

Petroleum Remediation Refresher Course:
Subsurface Interactions, Assessment, Cleanup, Site Closure Criteria


U.S. Environmental Protection Agency

Most of the visuals were taken from the Interstate Regulatory Council (ITRC) LNAPL course

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Introduction

- Petroleum products are mixtures of compounds that are immiscible with air and water;
- Hence, they are referred to a **light nonaqueous phase liquids (LNAPLs):**
  - Light because they are less dense than water;
- Oil-water, and air-oil interfaces are formed between the fluids in a three fluid system with water the wetting fluid, oil the intermediate wetting, and air the nonwetting fluid.
- LNAPL constituents cross the interfaces: dissolve in the water (dissolution), and partition to air (volatilization) to form plumes.

LNAPL: What is it?

Multi-component LNAPL

Oil/LNAPL – an immiscible organic liquid that is less dense than water

e.g., crude, gasoline, diesel, lube oils, benzene, toluene, etc

Water

Single component LNAPL

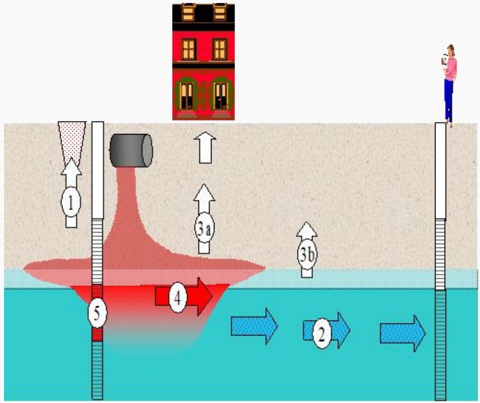
Key Point: You will learn that although LNAPL floats neatly on water in a glass, it doesn't behave as neatly in the subsurface

LNAPL is also referred to as:
oil**,** product, free product, separate-phase hydrocarbons, separate phase and phase-separated hydrocarbons

(Source: ITRC LNAPL Course)

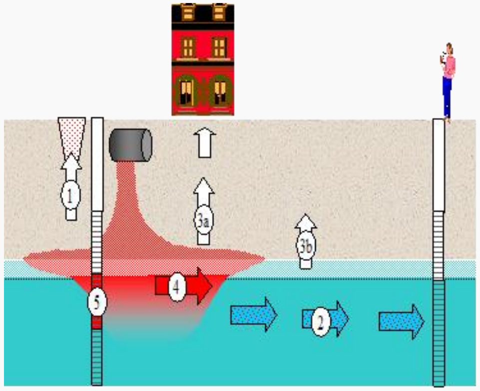
Introduction Cont'd

- In the event of a subsurface release, the LNAPL body, the dissolved and vapor plumes pose risks to the environment.
- The focus of a site assessment: delineate the extent of the LNAPL body, the dissolved and vapor plumes, and the hydrogeology.
- Integrate data in a conceptual site model (CSM):
  - Identifies impacted/potential receptors;
  - Informs risk assessment/management.



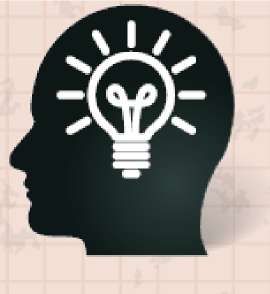
Development of a CSM/LCSM

- The CSM is developed through an iterative process of site discovery
- The CSM is an essential understanding the overall site and informs the risk management process. The CSM presents the current understanding of the site, identifies data gaps, and focuses data collection. The CSM is maintained and iteratively improved throughout the project life cycle, including during remediation.
- The LCSM is a subcomponent of the CSM: integrates LNAPL source, hydrogeologic data, and their interactions.
- ***The LCSM is the focus of this training***



About the Course and Objectives

- In order to build an LNAPL Conceptual Site Model (LCSM) to inform site management, an understanding of subsurface LNAPL science is germane: How does oil move through the vadose and saturated zones? How does oil interact with subsurface media?



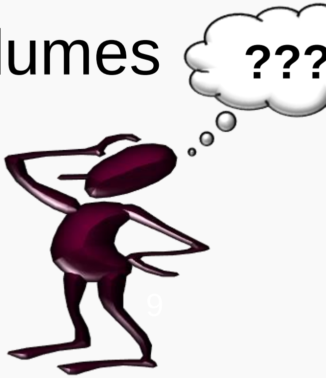
How does oil interact with subsurface media?

- Does oil float on top of the water table?
- Can oil from a shallow release penetrate deep below the water table(depths of 100’ or more)?
- Can oil be confined or perched like groundwater?
- When LNAPL is present, does it occupy the entire pore space?
- Can a dissolved hydrocarbon plume persist without an LNAPL source?

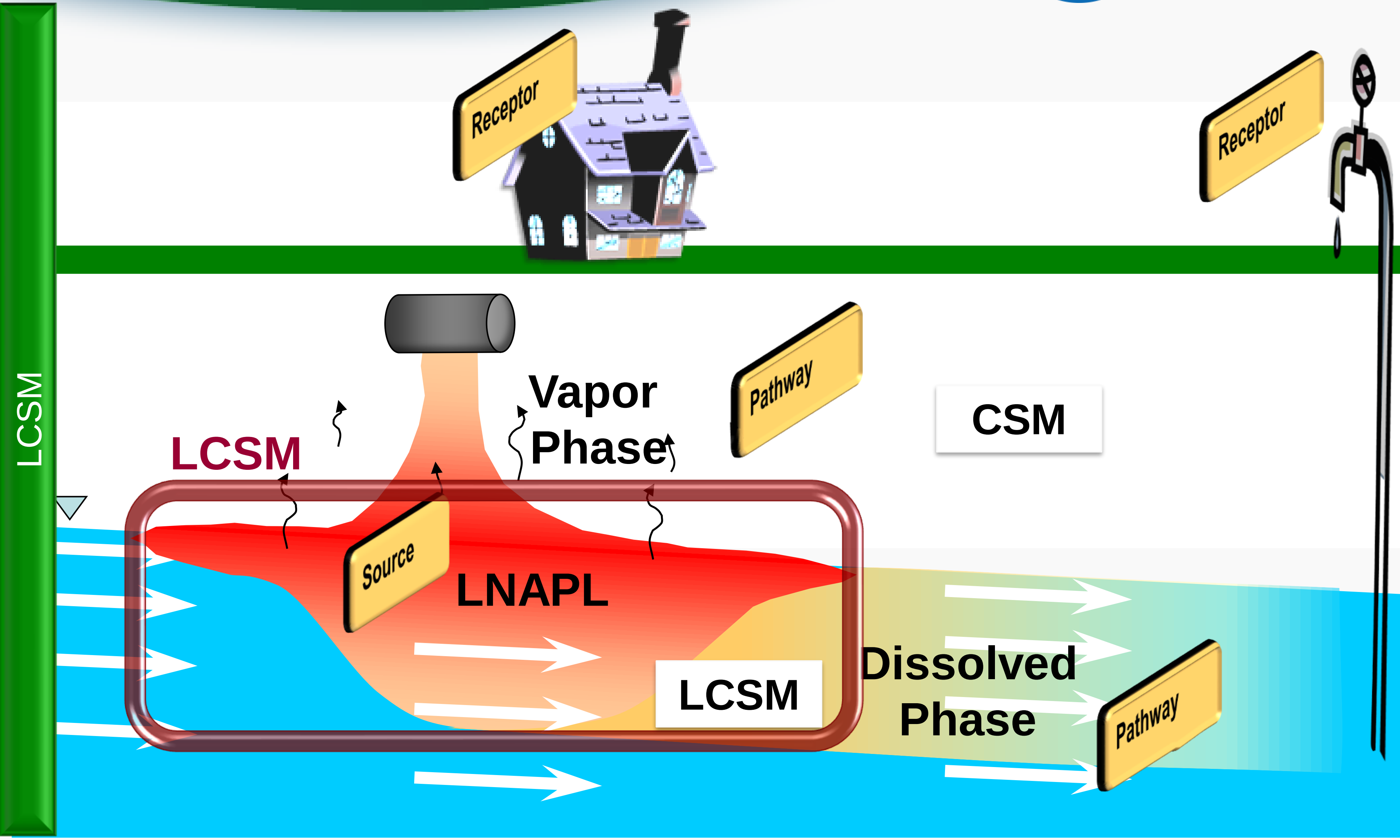
Course Objectives

Participants in this course will learn the following:

- The physics and chemistry of oil interactions as it moves through the subsurface
- How LANPL exist in the subsurface: residual, trapped or immobile; mobile or free; or it can be migrating?
- Aquifer conditions of LNAPL: Can LNAPL be confined, unconfined, or perched?
- Can/how About the partitioning of hydrocarbon compounds between LNAPL and the other phases
- The nature/behavior of hydrocarbon dissolved plumes



LNAPL Conceptual Site Model (LCSM)

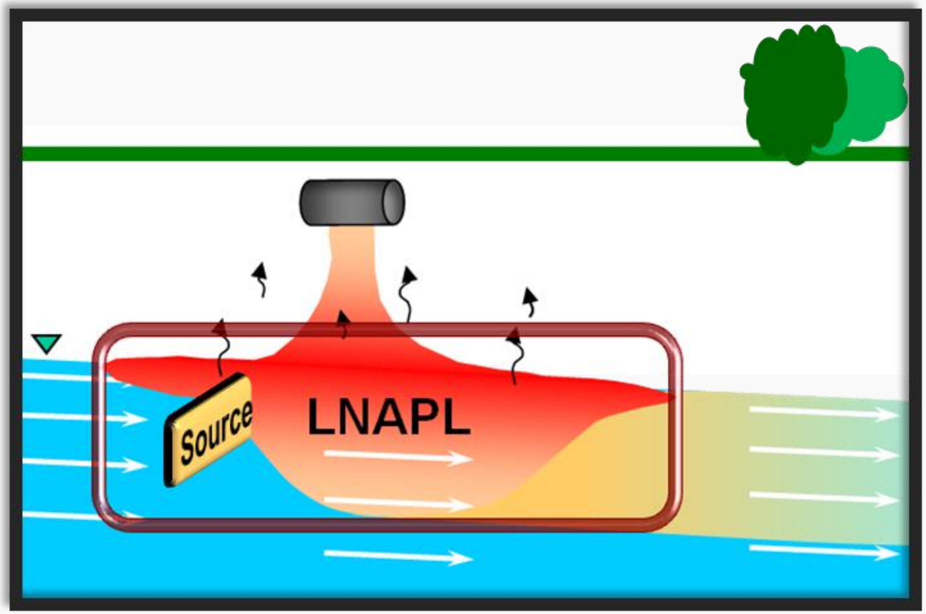


(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LCSM Key Components

- LNAPL source delineation: where and what
- hydrogeology, and it's interaction with LNAPL
- LNAPL migration potential and stability
- LNAPL transmissivity – to assess recoverability



(Source: ITRC LNAPL Course)

Roadmap for LCSM Section

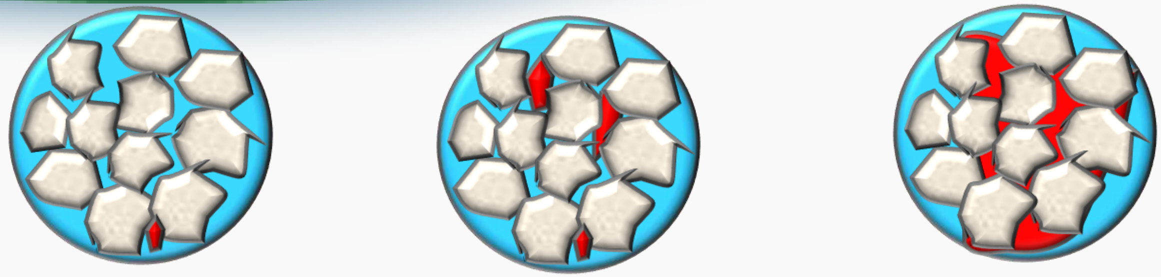
- What happens following a release?
- Source delineation - where and what
  - Anatomy
    - LNAPL shares pores with groundwater
  - Indicators
    - Direct, dissolved phase, conventional, specialized
  - Interpreting in-well thickness
    - Vertical LNAPL distribution in unconfined conditions
- Conceptual challenges
  - Residual LNAPL saturation
  - Water-table fluctuations
  - Confined LNAPL
  - Deep LNAPL penetration below water table
  - LNAPL in fractures and preferential pathways

Roadmap for LCSM Section (cont'd)

LCSM

- LNAPL migration potential/stability
  - Darcy's Law
  - Pore entry pressure
  - Lines of evidence for LNAPL stability
- Parameter to understand LNAPL conditions and assess LNAPL recoverability
  - LNAPL transmissivity
- Partitioning of LNAPL between phases
- Behavior and characteristics of hydrocarbon plumes

LNAPL Name Game



LNAPL

LNAPL is present, but does <u>not</u> flow into wells	LNAPL flows into wells

Terminology Changes

C_{sat} ⇨ Residual ⇨ Mobile ⇨ Migrating

(Source: ITRC LNAPL Course)

LNAPL Saturation and Residual Saturation

LNAPL In The Formation

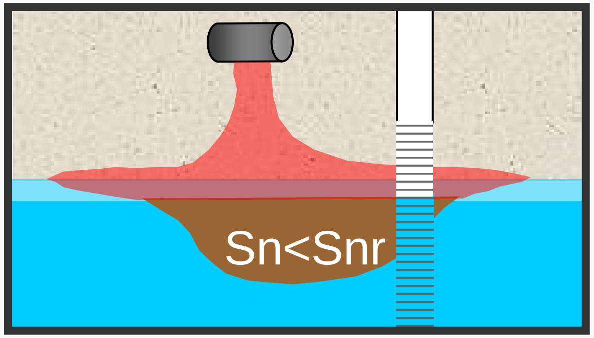
Mobile LNAPL = The LNAPL saturation in the soil exceeds the "LNAPL Residual Saturation" of the soil

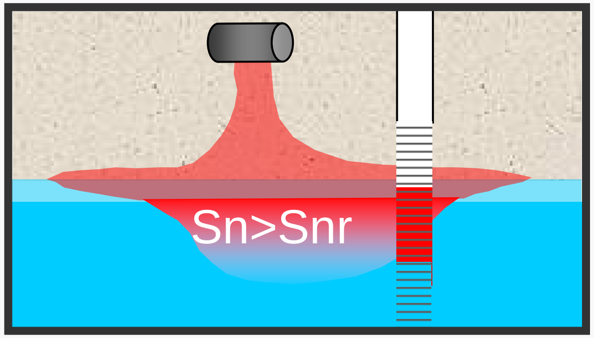
LNAPL Saturation in the soil (Sn)

Fraction of the soil pore space occupied by LNAPL

LNAPL Residual Saturation (Snr)

Oil trapped by capillarity (vadose zone) or by discrete blobs or ganglia (saturated zone)

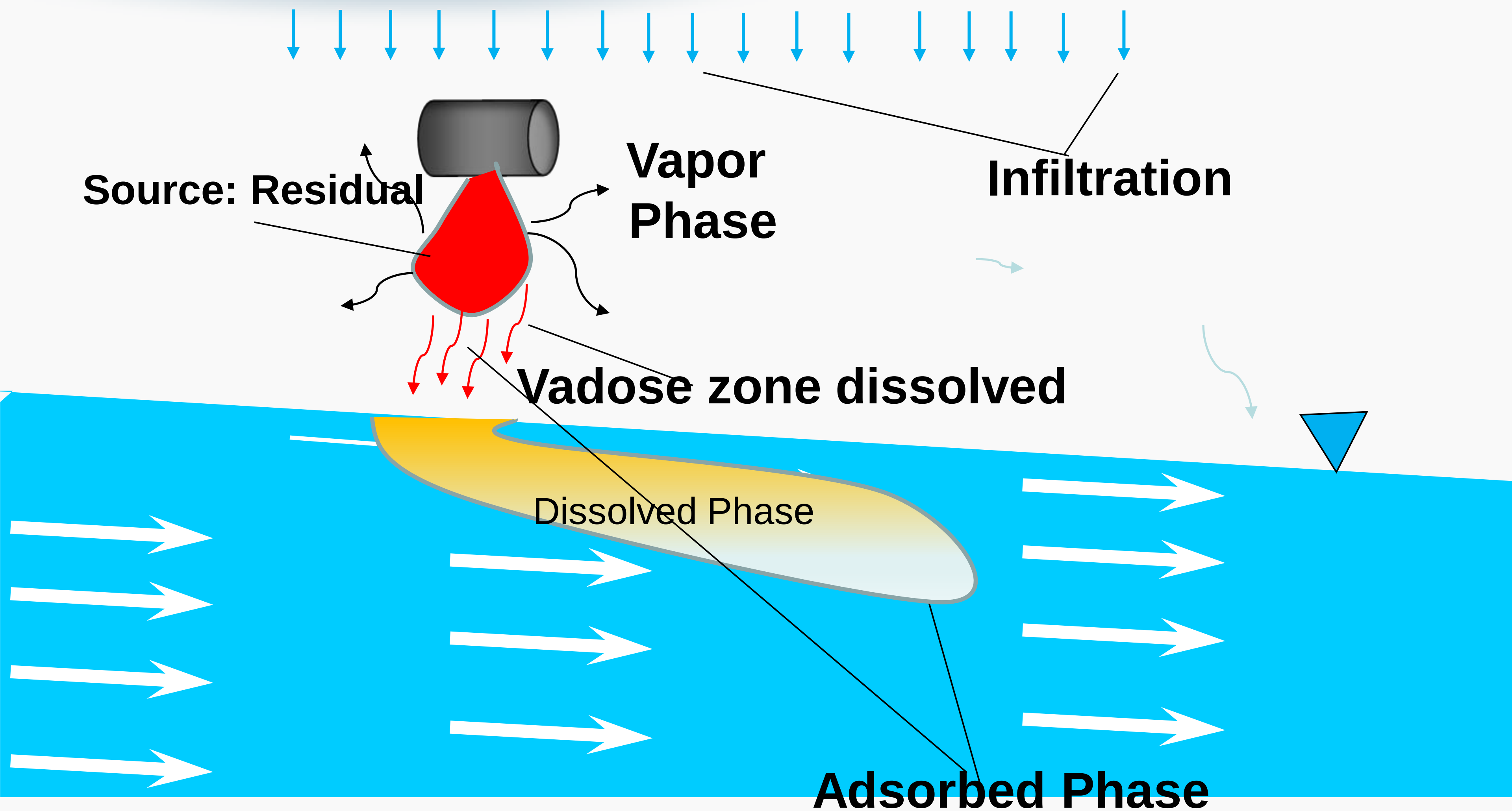




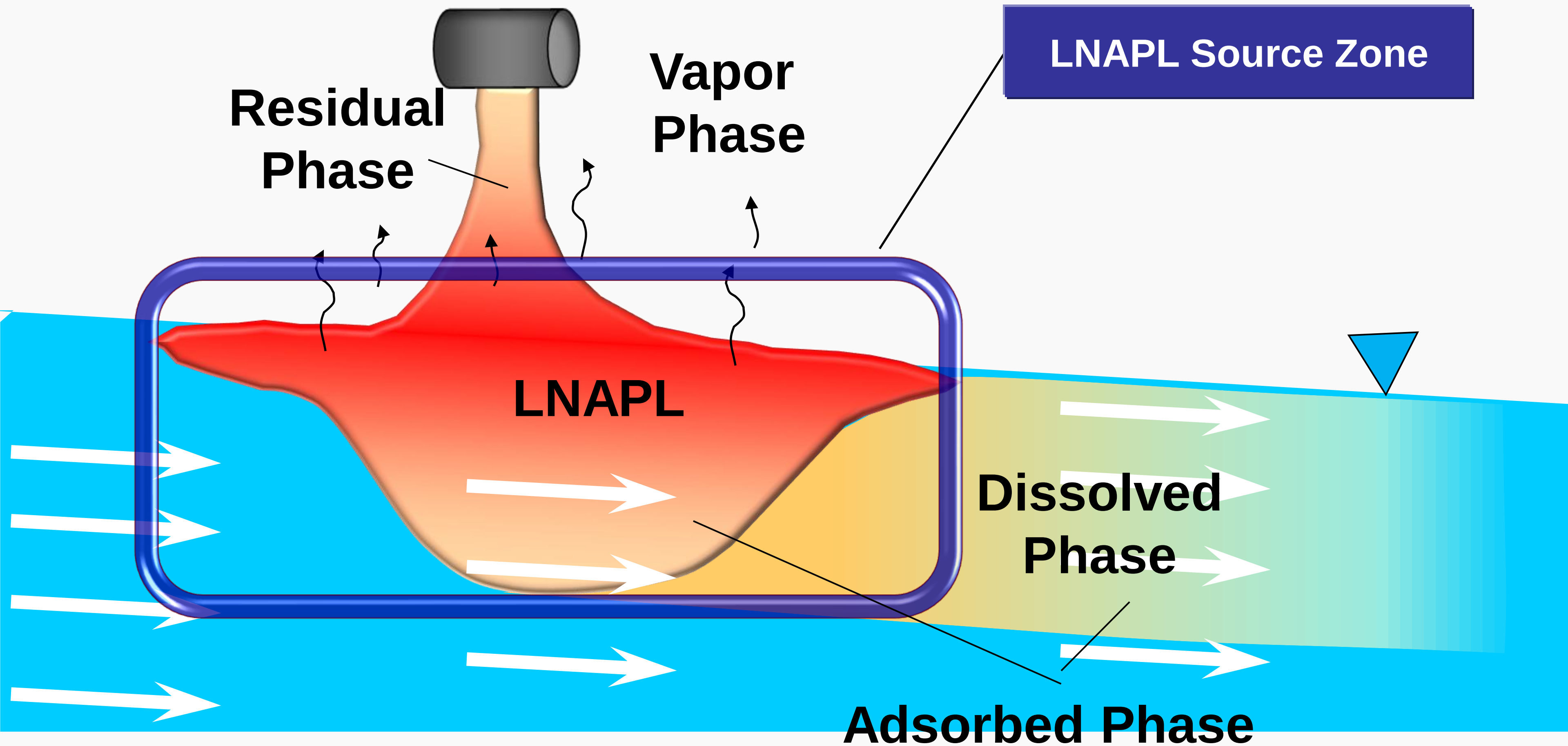
Following a Vadose Zone Release

- The LNAPL follows the path of least resistance (larger pores) downward due to gravity
- Leaves a trail behind the leading edge: vadose zone residual
- If release is small, relative to water table depth, LNAPL will not get to the water table
- If spill is large, an LNAPL body develops in the saturated zone

Oil Does Not Have to Reach Groundwater



Oil Leak can penetrate the Water table



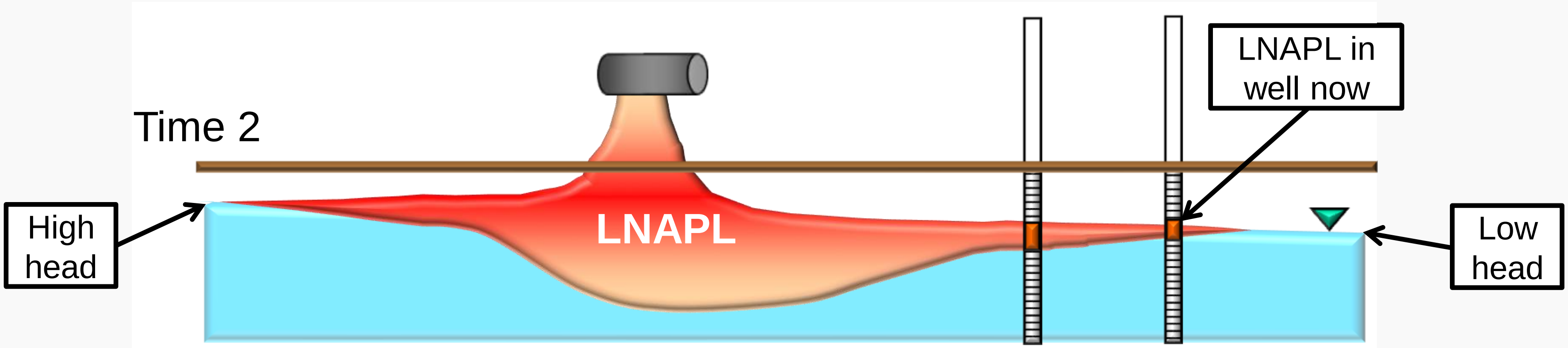
(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

Migrating LNAPL is Mobile LNAPL With a High LNAPL Saturation and LNAPL Head

Mobile vs Migrating

Migrating LNAPL = The LNAPL body/footprint is expanding



Key Point: To migrate, mobile LNAPL must have an LNAPL head (or gradient) and high saturation.

(Source: ITRC LNAPL Course)

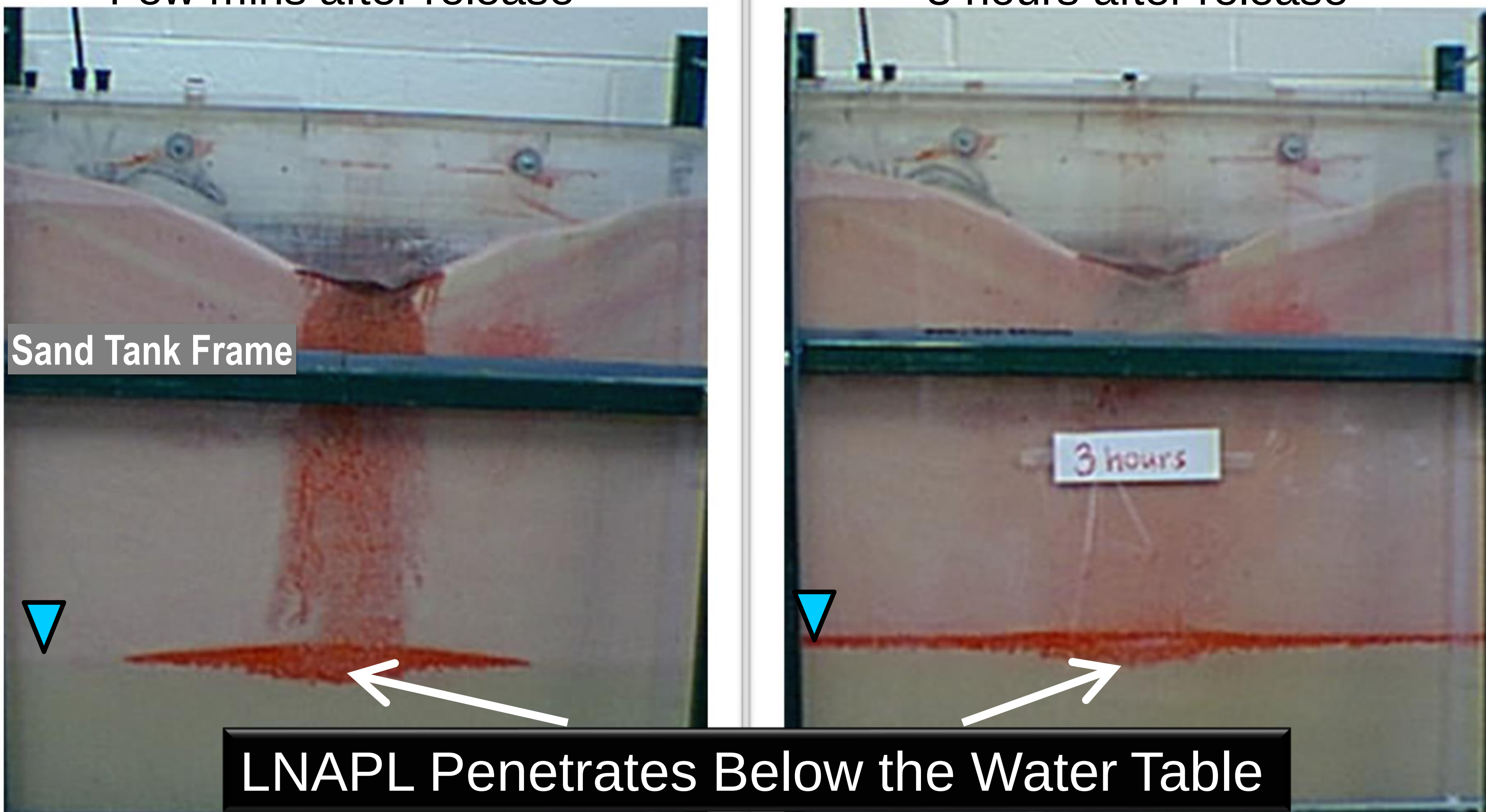
Source: ITRC LNAPL Course (ITRC)

Tank Experiment: LNAPL Penetrates Below the Water Table

Anatomy of an LNAPL Body

Few mins after release

3 hours after release



U.S. Environmental Protection Agency **(Source: ITRC LNAPL Course)**

LNAPL Penetrates Below The Water Table

Not this….

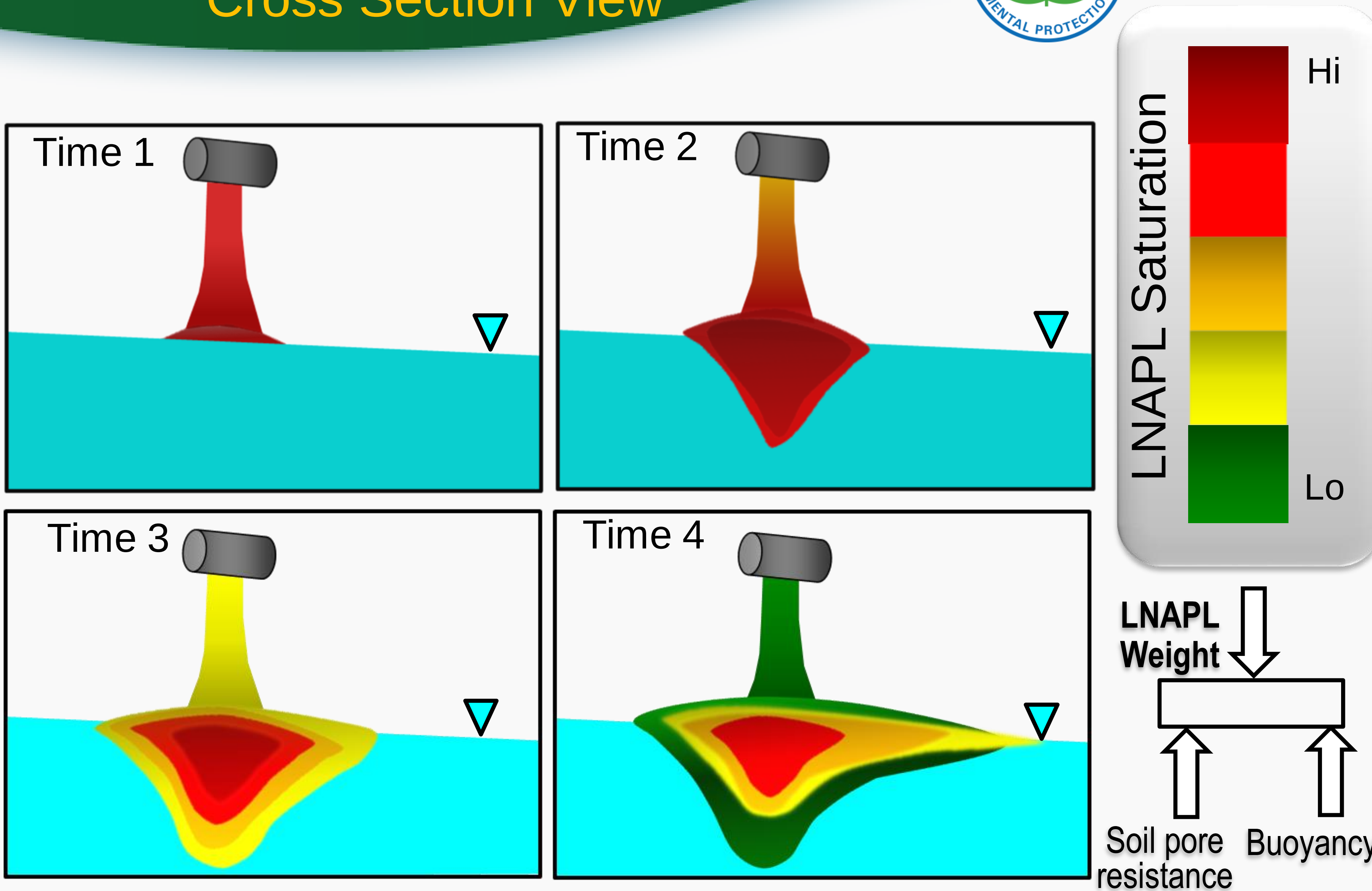
….But This

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

Time Series LNAPL Body Development: Cross Section View

Anatomy of an LNAPL Body

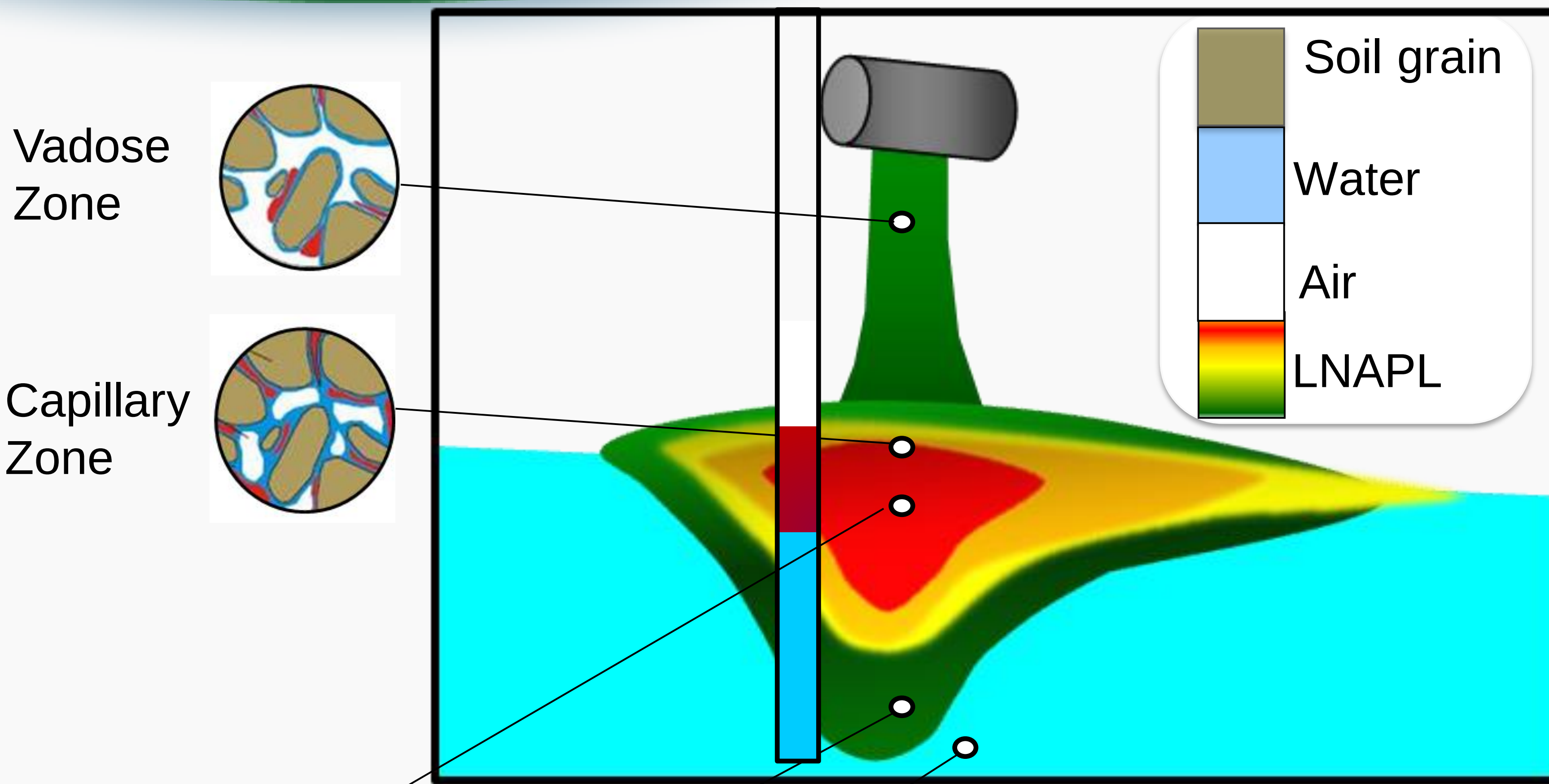


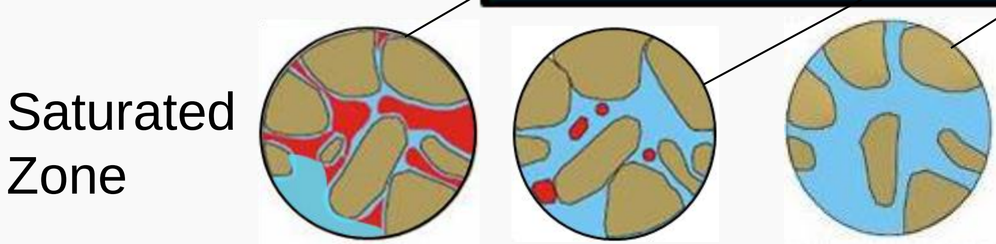
(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

Pore Scale LNAPL Distribution

Indicator: In-well LNAPL Thickness





Key Points:

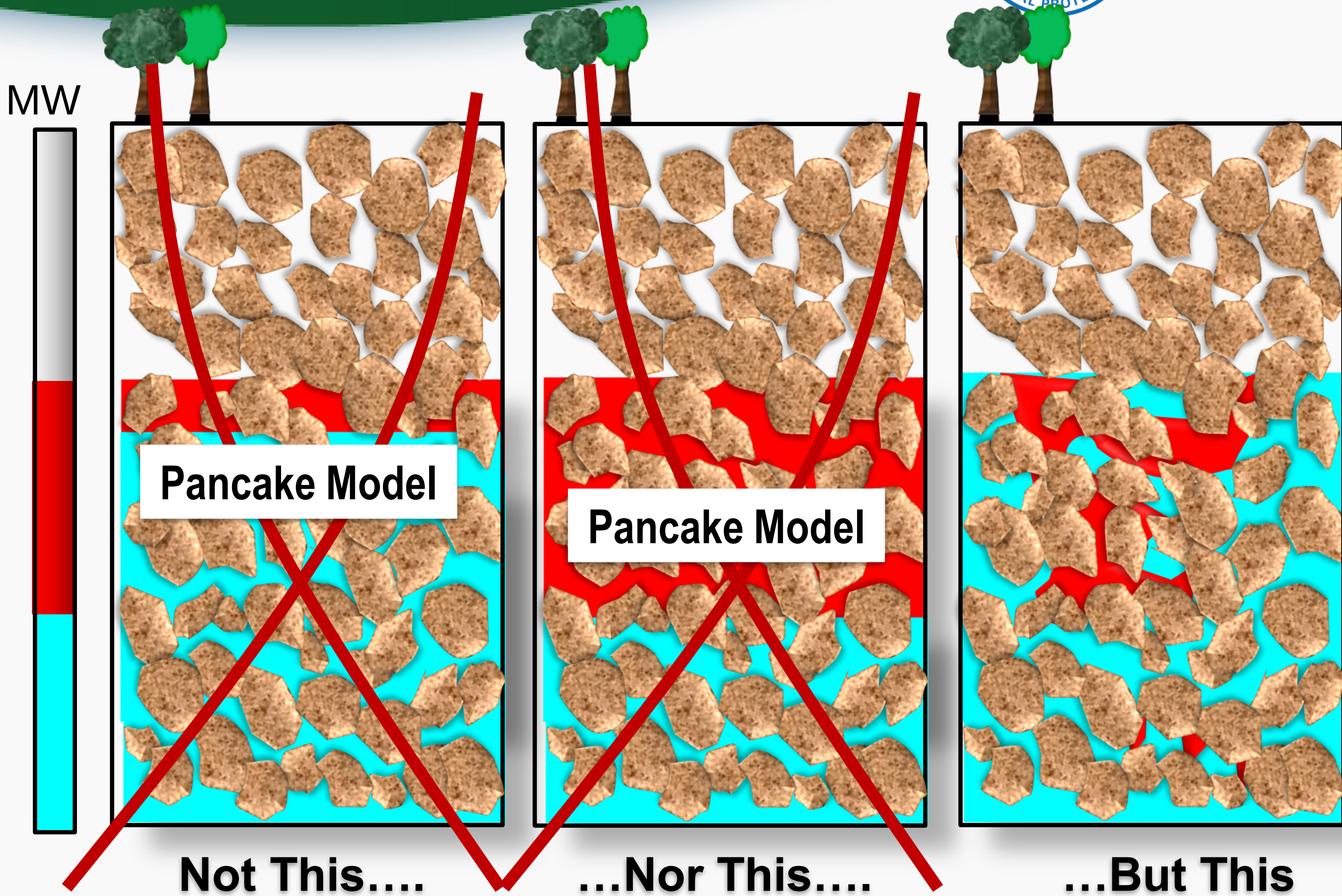
1. Soil pores contain LNAPL, groundwater and soil air.
2. Mobile oil occupies a fraction of the LNAPL contaminated zone

