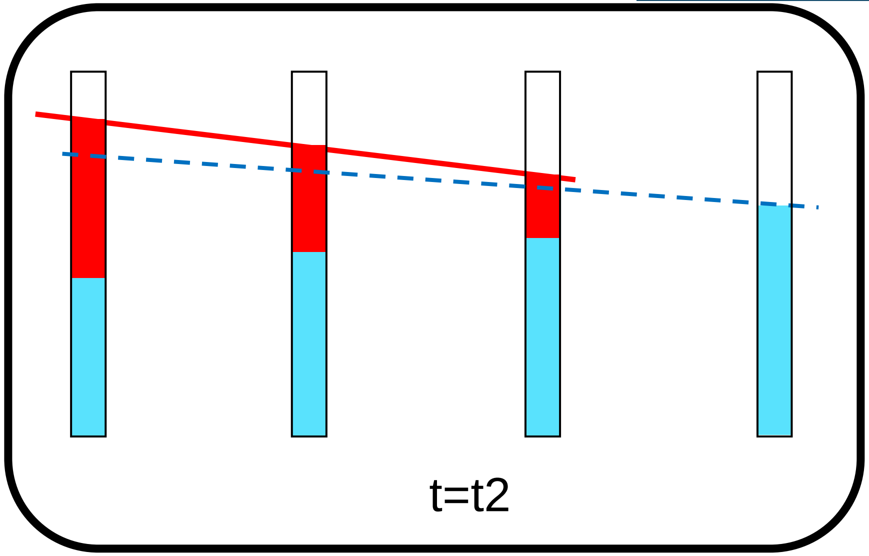


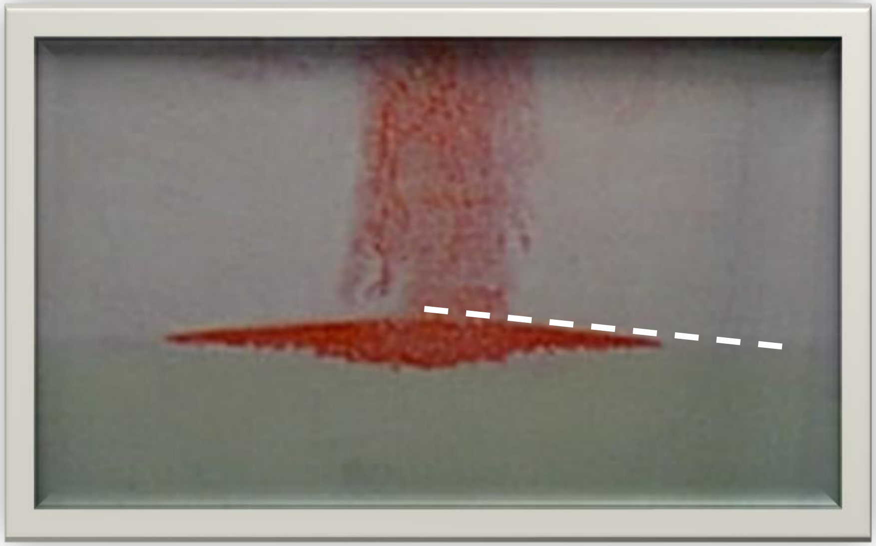


LNAPL Gradient: For a Finite Release Flattens over Time

Darcy's Law: Applicable to LNAPL



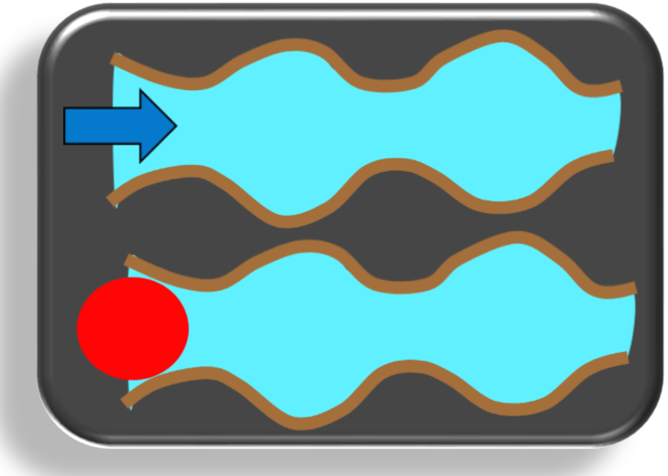




Pore Entry Pressure: LNAPL Behavior

- Similar behavior when LNAPL tries to enter pores with pre-existing fluids
  - Fluid does not encounter resistance when flowing into like (e.g., groundwater flow)
  - Soil pores less wetting to LNAPL than water: LNAPL encounters resistance
  - Soil pores more wetting to LNAPL than air: LNAPL displaces air easily
- LNAPL only moves into water-wet pores when entry pressure (resistance) is overcome
  - To distribute vertically and to migrate laterally

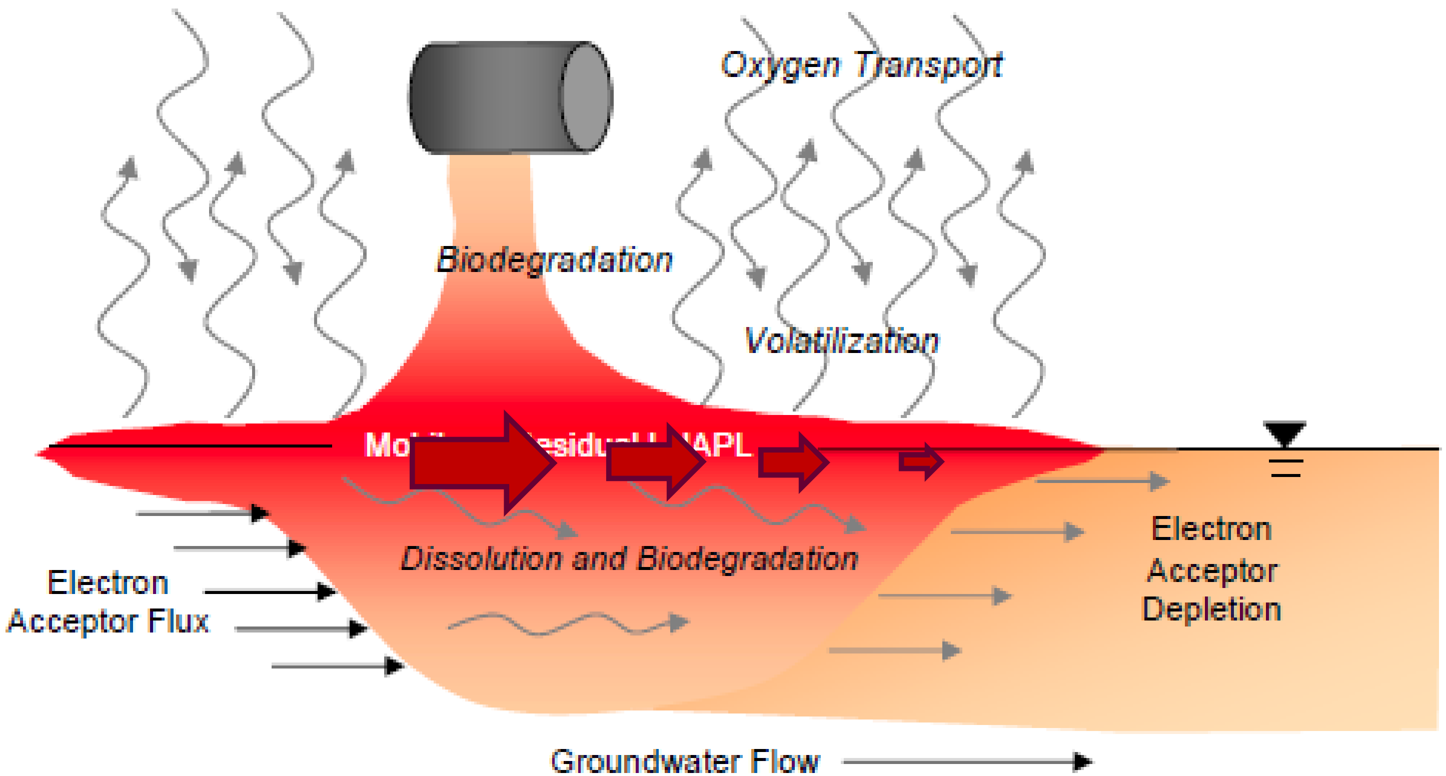
For water-wet media



Key Point: Pore Entry Pressure is the resistance that LNAPL encounters when flowing into a pore with preexisting groundwater

NSZD (Natural Source Zone Depletion) Contributes to LNAPL Stability

- Rates have been measured at about 100 to 1000 gallons per year per acre *(Lundegard & Johnson 2006; ITRC 2009; Sale 2011)*