(Source: ITRC LNAPL Course)

Nature of LNAPL Impacts in the Formation:

Below Water Table And Saturation Varies

Anatomy of an LNAPL Body



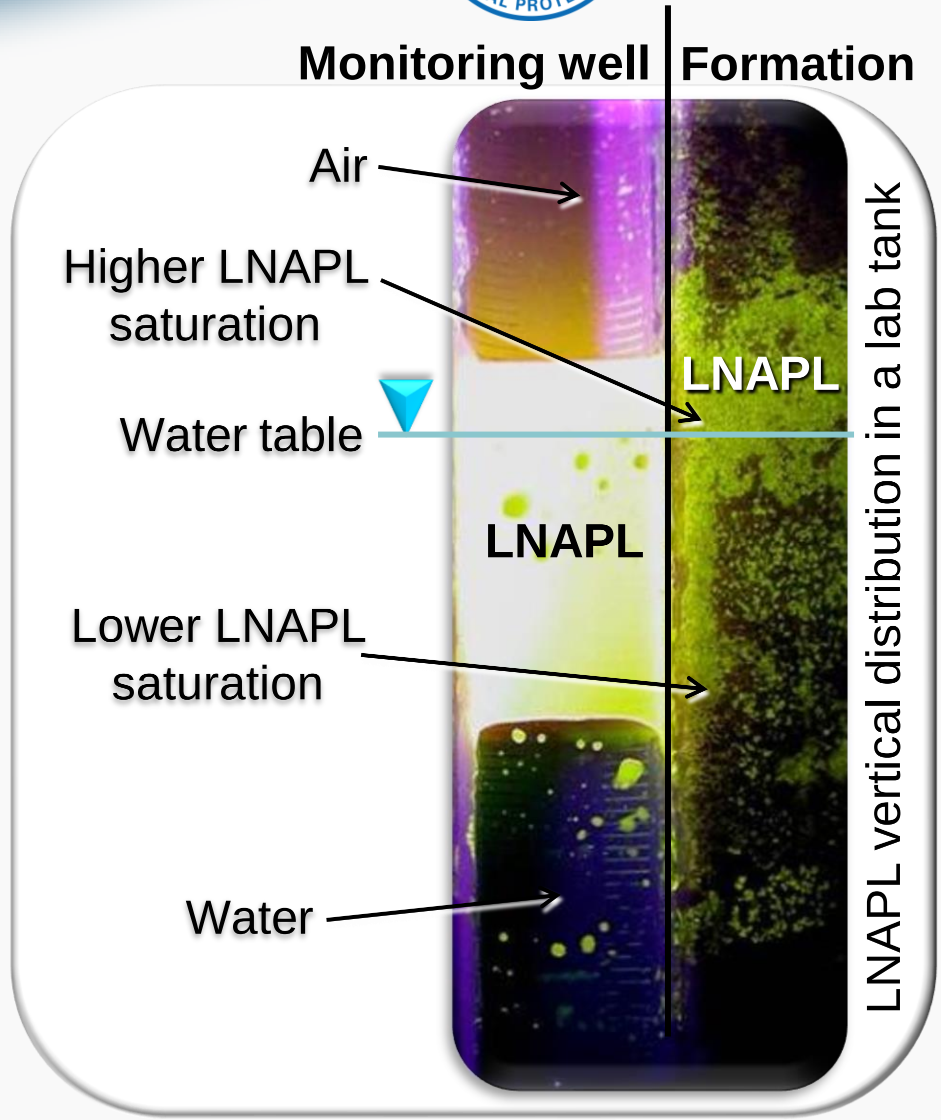
(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

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



Photograph From Andrew Kirkman

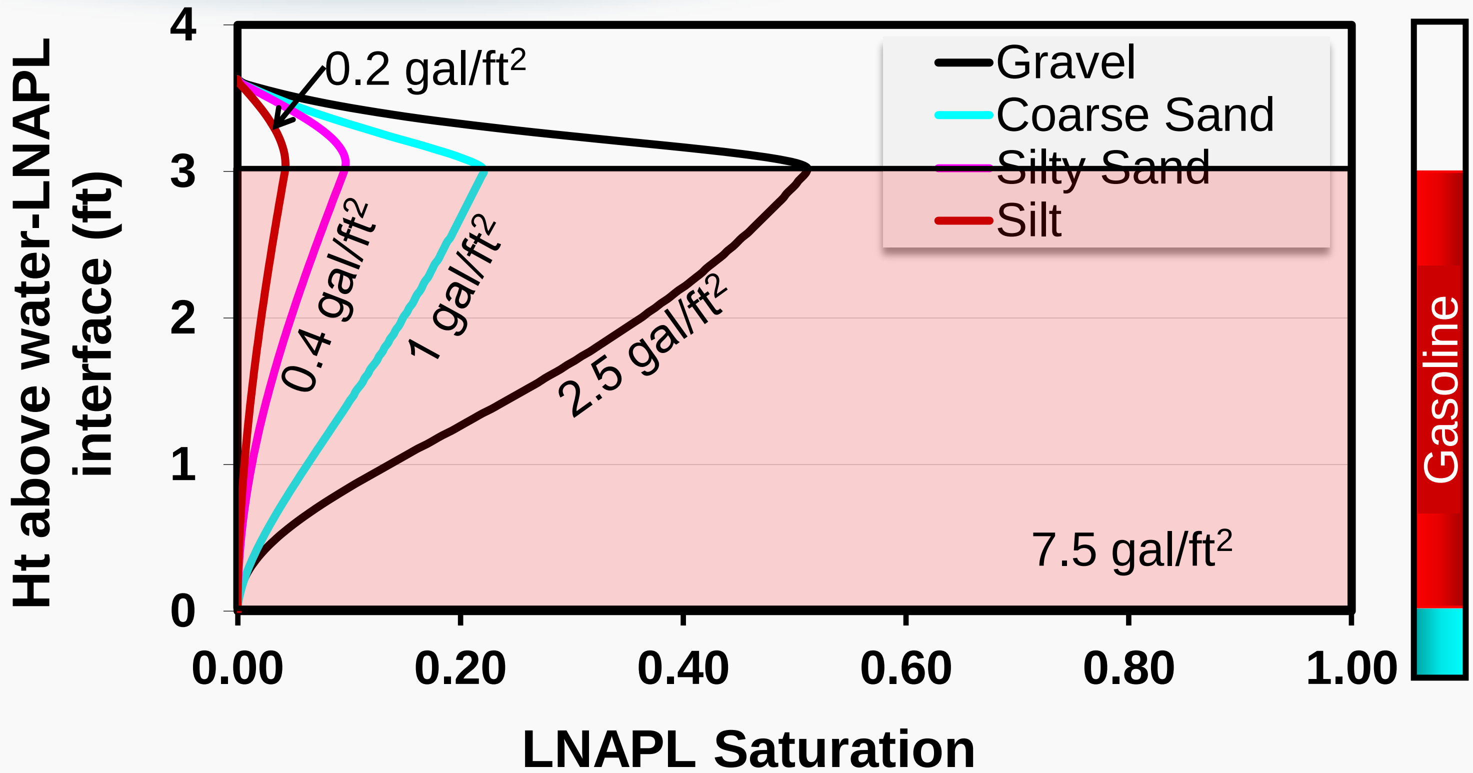
(Source: ITRC LNAPL Course)

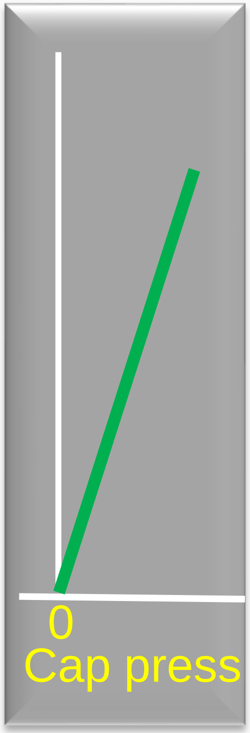
Source: ITRC LNAPL Course (ITRC)

Texture and Vertical LNAPL Distribution

(assumed in-well LNAPL: 3 ft)

Interpreting In-well Thickness





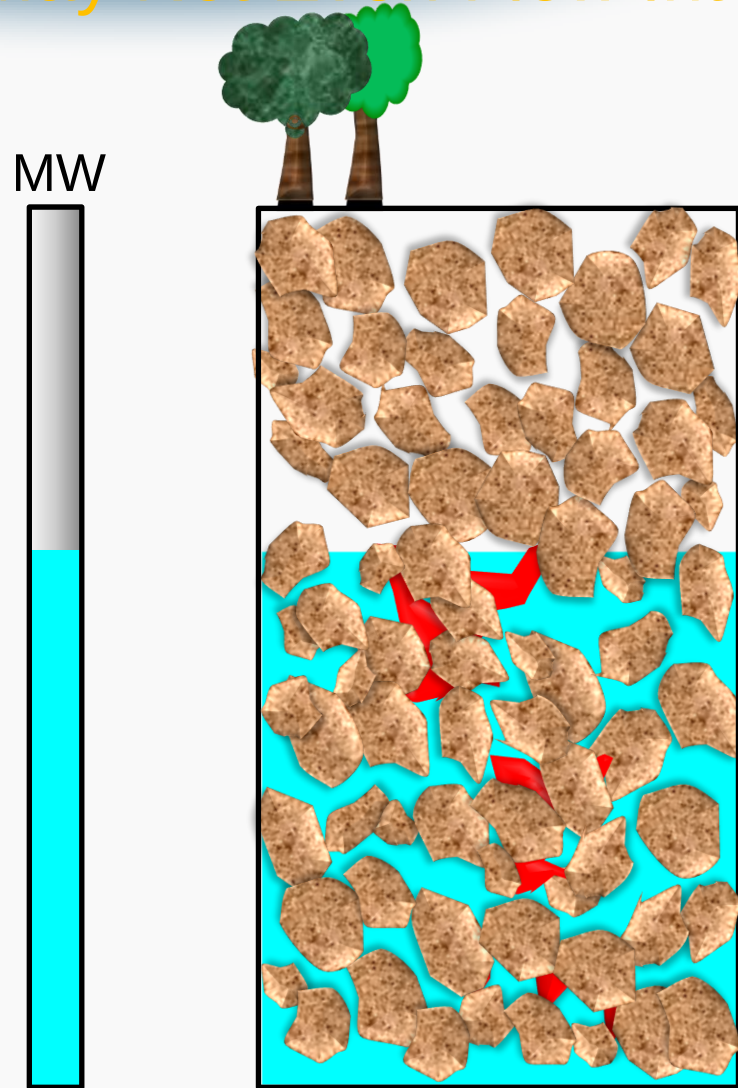
- For a given LNAPL thickness, LNAPL saturations and volumes are different for different soil types (greater for coarser-grained soils)

(Source: ITRC LNAPL Course)

Nature of LNAPL Impacts in the Formation:

LNAPL May Not Even Flow Into A Well

Anatomy of an LNAPL Body



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

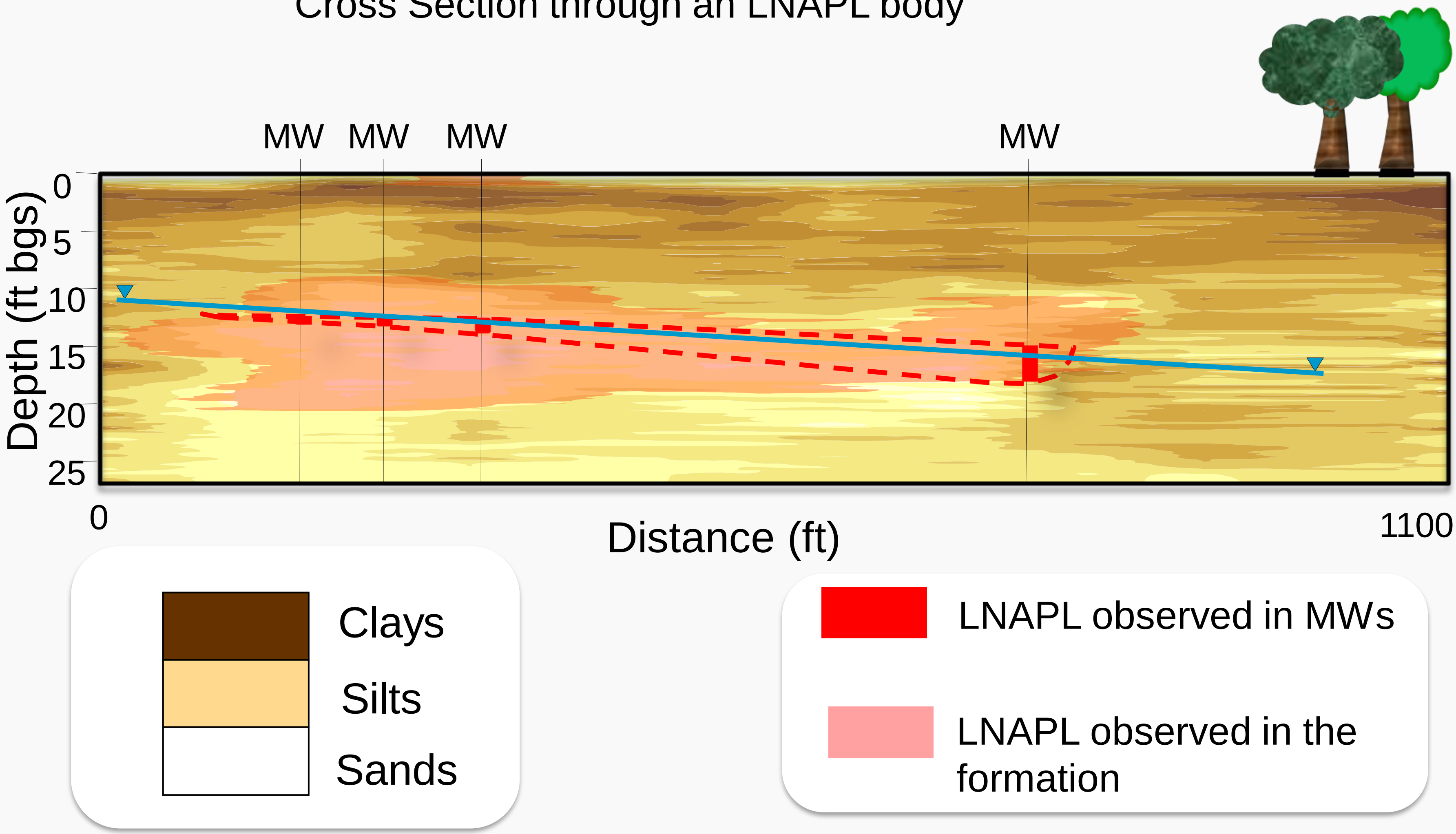
(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL *Vertical* Extent typically Greater Than In-Well LNAPL Thickness

Indicator: In-well LNAPL Thickness

Cross Section through an LNAPL body



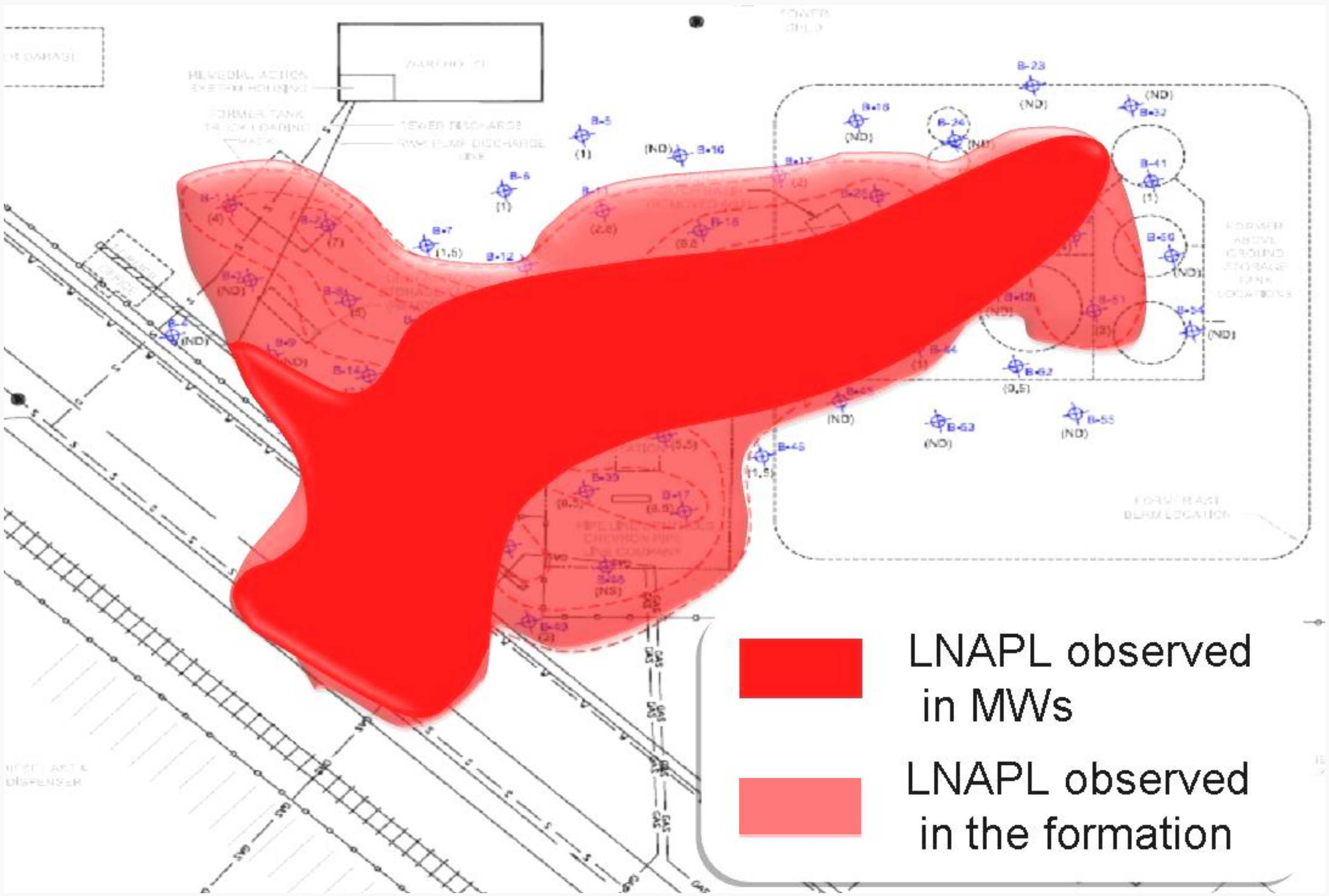
(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL *Lateral* Extent Typically Greater than that Inferred from In-Well Thicknesses

Indicator: In-well LNAPL Thickness

Plan View at an LNAPL site

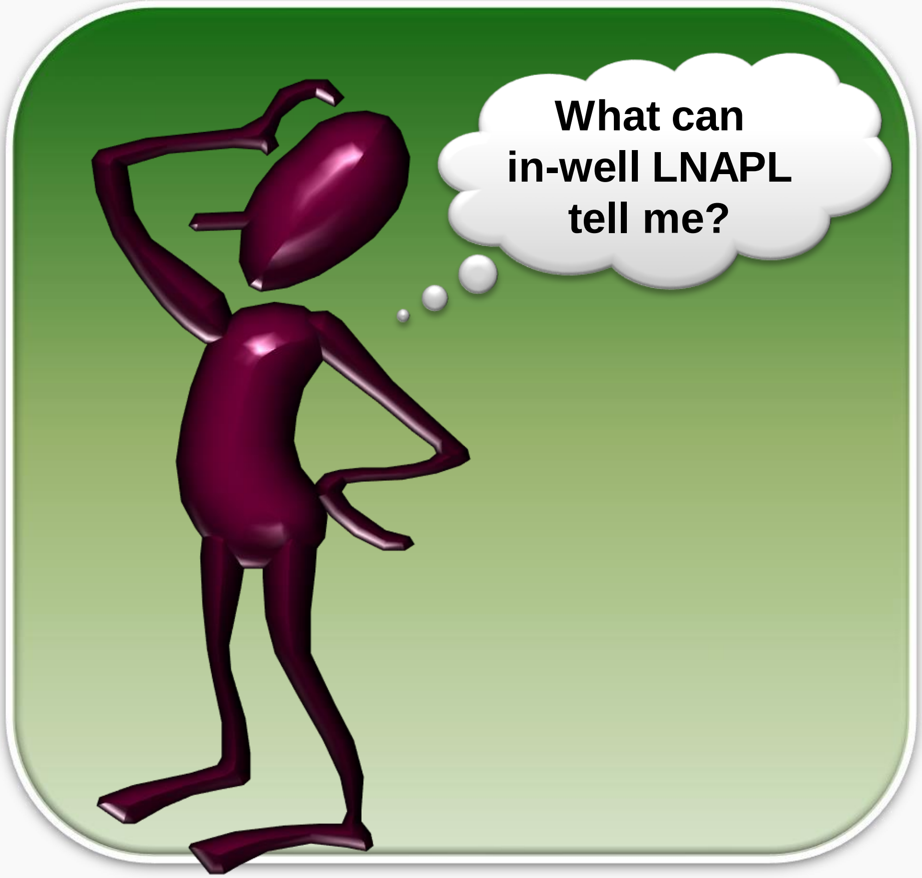


(Source: ITRC LNAPL Course)

Role Of In-Well LNAPL Thickness In Delineation?

If the LNAPL lateral and vertical extent is not the same as the in-well LNAPL thickness (‘free product’) then:

- What is the extent of LNAPL, and how can it be determined?
- What is the use of in-well LNAPL thickness?



(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

In-Well LNAPL Thickness:

Interpreting In-well Thickness

The Good

- A direct indicator of LNAPL presence
  - LNAPL in well means LNAPL in the formation
- Informs the feasibility of hydraulic recovery

The Bad

- Not a reliable indicator of LNAPL vertical and lateral extent
  - Vertical extent (i.e., smear zone) can be larger or smaller than in-well thickness
  - Footprint of LNAPL impact in the formation can be larger
- Not a good indicator of volume by itself
- Absence/removal of in-well LNAPL does not eliminate source

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

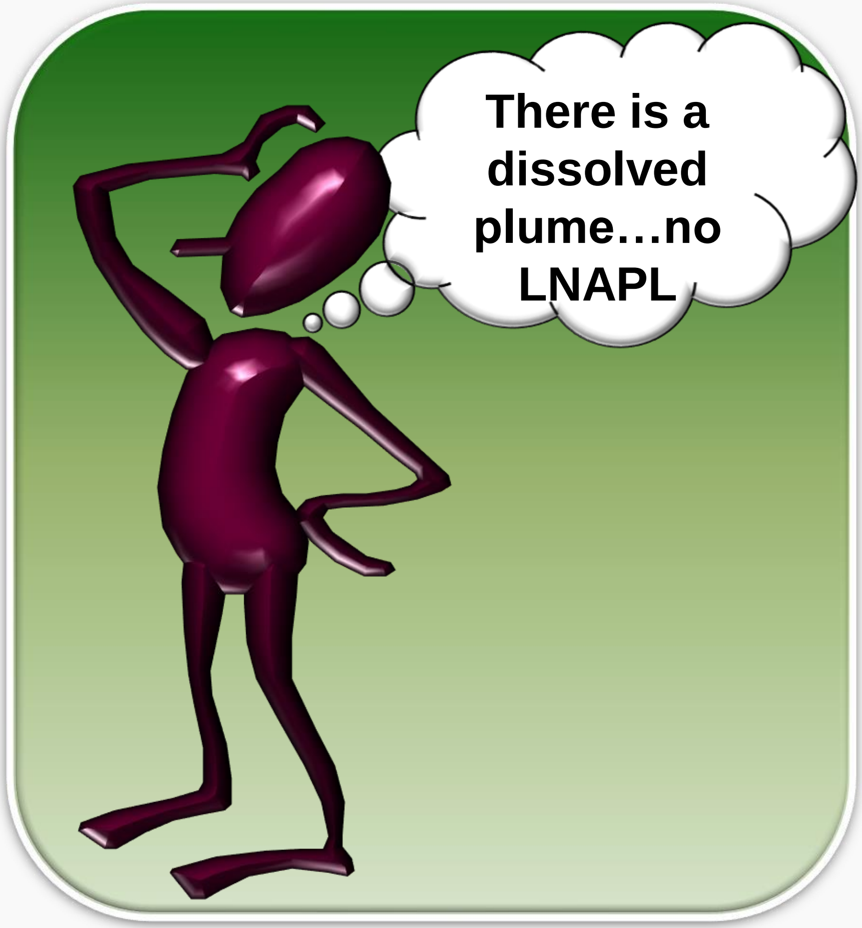
LNAPL Presence: Indicators

Inferring From Dissolved Phase

Indicator: Dissolved Phase

Learning Objectives:

- Determine the presence of LNAPL using dissolved-phase concentration data



Source: ITRC LNAPL Course (ITRC)

Dissolved Phase Persistence

Indicator: Dissolved Phase

If There Is Smoke….

……there is a fire

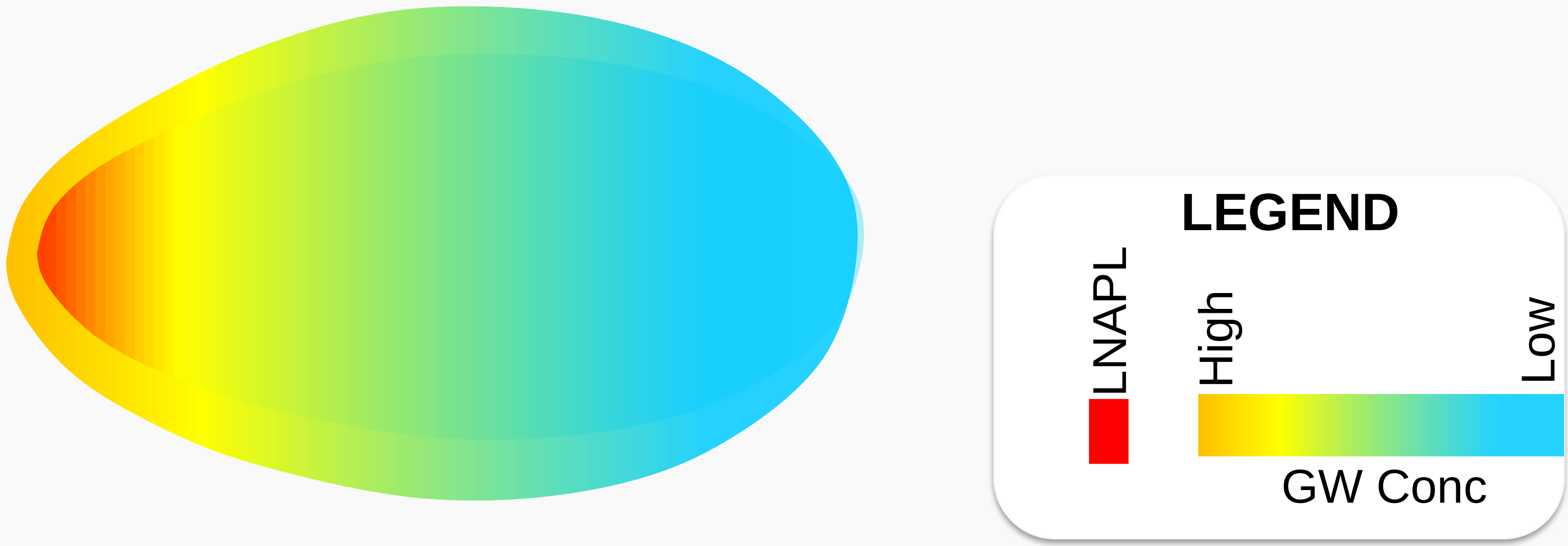
Source: ITRC LNAPL Course (ITRC)

(Source: ITRC LNAPL Course)

Dissolved Phase Persistence

Indicator: Dissolved Phase

If There Is a Persistent Groundwater Plume….



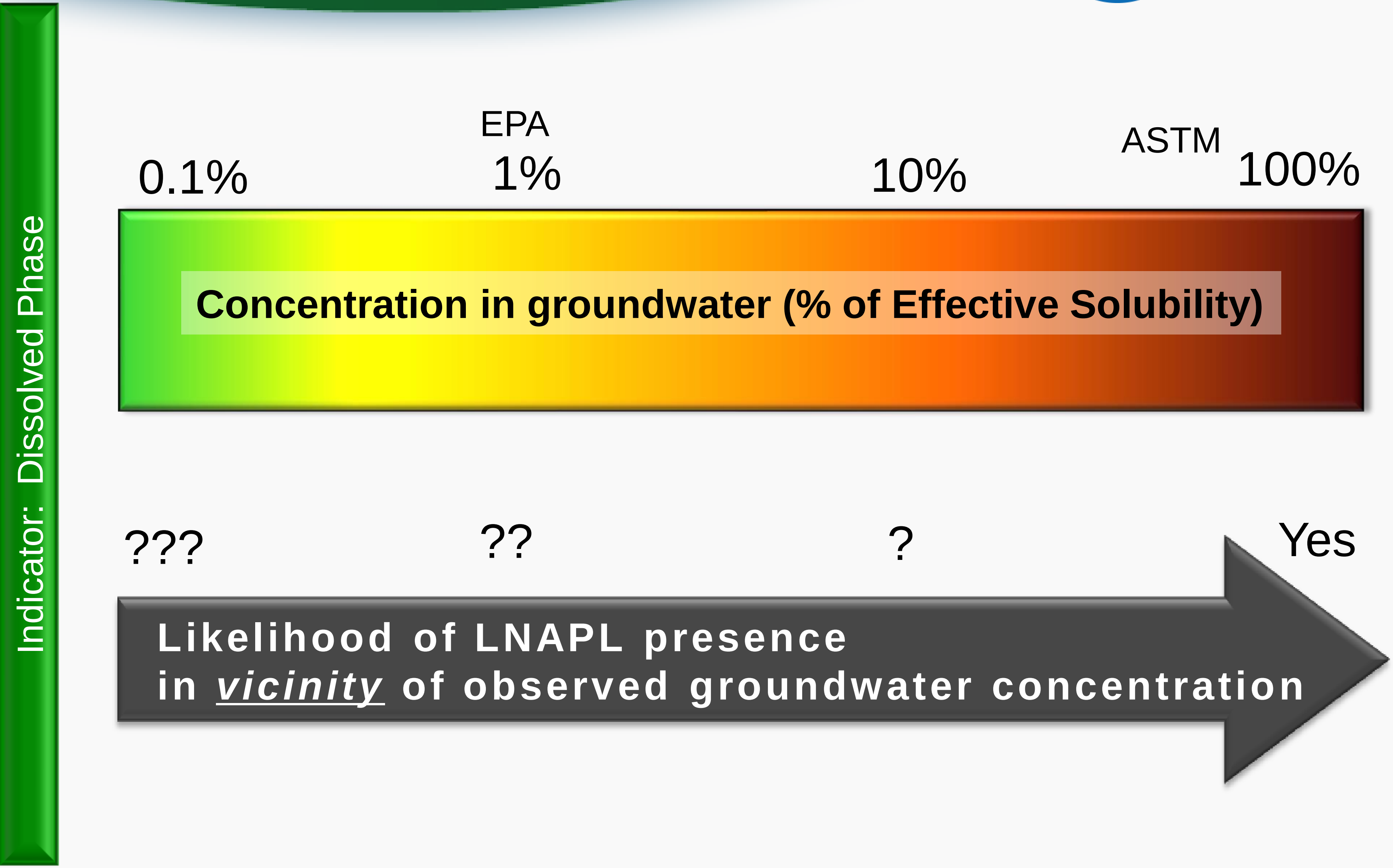
……there is an LNAPL source

…………...it may or may not flow into a well

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

Groundwater Concentrations as an Indicator of LNAPL



(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

Persistent Dissolved-Phase Plume Versus Groundwater Concentrations

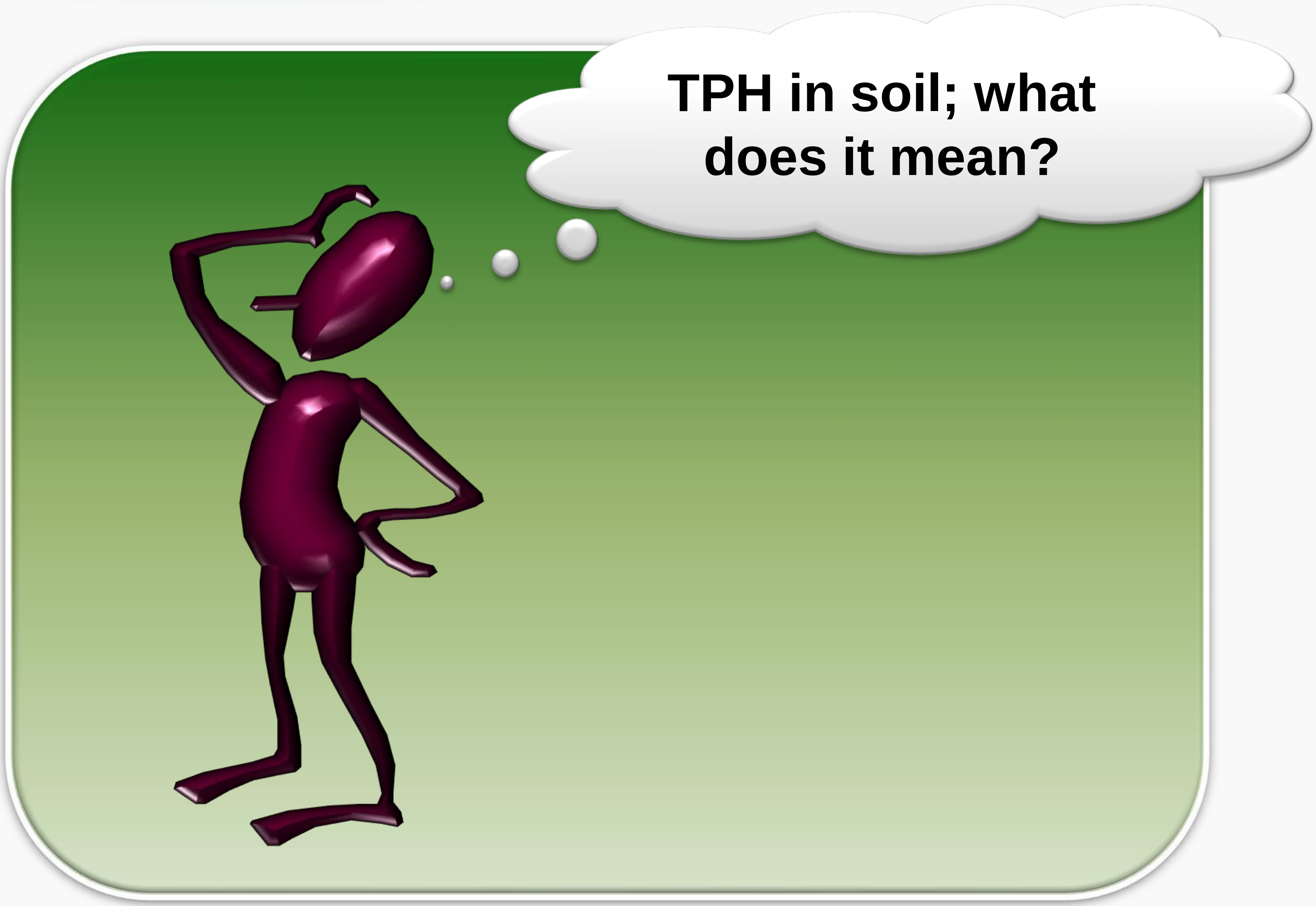
Indicator: Dissolved Phase

- If there is a persistent dissolved-phase plume, there is LNAPL *somewhere*
- The higher the groundwater concentration relative to effective solubility, the higher is the likelihood of a *nearby* LNAPL source

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

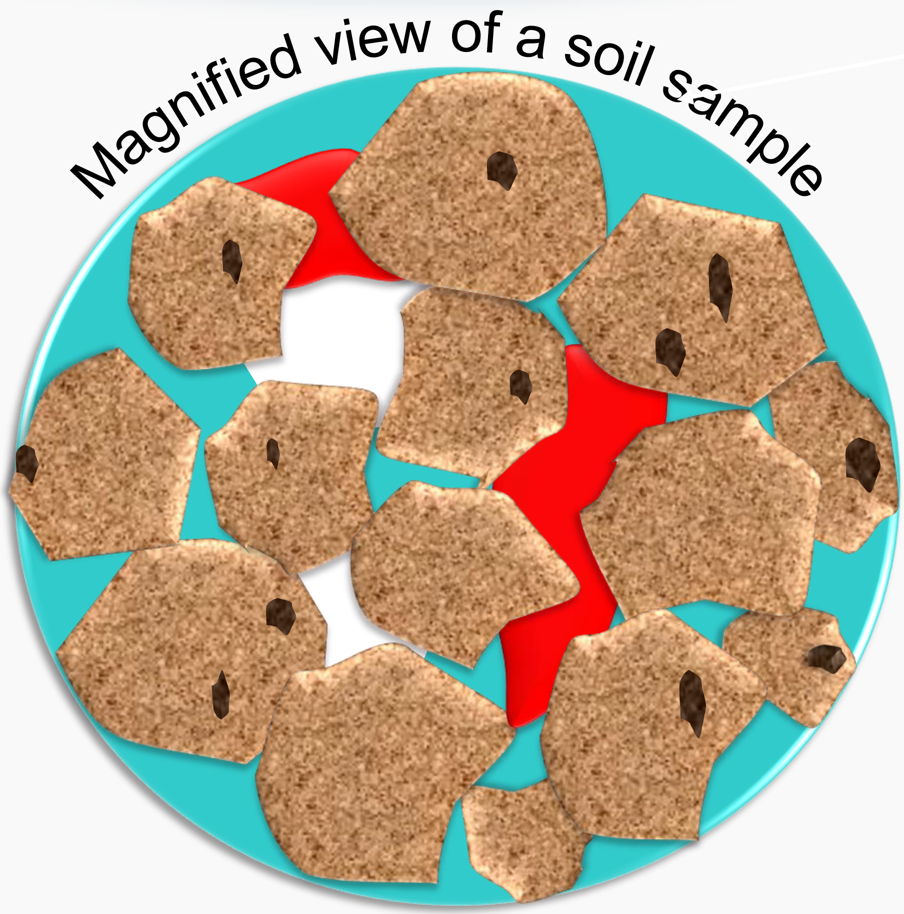
LNAPL Presence Indicators:
*Inferring From Soil Sampling Data- **TPH***



Source: ITRC LNAPL Course (ITRC)

Total Petroleum Hydrocarbon (TPH) In Soil

Indicator: Conventional Assessment



- Soil grain with organic carbon
- Water
- Air
- LNAPL

TPH Units: mg/kg (ppm mass)