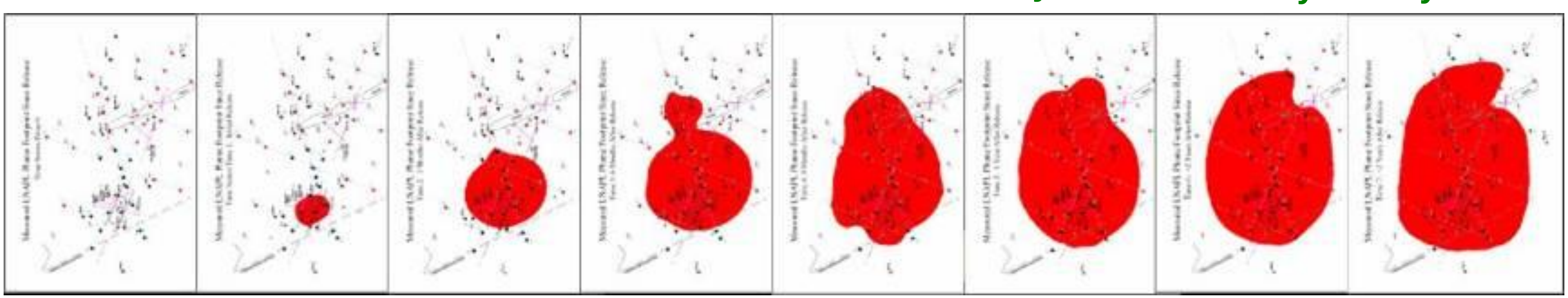


Lines of Evidence:
1. Gauging Data

- Monitoring results (assumes adequate well network)
  - Stable or decreasing thickness of LNAPL in monitoring wells
  - Sentinel wells outside of LNAPL zone remain free of LNAPL

Caution: Need to account for water-table fluctuations when evaluating thicknesses

time = 0 - **0+** **3 months** **6 months** **9 months** **1 year** **2 year** **3 year**



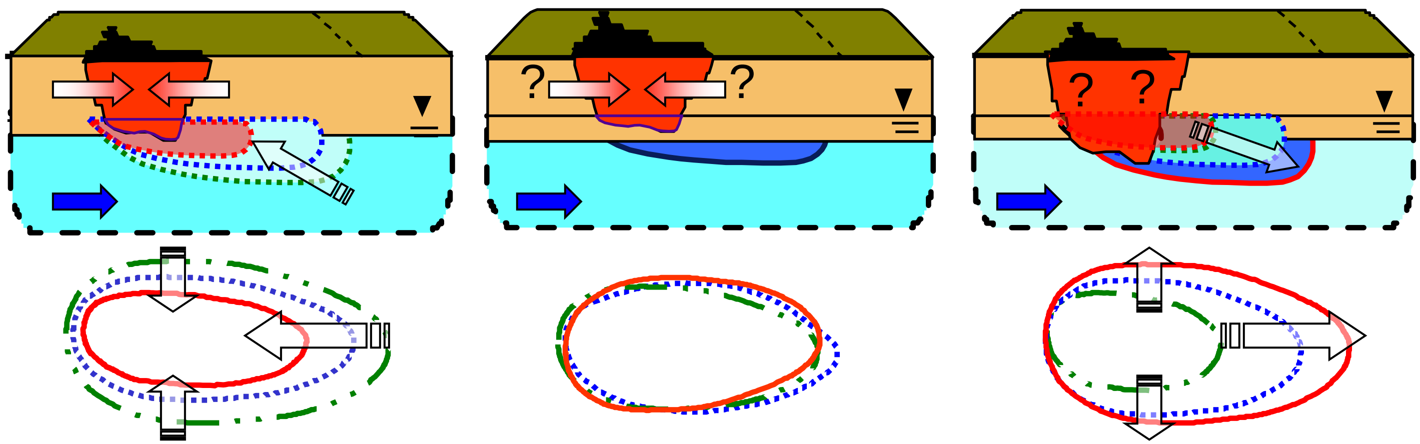
Lines of Evidence:
2. Groundwater Data

- Dissolved-phase plume maps
  - Characterize source area shape, size and depth
  - Assess if natural attenuation on-going
  - Shrinking/stable GW plume = shrinking/stable LNAPL body

Shrinking GW = Shrinking LNAPL

Stable GW = Stable/Shrinking LNAPL

Expanding GW= Shrinking/Stable/Expanding LNAPL

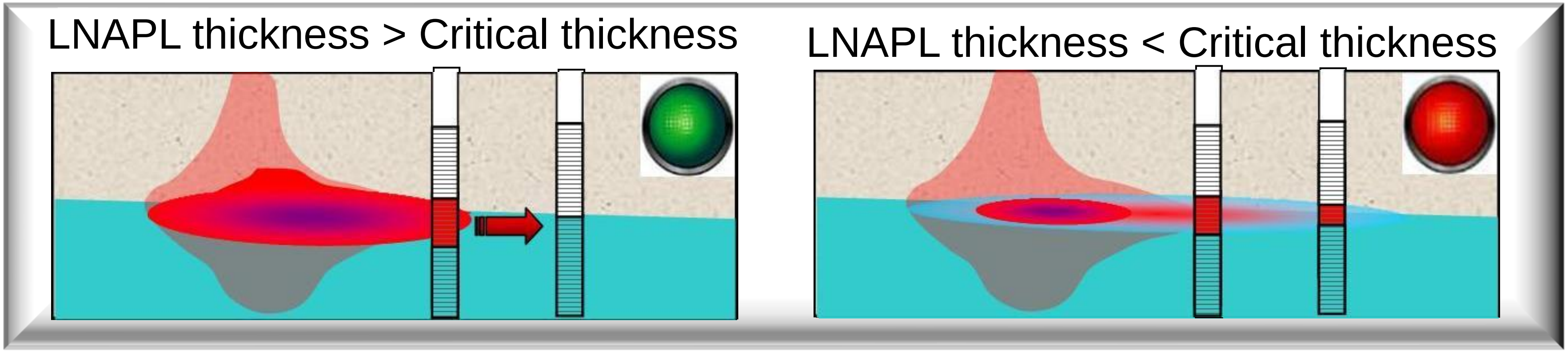


Groundwater Iso-Concentrations vs. Time

Initial time Mid-time Later time

Lines of Evidence: 3. Measured LNAPL Thickness < Critical Thickness

LNAPL Footprint Stability LOE



Soil Type	Capillary Fringe Height (ft)	Critical LNAPL Thickness for Gasoline (ft.)	Critical LNAPL Thickness for Diesel (ft.)
Sand	0.23	0.7	1
Sandy Loam	0.43	1.4	2.1
Loam	0.92	2.8	3.6
Silt	2.03	4.8	5.9
Sandy Clay	1.21	3.9	4.9
Clay	4.10	6.6	9.5
Silty Clay	6.56	8.7	13.8

Ref: Charbeneau et al. (1999)
API Publication No. 4682

Other Lines Of Evidence Of LNAPL Footprint Stability

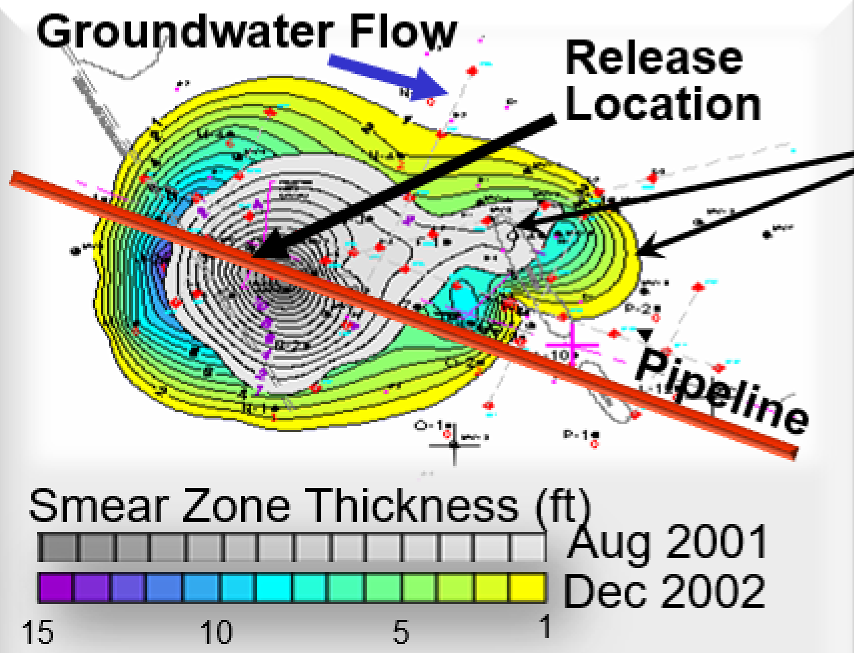
4. Low LNAPL Transmissivity
   - Low Kn
   - Site measurements yield average values – can have higher Kn lenses
5. Age of the release
   - Abated release
   - Timing of release (if known)
   - Weathering indicators
6. Recovery rates
   - Decreasing LNAPL recovery rates
7. Laboratory tests
   - Saturation and residual saturation values
8. Tracer test
   - Measures rate of dilution of hydrophobic tracer

LNAPL Migration: Case Examples

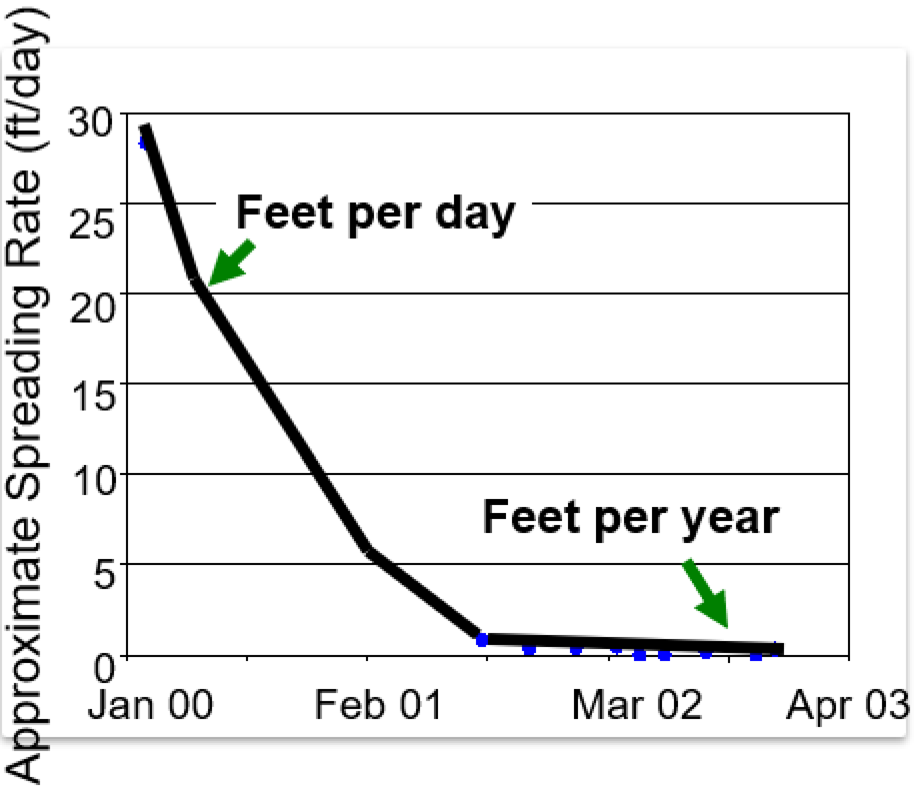
What we have observed at sites:

- LNAPL can initially spread at rates higher than the groundwater flow rate due to large LNAPL hydraulic heads at time of release
- LNAPL can spread opposite to the direction of the groundwater gradient (radial spreading)
- After LNAPL release is abated, LNAPL bodies come to be stable configuration generally within a short period of time

Case Example 1:
LNAPL Release and Spreading



Change in LNAPL footprint from Aug '01 to Dec '02

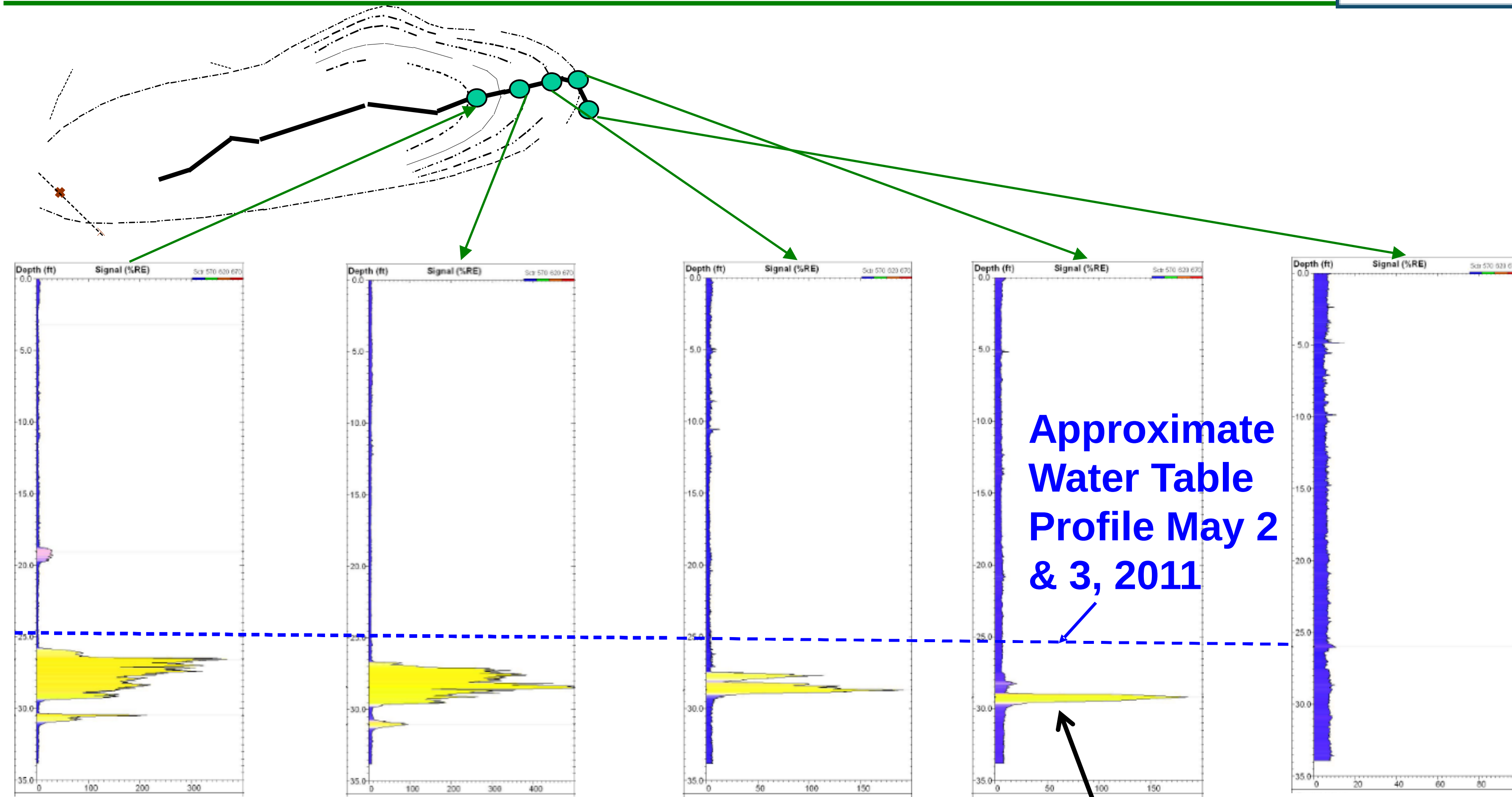


Pipeline release in Feb 2000

- Sweet Texas crude
- Unknown release volume

Case Example 2: Bemidji, MN North

Pool Transect LIF Signatures

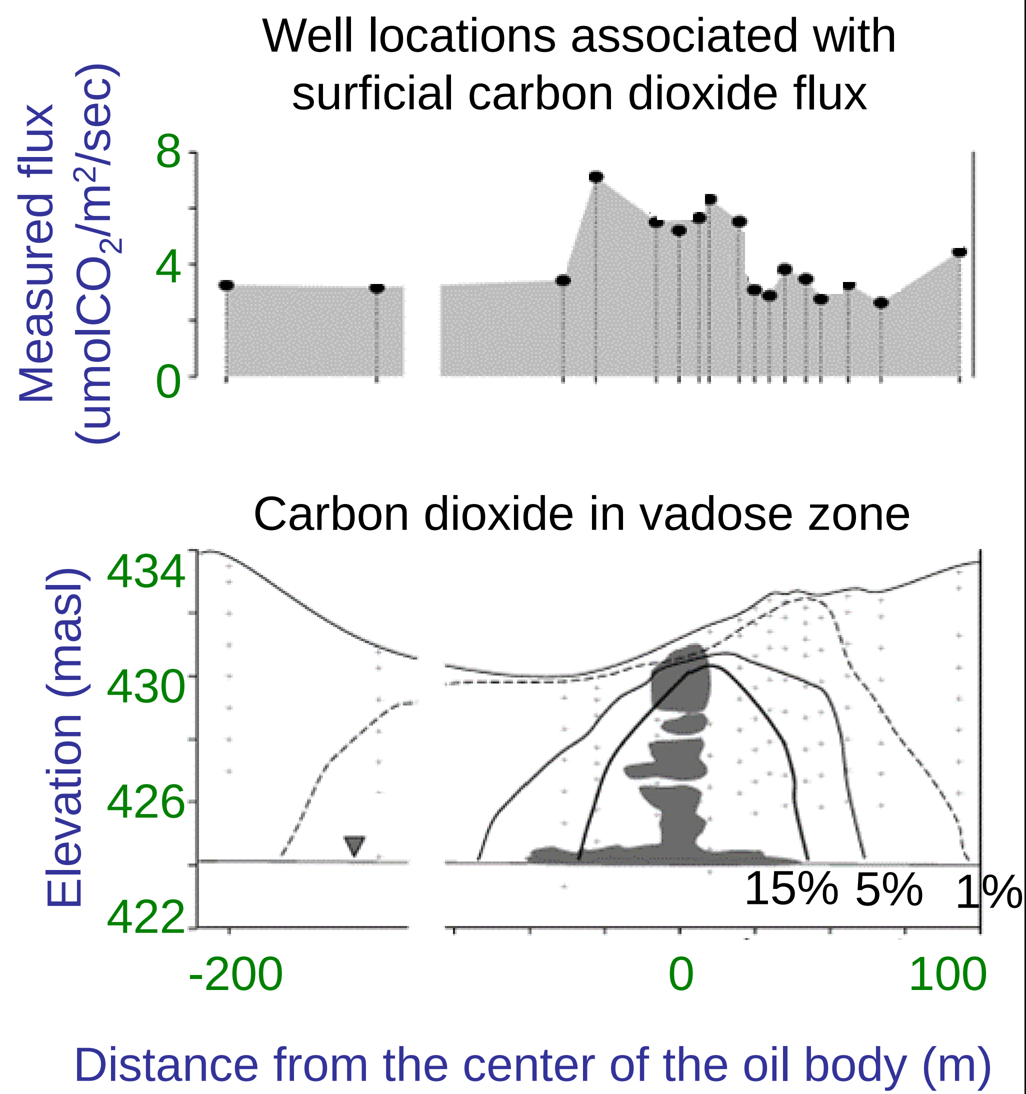


Oil thickness ~0.7 ft (0.2 m) is less than calculated critical thickness of 1.2 to 1.6 ft

Lundy, 2012

Case Example 2: Bemidji, MN Preliminary Estimates of Rates of Spreading vs Mass Depletion