TPH analyses

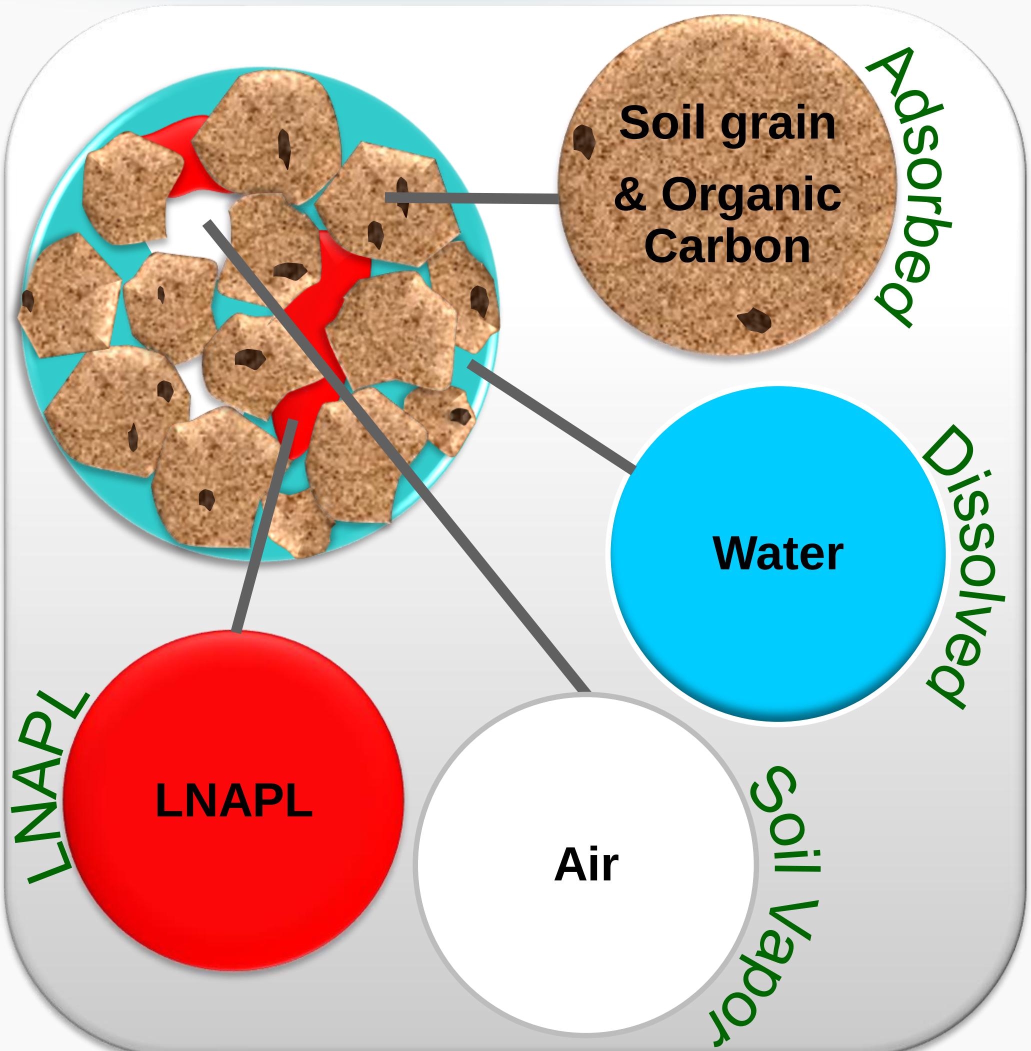
Typical Carbon No.	**Range**
Gasoline	(C6 - C10)
Diesel	(C11- C28)
Residual	(C29 - C35)

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

TPH Concentrations in Soil: An Indicator of LNAPL

Indicator: Conventional Assessment



- Adsorbed, dissolved, and soil gas have a finite capacity for organic chemicals.
  - C_{sat}
- When the TPH concentration exceeds C_{sat}, then a fourth phase, LNAPL, must exist
  - TPH > C_{sat} →LNAPL

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL Mixture	Soil Type	C_{sat} (mg TPH/Kg Soil)
Gasoline	Coarse to medium sand	143
Gasoline	Medium to fine sand	215
Gasoline	Fine sand to silt	387
Kerosene/Diesel Family	Medium to fine sand	9
Kerosene/Diesel Family	Fine sand to silt	18

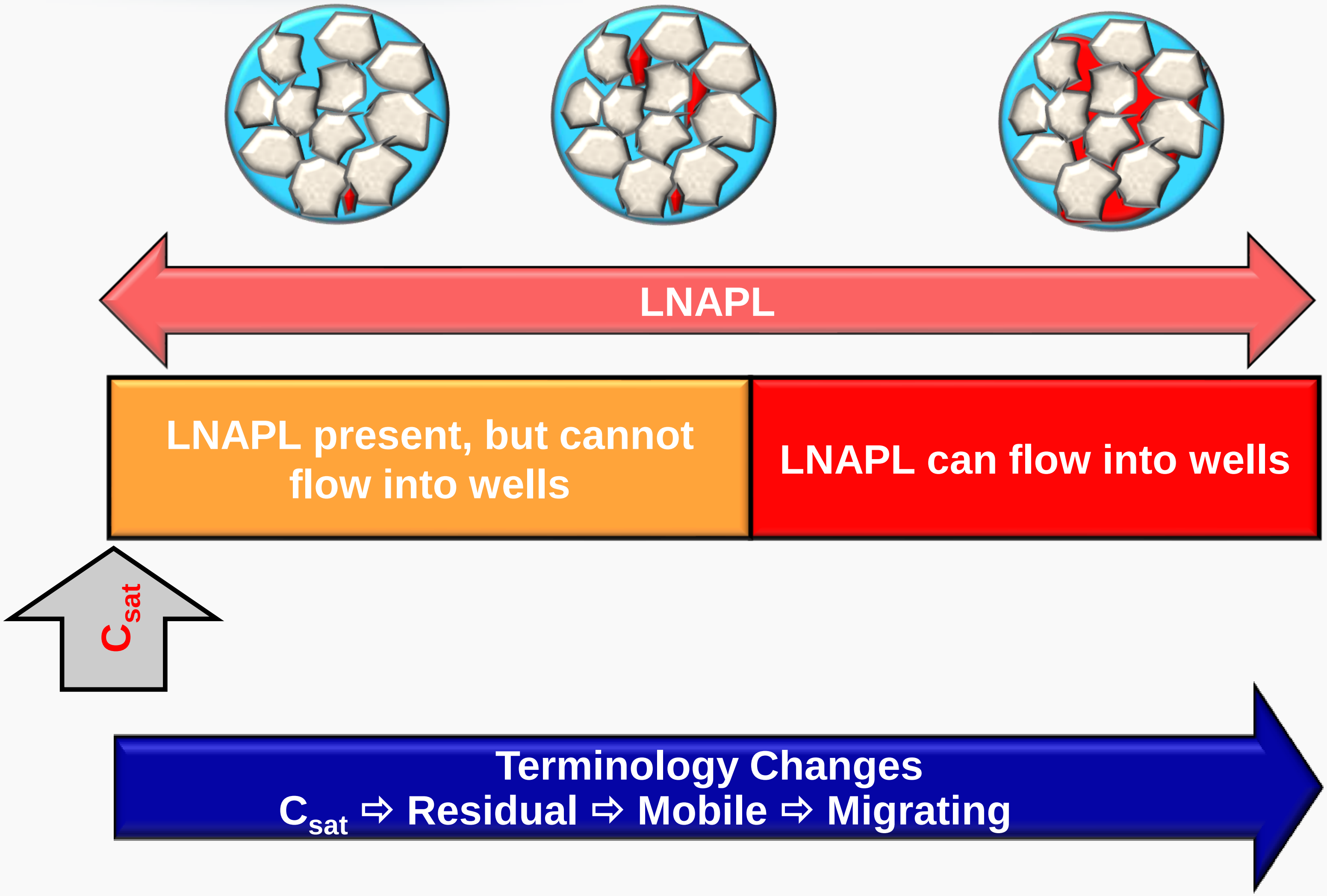
Brost and DeVaull, 2000. API Bulletin 9.

- C_{sat} is a theoretical value, above which LNAPL is likely to exist in the soil pores
- C_{sat} is significantly lower than concentrations at which LNAPL may actually be observed

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

The Name Game



(Source: ITRC LNAPL Course)

Relationship between LNAPL Saturation and Soil TPH

Indicator: Specialized Assessment

- Both measure the LNAPL in soil
- Sample handling and analysis techniques are different:
  - Saturation – Gravimetric
  - TPH- GC/FID
- Results are expressed in different forms (units):
  - Saturation – cm^3 LNAPL/ cm^3 pores
  - TPH- mg LNAPL/Kg soil
- TPH can measure up to C 35

Mathematical Relationship

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

S_n = LNAPL saturation (unitless)
ρ_b = dry soil bulk density (g/cm^3)
TPH = total petroleum hydrocarbons (mg/kg)
ρ_n = NAPL density (g/cm^3)
n = porosity

(Parker et al, 1994)

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL Flow/Migration

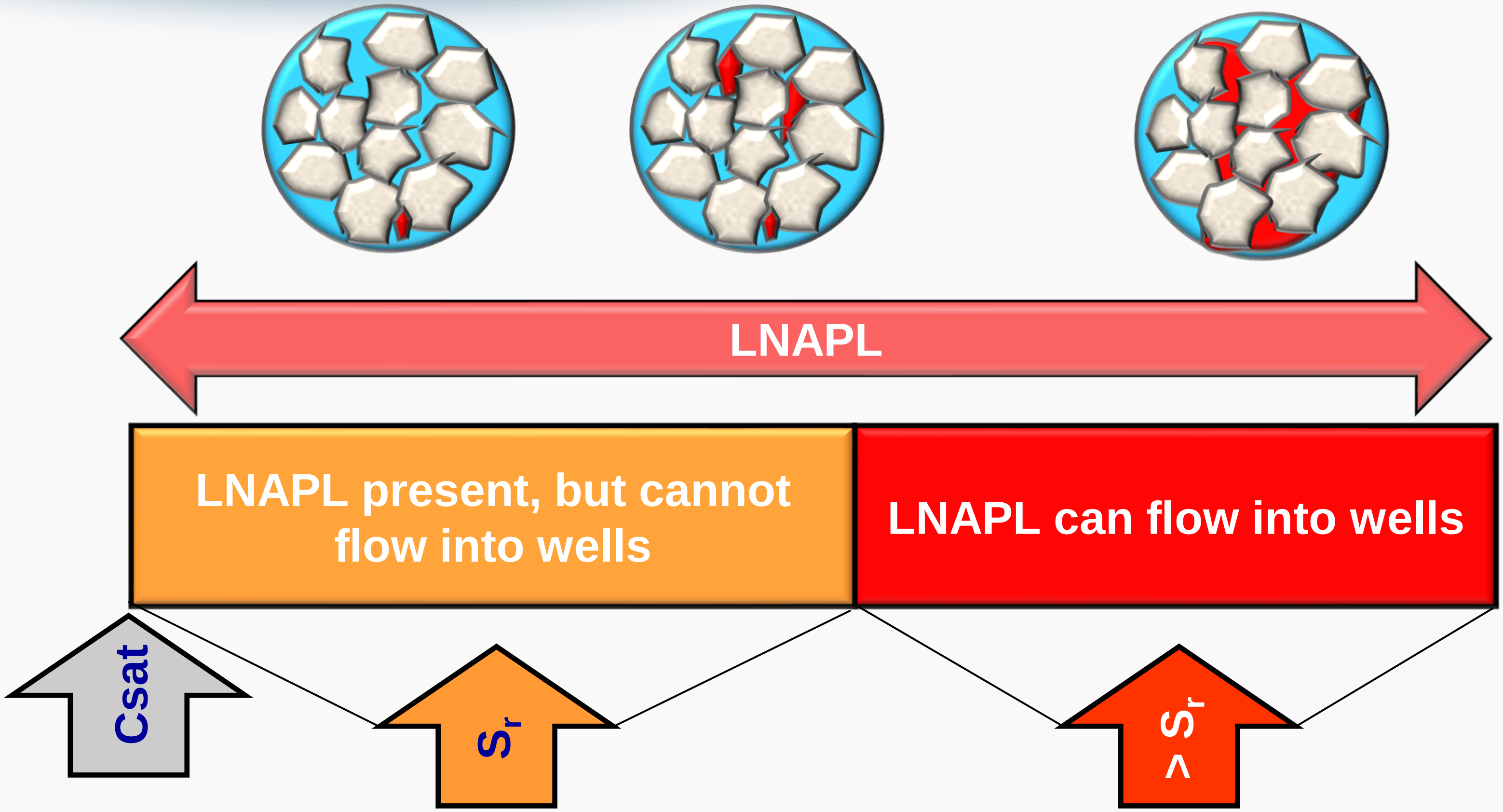
Learning Objectives:

- Understand under what conditions does in-well LNAPL (**Mobile LNAPL**) migrates; i.e., invade pristine territory.

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

The Name Game



S_r= Residual Saturation
$>S_r$= Mobile
S_m= Mobile Saturation

Terminology Changes
Csat ⇨ Residual ⇨ Mobile ⇨ Migrating

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL Migration – Darcy's Law

Learning Objectives:

- Apply Darcy's Law to show LNAPL migration is *somewhat* analogous to groundwater flow

Source: ITRC LNAPL Course (ITRC)

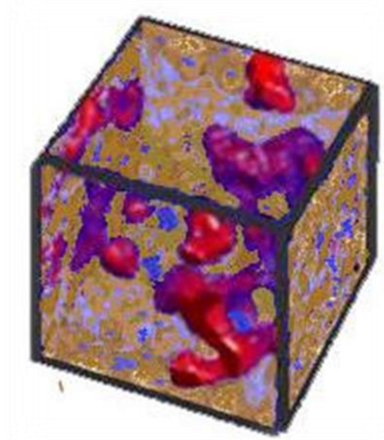
Darcy's Law for LNAPL

Darcy's Law: Applicable to LNAPL

- Darcy's Law:
  - $q = K\, i$
- Two components of flow: conductivity and gradient
- In a water/LNAPL system: not just single fluid, but two--groundwater and LNAPL.
- Darcy's Law applicable to each fluid.

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

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

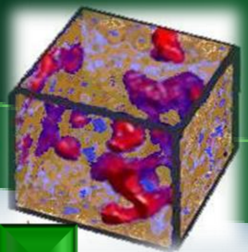


q= Darcy flux (L/T)
K = fluid conductivity (L/T)
i = gradient
w = water
n = LNAPL

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

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)



LNAPL Conductivity

Darcy's Law: Applicable to LNAPL

Hydraulic conductivity water only (saturated)

$$K_{w,sat} = \frac{\rho_w \cdot g \cdot k}{\mu_w}$$

Hydraulic/Water conductivity with LNAPL:

$$K_w = \frac{\rho_w \cdot g \cdot k}{\mu_w} k_{rw} = K_{w,sat} \, k_{rw}$$

LNAPL conductivity (groundwater is always present):

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

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

K = liquid conductivity
k = intrinsic permeability
k_r = relative permeability
ρ = density
μ = viscosity
n = LNAPL
w = water
g = acceleration due to gravity

Parameter	Parameter Trend	K_n	Effect on LNAPL Flow (q_n)
Relative Permeability of LNAPL (k_{rn})	↑	↑	↑
LNAPL Density (ρ_n)	↑	↑	↑
LNAPL Viscosity (μ_n)	↑	↓	↓

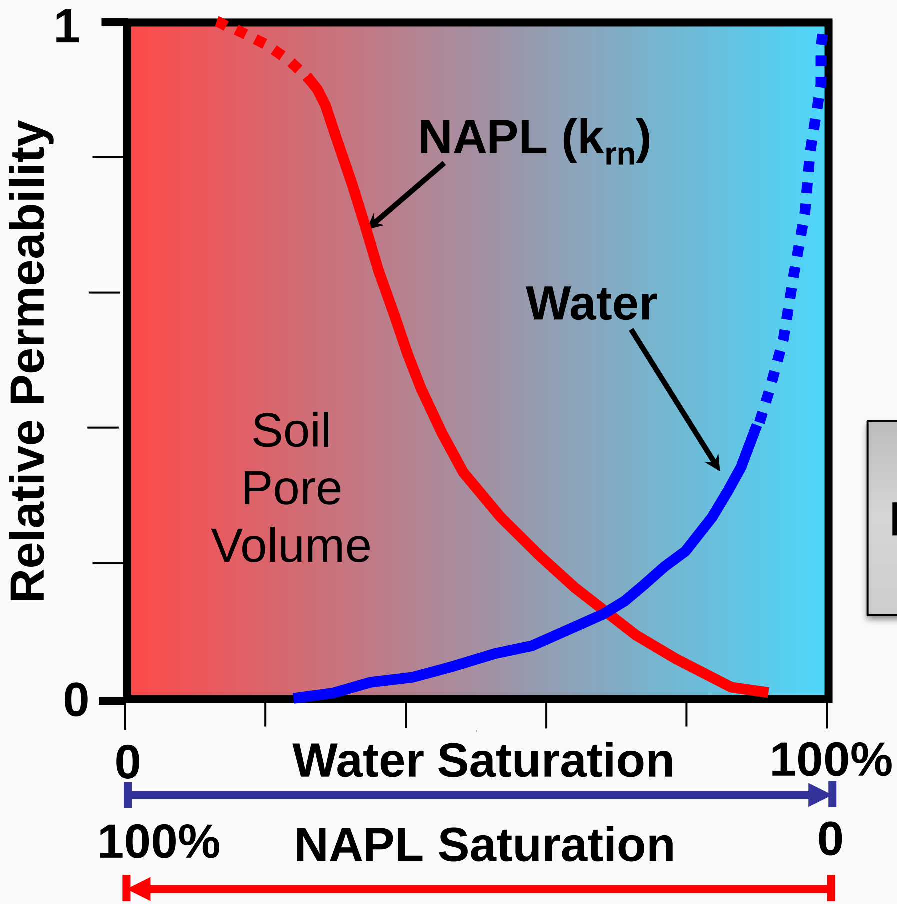
(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL Conductivity: Relative Permeability (k_r)

Darcy's Law: Applicable to LNAPL

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



Consider water/LNAPL in soil:

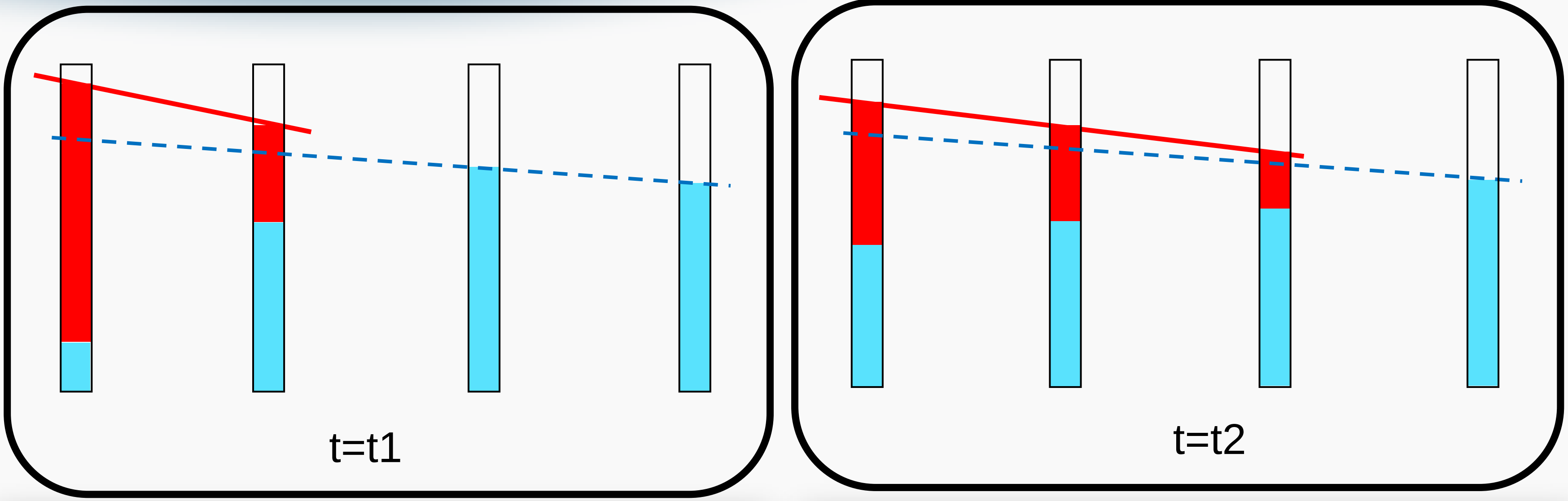
- Saturation → relative permeability
- Relative permeability of soil for water or LNAPL at 100% saturation = 1

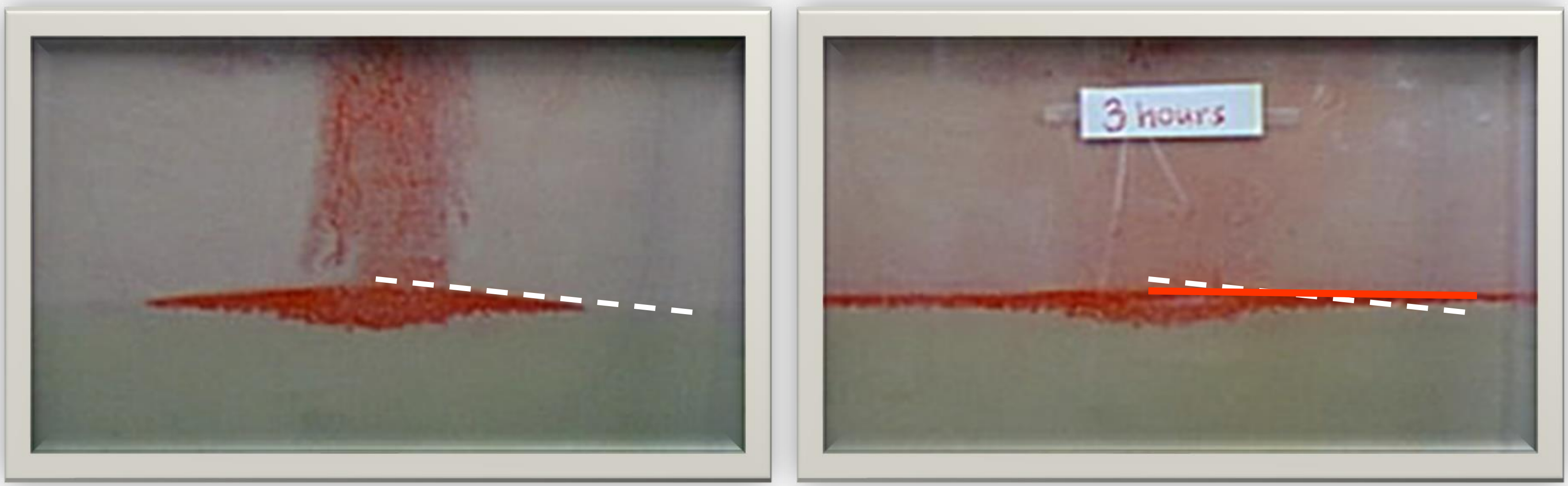
Relative permeability for both LNAPL and water decreases rapidly as saturation declines from 100%

(Source: ITRC LNAPL Course)

The Next Flow Component: Gradient
(Flattens over Time for Finite Releases)

Darcy's Law: Applicable to LNAPL

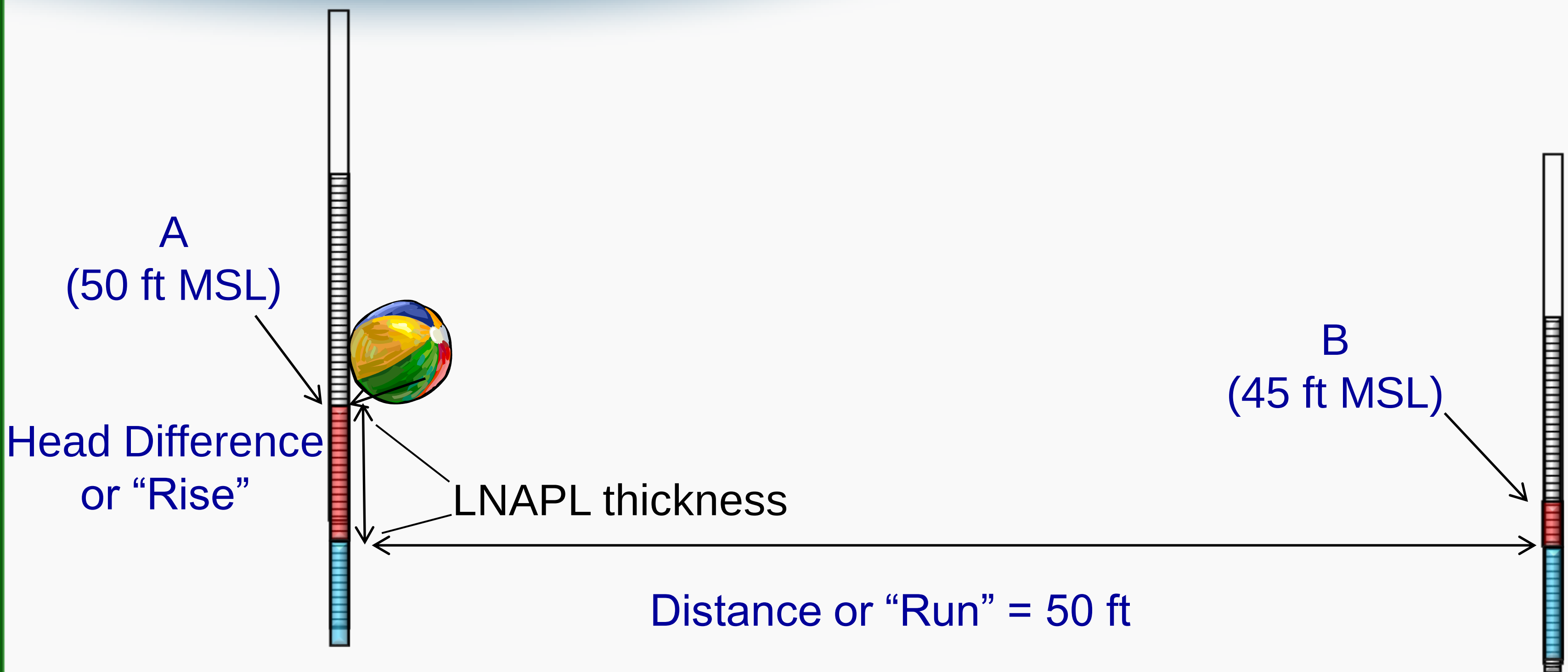




(Source: ITRC LNAPL Course)

Key Concept Behind Migrating LNAPL: Gradient

Fluid Movement



LNAPL Head: Elevation of air-LNAPL interface above a specified datum. The LNAPL elevation at point A = 50 ft MSL.

LNAPL Gradient: Head difference between two well divided by the distance between them: between wells A and B gradient = 5 ft rise / 50 ft run = 0.1 ft/ft

Key Point: Liquids (water or LNAPL) flow from high head to low head at a rate that is proportional to the gradient.

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

Take-Home Points Regarding Darcy's Law & LNAPL

Darcy's Law is applicable to LNAPL flow, just as it is to groundwater, but:

- For a finite release, LNAPL conductivity and gradient decrease with time as a result of
  - Spreading (sat↓)
  - Recovery (sat↓)
- LNAPL migration is a self-limiting process as it spreads, and gradient diminishes.

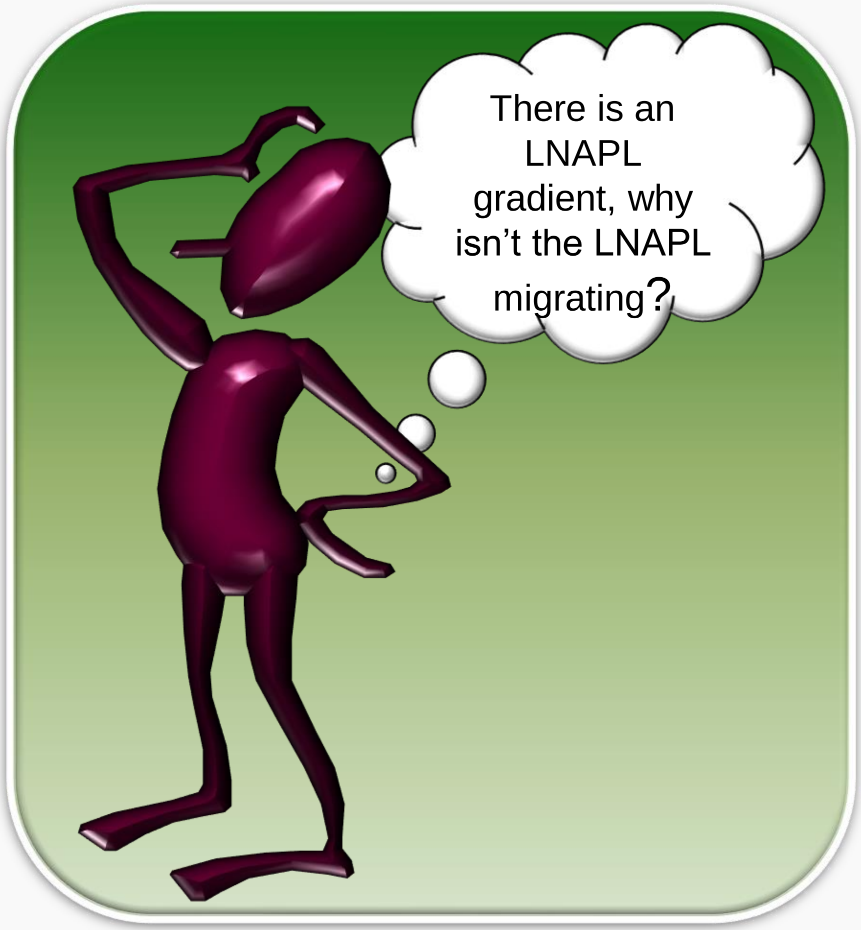
(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

What Else Limits LNAPL Migration? – Pore Entry Pressure

Learning Objectives:

- Understand pore entry pressure as an opposing force to LNAPL migration
  - Darcy's Law induces migration, but the pores push back.



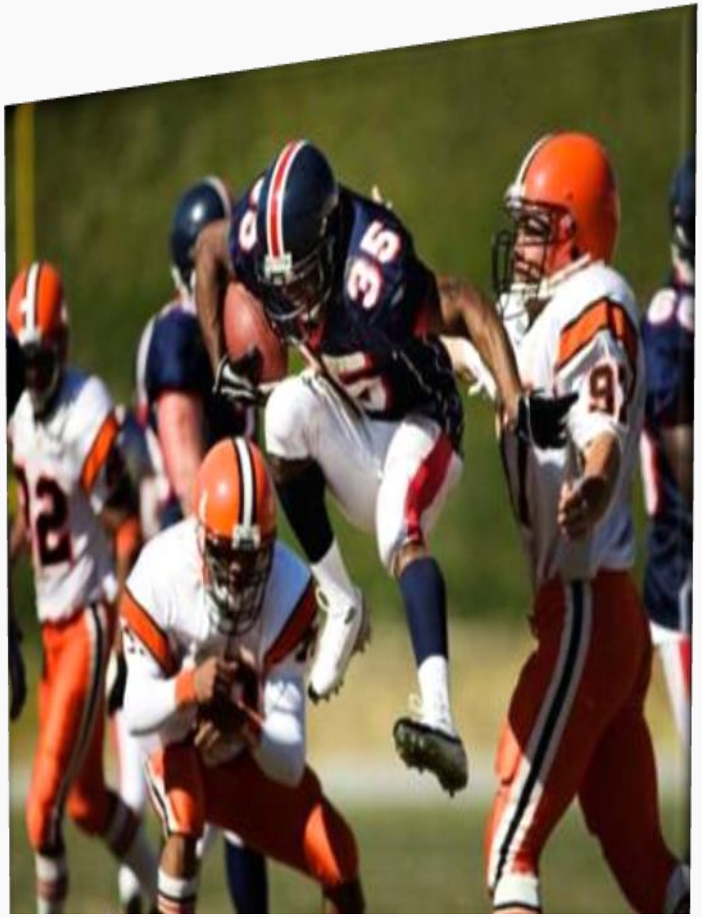
(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

Wettability and Pore Entry Pressure: Real Life Analogy

Pore Entry Pressure

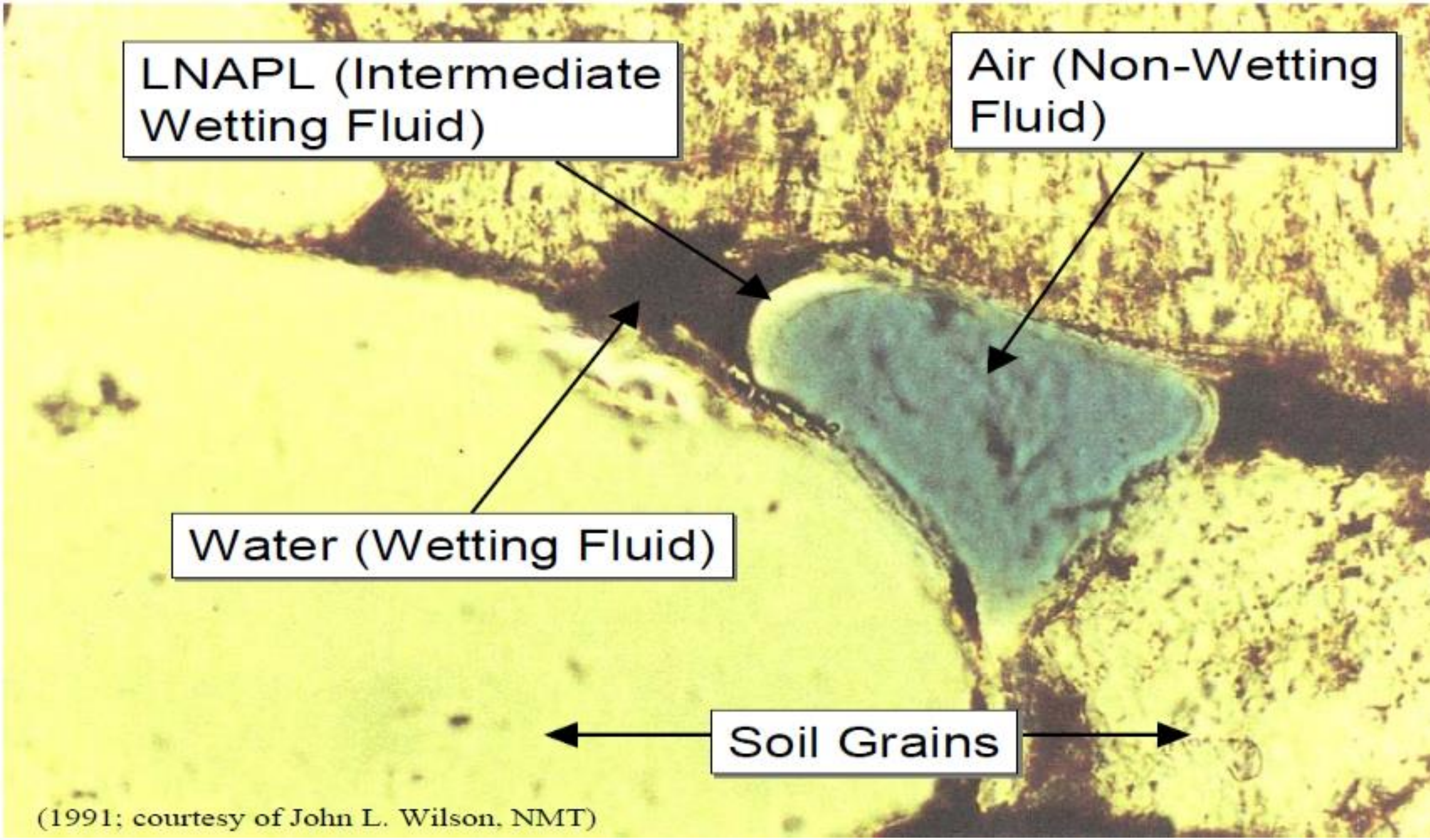
- What happens when you try to get into someone else’s territory?
  - If they like you – no problem
  - If you’re stronger – some problem
  - If you’re weaker – then there is resistance, and you cannot get in until you build enough forces



(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

Pore Scale the Fluid Vadose Zone System: Air, Oil, Water



(Source: ITRC LNAPL Course)

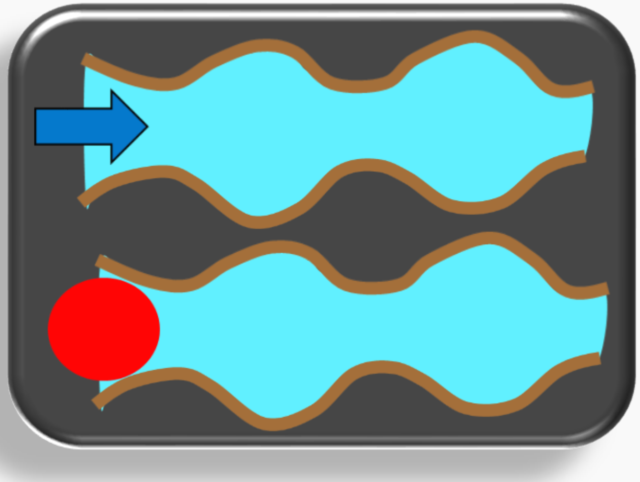
Source: ITRC LNAPL Course (ITRC)

Pore Entry Pressure (PEP): LNAPL Behavior

Pore Entry Pressure

- Behavior when LNAPL tries to enter pores with pre-existing fluids
  - No resistance when like flows displaces like (e.g., groundwater flow)
  - Vadose Zone: Pores more wetting to LNAPL than air: LNAPL displaces air easily
  - Sat. Zone: Pores less wetting to LNAPL than water--LNAPL encounters resistance

For water-wet media



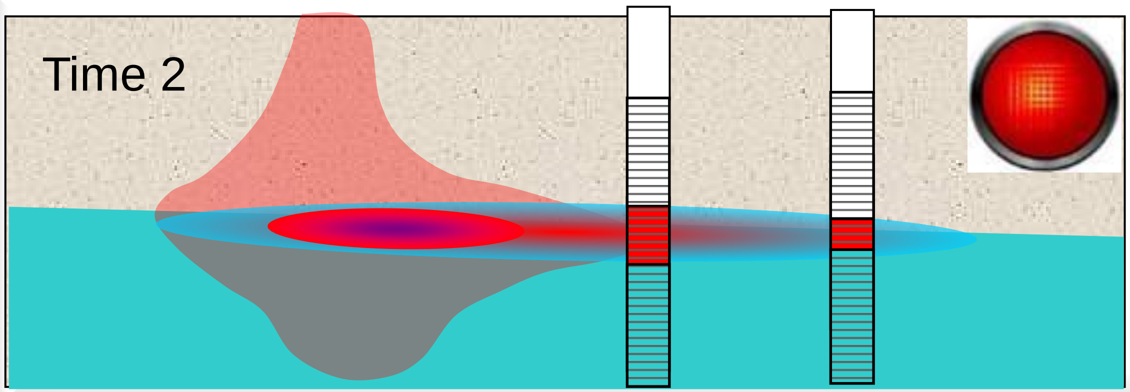
(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL Migration:

LNAPL Body Stabilizes Due to PEP

Pore Entry Pressure (PEP)



LNAPL thickness at the leading edge NOT sufficient to overcome PEP → LNAPL *Stable*

Residual LNAPL Sat

Key Point: Water acts as capillary barrier against continued LNAPL spreading at the LNAPL body edges

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL Migration

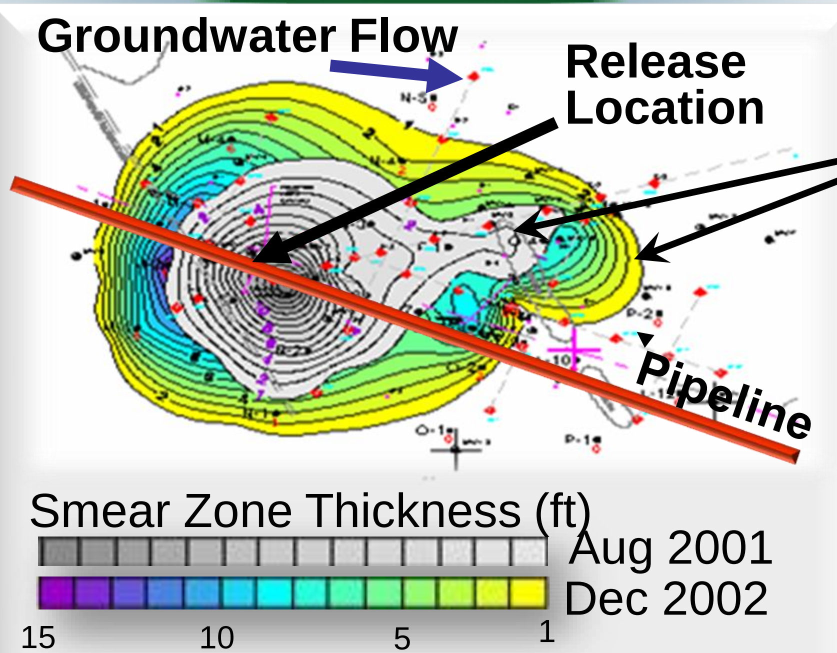
What we have observed at sites:

- LNAPL can initially flow faster than the groundwater due to high LNAPL gradients at early times
- Typically, LNAPL migrates radially following a release—i.e., upgradient as well
- After release is abated, LNAPL bodies come to a stable configuration within a short time for most LNAPLS—PEP constraints