- Oil discharge from oil infiltration zone
  - Baildown test oil transmissivity, T_{oil}
  - $Q_{oil} = K_{oil}\, i_{oil}$ Area
  - 2.2 kg/d leaving infiltration area
- CO_2 flux, proxy for LNAPL mass depletion
  - 4.3 kg/d over downgradient area



Lundy, 2012 and Sihota et al. 2011

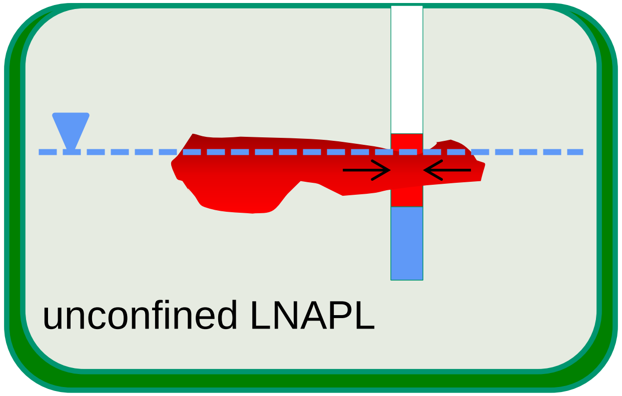
LNAPL Migration Potential / Stability Summary

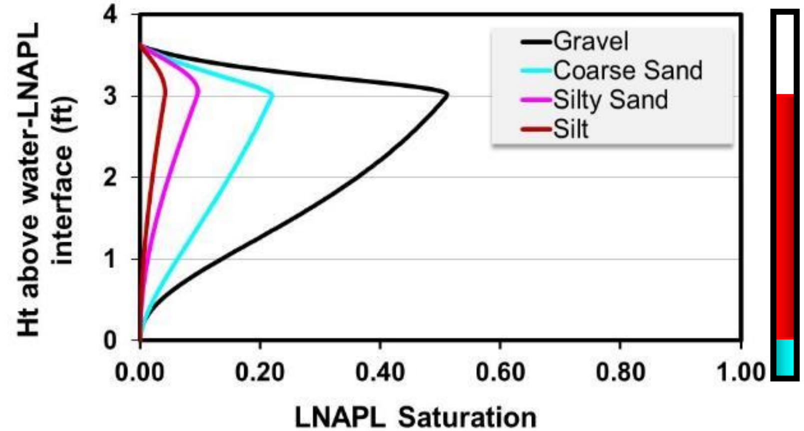
- Mobile LNAPL is not necessarily migrating LNAPL
  - In-well LNAPL does not mean it is moving
- Principles of Darcy's Law apply
  - LNAPL can spread upgradient and migrate rapidly in the early phases following a release
  - Self-limiting process, once the release is abated
- LNAPL needs to overcome pore-entry pressure to move into a water-saturated pore
- NSZD (Natural Source Zone Depletion) contributes to LNAPL stability
- Use multiple lines of evidence to assess LNAPL stability

Key Message 7

LNAPL Transmissivity is a better indicator of recoverability

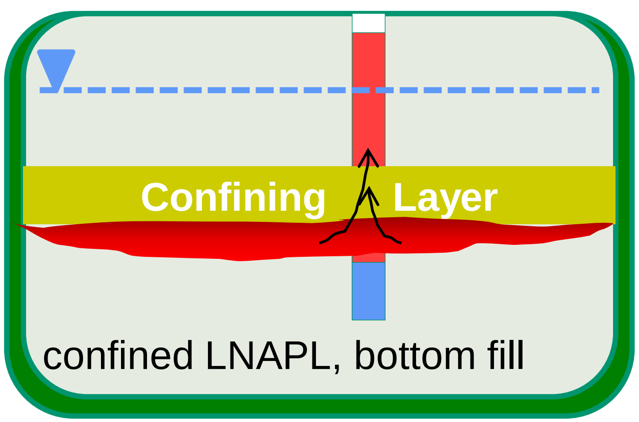
Apparent LNAPL Thickness Not a Good Indicator of Recoverability

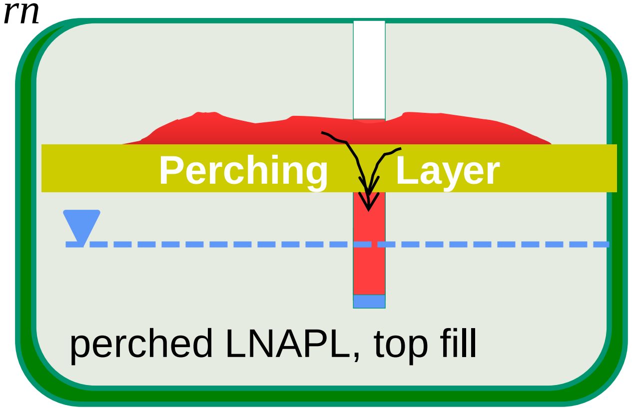




LNAPL conductivity:

$$K_n = \frac{\rho_n \cdot g \cdot k}{\mu_n} k_{rn}$$





Need a metric that is indicative of LNAPL recoverability!

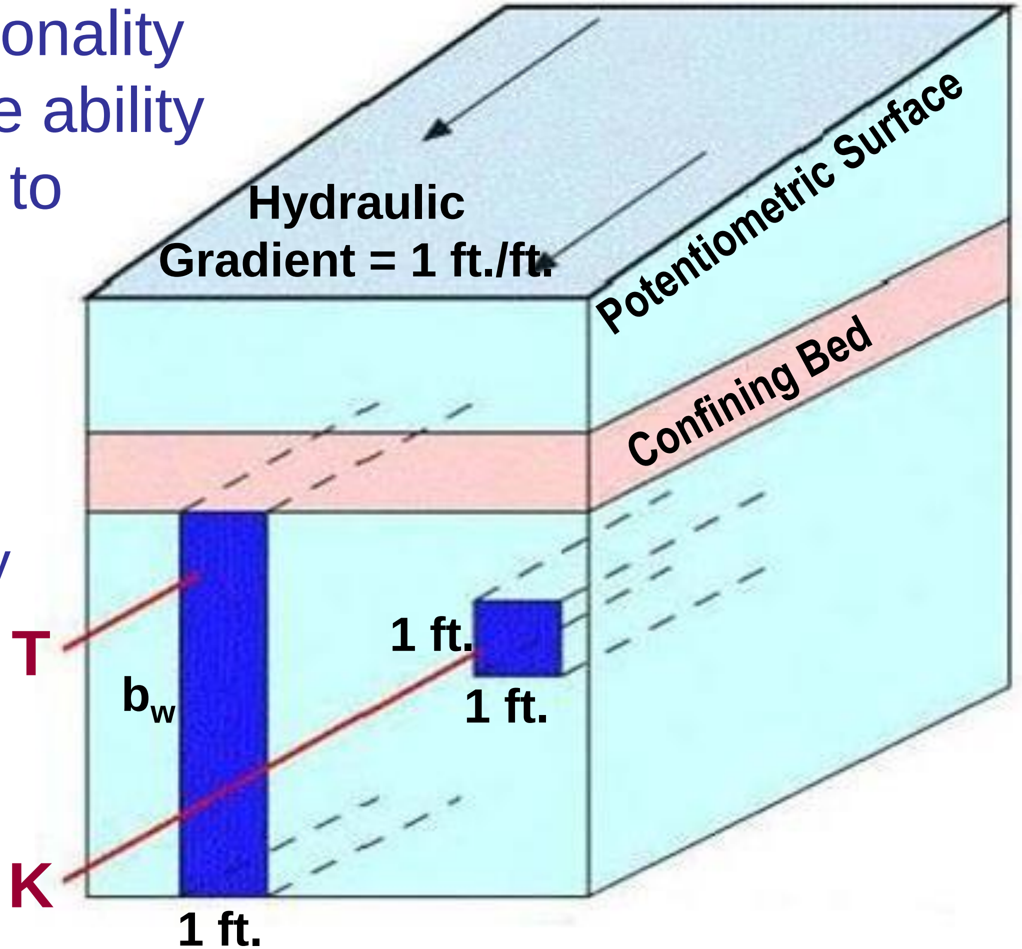
Groundwater Transmissivity – The Standard for Groundwater Producibility

- **Transmissivity** - proportionality coefficient describing the ability of a permeable medium to transmit water

$T_w = K_w \cdot b_w$

K_w = hydraulic conductivity

b_w = aquifer thickness



Modified from Driscoll (1989)

LNAPL Transmissivity – The New Standard for LNAPL Recoverability

LNAPL Transmissivity (T_n) is a proportionality coefficient that represents the ability of a permeable medium to transmit LNAPL

$$q_n = K_n i_n$$

$$q_n b_n = K_n b_n i_n$$

$$Q_n = T_n i_n$$

T_n represents *averaged* aquifer & fluid properties (soil permeability, density, viscosity, saturation) AND thickness of mobile LNAPL interval

$$T_n = K_n b_n \qquad K_n = \frac{\rho_n \cdot g \cdot k}{\mu_n} k_{rn}$$

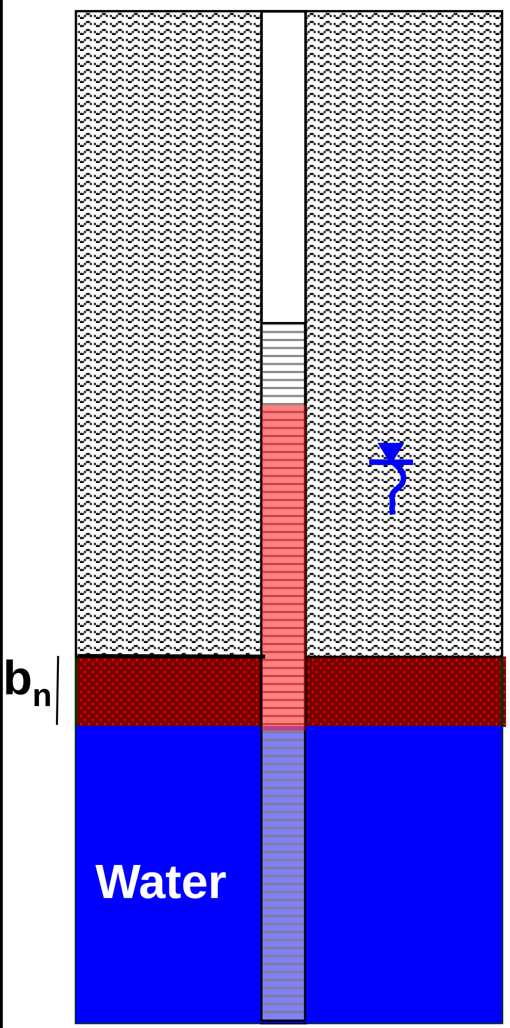
T_n is an averaged indicator of recoverability

- K_n varies with saturation

From Andrew Kirkman

Formation Thicknesses for Confined/Perched Conditions

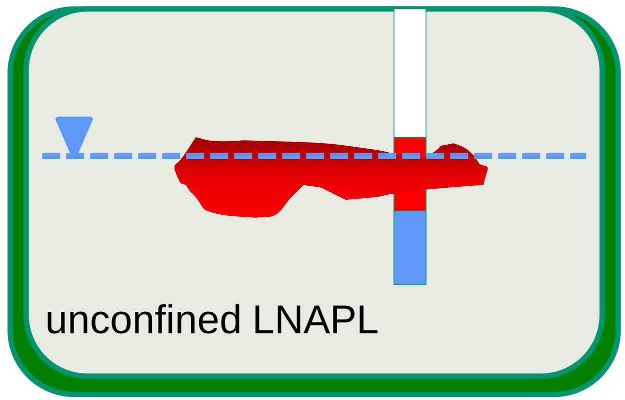
Confined LNAPL



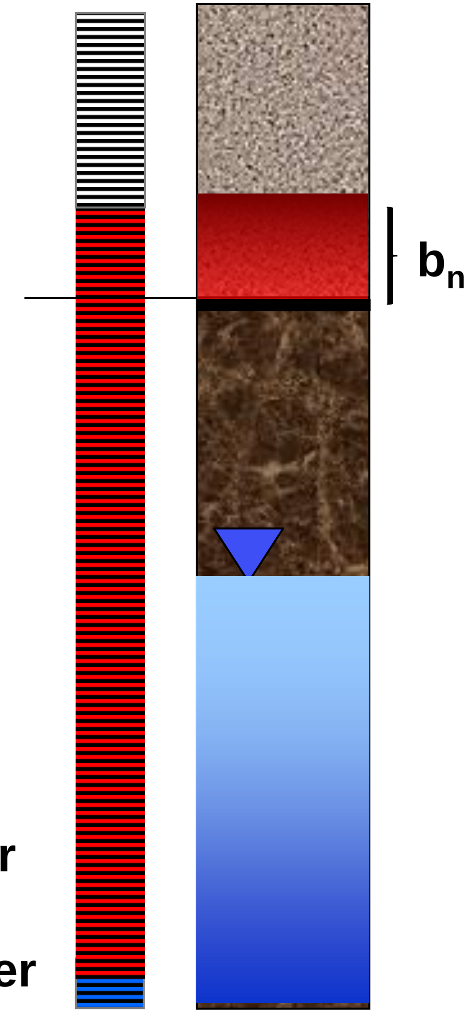
b_n = lower elevation of confining layer – elevation of LNAPL water interface

Unconfined LNAPL

b_n = LNAPL thickness in MW



Perched LNAPL



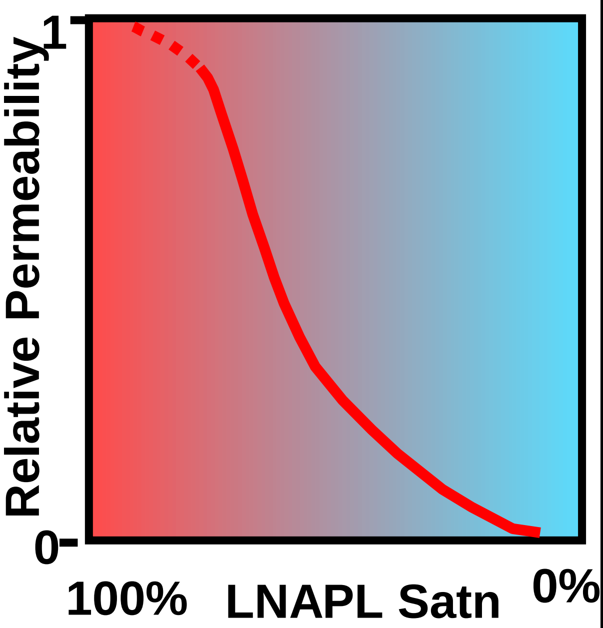
b_n = elevation of LNAPL-air interface – upper elevation of low permeability layer

T_n Values for Gasoline/Diesel

USDA Soil Type	Saturated Hydraulic Conductivity (ft./day)	LNAPL Thickness (ft.)	T_n gasoline (ft^2/day)	T_n diesel (ft^2/day)
Medium Sand	100	1	8.5	0.2
		2	58	2.4
		5*	335	38
Fine Sand	21	1	1.6	0.03
		2	11	0.4
		5*	67	7.4
Sandy Loam	1.25	1	0.3	0.03
		2	1.0	0.1
		5	4.4	0.6
Silt Loam	0.6	1	0.006	0.0
		2	0.05	0.005
		5	0.5	0.05

LNAPL-2 = 0.1 - 0.8 ft^2/day

T_n modeled assuming homogenous soils

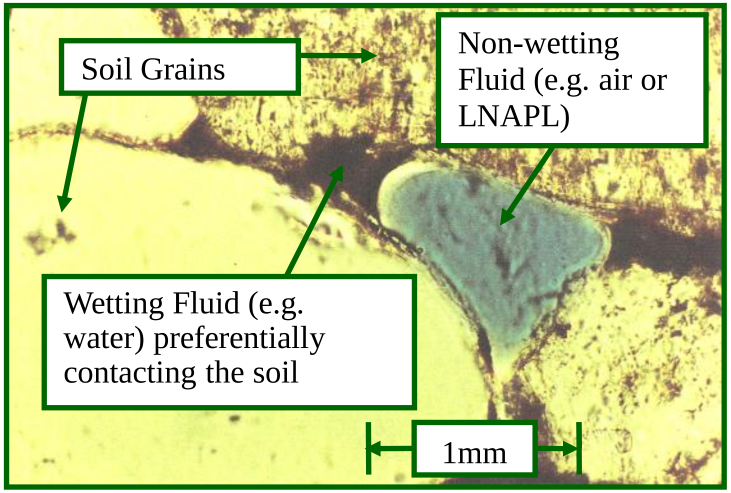


***5 ft formation thickness unlikely at old sites**

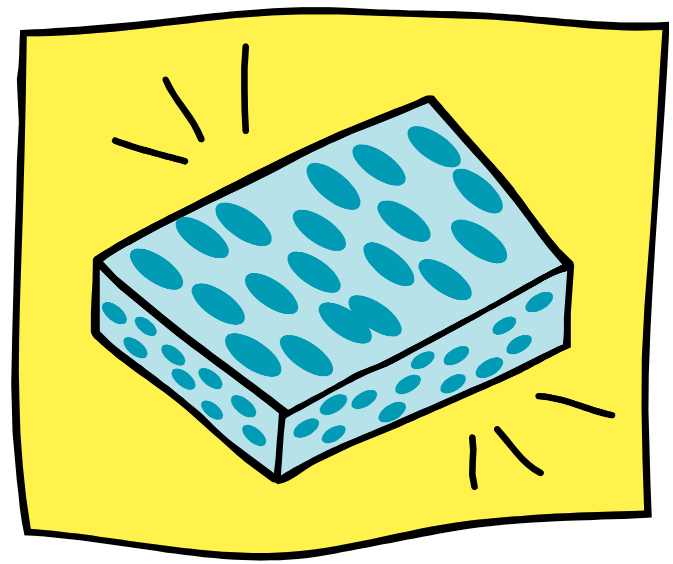
Residual Saturation and Transmissivity

Transmissivity – Indicator of recovery

- **"the oil that remains in an oil reservoir at depletion"**
  Pet. Eng. Handbook, 1987
- **"oil that remains after a water flood has reached an economic limit"**
  Morrow, 1987
- **"saturation at which the NAPL becomes discontinuous and is immobilized by capillary forces"**
  Schwille, 1984; Domenico and Schwartz, 1990; and Mercer and Cohen, 1990



From Wilson et al., (1990)



When LNAPL saturation approaches Residual Saturation, LNAPL Transmissivity approaches Zero

Knowledge Check

Background: A site has 7 ft. of LNAPL in a well. After a heavy rainfall season the LNAPL thickness increased to 9 ft.

Question: How would one make decision regarding recoverability?