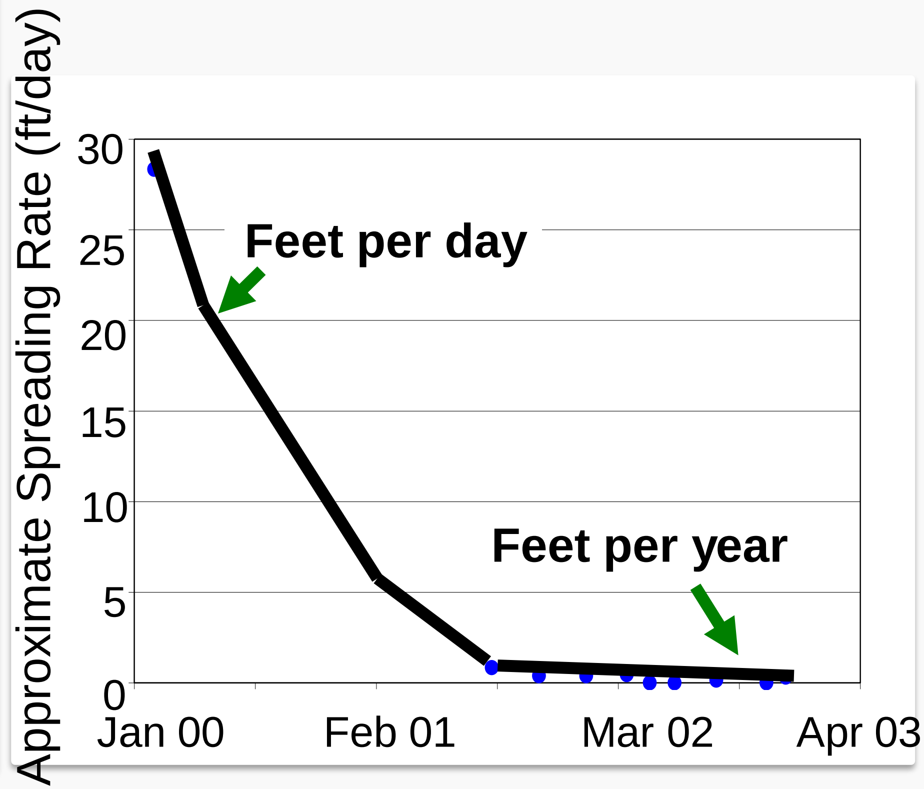
(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL Release and Spreading over Time



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



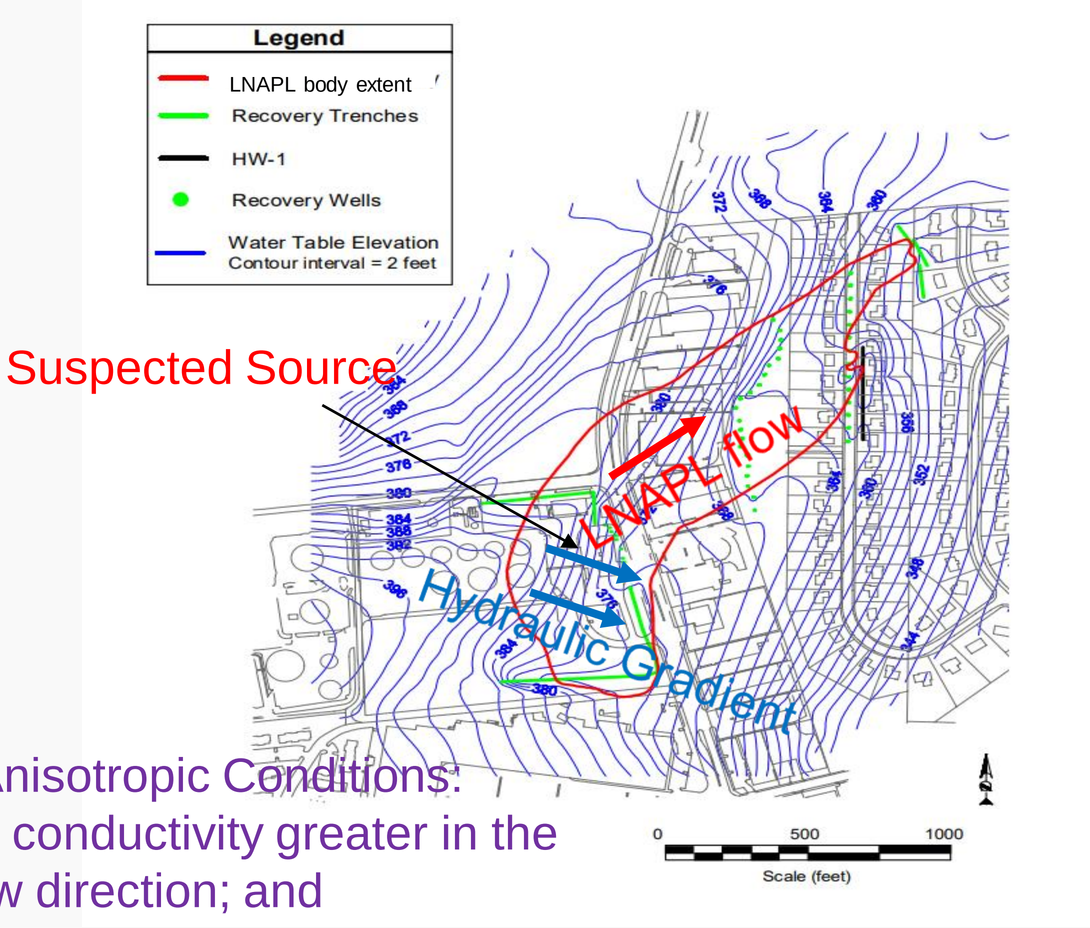
Pipeline release in Feb 2000

- Sweet Texas crude
- Unknown release volume

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL Flow: Anisotropic Conditions



Key Point

Horizontal Anisotropic Conditions:

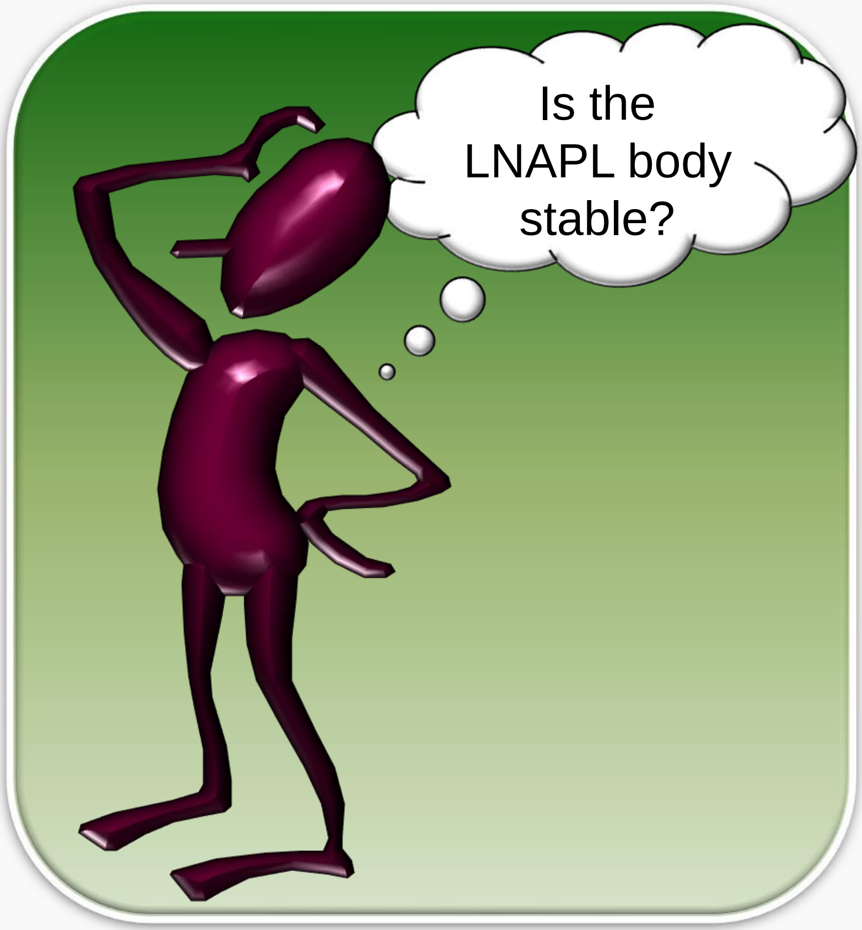
1. Hydraulic conductivity greater in the principal flow direction; and
2. Flow (groundwater and LNAPL) and transport (dissolved plume) NOT parallel to hydraulic gradient

LNAPL Migration – Lines of Evidence

LNAPL Footprint Stability LOE

Learning Objectives:

- Apply lines of evidence (LOE) to evaluate LNAPL footprint stability



Source: ITRC LNAPL Course (ITRC)

Lines of Evidence of LNAPL Footprint Stability

LNAPL Footprint Stability LOE

1) Stable or decreasing thickness of in-well LNAPL, and mobile LNAPL extent by extension

2) If Monitoring well dissolved concentrations are stable or decreasing and the dissolved plumes by extension

3) If a discharge, say to surface water, abates

4) Age of the release
   - Elapse time since release abated (if known)

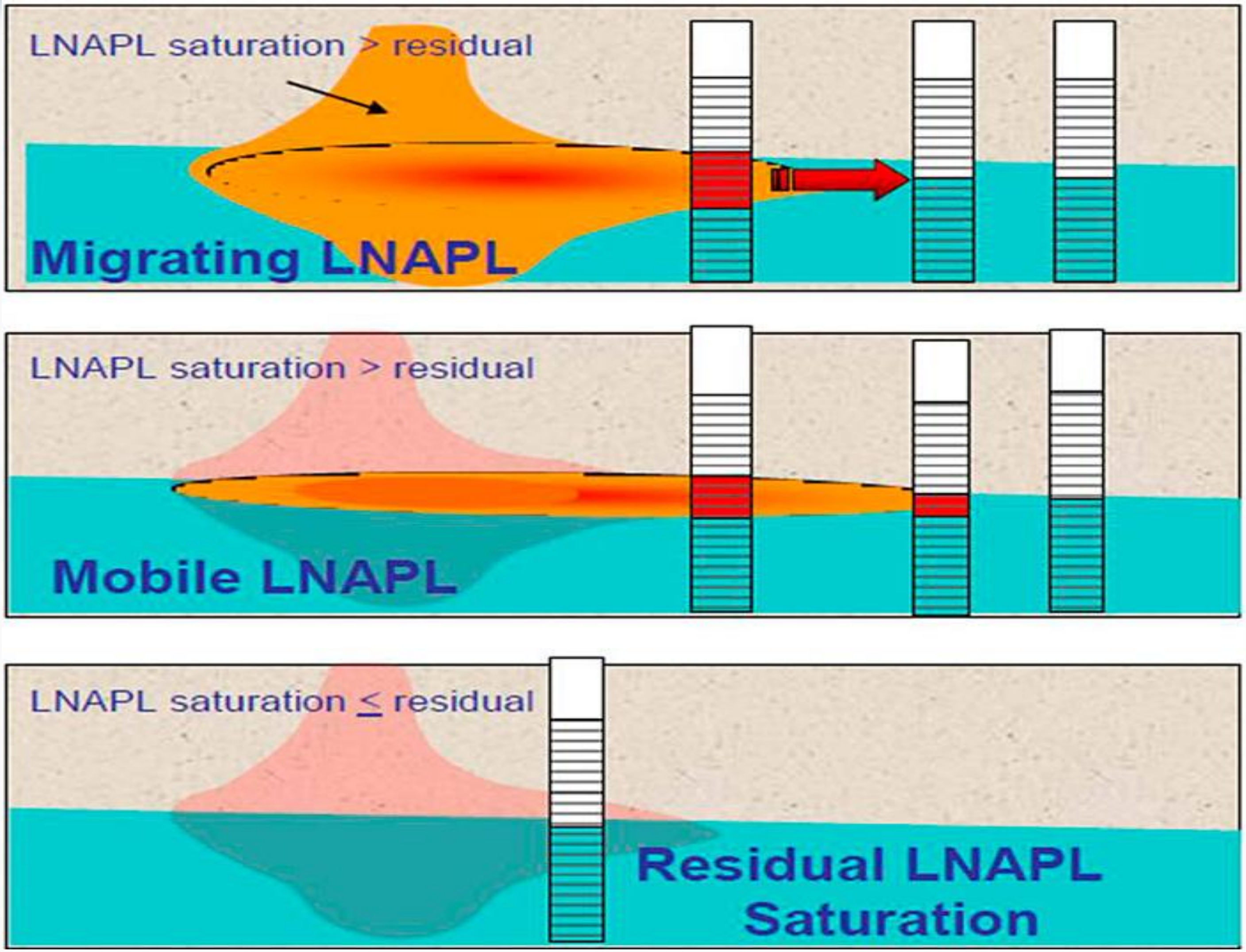
5) Decreasing Recovery rates from a Recovery system

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

Summary: LNAPL Body Life Cycle

LNAPL Footprint Stability LOE



Early in the Lifecycle

Later in the Lifecycle

Late in the Lifecycle

LNAPL Transmissivity

Learning Objectives:

- Discuss LNAPL Transmissivity as a parameter to determine LNAPL recoverability

Discussion Points

- Introduce the LNAPL transmissivity (Tn) parameter
- Demonstrate its analogy & relation to other flow parameters
- Demonstrate how Tn is a summary metric: soil and LNAPL properties, formation thickness and LNAPL saturation

(Source: ITRC LNAPL Course)

Definition and Context

- LNAPL Transmissivity (T_n)
  - Definition: proportionality coefficient describing the ability of a permeable medium to transmit LNAPL
    - Units: length^2/time (volume/unit width/time)
  - A coarse-textured soil (more permeable) will deliver more LNAPL than a fine-textured, less permeable, soil for similar LNAPL type, formation thickness and LNAPL gradient
- Assumptions inherent in T_n
  - Vertical (hydrostatic) equilibrium
  - Aquifer type (horizontal) flow

(Source: ITRC LNAPL Course)

LNAPL Transmissivity

LNAPL Transmissivity

- Discussed LNAPL conductivity (Kn) in Darcy's Law for LNAPL flow
  - Kn is a point parameter; i.e., varies in three dimensions
  - Not measureable in the field, hence, has limited practical utility in site characterization and evaluating LNAPL recoverability
- LNAPL Transmissivity (Tn): will be discussed for evaluating LNAPL flow and recoverability
  - Tn is a vertically integrated parameter; i.e., varies areally between wells
  - Easily measured in the field, hence more practical for site characterization/LCSM development (need one Tn per monitoring well/time)

(Source: ITRC LNAPL Course)

Relationship to LNAPL Conductivity (K_n)

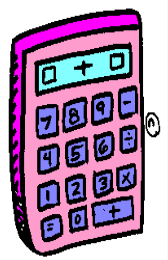
LNAPL Transmissivity

- Tn is proportionality coefficient like LNAPL conductivity (K_n); i.e., no gradient, no flow

$$q_n = K_n\, i_n$$
$$q_n\, b_n = K_n\, b_n\, i_n$$
$$Q_n = T_n\, i_n$$

q_n = LNAPL flow per unit area perpendicular to flow/gradient
Q_n = LNAPL discharge per unit width perpendicular to flow/gradient
i_n = LNAPL gradient
b_n = LNAPL formation thickness

Key Point: Higher T_n, higher Q_n potential



(Source: ITRC LNAPL Course)

LNAPL Transmissivity (T_n) Analogous to Hydraulic Transmissivity (T_w)

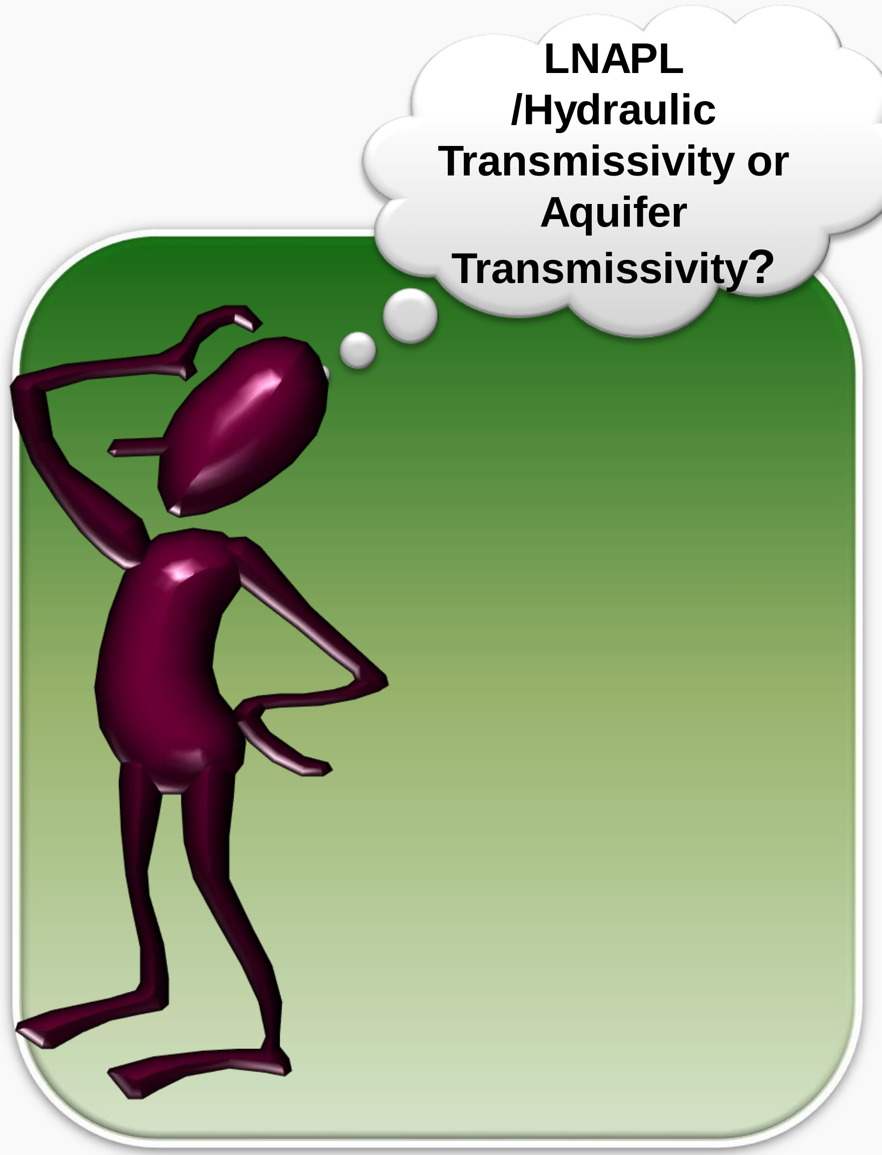
LNAPL Transmissivity

T_n analogous to T_w

- T_w water transmissivity
- T_n LNAPL transmissivity

Correct term: aquifer transmissivity to water/LNAPL

- Aquifer that allows fluids to flow



(Source: ITRC LNAPL Course)

Analogous to Water Transmissivity (T_w)

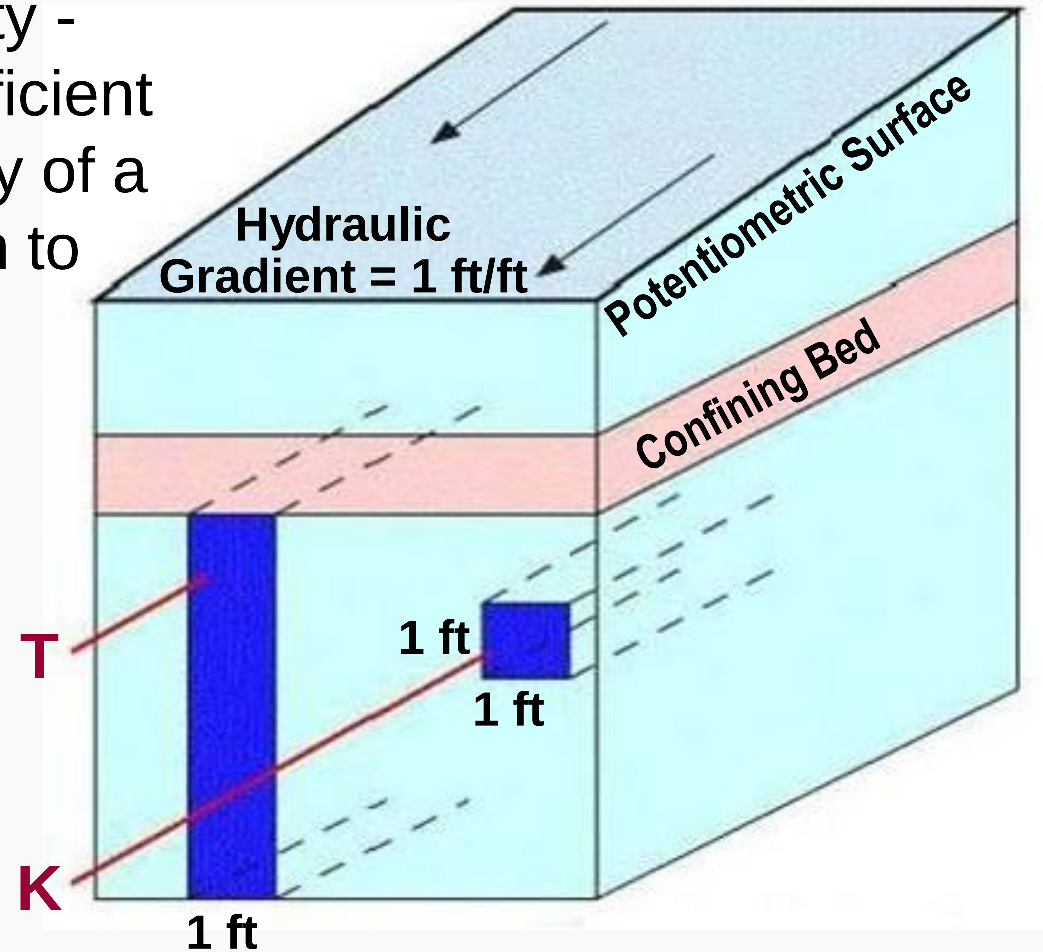
LNAPL Transmissivity

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

$T_w = K_w \cdot b$

K = hydraulic conductivity

b = aquifer thickness



Modified from Driscoll (1989)

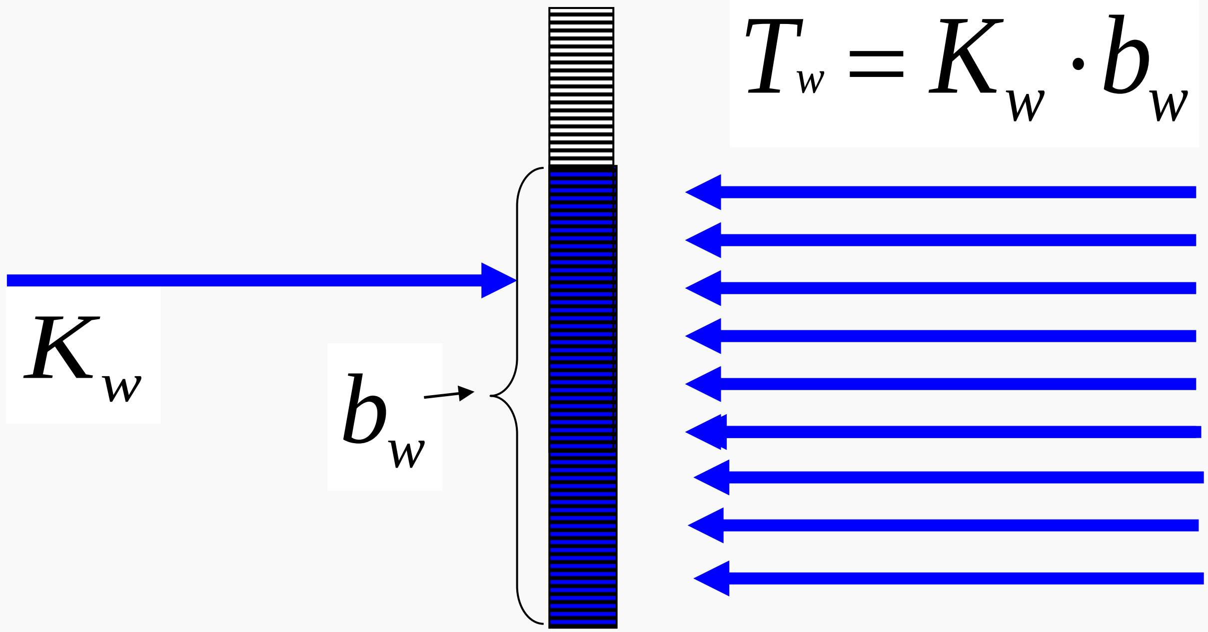
(Source: ITRC LNAPL Course)

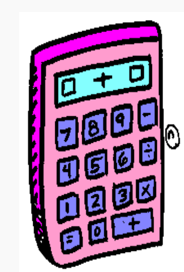
Water Transmissivity (T_w)

T_w integrates hydraulic conductivity (K_w) over entire water column (b_w)

For homogenous soil

$$T_w = K_w \cdot b_w$$





(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

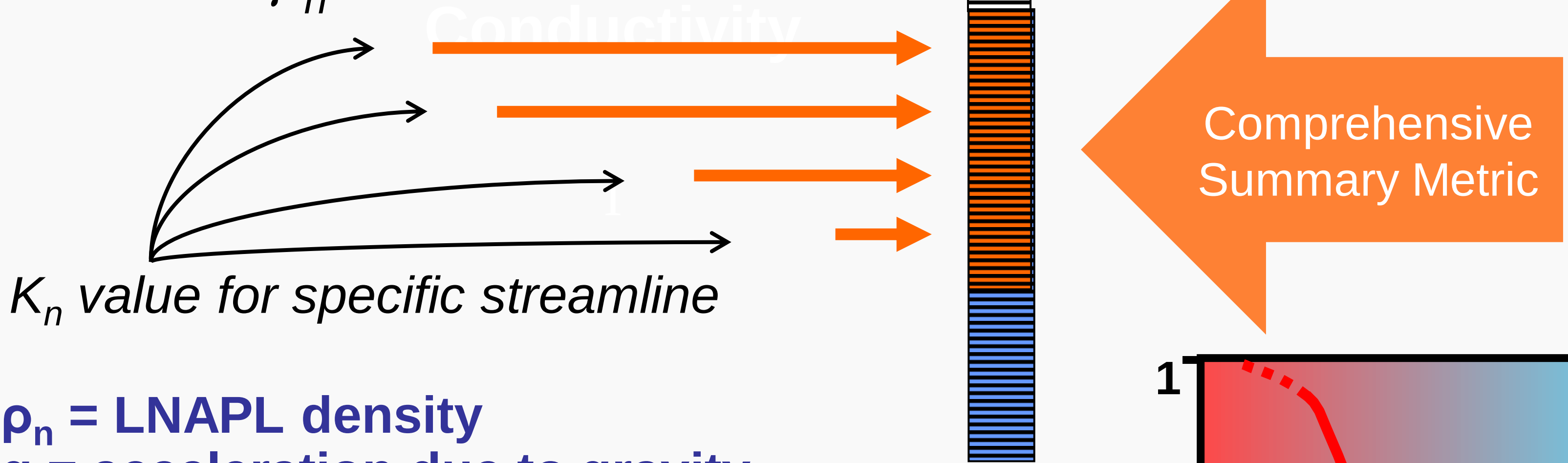
LNAPL Transmissivity (T_n)

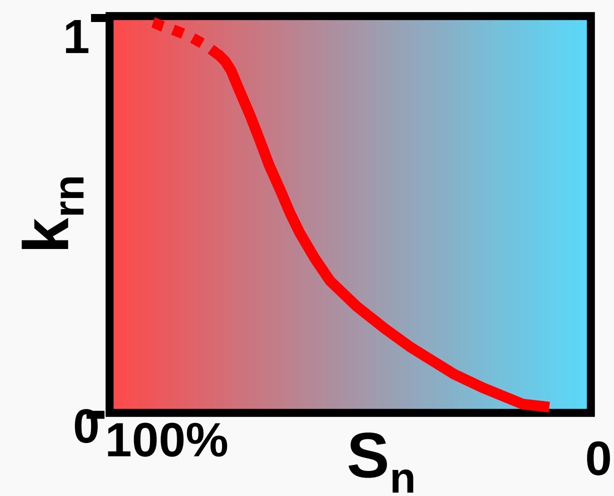
LNAPL Transmissivity

T_n integrates K_n over the formation LNAPL thickness (b_n)

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

$$T_n = \sum K_n$$





ρ_n = LNAPL density
g = acceleration due to gravity
k = soil permeability
k_{rn} = LNAPL relative permeability
μ_n = LNAPL viscosity
S_n = LNAPL saturation

(Source: ITRC LNAPL Course)

Relation to LNAPL Saturation

LNAPL Transmissivity

Zone of highest LNAPL saturation has highest LNAPL conductivity

Low LNAPL saturation results in low LNAPL conductivity

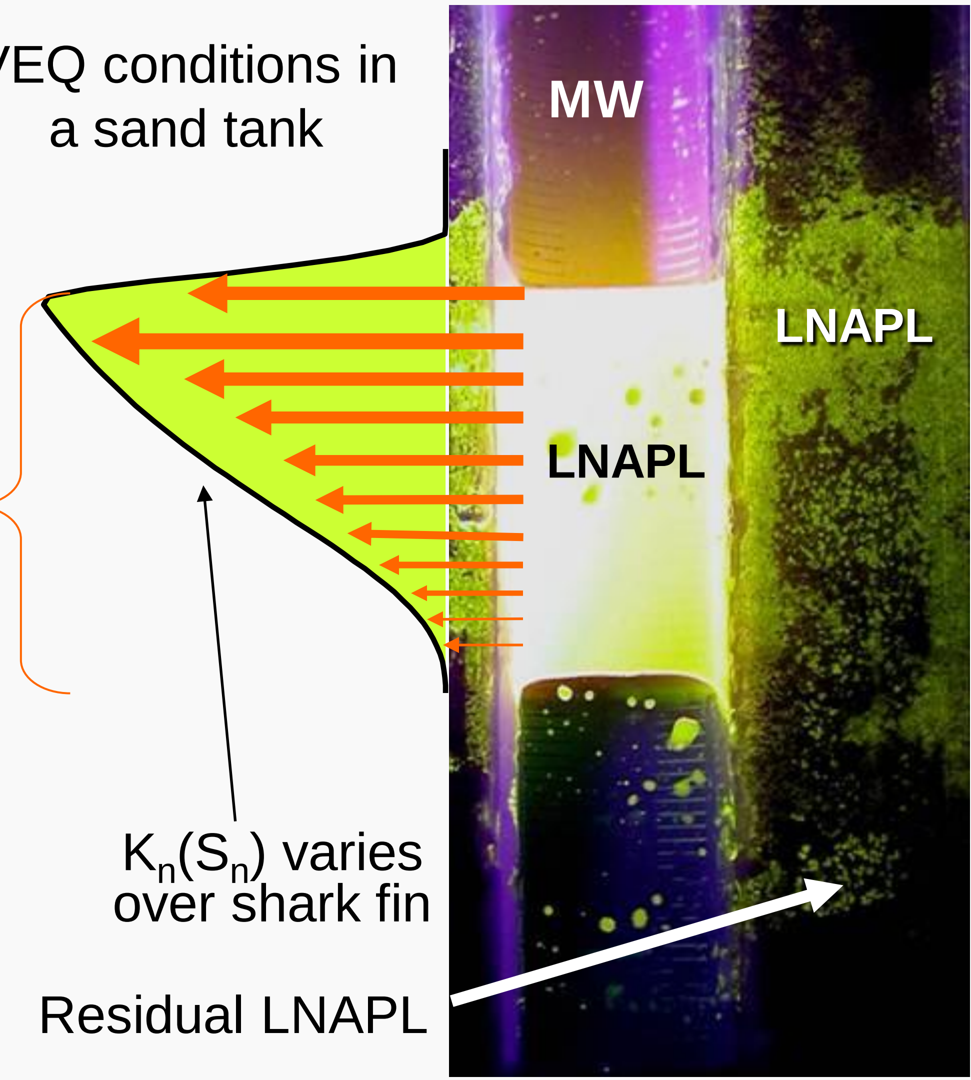
$T_n = \sum K_n$ over b_n

$$T_n = \overline{K}_n \cdot b_n$$

Hydraulic recovery rate proportional to T_n for given technology

Well thickness does not dictate relative recoverability

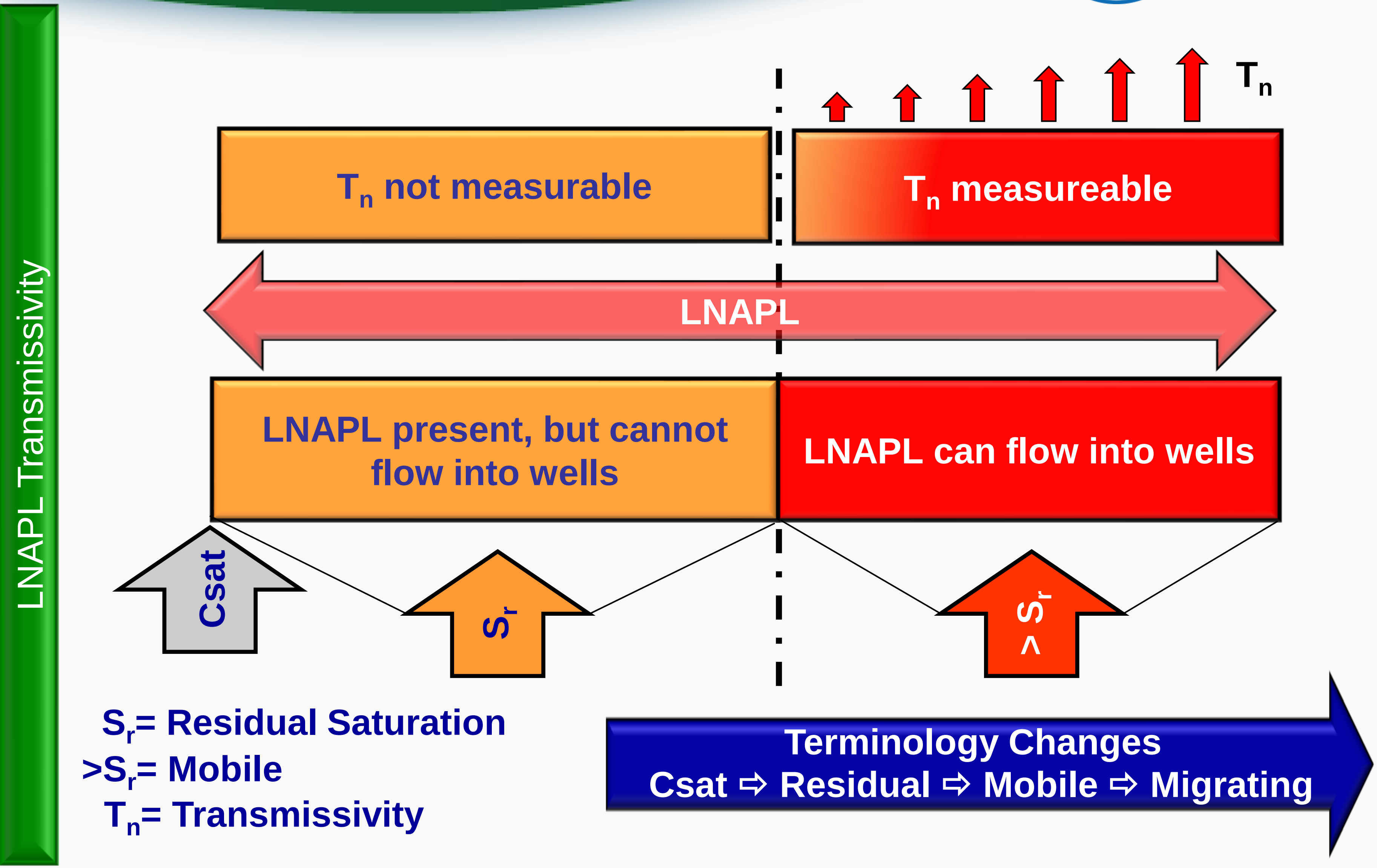
VEQ conditions in a sand tank



(Source: ITRC LNAPL Course)

Sources: ITRC LNAPL Course (ITRC), and Andrew Kirkman

The Name Game & T_n Measurement



S_r= Residual Saturation
>S_r= Mobile
T_n= Transmissivity

(Source: ITRC LNAPL Course)

Upcoming Discussion Points

Recovery Metric: Transmissivity

- Transmissivity and how it is used as an LNAPL Recovery Metric
- Typical range of T_n values Transmissivity values and what they mean

Source: ITRC LNAPL Course (ITRC)

Leading Metrics

Learning Objectives:

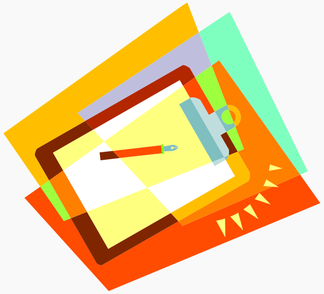
- Understand LNAPL recovery metrics, and why transmissivity is a good recovery metric

Source: ITRC LNAPL Course

LNAPL Recoverability Metrics: General Categories

Recovery Metric: Transmissivity

- **Leading Metrics** – to determine if LNAPL can be recovered and where
  - In-well thickness, LNAPL skimming test, and LNAPL transmissivity
- **Lagging Metrics** – to determine when recovery should end
  - In-well thickness, LNAPL transmissivity, asymptotic recovery, decline curve analysis, LNAPL-water recovery ratio (cost)



Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

In-Well LNAPL Thickness as a Recoverability Metric

- Traditional metric: recover LNAPL from areas with the largest in-well thicknesses down to a specified minimum
  - Poor metric: correlates unfavorably with LNAPL recoverability
  - Does not account for soil and LNAPL properties, soil heterogeneity, and LNAPL occurrence conditions (unconfined/perched/confined)
  - Use to be the default standard
  - Easy to understand
  - Inexpensive/very accessible

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL Transmissivity Reliable Metric

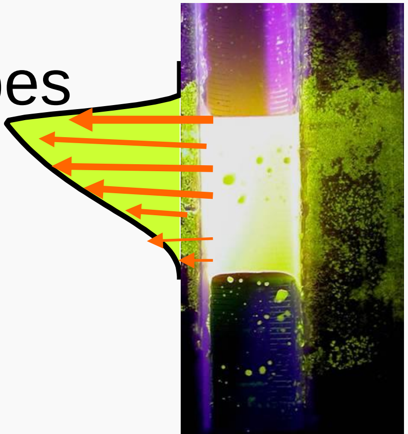
Recovery Metric: Transmissivity

- Incorporates:
  - Soil and LNAPL properties
  - LNAPL saturation
  - In well thickness
  - Soil heterogeneity
  - LNAPL occurrence (confined, perched, unconfined), etc.

$$T_n = \overline{K}_n \cdot b_n$$

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

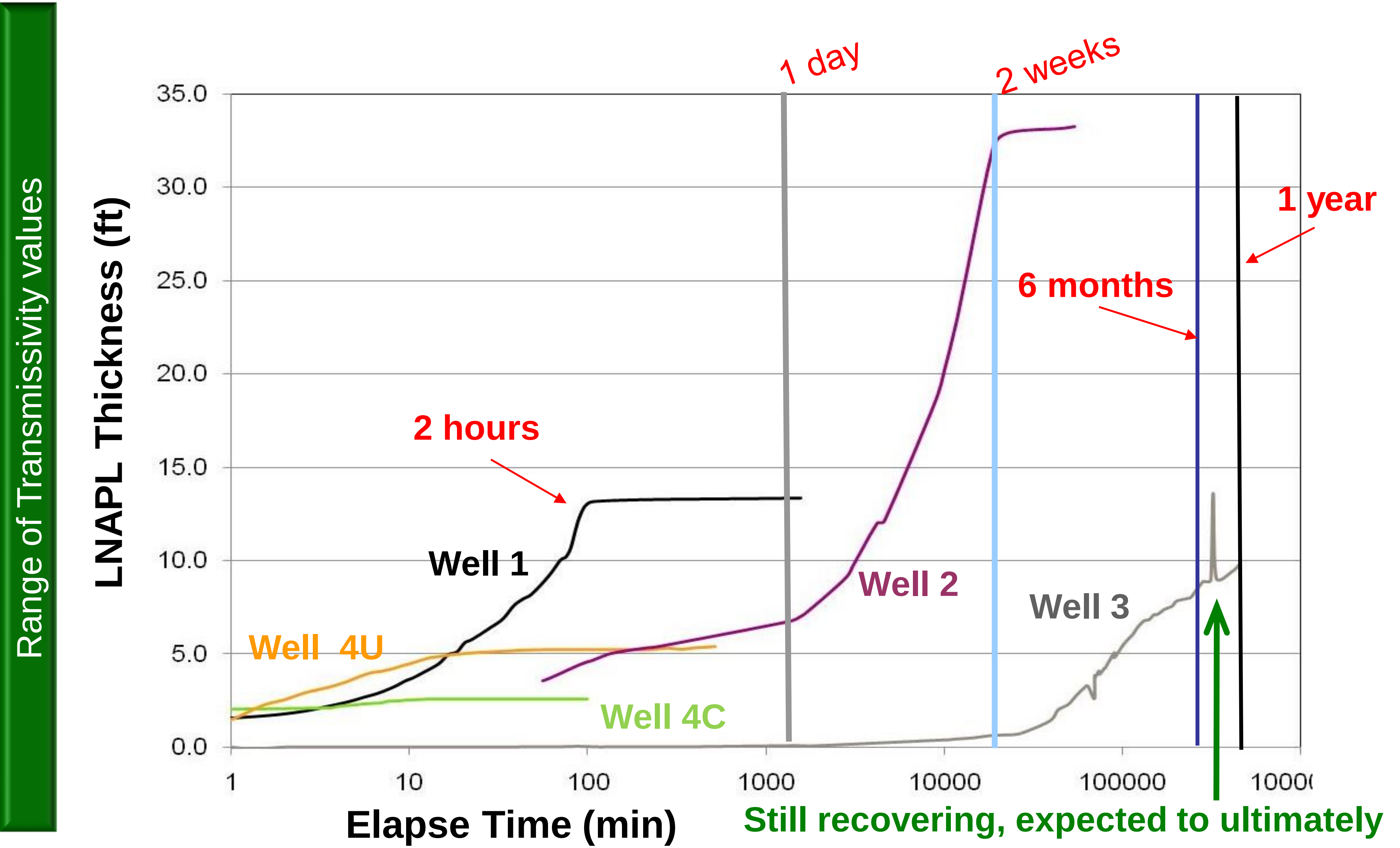
- Varies directly with recoverability: the higher the transmissivity, the higher the recoverability.
- Compared across soil, LNAPL and aquifer types
- **Relatively inexpensive to determine**



(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

LNAPL Baildown Test: Recovery Time Variability



Source: ITRC LNAPL Course (ITRC)

Metrics Comparison: T_n vs. LNAPL Well Thickness

Recoverability and Recovery Metric

Well No.	Approximate Gauged Thickness (ft)	Recovery Rate Based on Baildown Test Data		TechReg = 0.1-0.8 ft²/day LNAPL Transmissivity (ft²/day)
		LNAPL Skimming (GPD)	1 GPM - Water Enhanced Recovery (GPD)	
1	**15**	**40**	**115**	**4**
2	**34**	**2**	**5.7**	**0.2**
3	**30**	**0.4**	**0.7**	**0.01**
4 U	**2.6**	**120**	**800**	**31**
4C	**5.4**	**120**	**900**	**35**

	Recoverability Indicator Reliability	Incorporates Site Variables?	Metric/Recoverability Correlation
LNAPL Thickness	Poor	No	Not consistent
LNAPL Transmissivity	More reliable	Yes	Varies directly

Site Variables: Soil and LNAPL properties, LNAPL saturation, in-well thickness, soil heterogeneity, and LNAPL occurrence (confined, perched, unconfined)

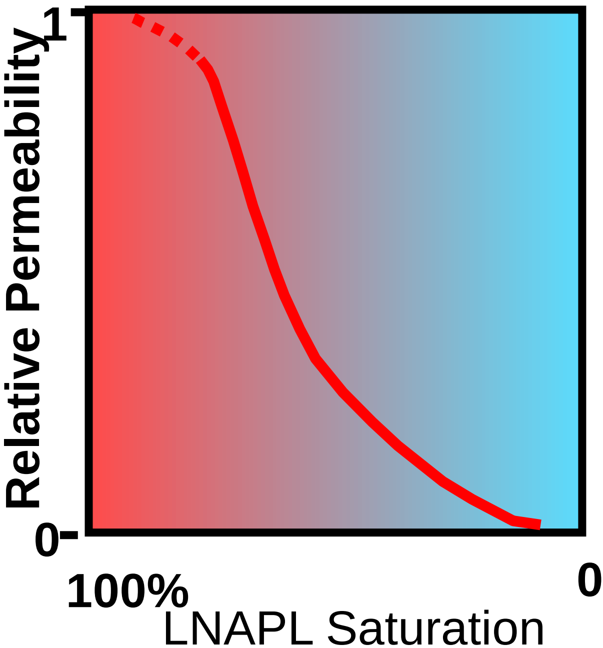
Source: ITRC LNAPL Course (ITRC)

Transmissivity 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

TechReg = 0.1 - 0.8 ft^2/day

T_n modeled assuming homogenous soils



***5' formation thickness unlikely at most legacy sites**

Source: ITRC LNAPL Course (ITRC)

What Did We Learn?

Take Aways

- LNAPL in-well thickness NOT a good recovery metric
- LNAPL transmissivity (T_n) is a good recovery metric
- That T_n is a function of soil properties, LNAPL properties, thickness and saturation
- That LNAPL T_n and flow rate higher under coarse textured material relative to fines
- About T_n measurement methods
- What T_n values may be expected for different soil types, LNAPL thickness and types
- Smart strategy to spend resources upfront to build a robust CSM/LCSM to enable good removal decision making

Source: ITRC LNAPL Course (ITRC)

Submodule Objectives:
Conceptual Challenges

- Recognize that LNAPL can penetrate deep in the saturated zone (100 ft or more)
- Effects of fluctuating water table on Mobile LNAPL
- Recognize that mobile LNAPL can exist under confined and perched conditions

Releases from can Penetrate very deep below the Water Table

earning Objective:

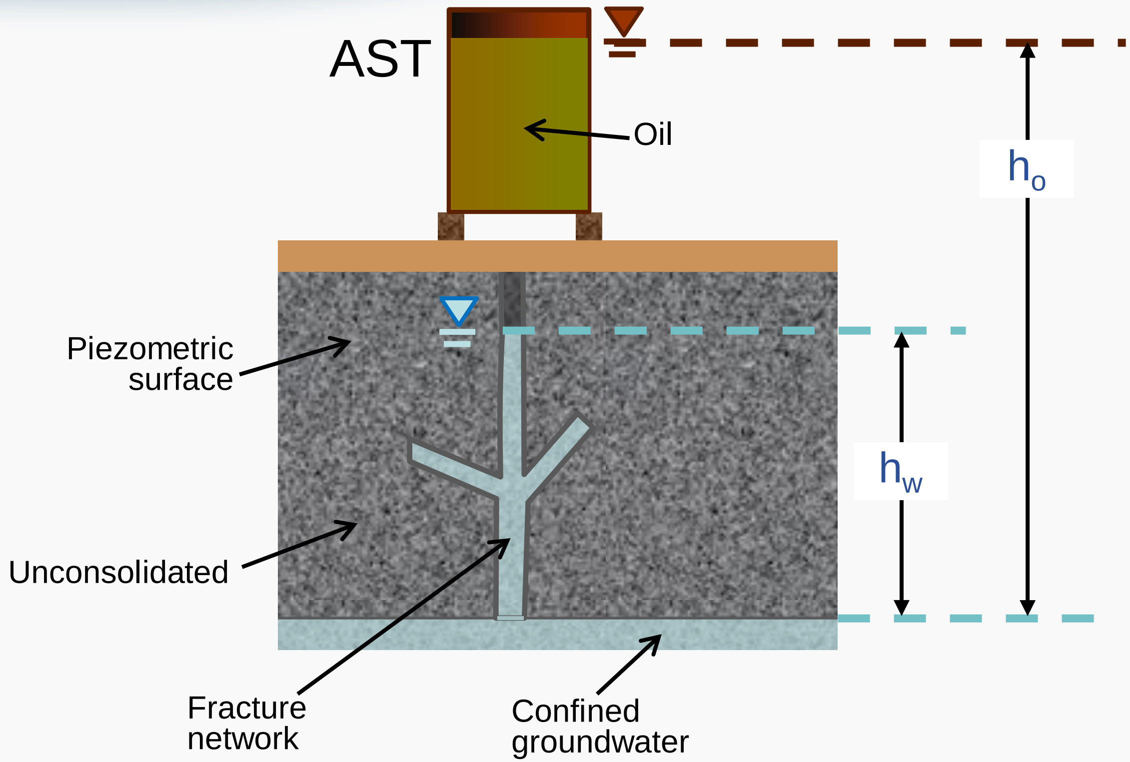
Recognizing that LNAPL can penetrate deep below the water table, for a shallow release

Source: ITRC LNAPL Course (ITRC)

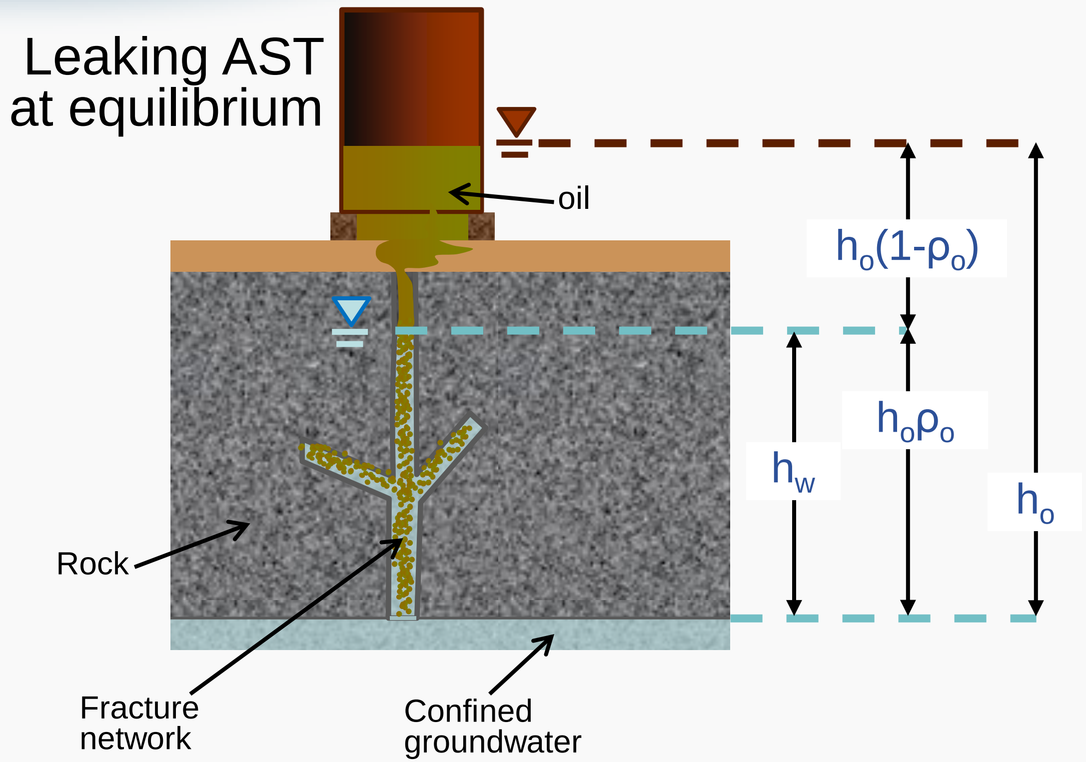
Releases can Penetrate very deep below the Water Table

- Provided source is connected hydraulically with the subsurface
  - oil has to penetrate very deep to attain this vertical equilibrium.
  - Source can an AST/UST

Oil Penetration Below Water Table



Oil Penetration Below Water Surface



At equilbrium: $h_w\rho_w = h_o\rho_o$

h_w – water head
h_o – oil head
ρ_w – water specific gravity
ρ_o – oil specific gravity

$h_o(1- \rho_o) + h_o\ \rho_o = h_o$

If $\rho_o = 0.8$, and $h_o(1- \rho_o) = 20'$

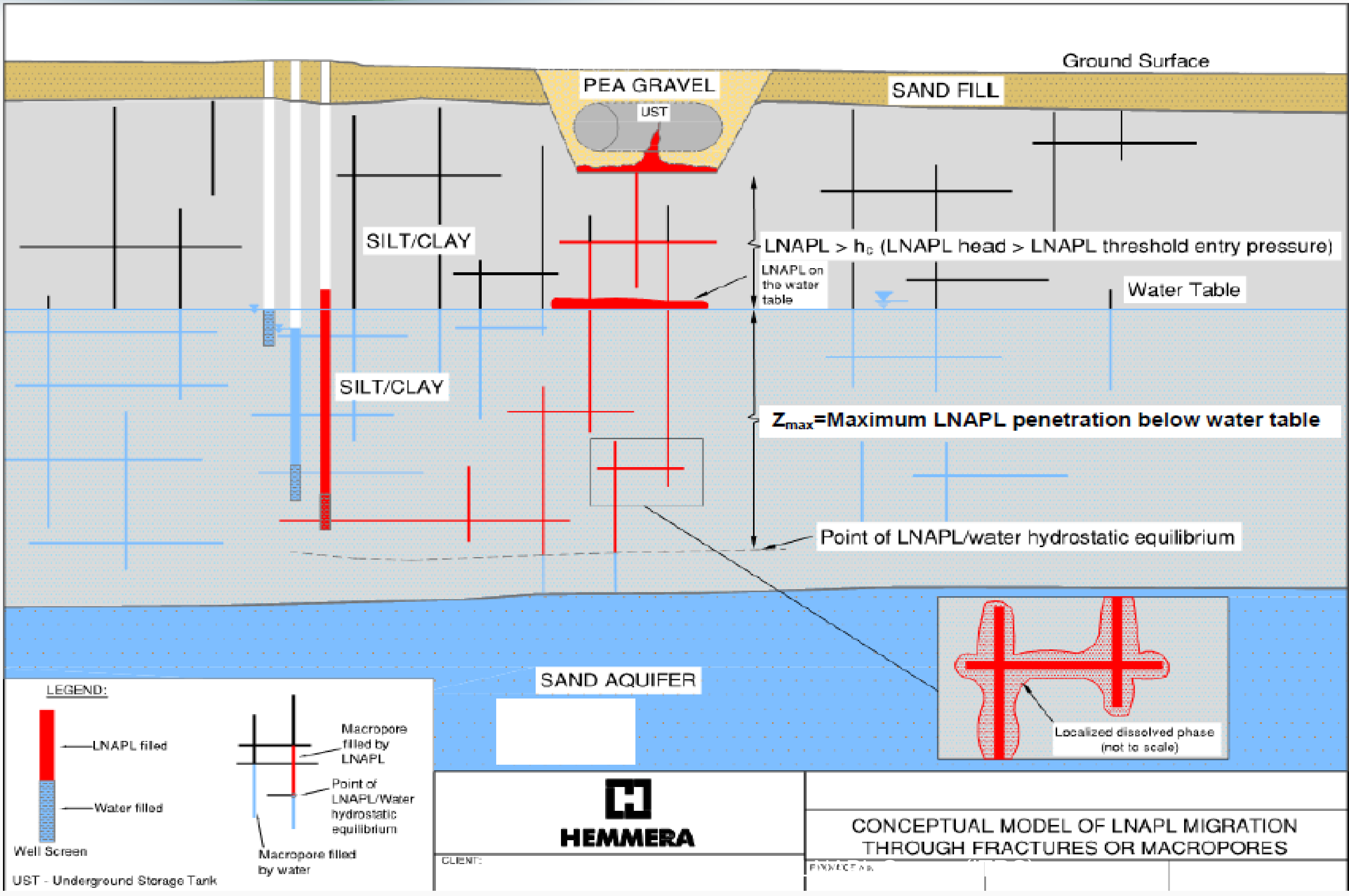
$h_o(1-0.8) = 20'$

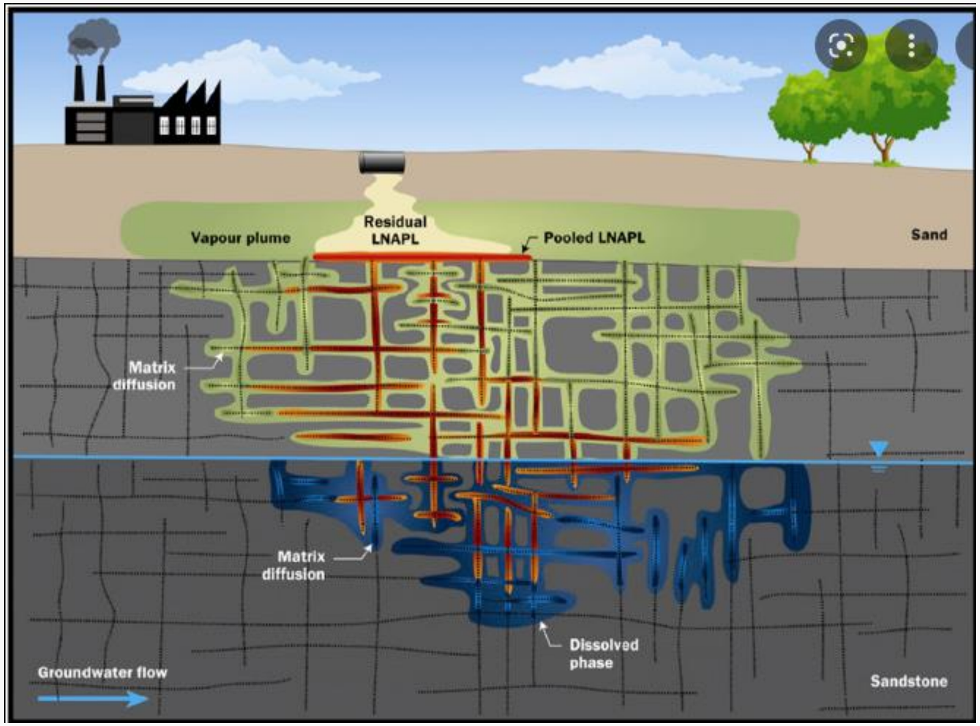
$h_o = 20/.2 = 100'$

Oil can penetrate 80′ below piezometric surface

Deep LNAPL in Fractured Setting

Conceptual Challenges – Deep LNAPL




Vapour plume
Residual LNAPL
Pooled LNAPL
Sand
Matrix diffusion
Matrix diffusion
Dissolved phase
Groundwater flow
Sandstone

Conceptual Challenges: Water-Table Fluctuations

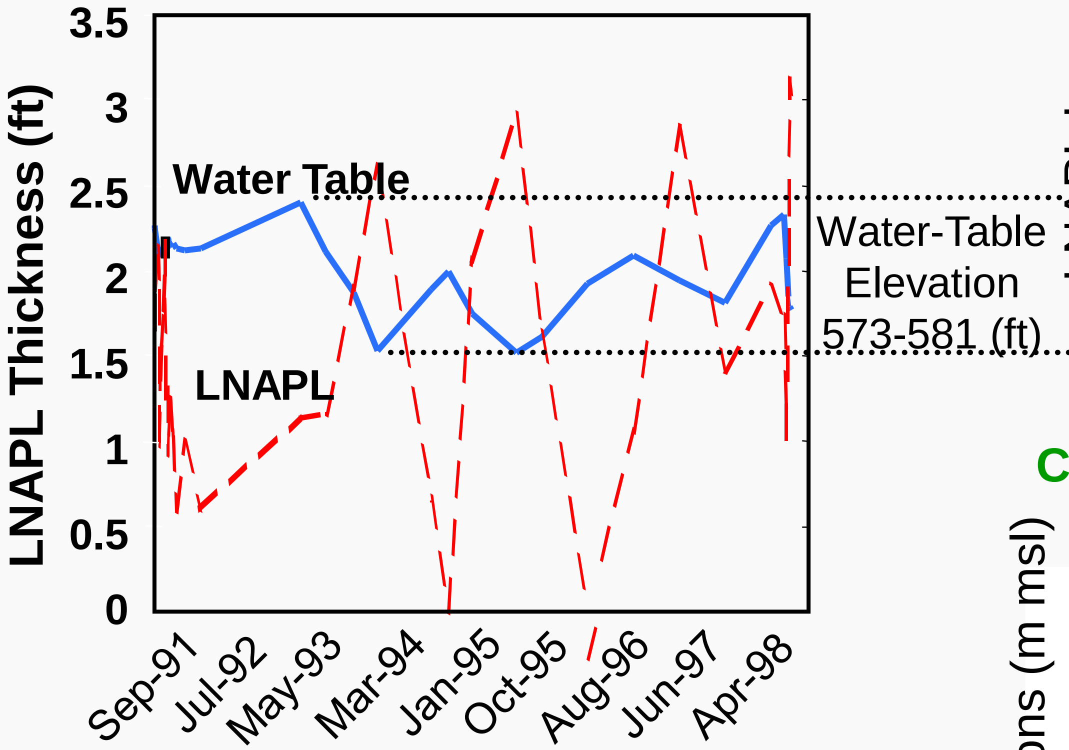
earning Objective:

Understand how water-table fluctuations impact in-well LNAPL thickness

Source: ITRC LNAPL Course (ITRC)

Effect of Water Table Fluctuation on In-Well LNAPL Thickness (Unconfined)

A:



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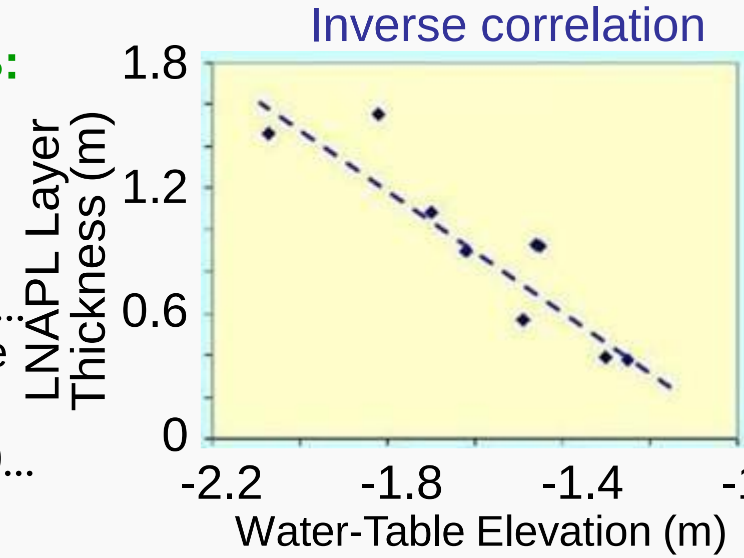

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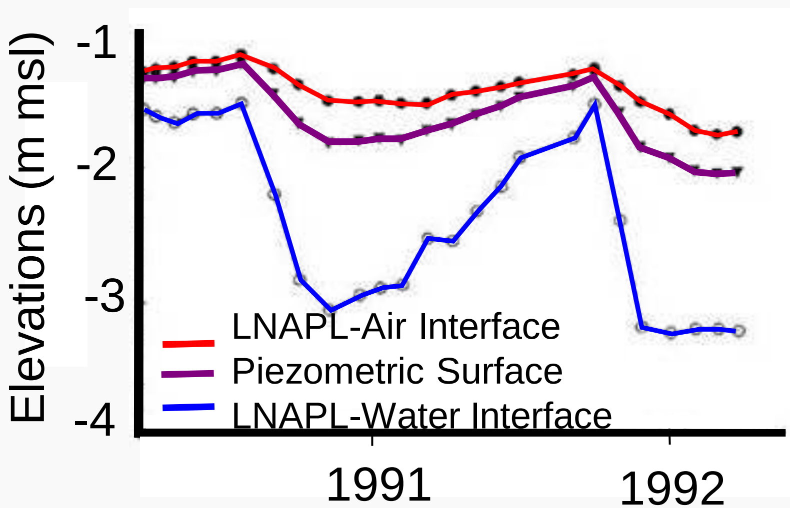
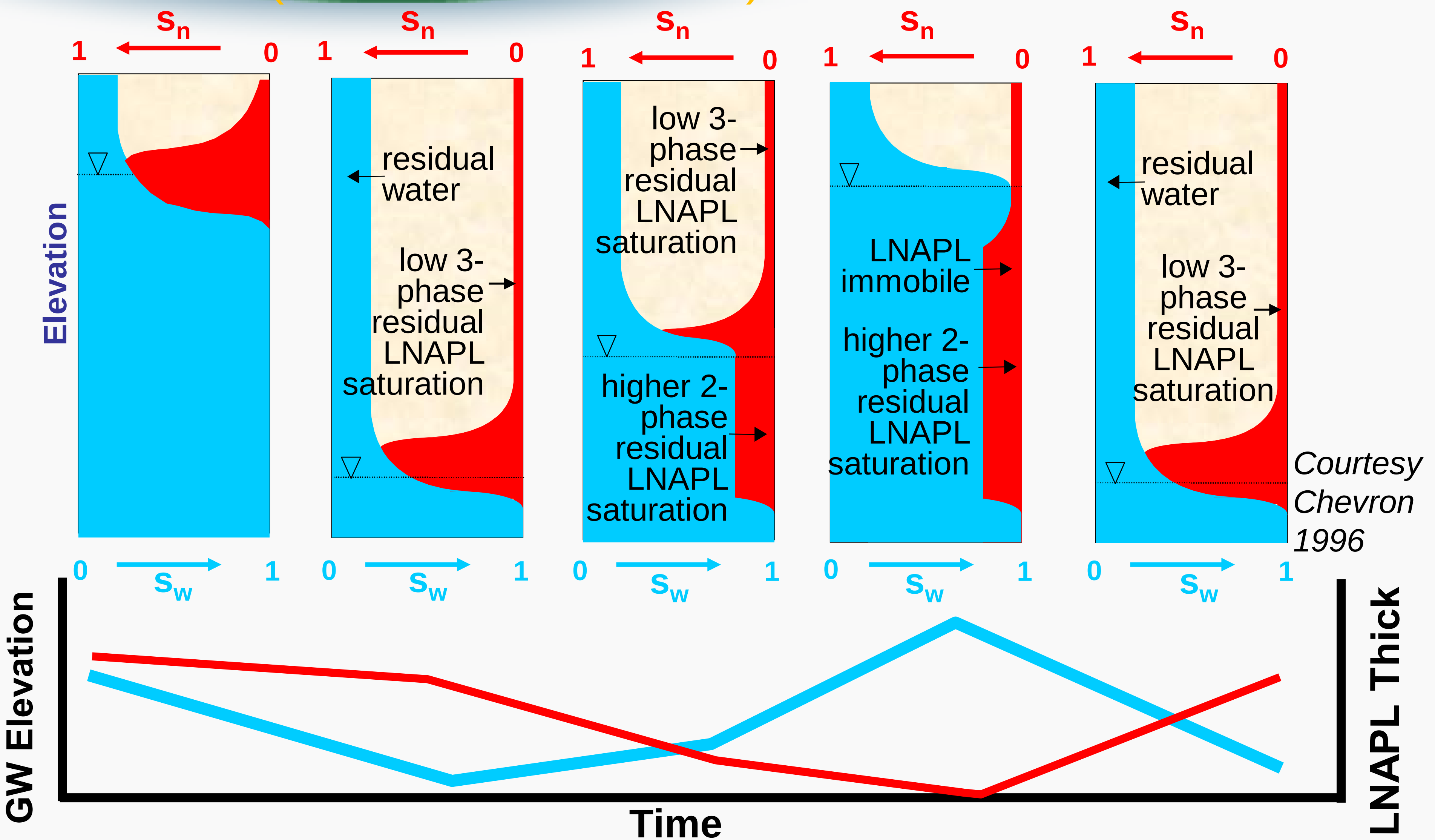


Three different types of graphs to show same type of information→ LNAPL thickness increase with water-table drops

(Source: ITRC LNAPL Course)

Why Does LNAPL Thickness in a Well Increase With a Water Table Drop?
(LNAPL Redistribution)

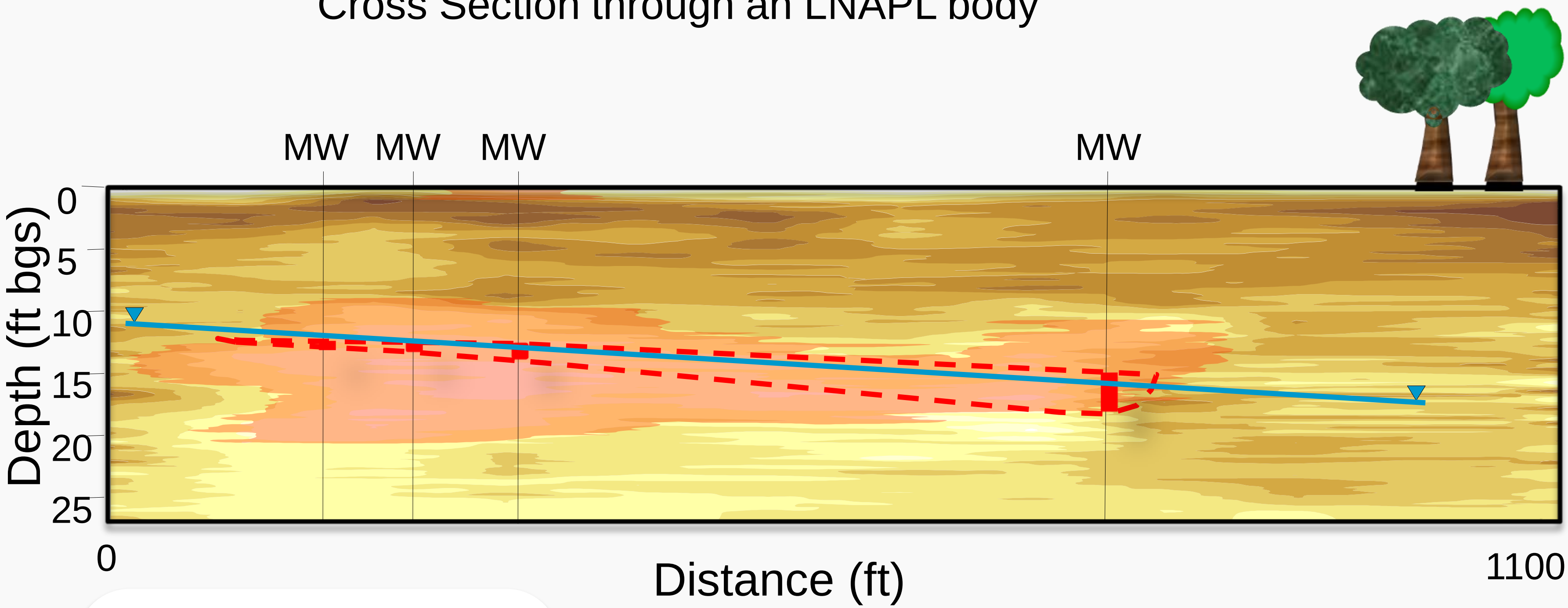


(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

Smear Zone due to water table Fluctuations

Cross Section through an LNAPL body



Clays

Silts

Sands

LNAPL observed in MWs

LNAPL observed in the formation

(Source: ITRC LNAPL Course)

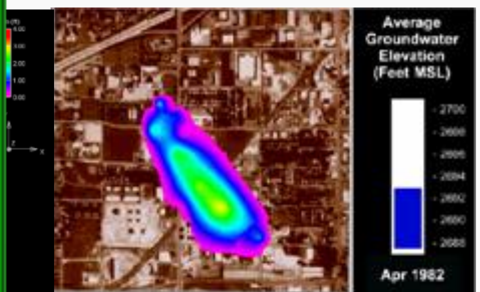
Source: ITRC LNAPL Course (ITRC)

Temporal Water Table Fluctuation on Mobile LNAPL Extents

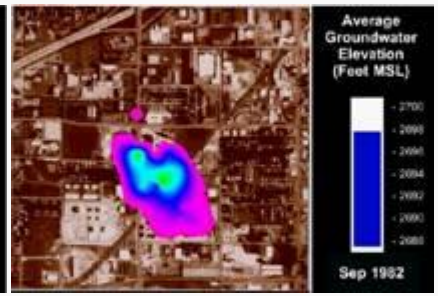
Conceptual Challenges – Water Level

LNAPL Monitoring Over Time - Refinery

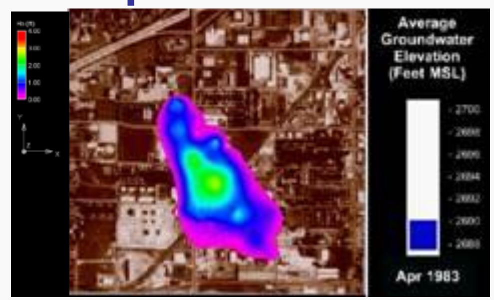
Low Water April 1982



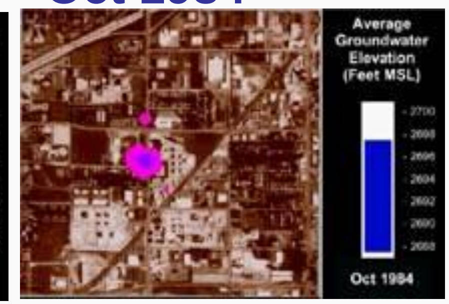
High Water Sept 1982



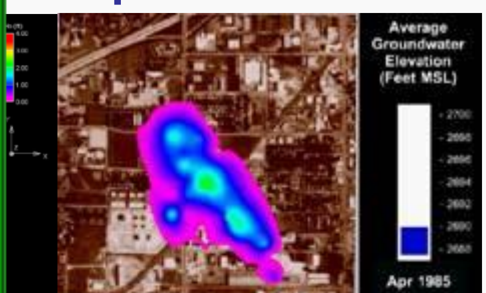
Low Water April 1983



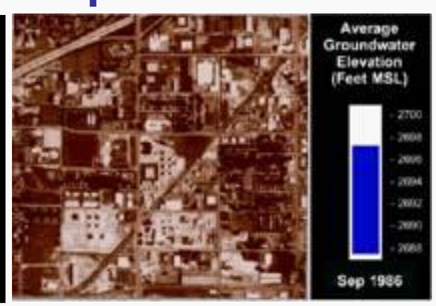
High Water Oct 1984



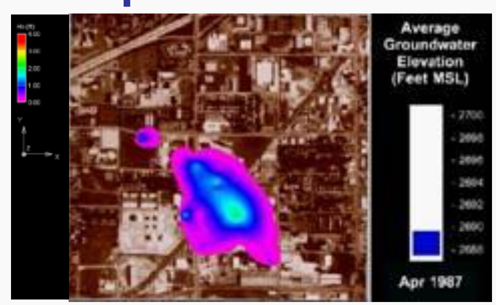
Low Water April 1985



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**

(Source: ITRC LNAPL Course)

Source: ITRC LNAPL Course (ITRC)

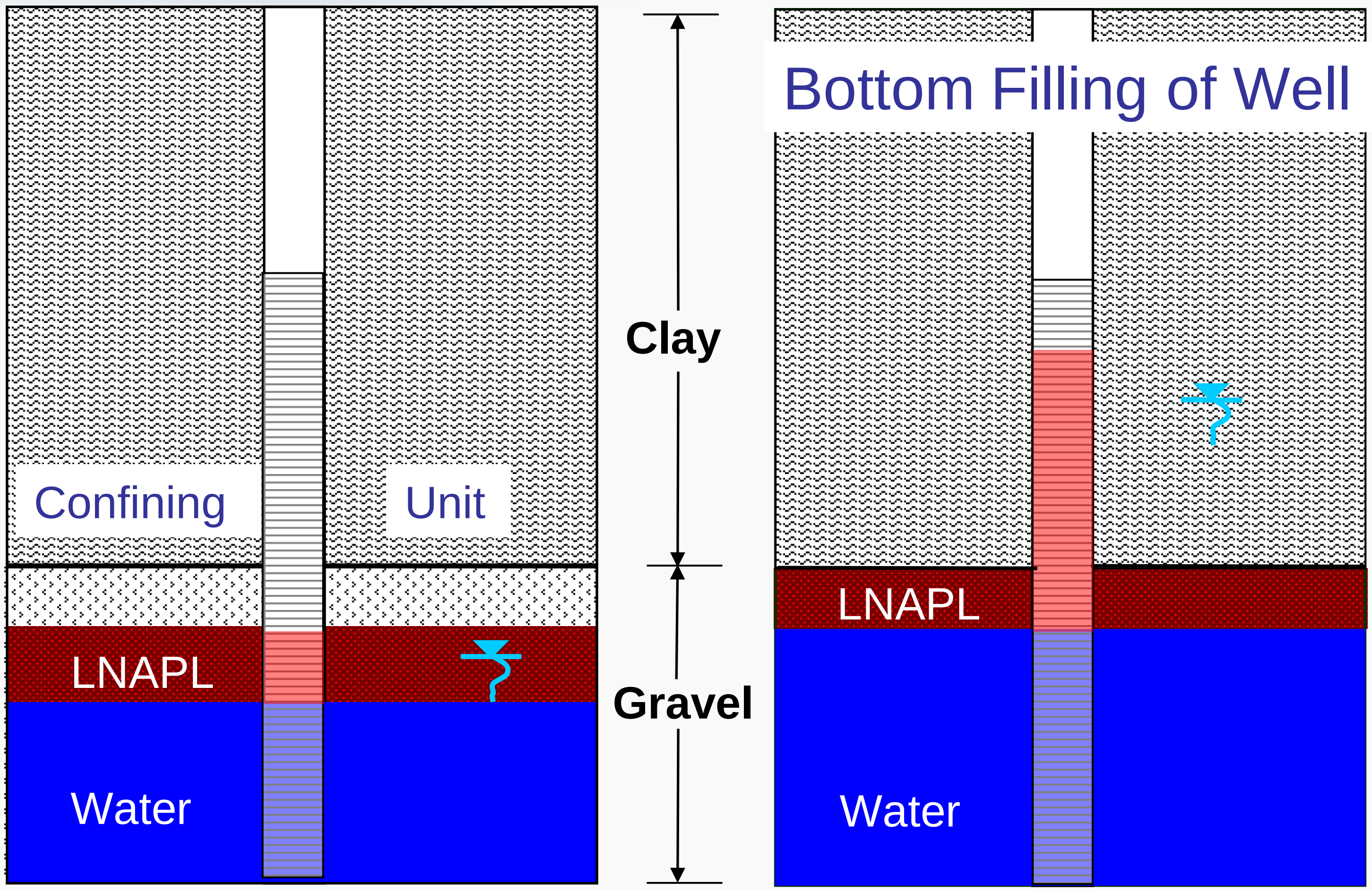
Conceptual Challenges: Confined LNAPL Conditions

earning Objective:

- Recognize confined LNAPL conditions and implications

Source: ITRC LNAPL Course (ITRC)

Confined LNAPL: Thickness in Well Changes With Hydrostatic Pressure

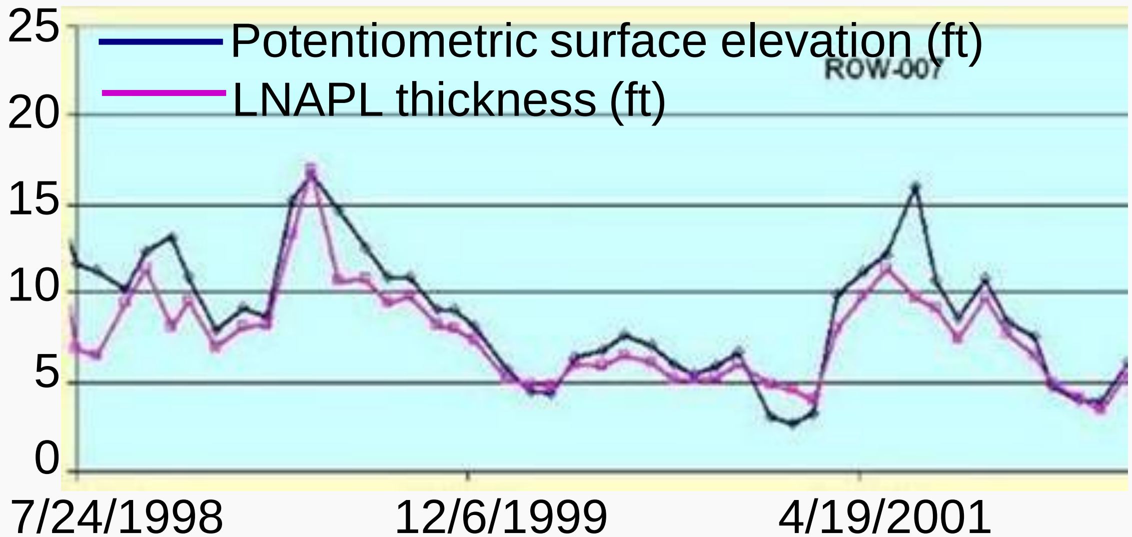


Monitoring well is a giant pore!