A. There is a lot of LNAPL at the site, and should be readily recoverable
B. LNAPL is confined and does not need to be recovered
C. Bail the LNAPL out and see how fast it recovers

Poll Question

Key Message 8

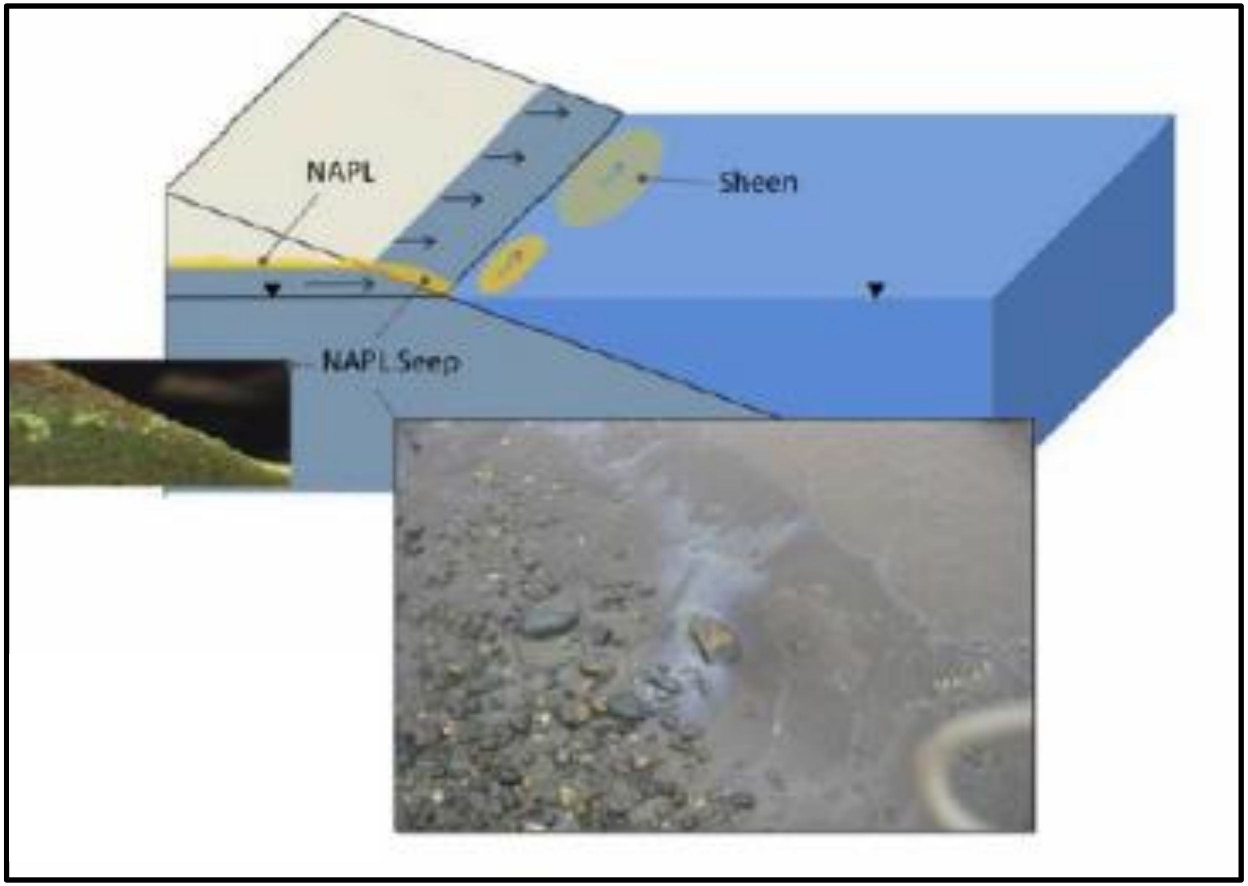
Causes for Sheens Not Necessarily LNAPL Migration

Petroleum Sheens

Originating from LNAPL in sediments at the groundwater surface water interface

Images: CH2M (2016)

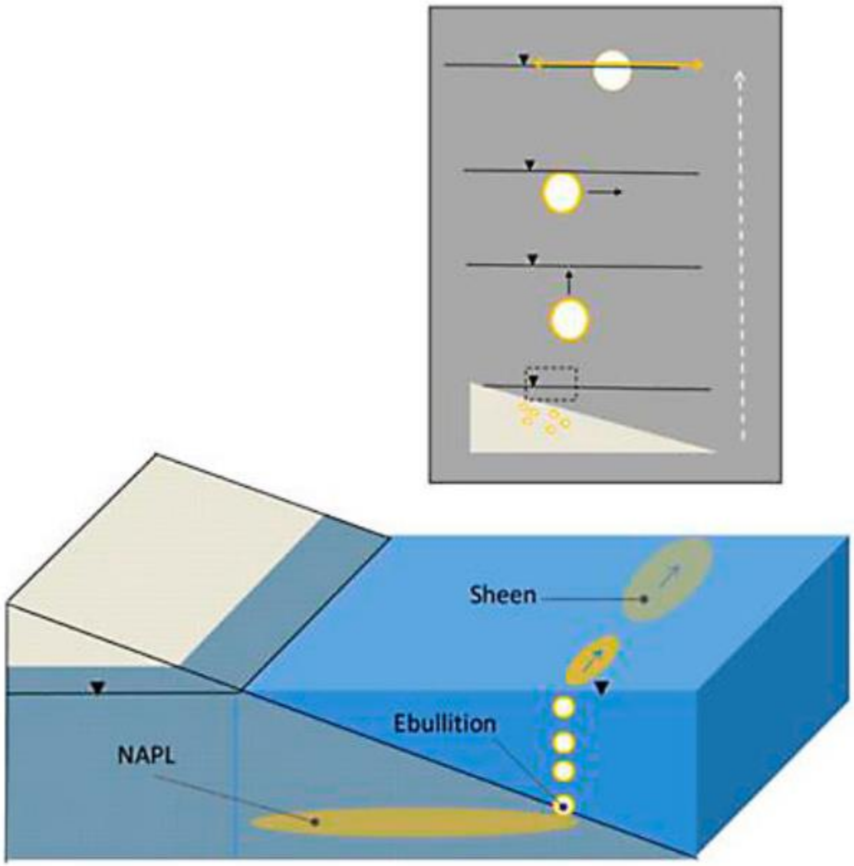
Sheen Release Mechanisms



1. Seep: Groundwater discharge carries LNAPL sheen

From Sale and Lyverse, 2014

Sheen Release Mechanisms

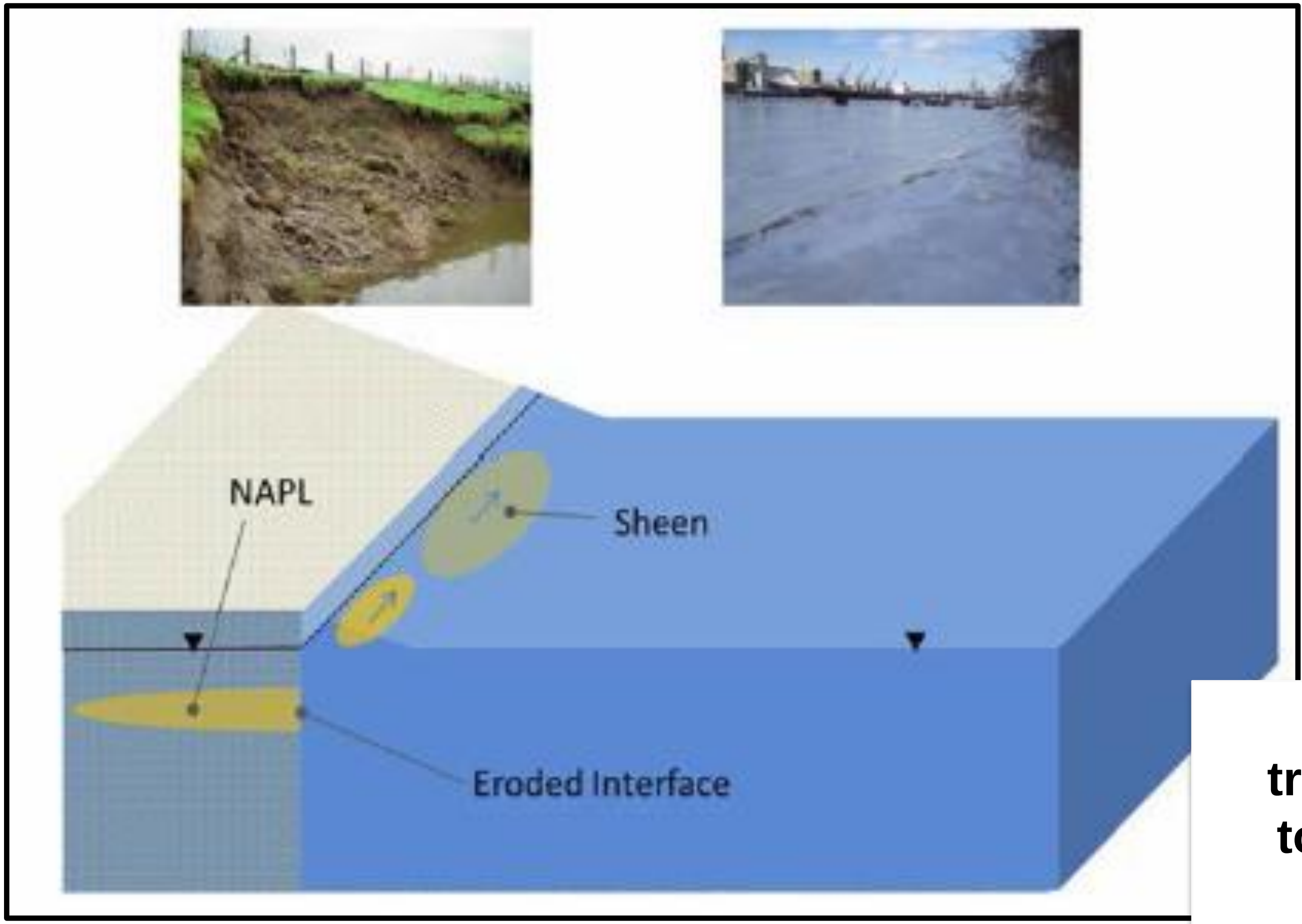


2. Ebullition: Gas generated from degradation carries LNAPL sheen

Photograph provided by Dr. Julio Zimbron, authorization to use by Author/Colorado State University