Source: ITRC LNAPL Course (ITRC)

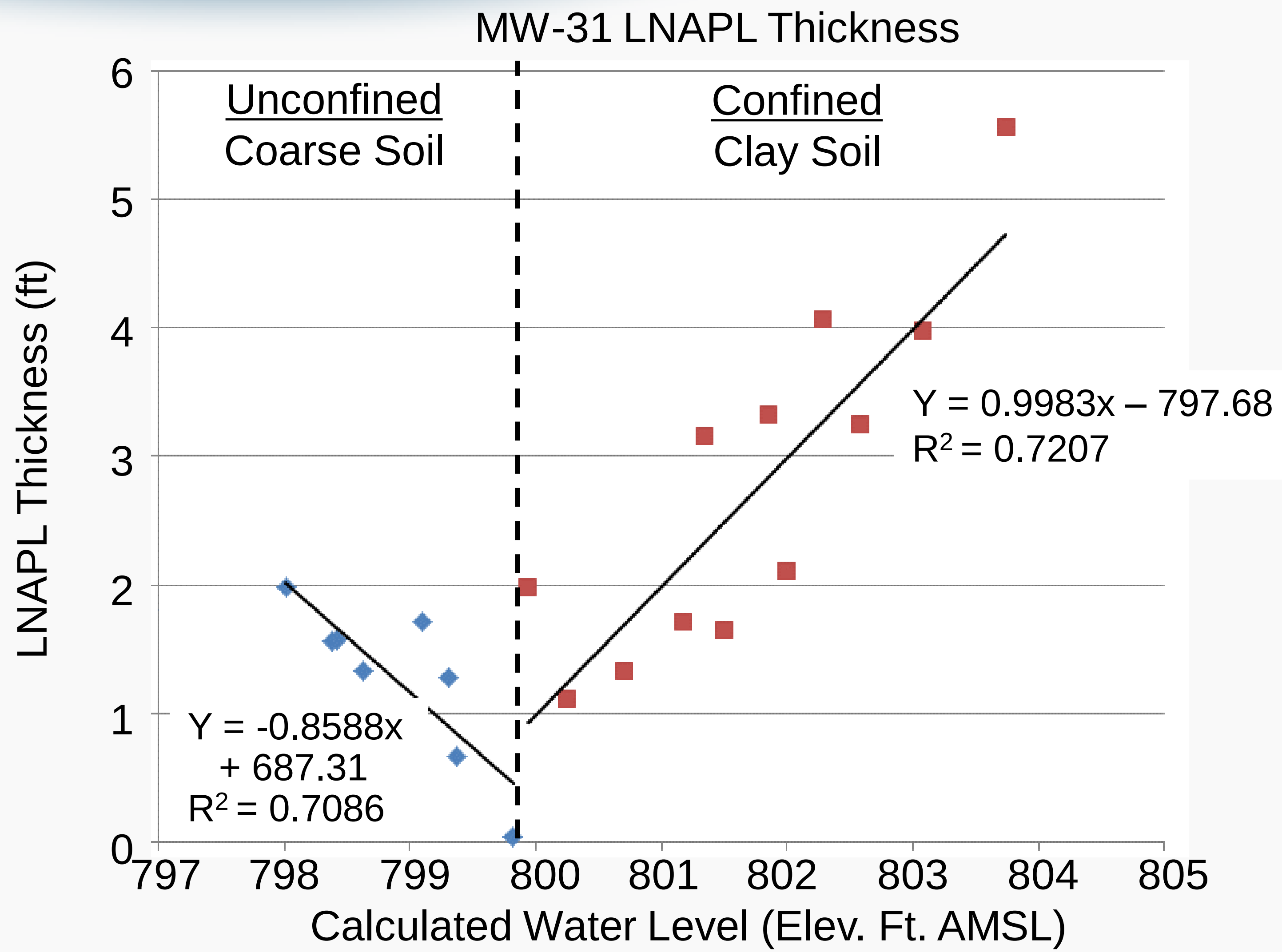
Confined LNAPL Thickness as a function of Potentiometric Surface

Confined systems (at equilibrium) have positively correlated potentiometric surface and LNAPL thickness.



Source: ITRC LNAPL Course (ITRC)

IN-Well LNAPL Thickness and Potentiometric Surface Elevation

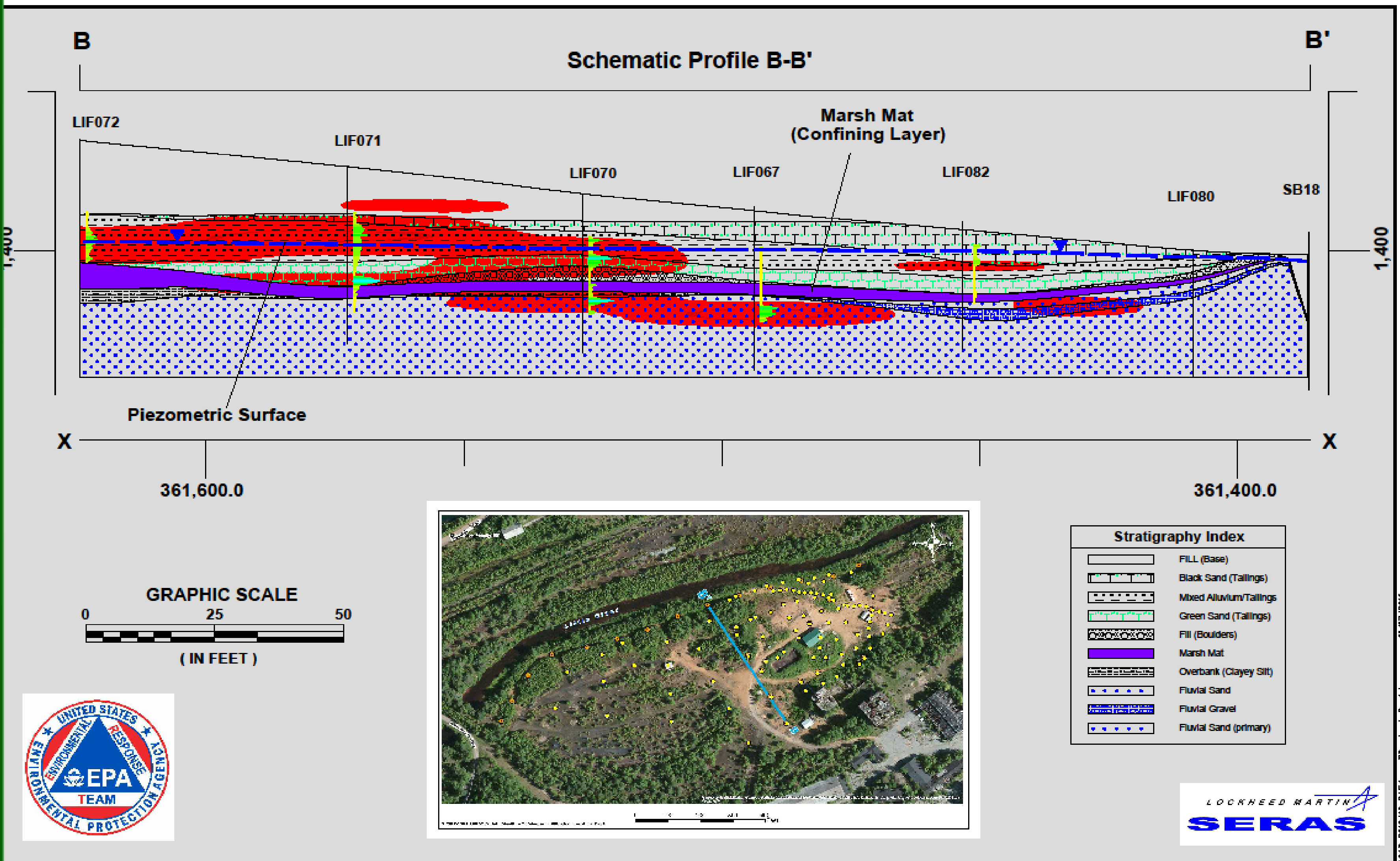


Conceptual Challenges - Confined

Source: ITRC LNAPL Course (ITRC)

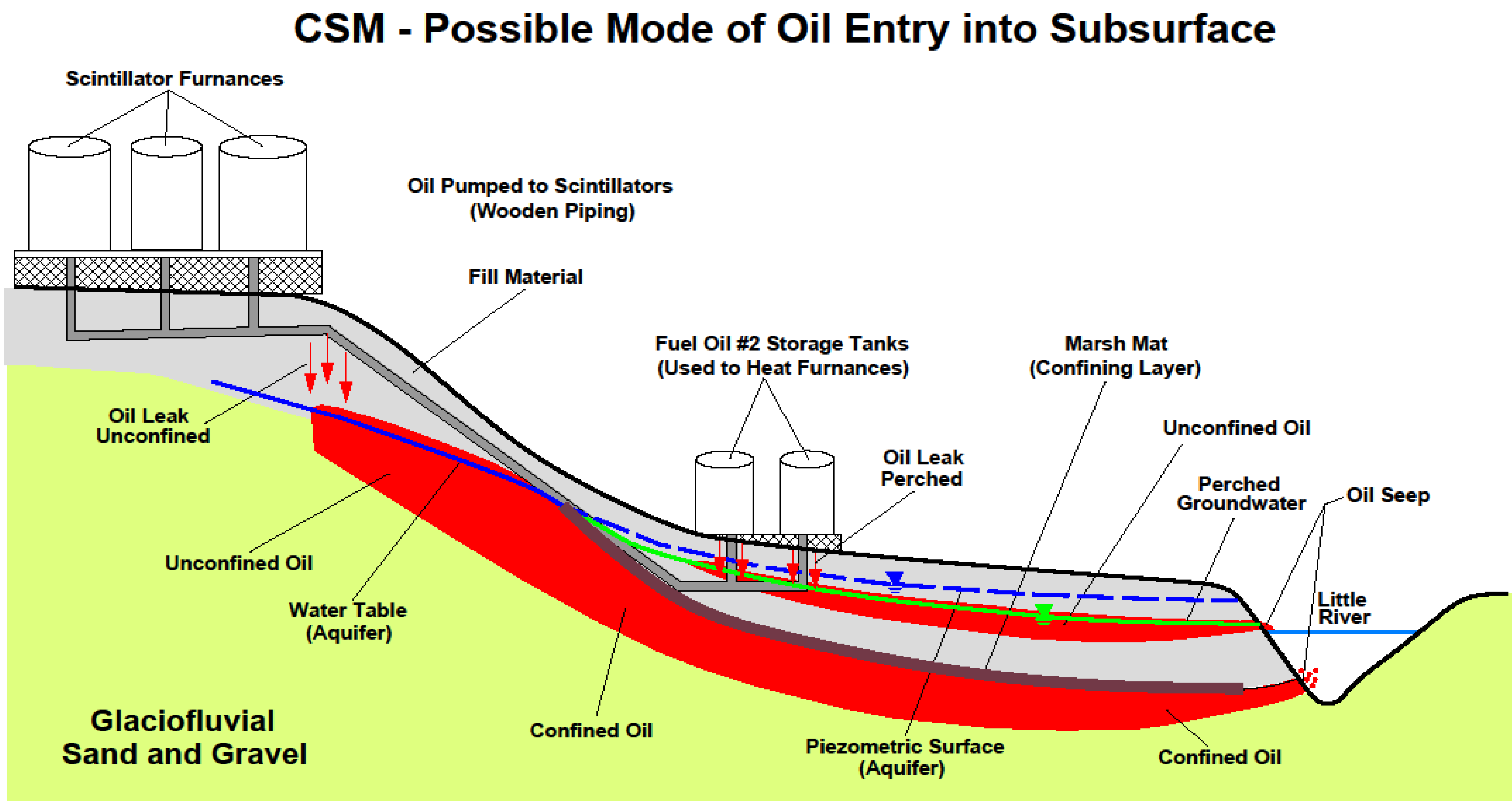
Confined LNAPL: Hydrogeologic Cross Section

Conceptual Challenges - Confined



How did the LNAPL get beneath the marsh mat?

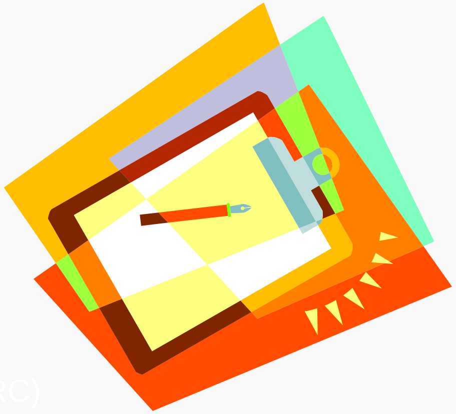
Conceptual Challenges - Confined



LOCKHEED MARTIN SERAS

Indicators of Confined LNAPL

- Large LNAPL thickness in wells at equilibrium (allowed to equilibrate for a month, may be years)
- LNAPL thickness increase with potentiometric surface (water level) rise
- Constant LNAPL-water interface elevation over time
- Constant rate of LNAPL recharge (as function of LNAPL / water interface) if in-well LNAPL removed



Source: ITRC LNAPL Course (ITRC)

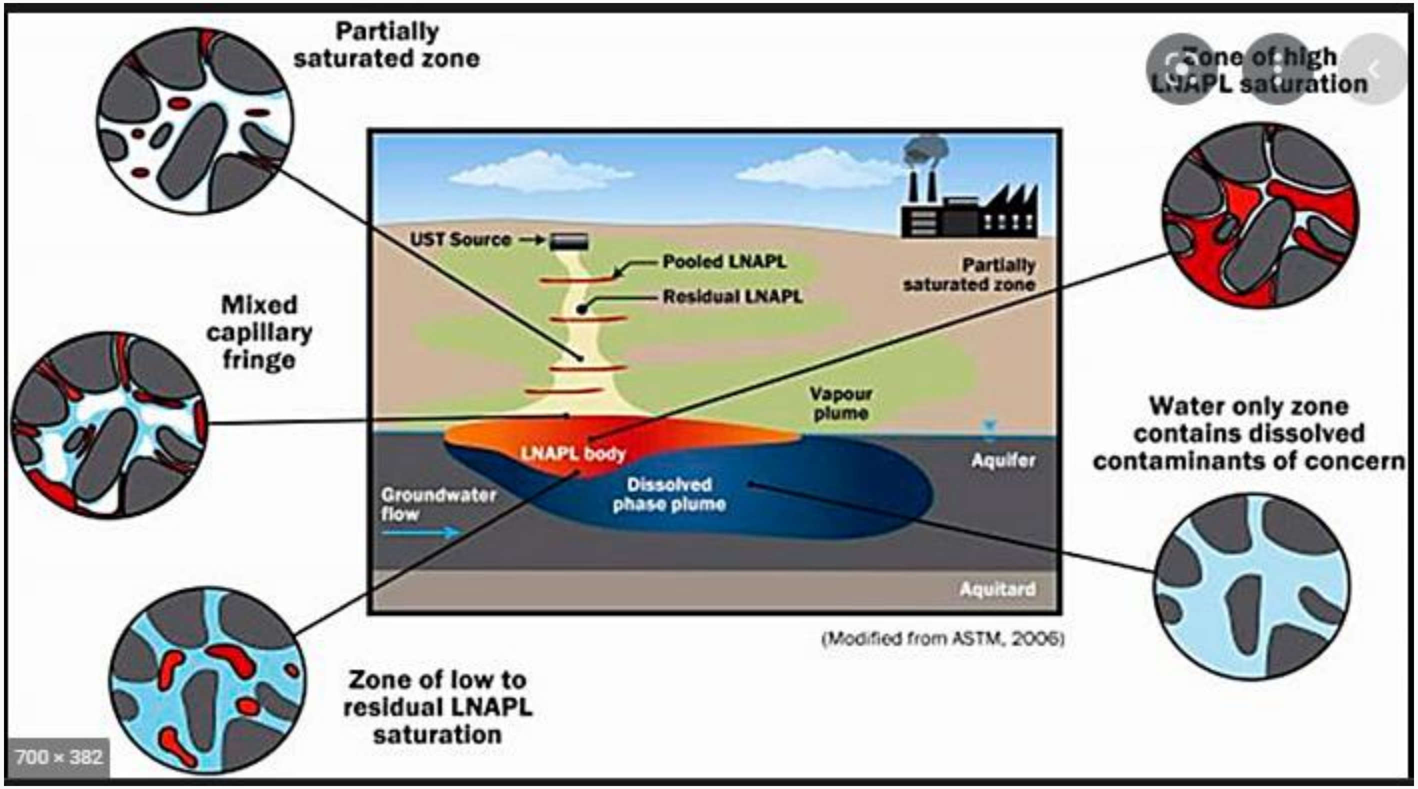
Conceptual Challenges: Perched LNAPL Conditions

earning Objective:

- Recognize when LNAPL is perched and its implications

Source: ITRC LNAPL Course (ITRC)

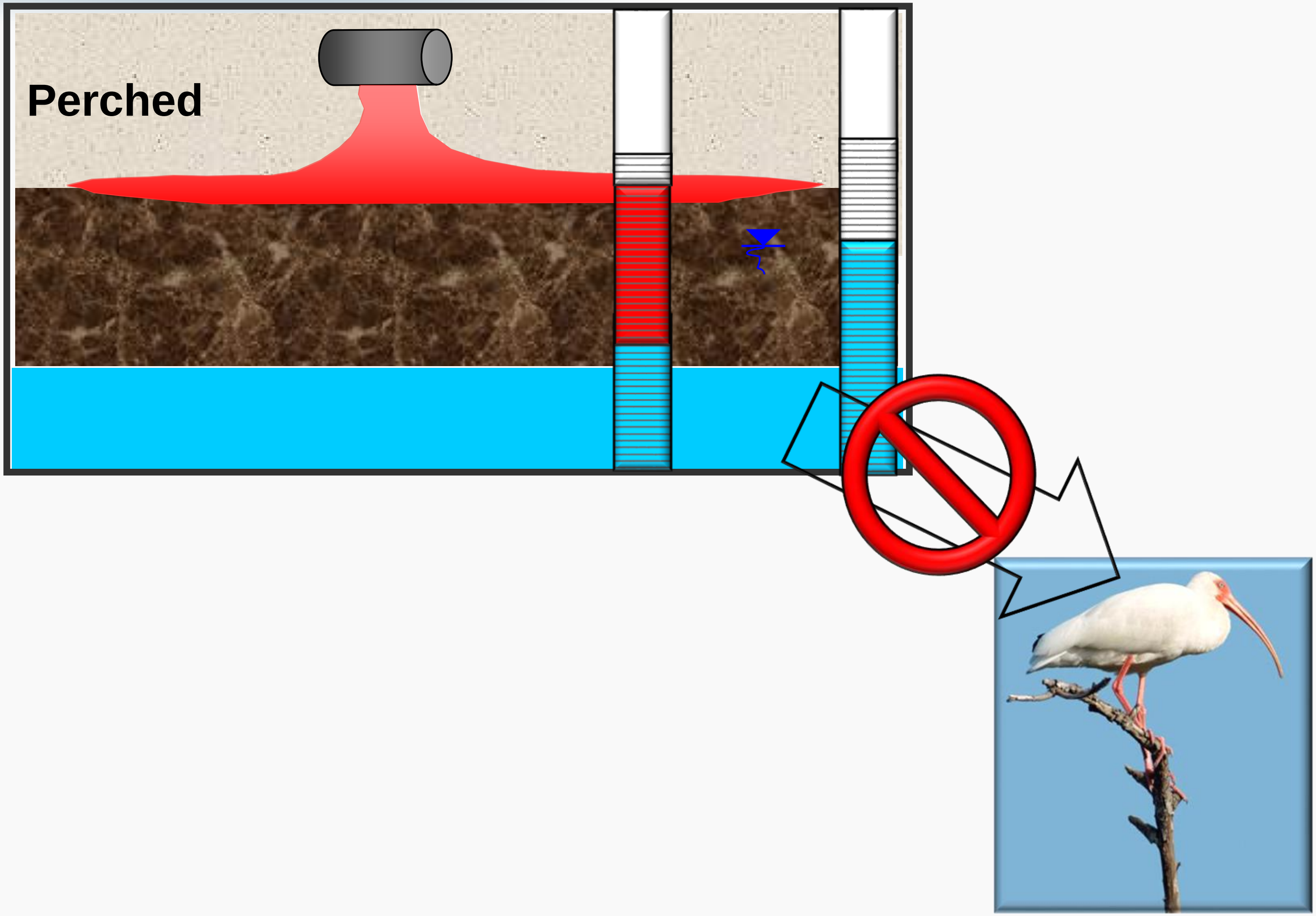
Perched LNAPL Conditions



Perched LNAPL Conditions

Screened Across the Water table

Conceptual Challenges - Perched

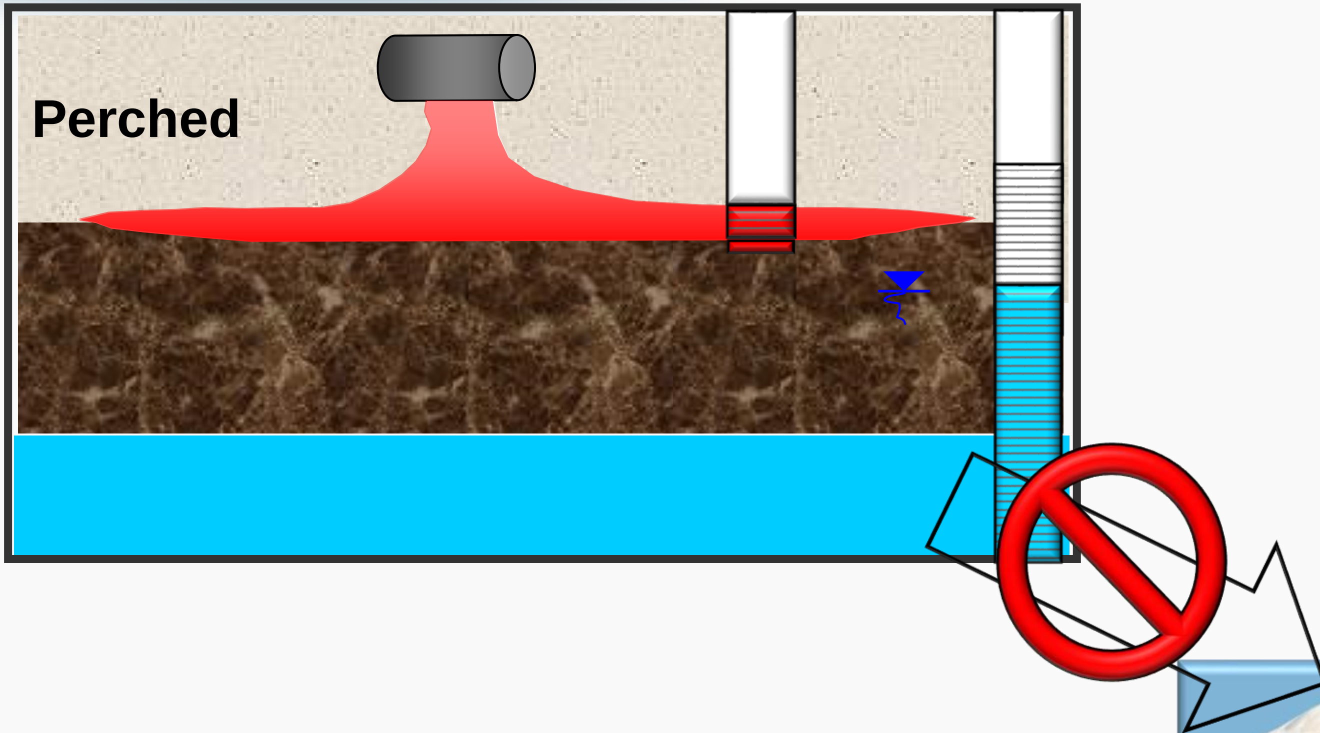


Source: ITRC LNAPL Course (ITRC)

Perched LNAPL Conditions

Properly Screened

Conceptual Challenges - Perched



Source: ITRC LNAPL Course (ITRC)

Significance of Identifying Conceptual Challenges

Conceptual Challenges - Significance

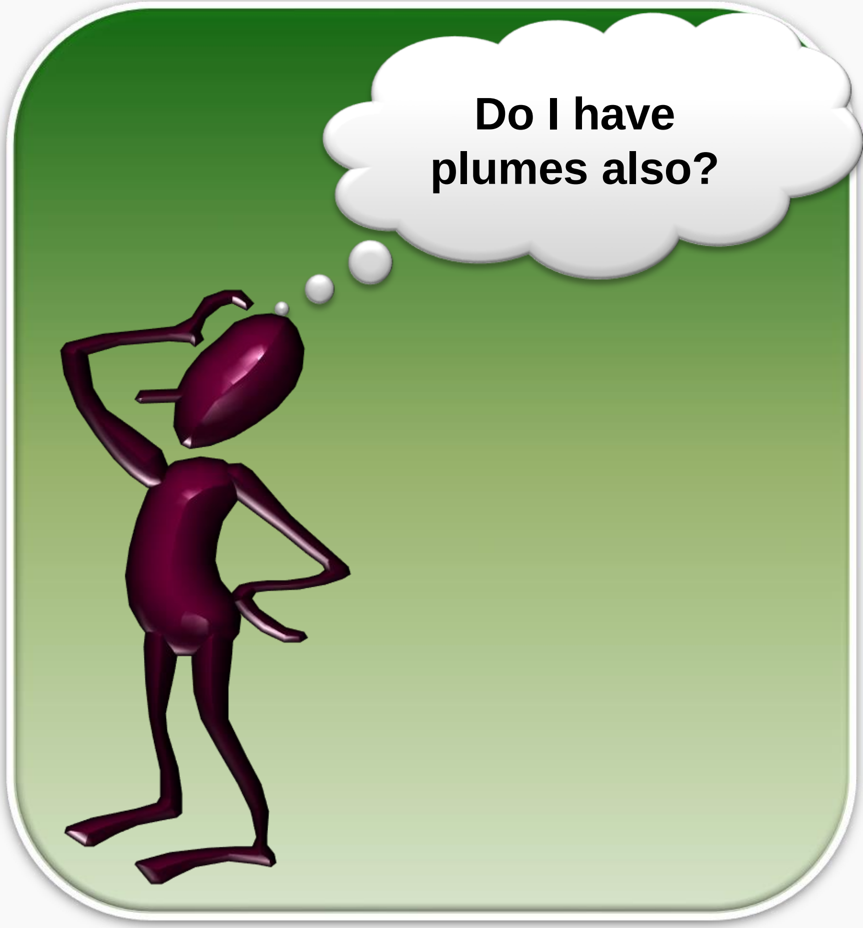
- Improves conceptual understanding of LNAPL subsurface Interactions—robust LCSM
  - Mobile/recoverable LNAPL can over time which has implications for recovery
  - Can exaggerates LNAPL thickness in wells relative to what’s in the formation
  - Can lead to overestimate of mobile/recoverable volume estimate
  - Understanding LNAPL migration pathways
- Development of effective LNAPL remedial strategy
  - Help optimizes recovery—Where/when to target LNAPL
  - Informs the remediation technology selection process

Source: ITRC LNAPL Course (ITRC)

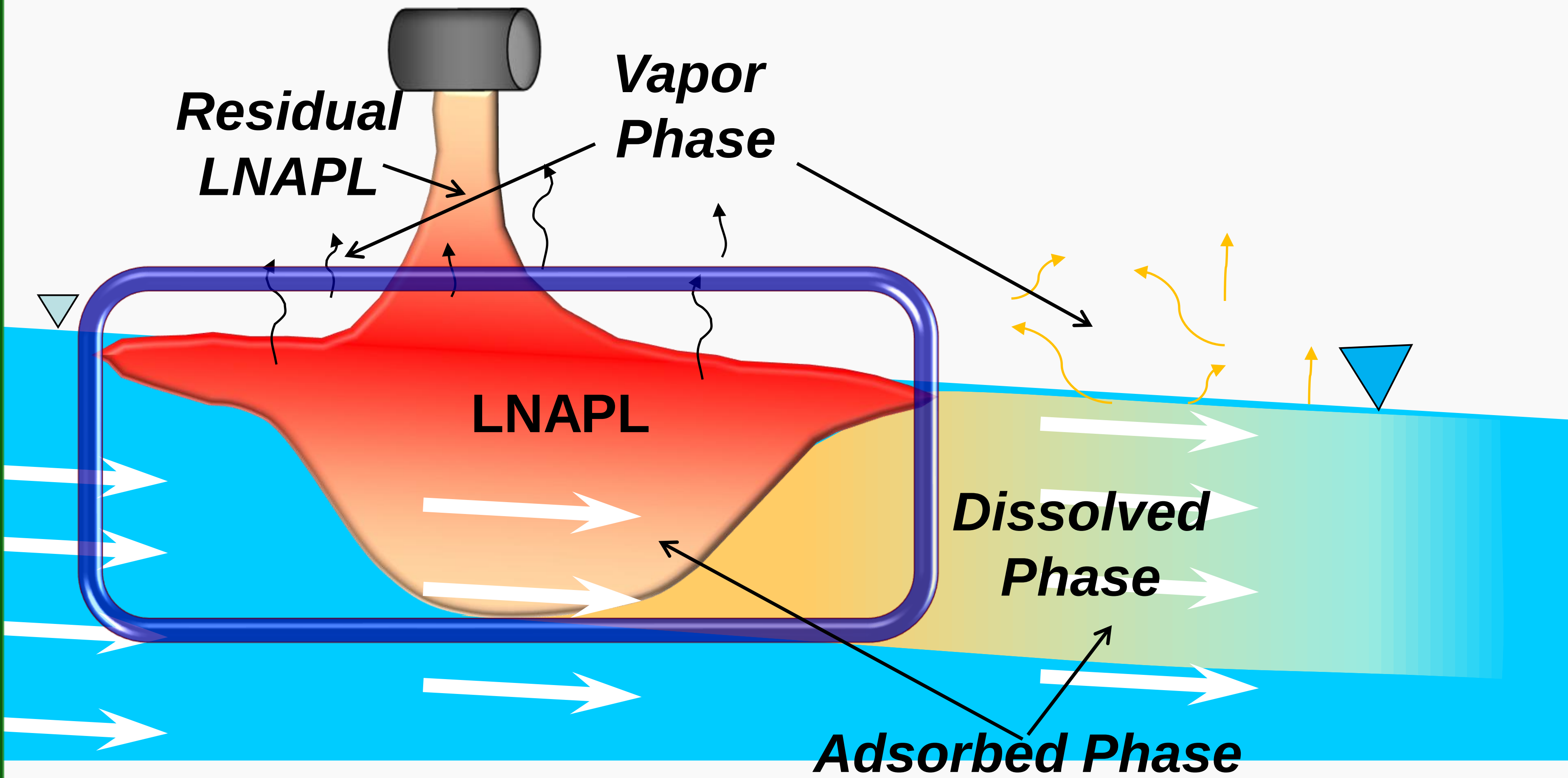
Partitioning of LNAPL in Subsurface Media

Learning Objectives:

- Discuss LNAPL partitioning to other phases in the subsurface—focusing on the dissolved phase

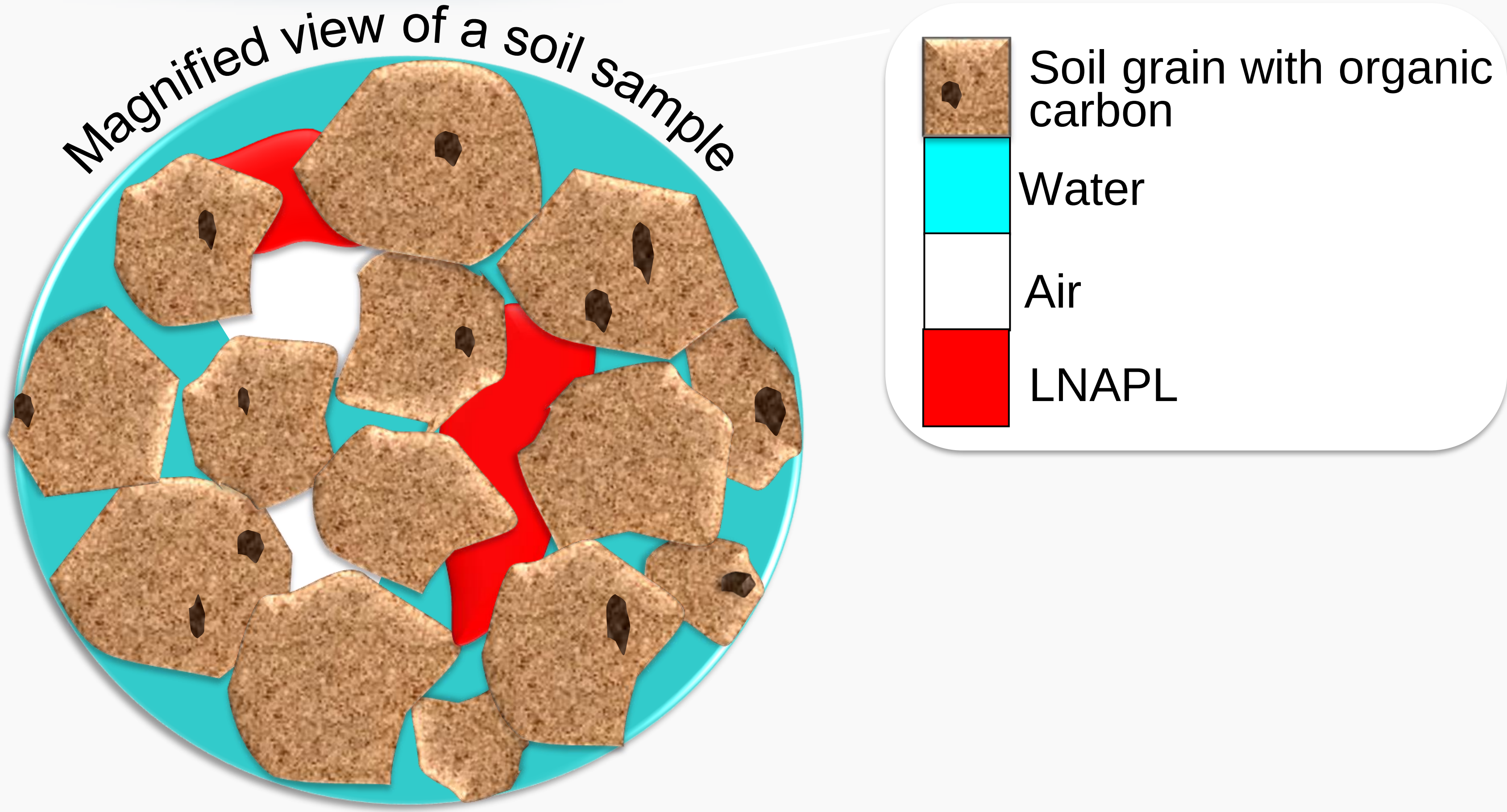


Partitioning of LNAPL in Subsurface Media



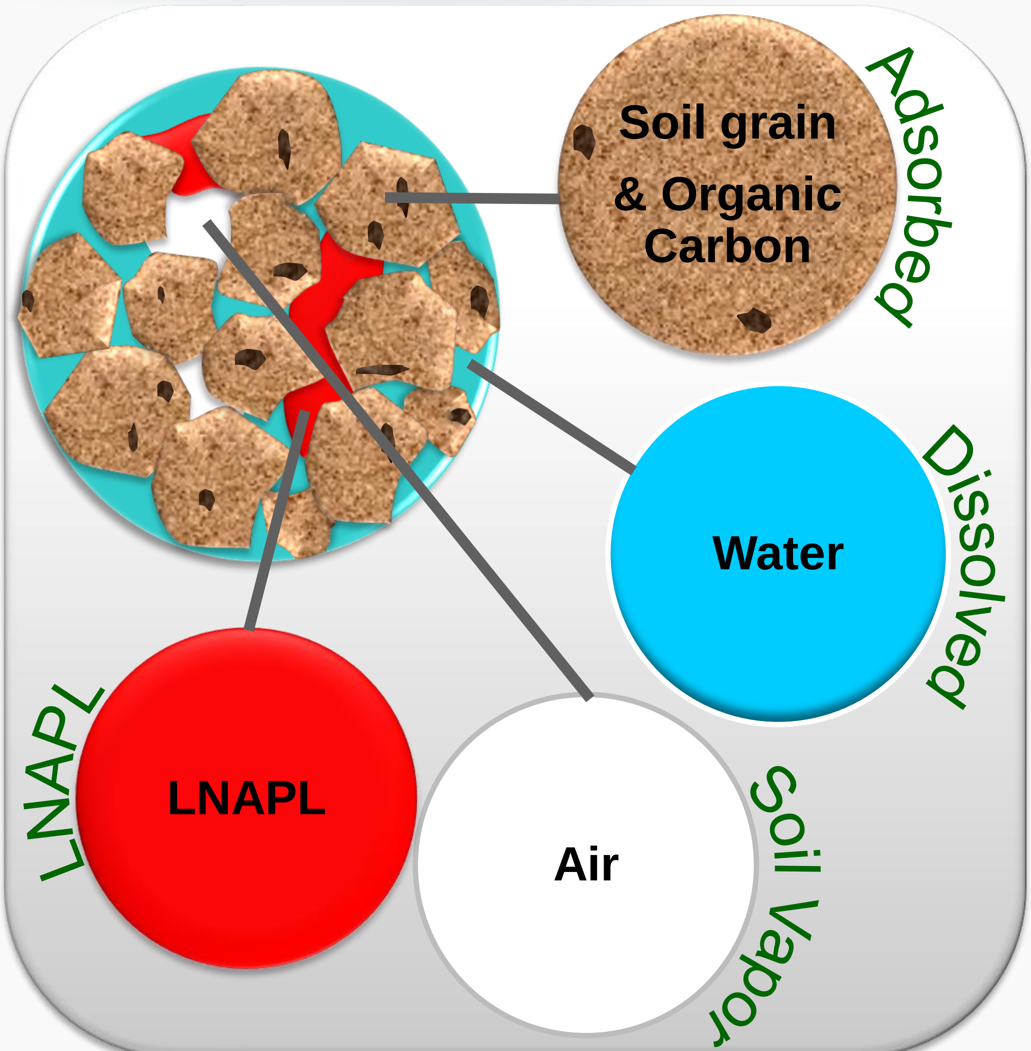
Partitioning of LNAPL in Soil

Subsurface LNAPL Interactions: Partitioning



Source: ITRC LNAPL Course (ITRC)

Partitioning Of LNAPL With Other Phases: Soil, Water, Gas



Adsorbed, dissolved, and soil gas have a finite capacity for organic chemicals.

Soil distribution coef. (K_d); dissolved (S_i^e), and soil gas (effective vapor pressure and Henry's Law)

Source: ITRC LNAPL Course (ITRC)

Properties Affecting Partitioning for Select Chemicals

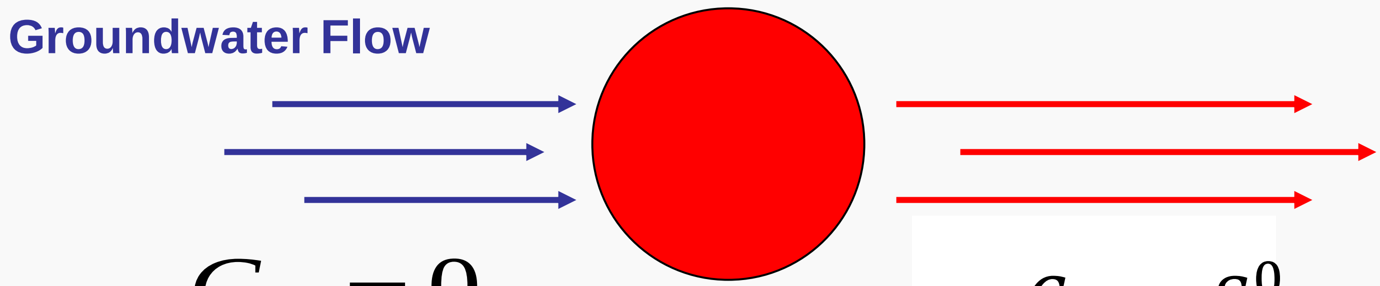
Compound	Molecular Weight (g/mol)	Solubility (mg/L) *1	Vapor Pressure (mmHg)	Unitless Henry's Law Constant	Organic Carbon Partition Coefficient, K_{OC} (L/kg) *2
Benzene	78.1	1780	76	0.24	66
Toluene	92.1	515	27	0.28	145
o-Xylene	106.2	152	5	0.22	241
Ethylbenzene	106.2	152	7	0.37	207

*1 Product of mole fraction and molecular weight determines maximum dissolved concentration (Raoult's Law)

*2 Product of K_{oc} and f_{oc} is the soil distribution coefficient $K_d = C_i^s / C_i^w$

LNAPL Dissolution to Groundwater (local equilibrium assumption)

Single Component NAPL blob



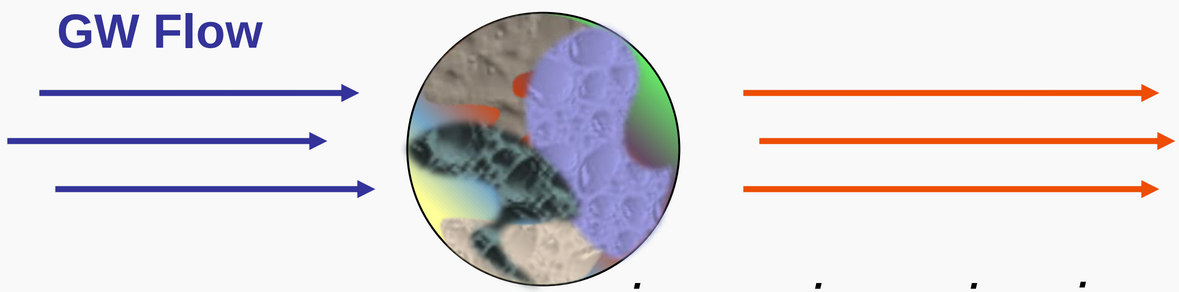
$$C_W = 0$$

$$C_w = S_i^0$$

Pure Compound	Solubility Limit (S_i^o)
Benzene	1800 mg/L
Toluene	515 mg/L
o-Xylene	152 mg/L

LNAPL Dissolution to Groundwater

Mixed LNAPL blob such as gasoline



$C_W^i = 0$

$$C_w^i = S_e^i = X_n^i \; S_0^i$$

Raoult's Law

Where C_w^i is dissoved concentration, S_i^0 is the pure phase solubility; X_n^i is the mole fraction of the ith LNAPL compound

$X_n^{Ben} = 0.01 \; and \; X_n^{Tol} = 0.1$

C_W^{Ben}= 0.01*1800 mg/L= 18 mg/L

C_W^{Tol}= 0.1*535 mg/L= 53.5 mg/L

} Effective Solubility (S_e^i)

LNAPL Mole Fraction vs. Weight Fraction

$$X_n^i = \frac{M_n^i}{\sum M_n^i} \quad ; \quad W_s^i = \frac{C_s^i}{TPH_s}$$

$$S_e^i = X_n^i S_i^0 \; ; \; S_i^e \approx W_s^i S_i^0$$

M_n^i – LNAPL number of moles component i

W_s^i – LNAPL weight fraction of component i

C_s^i – soil concentration of component i

TPH_s - soil TPH concentration from the source

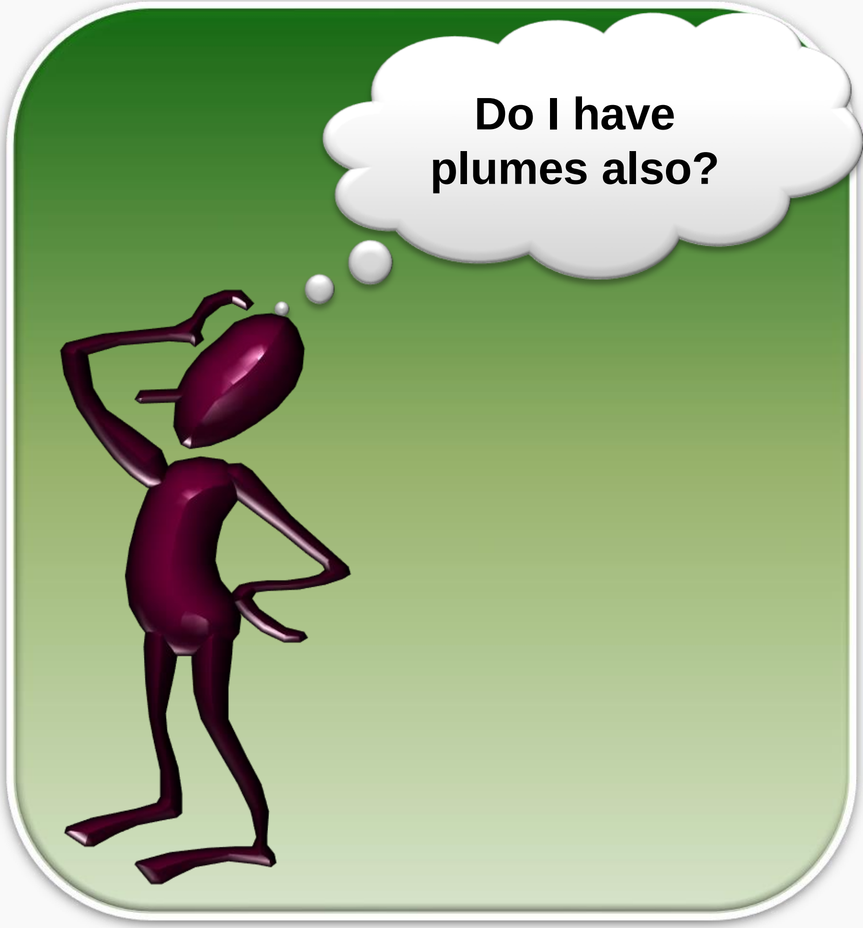
Effective and Estimated Effective Solubilities from Weight Fraction

Compound	Solubility (S_i) (mg/L)	Weight Percent (%)	Mole Fraction (%)	Effective Solubility (mg/L)	Estimated Effective Solubility ($W_s^i S_i^0$) (mg/L)
Gasoline					
Benzene	1780	1.94	2.49	44.39	34.53
Toluene	515	4.73	5.15	26.54	24.36
o-Xylene	152	2.27	2.15	3.26	3.54
m-Xylene	158	5.66	5.35	8.45	8.94
p-Xylene	200	1.72	1.63	3.25	3.44
Ethylbenzene	152	2.00	1.8	2.8	3.04
Diesel					
Benzene	1780	0.2	0.50	8.83	3.56
Toluene	515	0.3	0.63	3.25	1.54
o-Xylene	152	0.5	0.91	1.39	0.76
m-Xylene	158	0.5	0.91	1.44	0.79
p-Xylene	200	0.5	0.91	1.82	1.00
Ethylbenzene	152	0.2	0.36	0.5	0.30

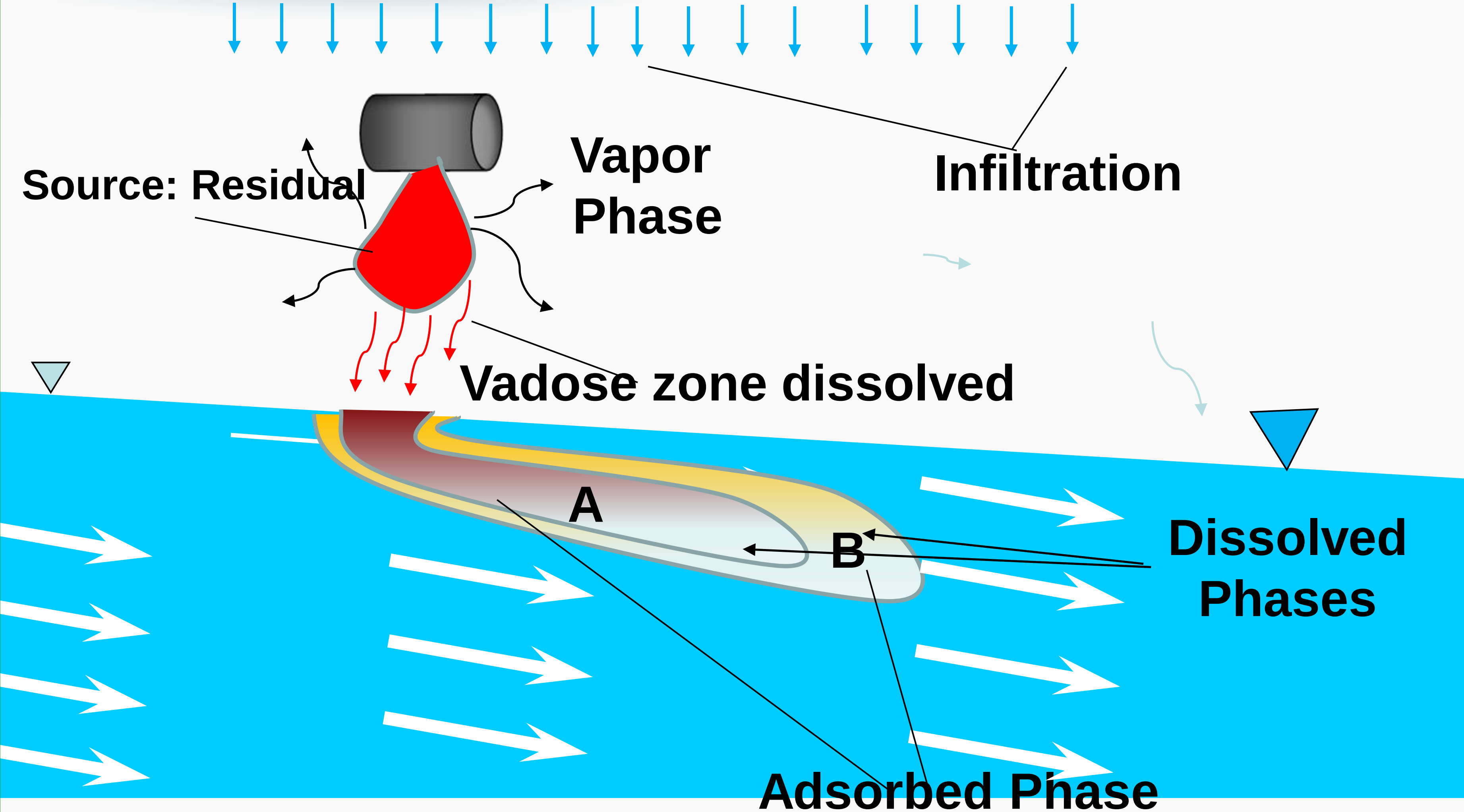
Nature and Properties of Dissolved Plume

Learning Objectives:

- Discuss the behavior and properties of the resulting dissolved hydrocarbon plumes

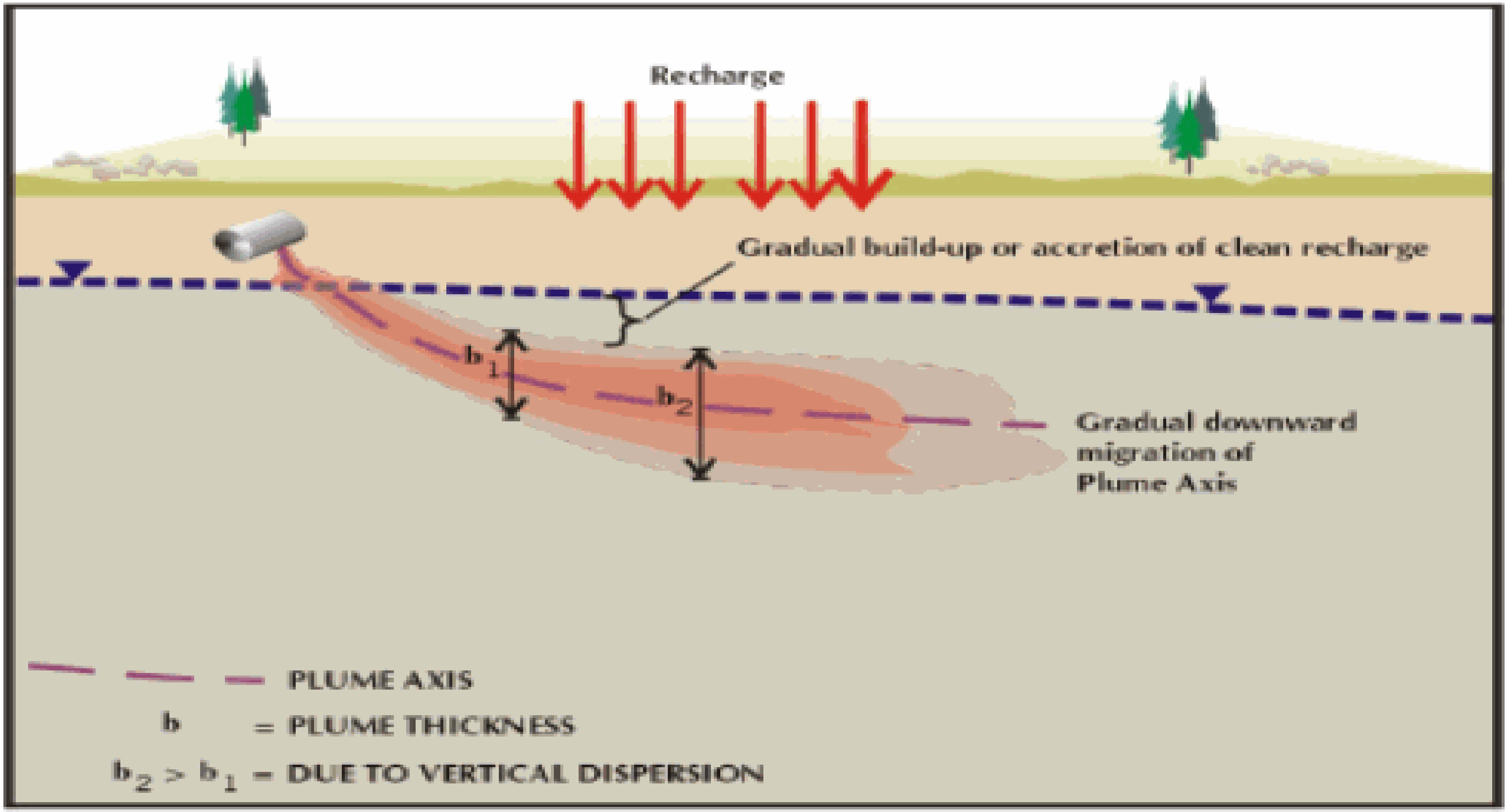


Interactions of LNAPL with Subsurface Media



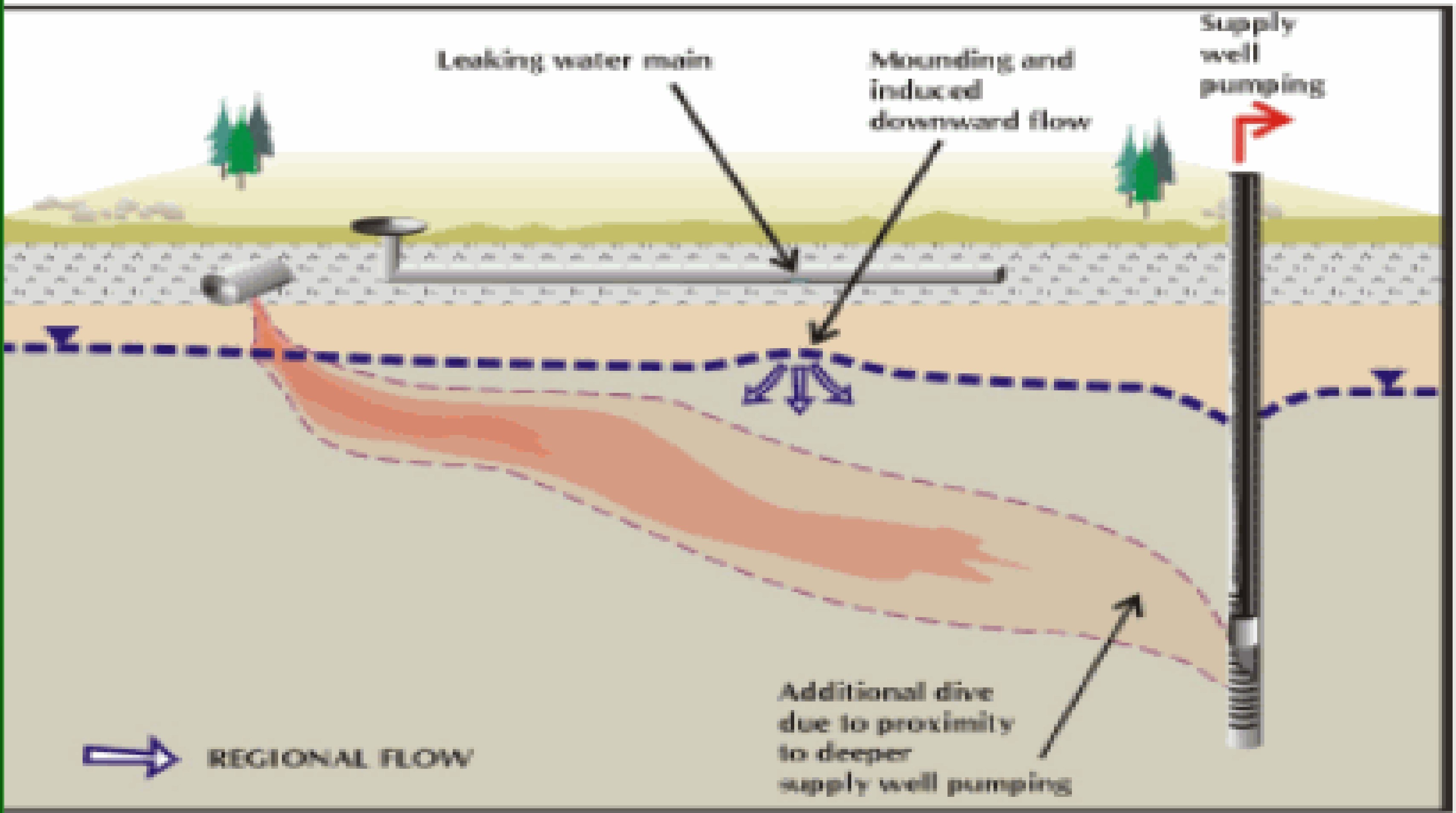
Behavior of Dissolved Plume

Behavior of Hydrocarbon Plumes



Source: API Soil and Groundwater Technical Task Force Bulletin 24 (April 2006), prepared by Eric M. Nichols, P.E., and Tracy L. Roth, R.G. LFR, Inc.

Behavior of Dissolved Plume



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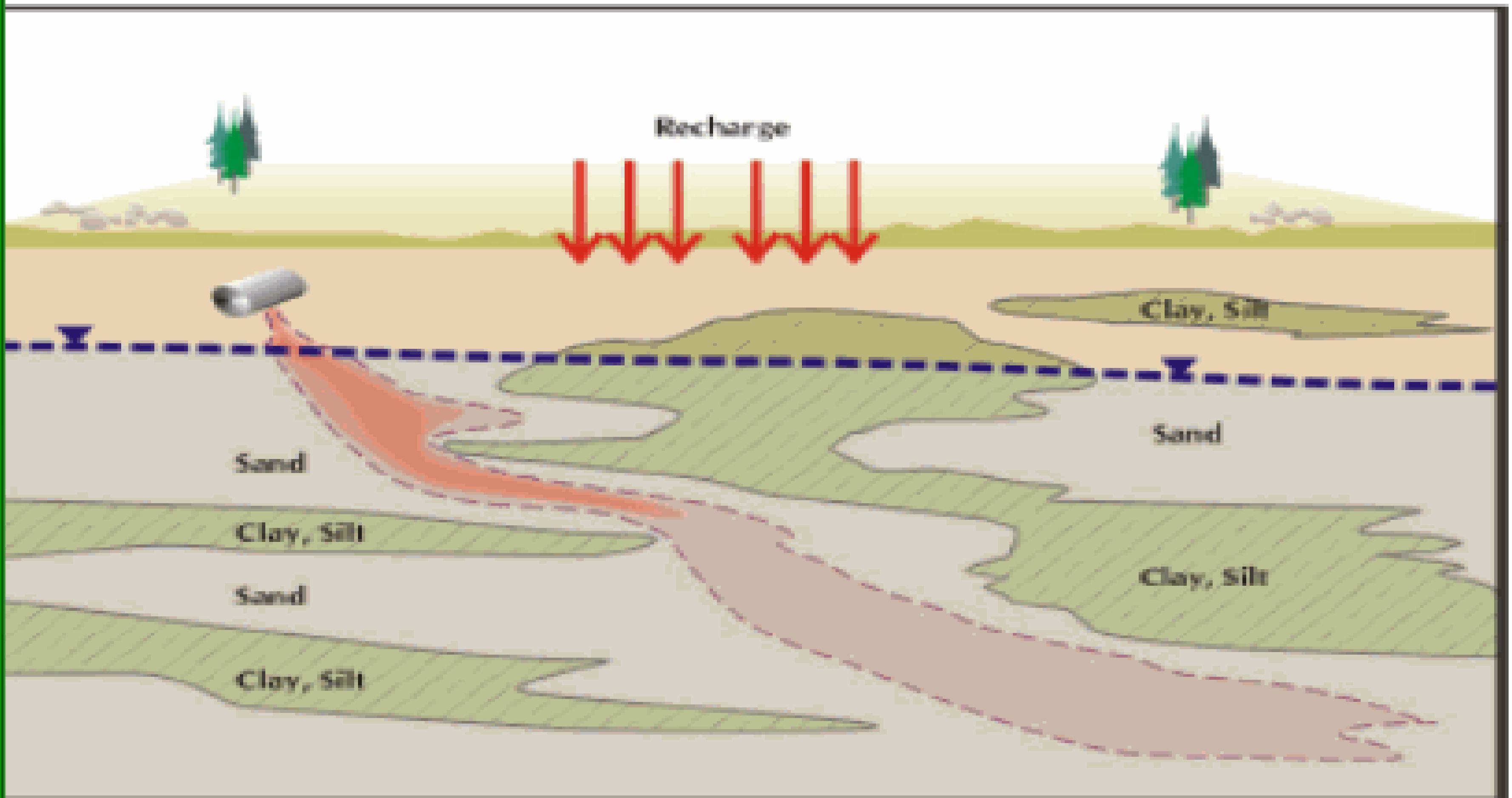
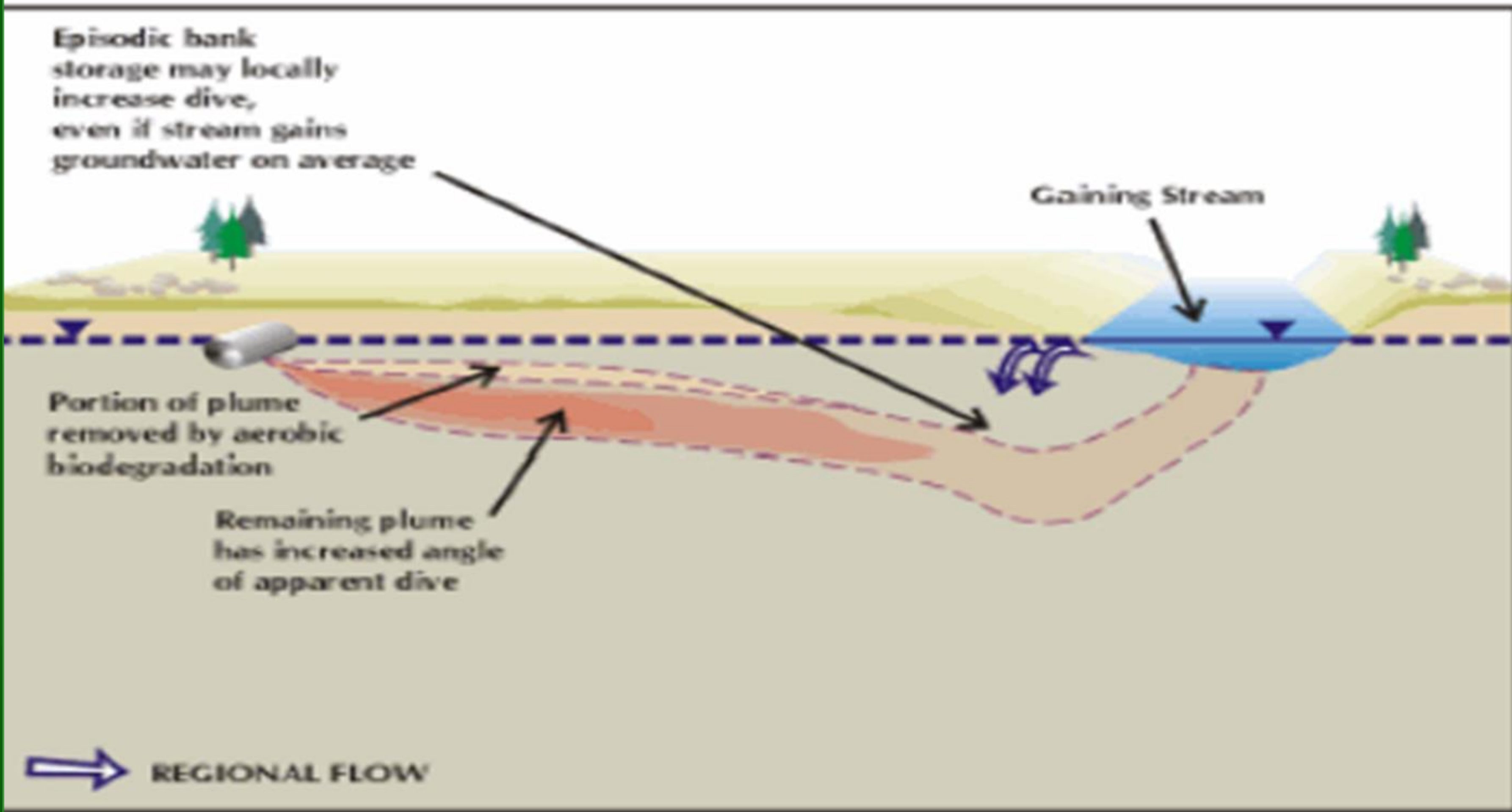
Behavior of Dissolved Plume



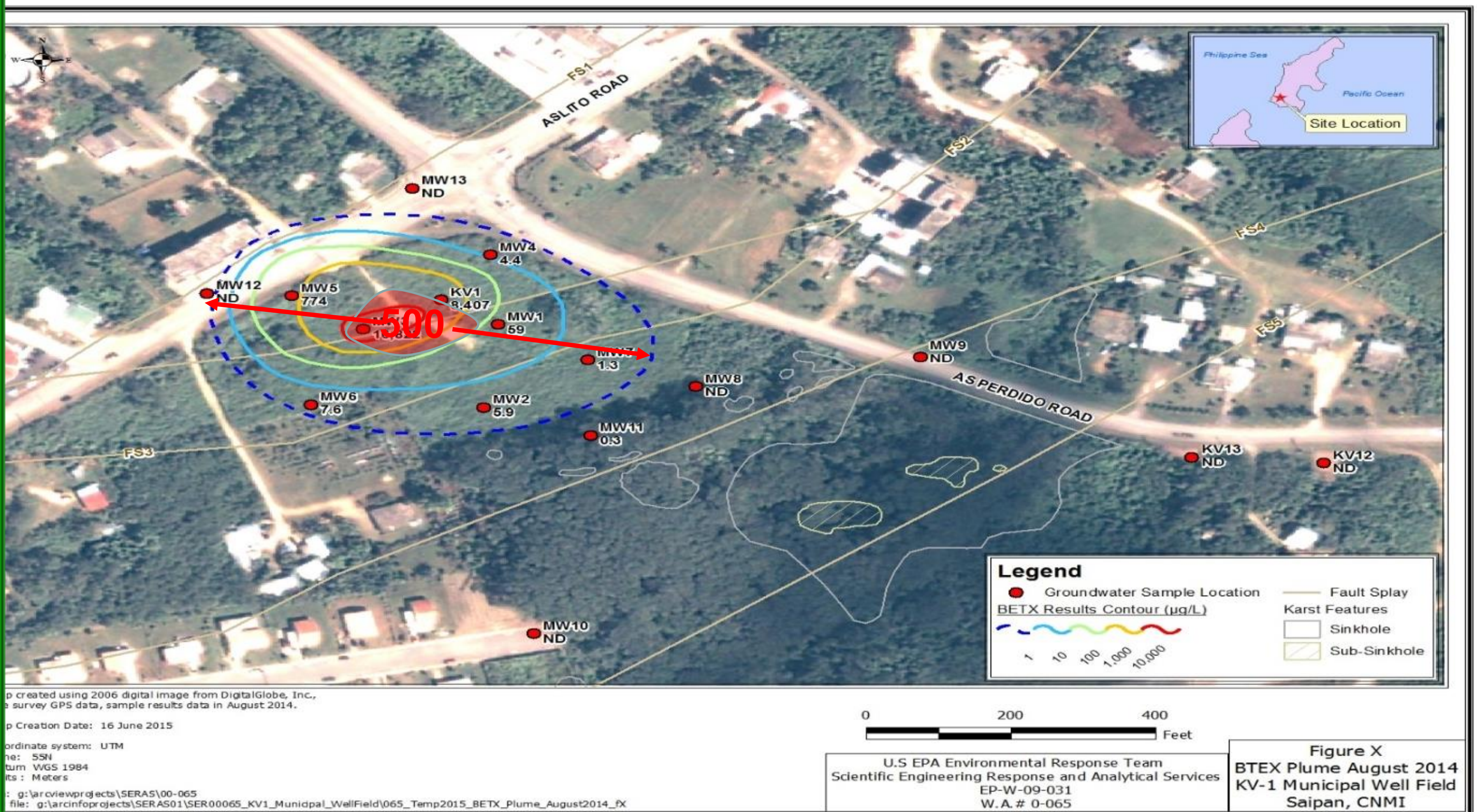
Source: API Soil and Groundwater Technical Task Force Bulletin 24 (April 2006), prepared by Eric M. Nichols, P.E., and Tracy L. Roth, R.G. LFR, Inc.

Dissolved Hydrocarbon Plume Behavior



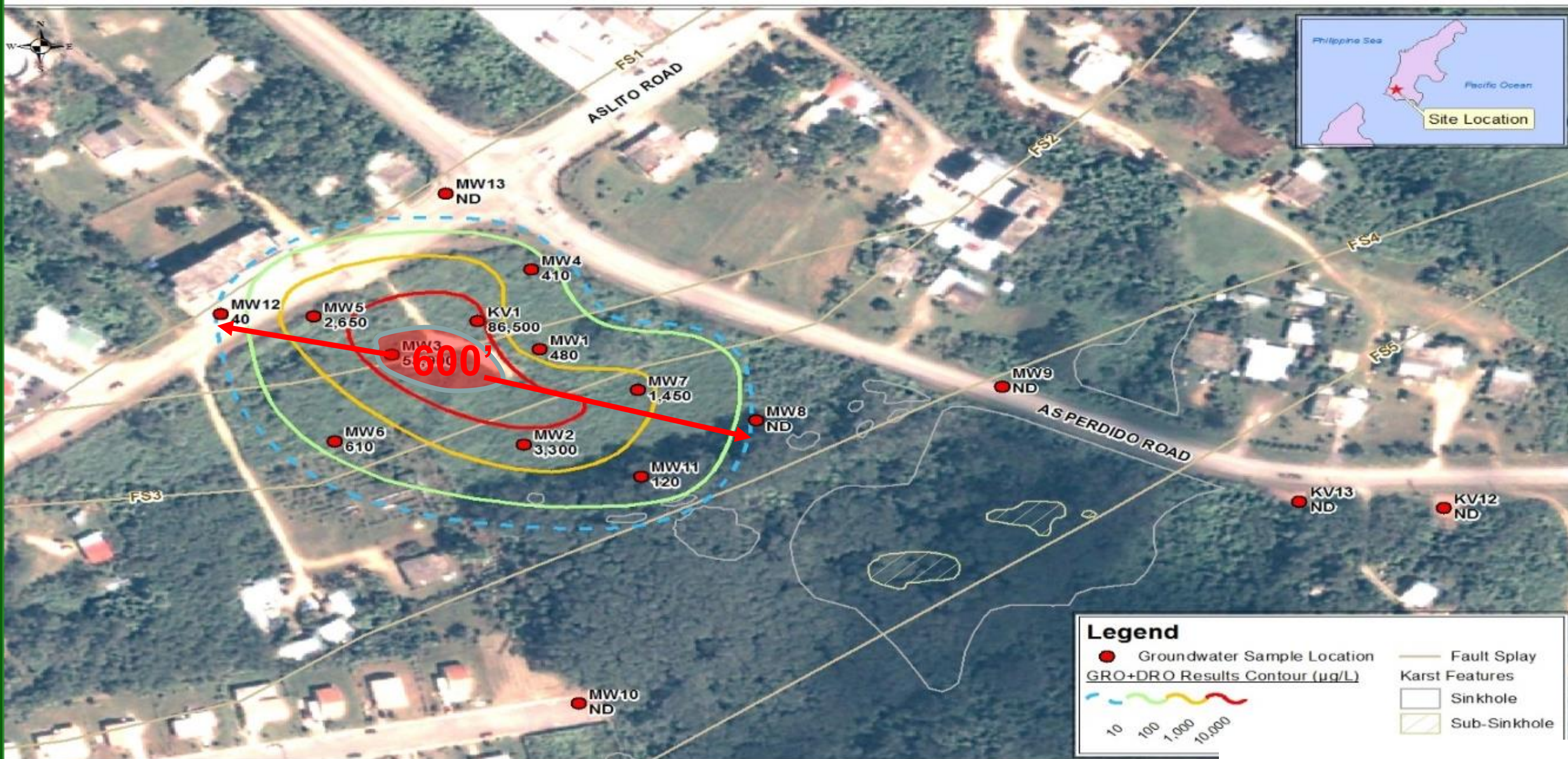
Source: API Soil and Groundwater Technical Task Force Bulletin 24 (April 2006), prepared by Eric M. Nichols, P.E., and Tracy L. Roth, R.G. LFR, Inc.

Hydrocarbon Plumes Limited in Extent: BTEX



Hydrocarbon Plumes Limited in Extent: TPH

Behavior of Hydrocarbon Plumes



created using 2006 digital image from DigitalGlobe, Inc., survey GPS data, sample results data in August 2014.

Creation Date: 16 June 2015

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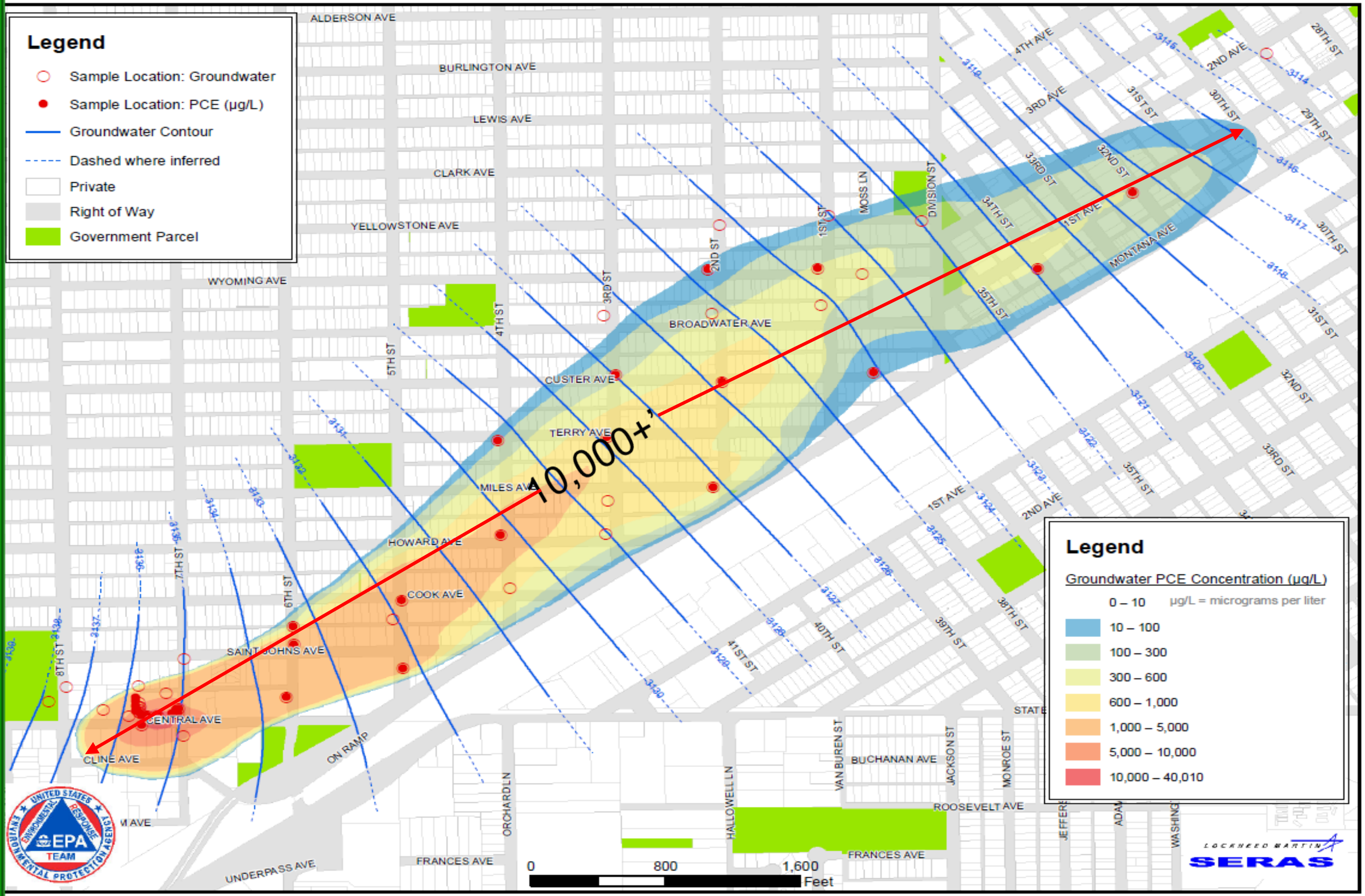
0 200 400 Feet

U.S EPA Environmental Response Team
Scientific Engineering Response and Analytical Services
EP-W-09-031
W.A.# 0-065

KV-1 Municipal Well Field
Saipan, CNMI

Chlorinated Solvents Plumes Very Long: PCE

Behavior of Hydrocarbon Plumes

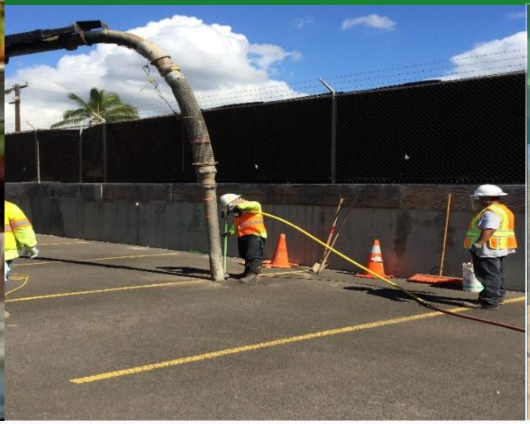


Summary of LNAPL Dissolution and Hydrocarbon Plume Behavior

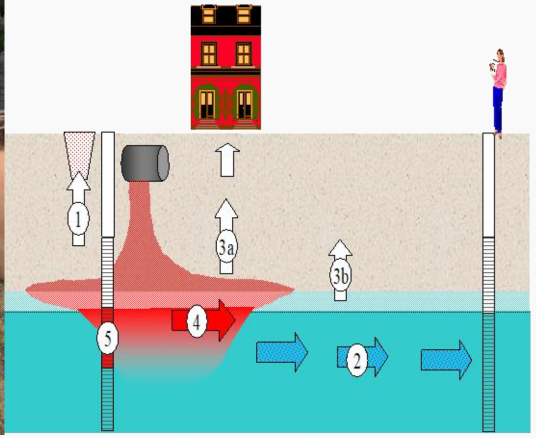
- Soluble Compounds Partitions to Groundwater—Raoult's Law
  - Equilibrium partitioning: groundwater velocity slow relative to kinetics of mass transfer
- The dissolved plume flows consistent with groundwater flow (convection and dispersion)and stratigraphy
- Providing source is stable, plume eventually stabilizes; i.e., it does not expand infinitely
  - Dilution and microbial activity on the edges constrain the dissolved plume `