From Sale and Lyverse, 2014

Sheen Release Mechanisms



3. Erosion:
Erosion of sediments with NAPL into water column

Key Message:
transport of LNAPL to surface water is not necessarily gradient-driven

From Sale and Lyverse, 2014

Key Message 9

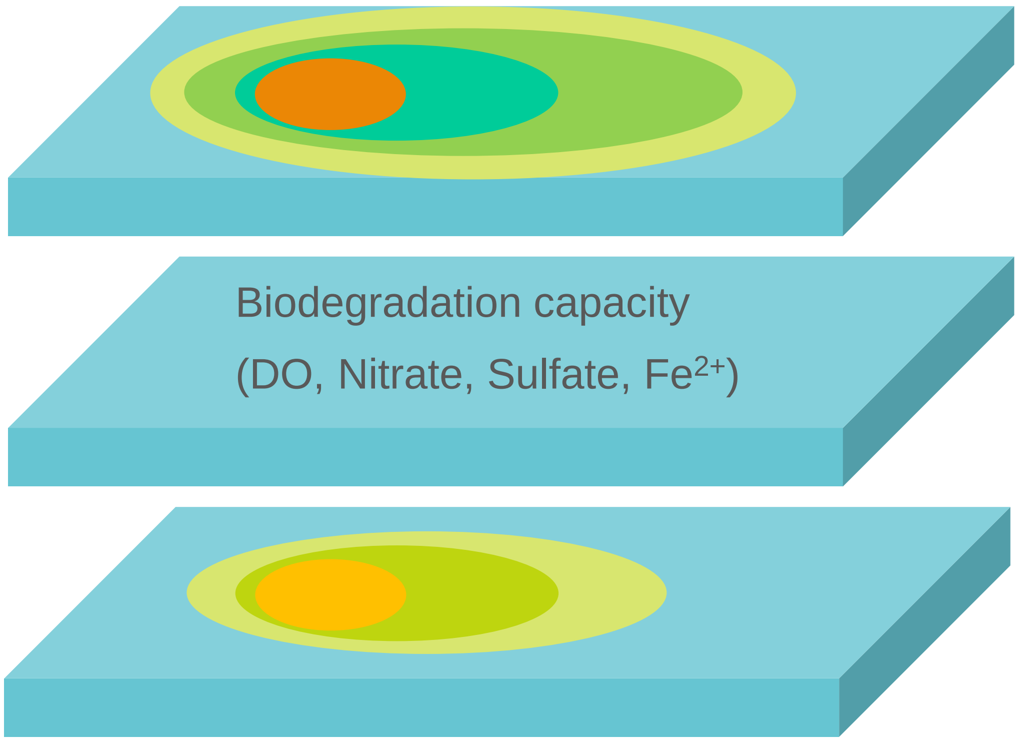
Biological processes are important

Biodegradation Capacity of Saturated-Zone Electron Acceptors

MNA focused on groundwater plume: how far and at what concentration

Typical Biodeg Capacity
<~50 gal/ac/yr

Garg et al., 2017



Source: Bioscreen documentation

KEY POINT

Electron acceptor mass-balance significantly <u>underestimated</u> LNAPL source zone biodegradation

NSZD Rates Being Observed

NSZD Study	Site-wide NSZD Rate (gallons/ acre /year)
Six refinery & terminal sites (McCoy et al., 2015)	2,100 – 7,700
1979 Crude Oil Spill (Bemidji) (Sihota et al., 2011)	1,600
Two Refinery/Terminal Sites (LA LNAPL Wkgrp, 2015)	1,100 – 1,700
Five Fuel/Diesel/Gasoline Sites (Piontek, 2014)	300 - 3,100
Eleven Sites, 550 measurements (Palaia, 2016)	300 – 5,600

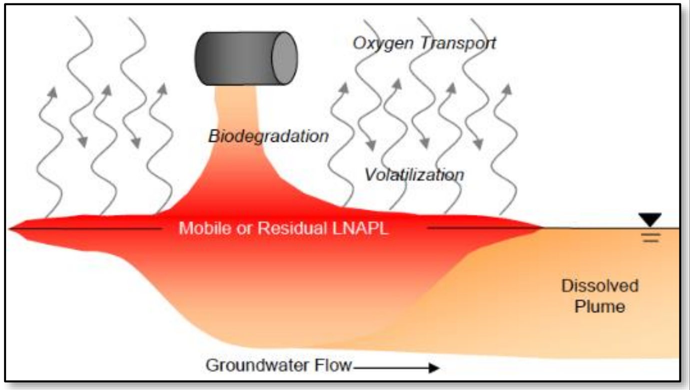
KEY POINT NSZD rates are in the range of 100s to 1000s of gallons/acre/year

Need Vapor Flux Also

Baedecker et al., 1993	*Mass transfer calculations indicated that the primary reactions in the anoxic zone are…and outgassing of CH_4 and CO_2*

Molins et al., 2010

"…the main degradation pathway can be attributed to methanogenic degradation of organic compounds …"



ITRC, 2009

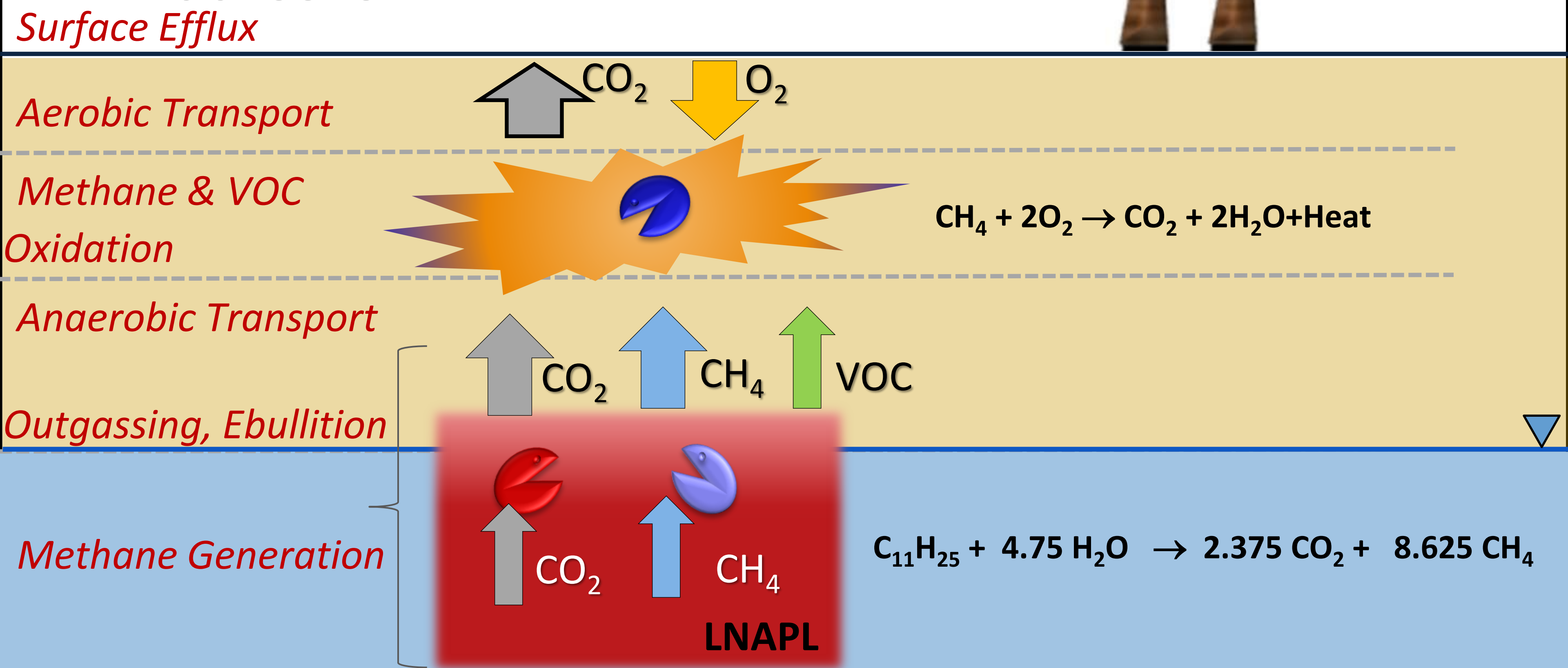
Amos & Mayer, 2006

transfer of biogenically generated gases from the smear zone provides a major control on carbon balance

Lundegard & Johnson 2006	*Mass loss associated with oxygen diffusion through the vadose zone is more significant (2 OOMs) than dissolution and biodegradation in the saturated zone*

NSZD Conceptual Model

KEY PROCESSES



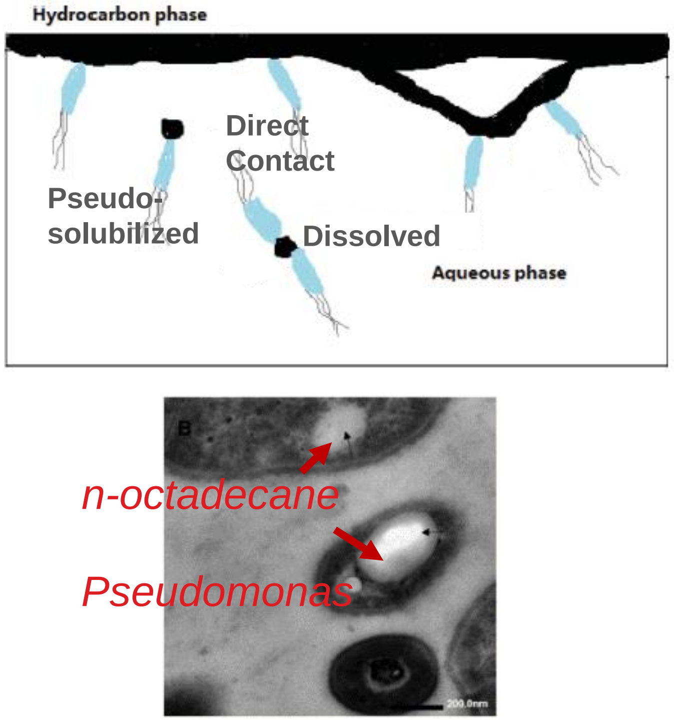
*Note: size of arrows indicates magnitude of flux

Garg et al., 2017

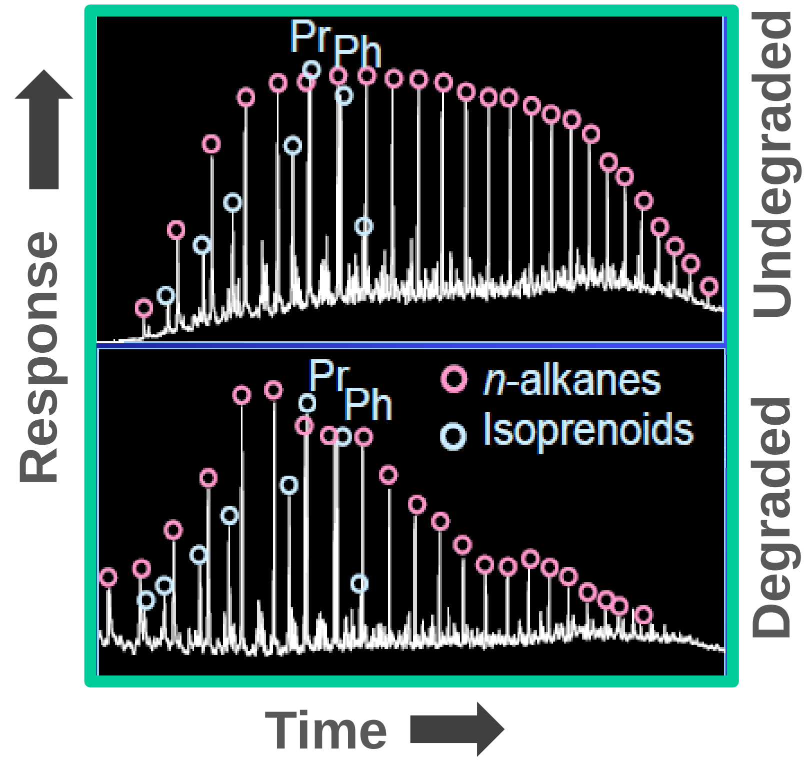
KEY POINT

- **Methanogenesis is a dominant process**
- **NSZD focuses on source depletion: how long**

Direct Outgassing



Hua et al., 2014

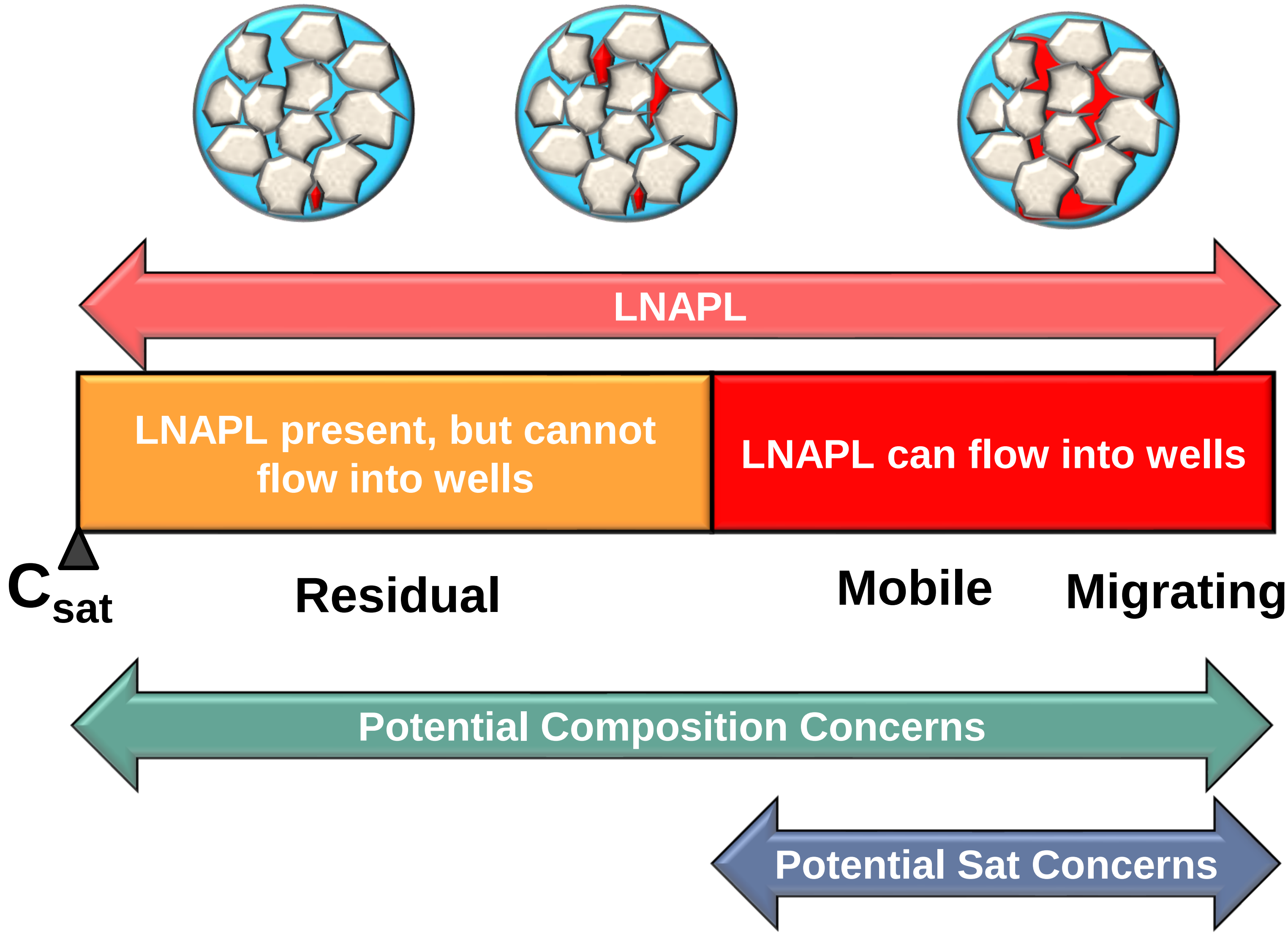


Bekins et al, 2005

KEY POINT

- Dissolution is not necessary for LNAPL biodegradation
- Biodegradation occurs in pore space near LNAPL

It is All LNAPL!



ITRC 3-Part Online Training Leads to YOUR Action

Part 1:
Connect Science to LNAPL Site Management
(Section 3)

NEXT

Part 2:
Build Your LNAPL Conceptual Site Model
(Sections 4 and 5)

Part 3:
Select / Implement LNAPL Remedies
(Section 6)

YOU
Apply knowledge at your LNAPL sites

Based on the ITRC LNAPL-3 Document: LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies

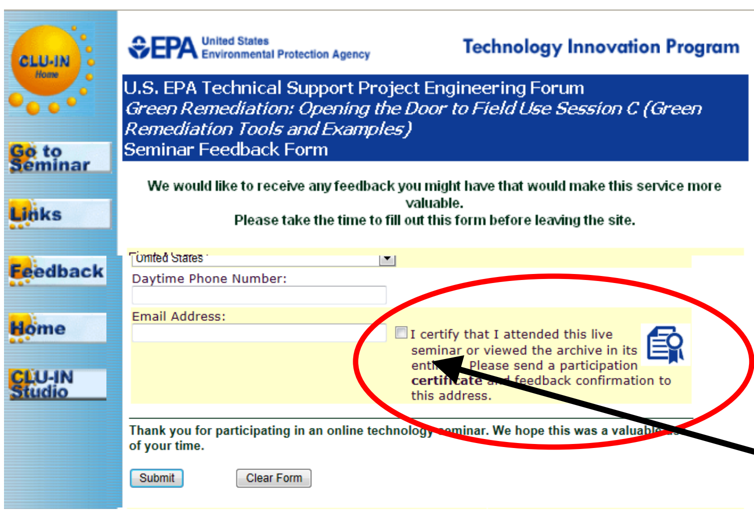
Apply Part 1 on the Job

- As you prepare to take Part 2 of the training series next week, think about how you can use the LNAPL science and key concepts presented today at your sites to develop your LCSM

Thank You

Follow ITRC

- 2nd Question and Answer Break
- Links to additional resources
  - http://www.clu-in.org/conf/itrc/LNAPL-3/resource.cfm
- Feedback form – *please* complete
  - http://www.clu-in.org/conf/itrc/LNAPL-3/feedback.cfm



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Fill out the feedback form and check box for confirmation email and certificate.

Poll Question