Summary of Hydrocarbon Plume Behavior

- Hydrocarbon plumes expand far beyond the source (within a few 100 ft of source)
  - Aerobic biodegradation around the edges limit spread
  - Most groundwater is aerobic
- Contrary to chlorinated compound plumes: can be miles long
  - Does not undergo aerobic biodegradation

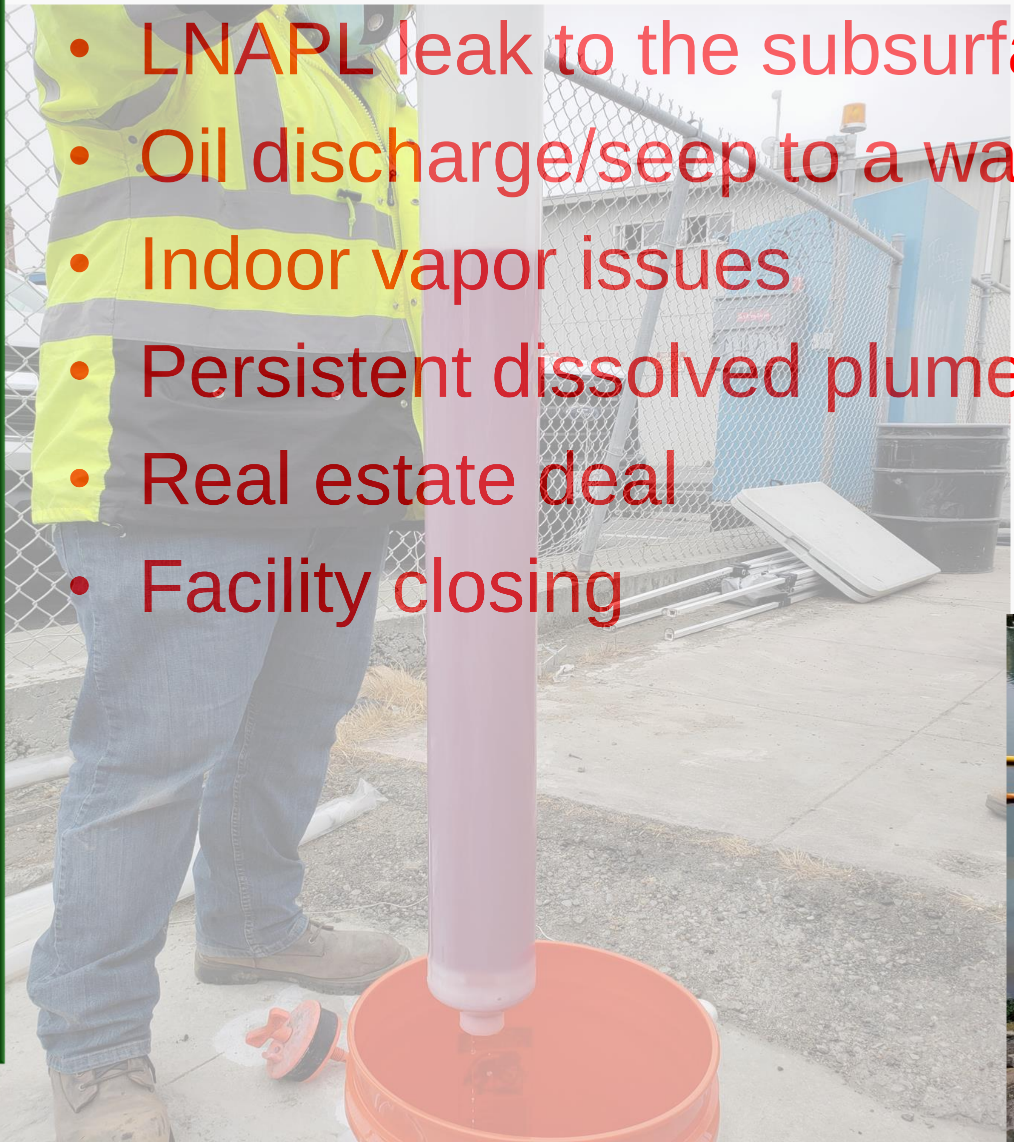


LNAPL Site Assessment Methodologies/Approaches



Why Conduct Subsurface LNAPL Assessment

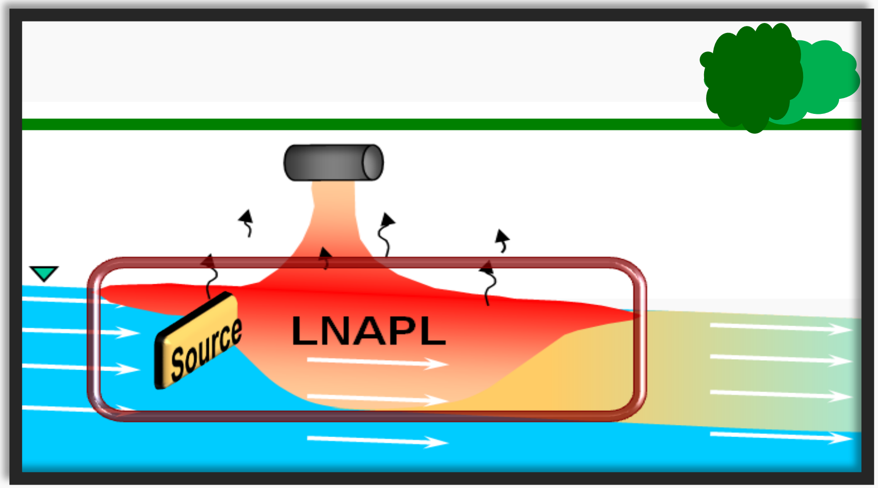
Why Site Assessment



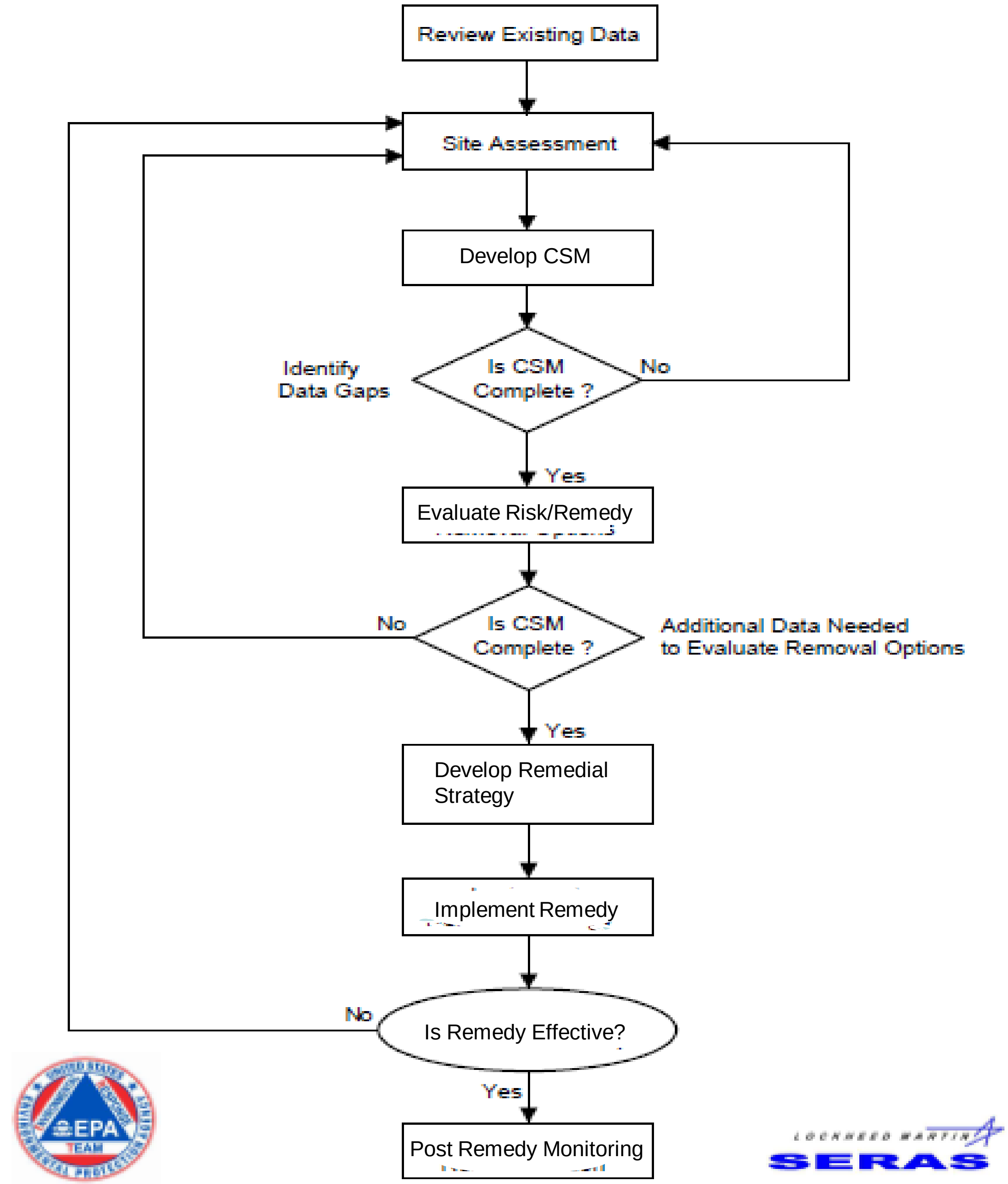
- LNAPL leak to the subsurface
- Oil discharge/seep to a water body
- Indoor vapor issues
- Persistent dissolved plume
- Real estate deal
- Facility closing

Objective of Assessment

- Gather data to build a robust CSM/LCSM to understand the subsurface conditions and guide the risk management
  - CSM focuses on the entire site: source, hydrogeology, pathways, receptors
  - LCSM focuses on the geometry of the source (oil) and the subsurface hydrogeologic interactions/processes
- As in the other course segments, we'll focus on assessment germane to the LCSM

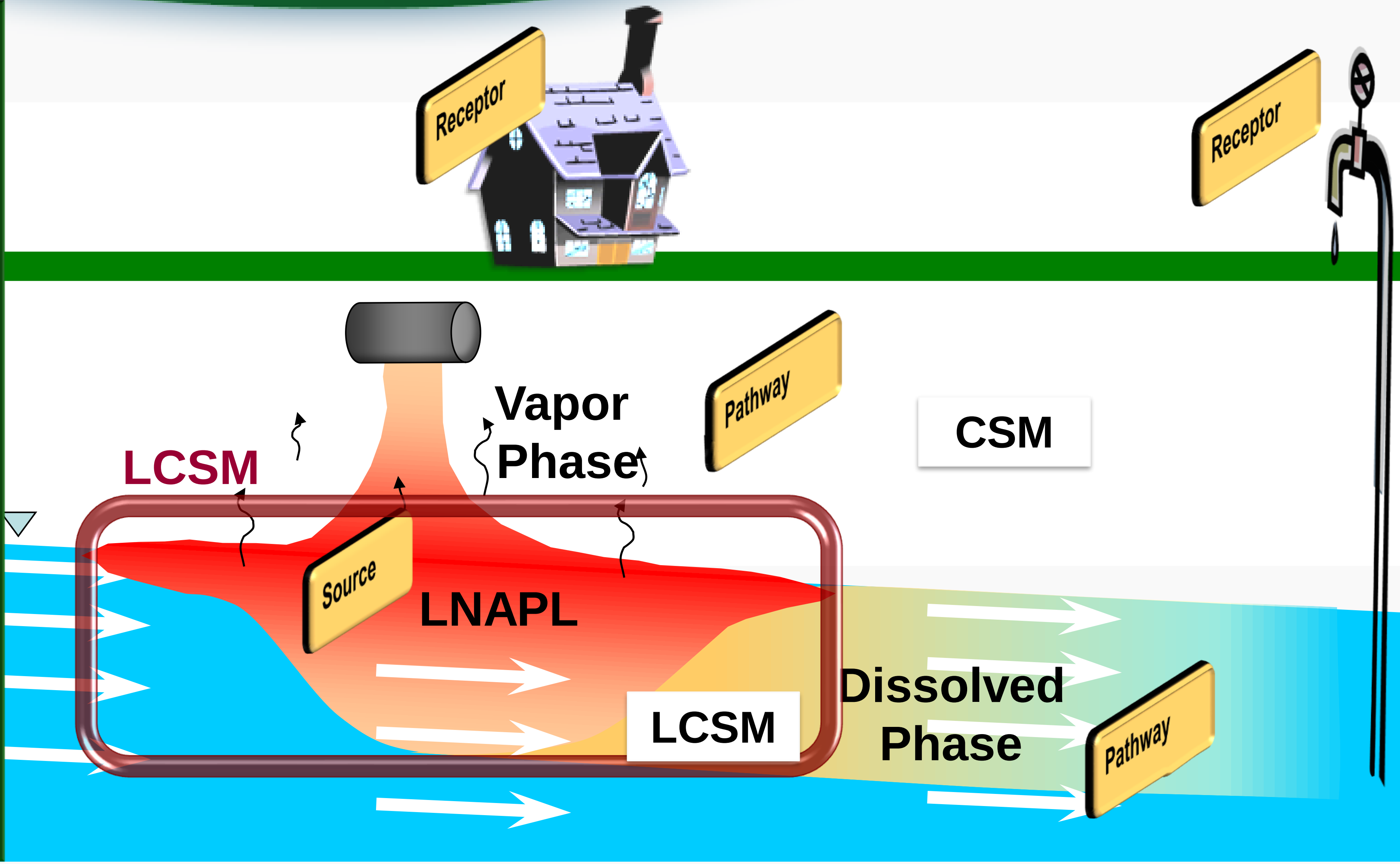


Iterative Site Assessment-CSM-Development Process



LNAPL Conceptual Site Model (LCSM)

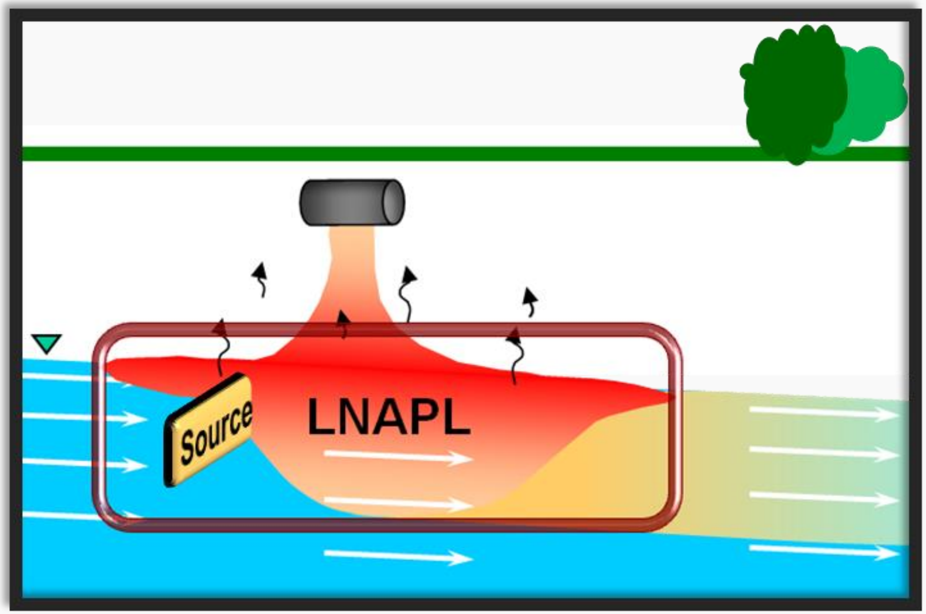
Why Site Assessment



Source: ITRC LNAPL Course (ITRC)

LCSM Key Components

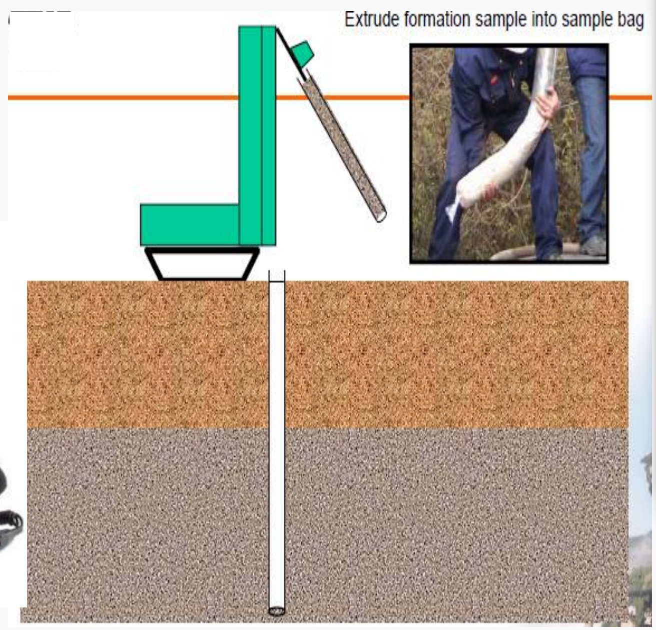
- LNAPL source delineation: where and what
- hydrogeology, and it's interaction with LNAPL
- LNAPL migration potential and stability
- LNAPL transmissivity – to assess recoverability



Conventional Assessment Technologies

Learning Objectives:

- Conventional assessment tools used to characterize the source three-dimensional extent and hydrogeology



Hydrogeology, Soil Sampling and Well Installation

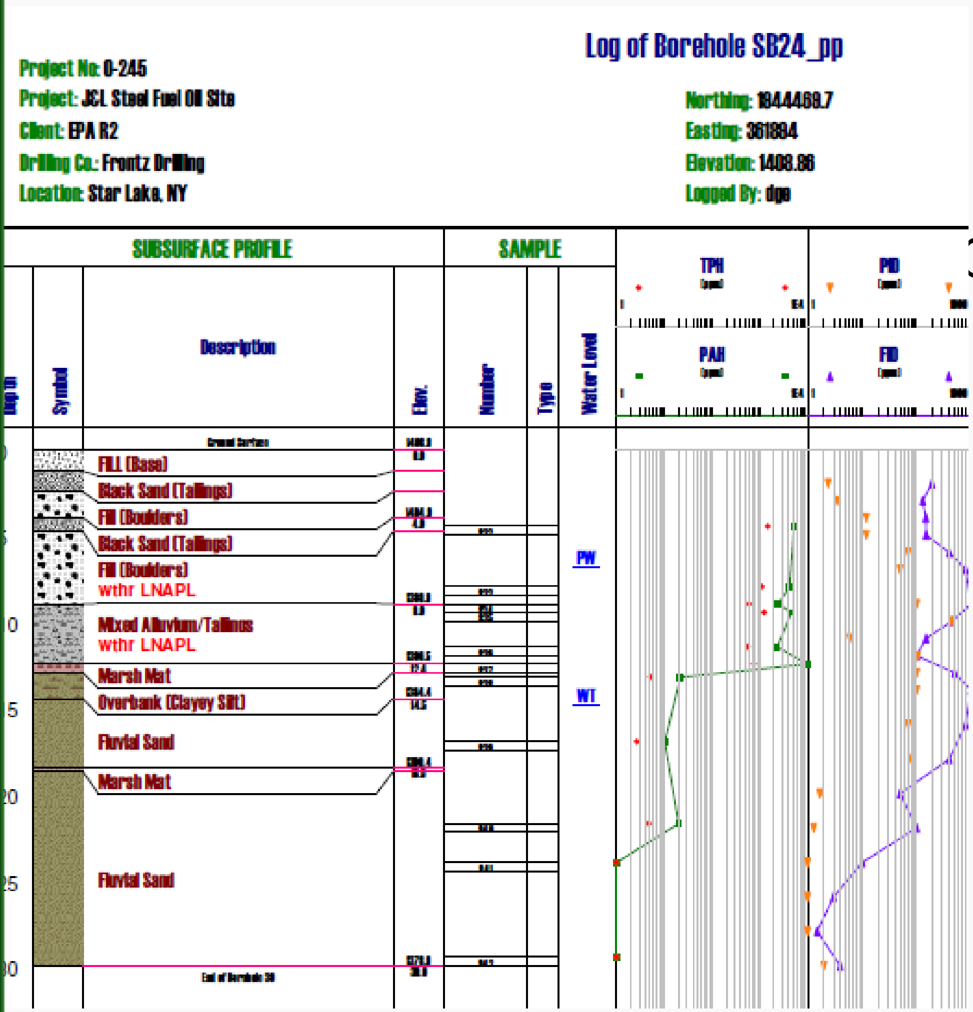
Conventional Assessment

Drilling Methods:

- Hollow Stem Auger
- Percussion/hammer
- Air/Mud Rotary
- Sonic: probably the method of choice—not cost prohibitive as it once was, continuous core, relatively quick, minimize cross contamination, and applicable to consolidated/ur material

Sonic: Continuous Core

Conventional Assessment

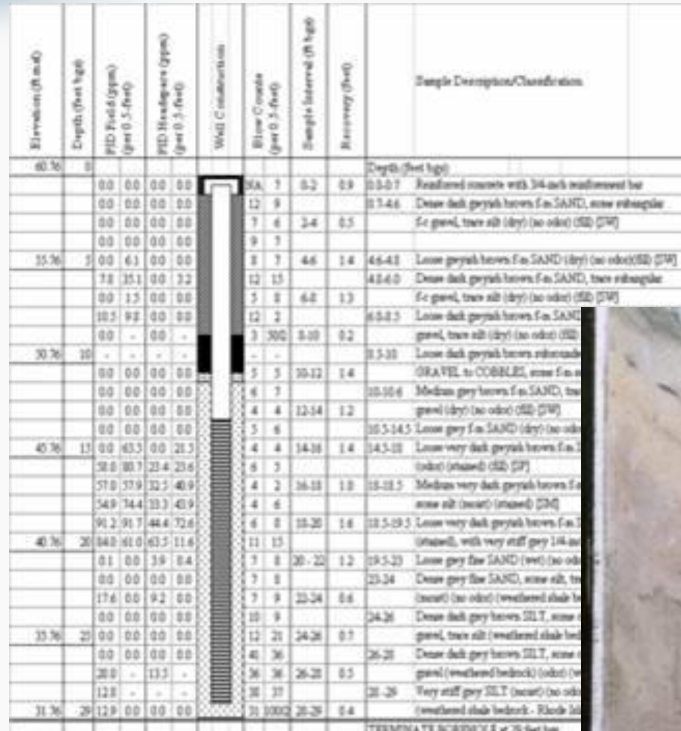


Mobile Oil Draining from Sonic Core

Continuous Core/Field Measurements

Conventional Assessment

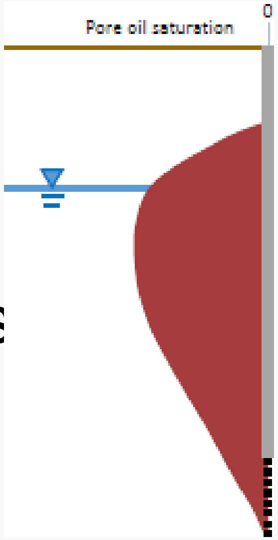
- Detailed soil boring logs through the zone of LNAPL are key includes
  - Lithology, water content, odor, soil structure, organic OVA meter readings
- Oleophilic dyes and ultra-violet (UV) light can aid assessment for presence of LNAPL
- Laboratory validates screening data



Soil Sampling and Analysis

Conventional Assessment

- Sample continuously–not at predetermined intervals
  - Use field screening, and hydrogeology to determine where to sample
- Do not stop sampling at the water table
  - If saturated zone impacted, most oil below water table
- Contaminant Concentrations:
  TPH (gro, dro and oro), VOC’s, BTEX, PAHs saturation, residual saturation, etc
- Soil Properties: bulk density, organic carbon fraction, porosity, etc.
- Analysis done at fixed laboratory



OVA Field Screening: PID/FID

FID

PID

FID/PID combined

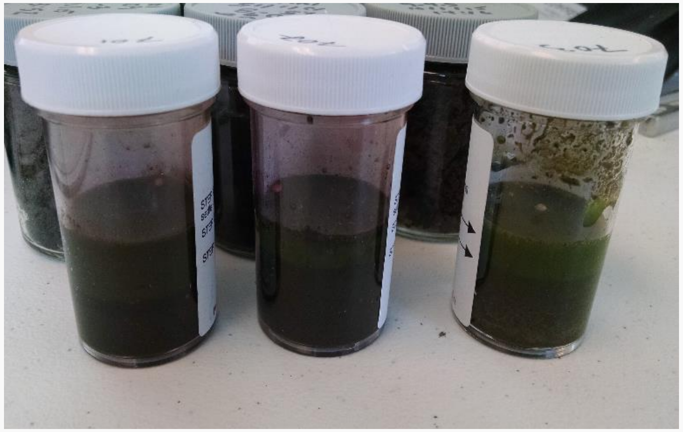
Field Screening: Oleophilic (Sudan) dyes

Specialized Methods/Tools

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

Picture cheiron-resources.com

Semiquantiative

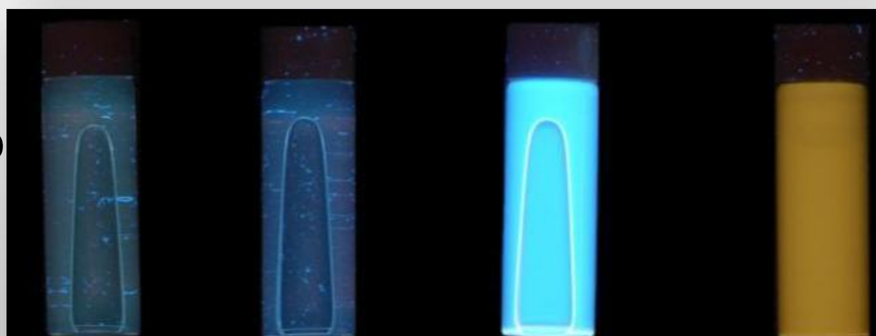


Field Screening: UV (black) Light

White light

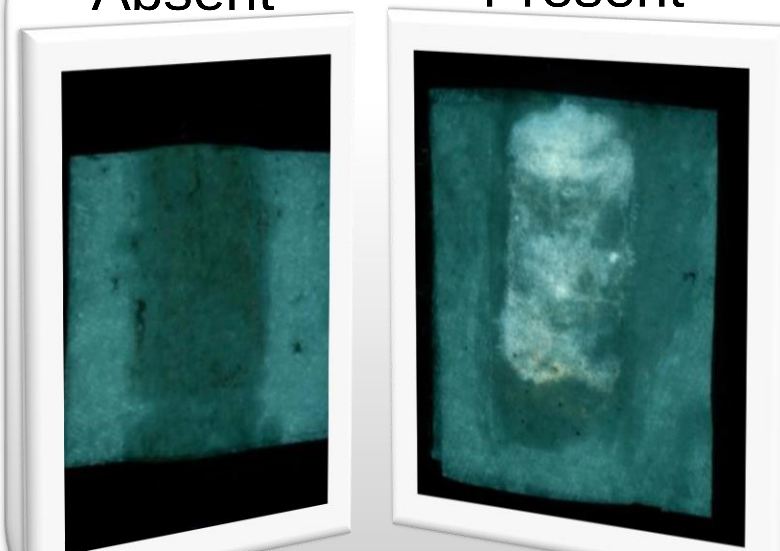
Gasoline Jet A Diesel Bunker C

UV light



Photographs: Courtesy of PTS Lab

LNAPL Absent LNAPL Present



Paper towels in UV light

Source: ITRC LNAPL Course (ITRC)

Laboratory Analyses

Specialized Methods/Tools

- Specialized laboratory analysis packages have been developed to support LNAPL evaluations for more complex LCSM
  - Core photography
  - Pore fluid saturations and soil properties
  - Fluid properties, e.g., density, viscosity
- Other optional analyses that may be performed at this time:
  - Fingerprinting
  - Residual saturation
  - Soil capillary properties
- Specialized soil sampling and handling procedures

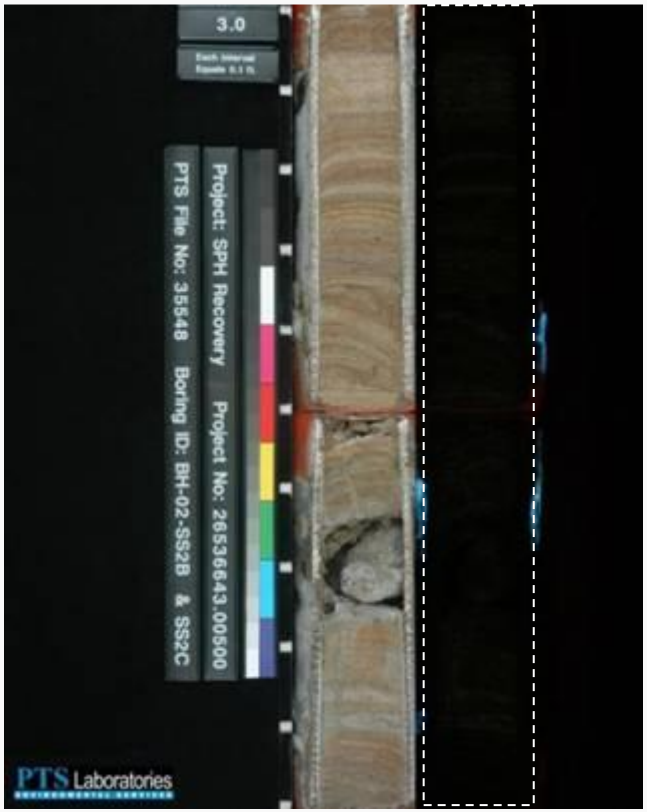
Preserving core using liquid nitrogen

Source: ITRC LNAPL Course (ITRC)

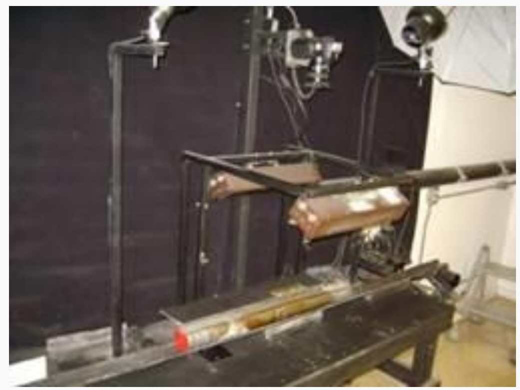
Laboratory Core UV Photography

Specialized Methods/Tools

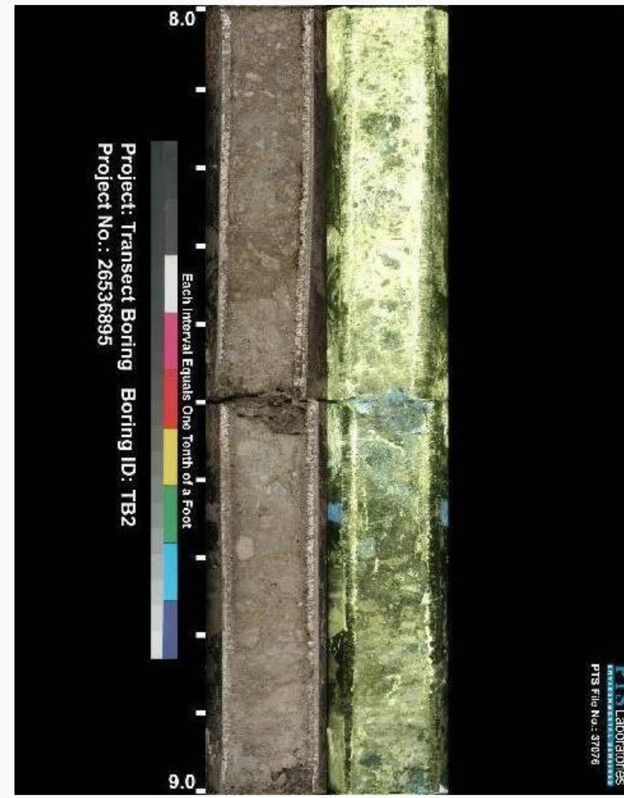
LNAPL Absent



Natural Light UV Light



NAPL Present



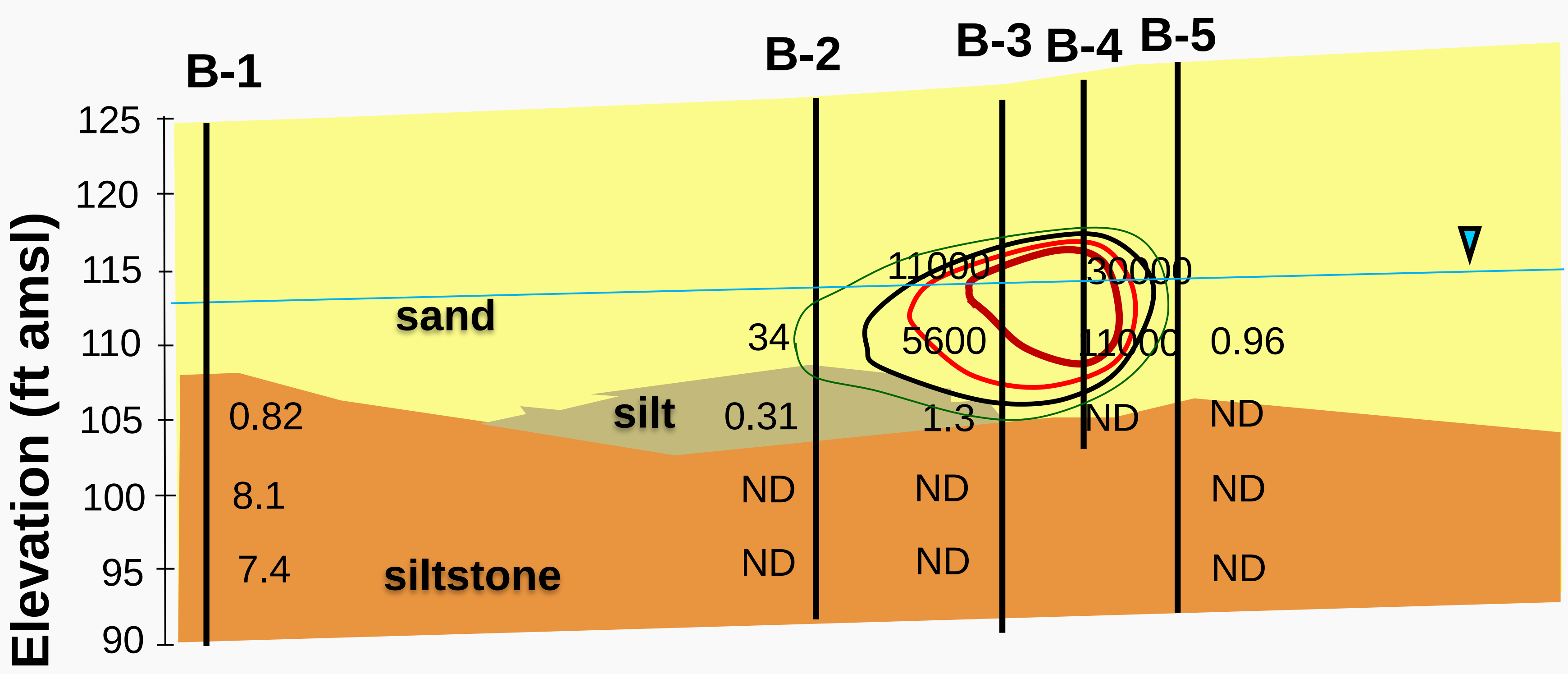
Natural Light UV Light

Fluorescence

Source: ITRC LNAPL Course (ITRC)

CSM: Hydrogeologic and TPH in Soil

CSM (data integration): Conventional Assessment

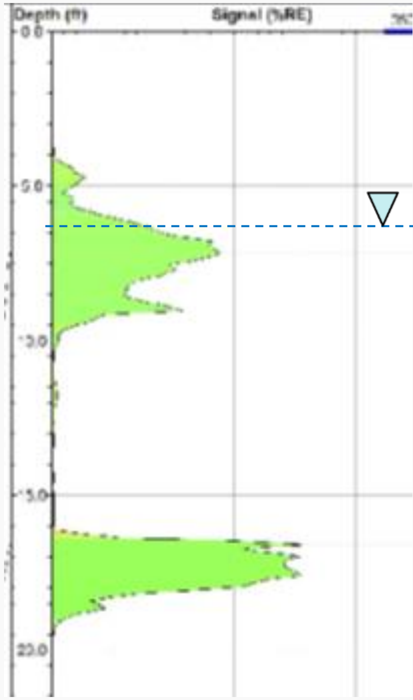


Source: ITRC LNAPL Course (ITRC)

Monitoring Well Installation

Conventional Assessment

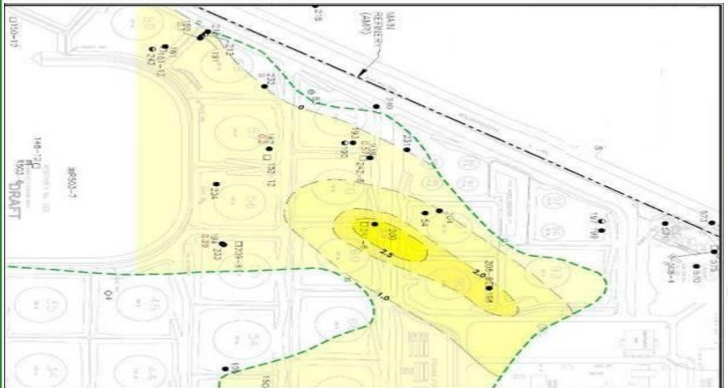
- Install wells and screens to target LNAPL zone(s)—could be multiple wells
  - Highest density of wells in LNAPL source area(s)
  - Also wells outside of source area(s)—upgradient, downgradient (sentinel), and lateral
- Screen wells to target LNAPL, paying special attention to lithology
  - The old precept to screen across the water table for LNAPL is not always correct.



Sampling/Monitoring for LNAPL

Conventional Assessment

- Depth to oil and water (interface probe)
  - LNAPL thickness, LNAPL thickness contours, LNAPL body stability, seasonal effects.
  - Groundwater elevation/gradient, oil thickness contours, piezometric surface, etc.
  - LNAPL body stability
- LNAPL mobility/recoverability—LNAPL Baildown test
  - Oil transmissivity (later)



Groundwater-LNAPL Monitoring/Sampling

- Soil Hydraulic Properties—Pump test, slug test
  - ✓ hydraulic conductivity, specific yield/storativity
  - ✓ Pump test, slug test
- LNAPL Sampling and Analysis:
  - ✓ Physical properties: density, viscosity, interfacial tensions, etc
  - ✓ Chemical Properties: fingerprint, composition, etc
  - ✓ Analysis by fix laboratory
- Groundwater Sampling Methods: Purge and sample, low flow, passive diffuser bags
  - ✓ Low flow/diffuser reduce/eliminate purge water

Test Pitting: LNAPL Monitoring

- Early in a response, heavy equipment may be available or recovery system installation phase
  - Getting a driller on site may take time
- Tells whether LNAPL is present or not
- Not very useful for lithologic information
- Could cross contaminate if oil layered

Test Pitting: LNAPL present or not

Be careful where there could be underground utilities

Excavators and backhoes are not finesse equipment

Air Knife

- High subsurface utilities density or inaccessible for utility clearance; or early in a response: refinery, tank farm, utility corridor, etc.
  - Use to clear shallow utility-clustered areas to allow drilling/direct push
  - If water table is shallow, used to install soil boring
  - Disadvantage: loose lithologic data

Summary

What Did You Learn?

- Discussed conventional assessment technologies
- Continuous coring preferred to approach to predetermined-discrete coring
- Do not sample soils at a predetermined interval; use field screening to determine where to sample
- Detailed soil log: lithology, soil structure, odor, OVA readings, photo documentation, etc
- Install monitoring wells based on soil sampling data
- Screen wells to target LNAPL—not always across the water table,
  - Do not screen across confining layers, and paired wells may be needed

Source: ITRC LNAPL Course (ITRC)

Summary Cont'd?

What Did You Learn?

- Groundwater sampling method: purge and sample, low flow, passive diffuser bags
- Monitor fluid levels periodically—is the LNAPL body stable, and seasonal effects
- Test pits and air knives can be useful assessment tool

Source: ITRC LNAPL Course (ITRC)

Field Determination of LNAPL Transmissivity

Learning Objectives:

- Discuss LNAPL Transmissivity field measurement methods
  - Transmissivity measurement methods
  - Review the LNAPL baildown test method

Transmissivity Tests Methods

- Short-term T_n estimation methods
  - Instantaneous applied stress
  - LNAPL baildown, LNAPL slug and LNAPL manual skimmer tests
- Long-term T_n estimation methods
  - Relatively long-term stress
  - LNAPL recovery data analysis, and LNAPL tracer test

Source: ITRC LNAPL Co

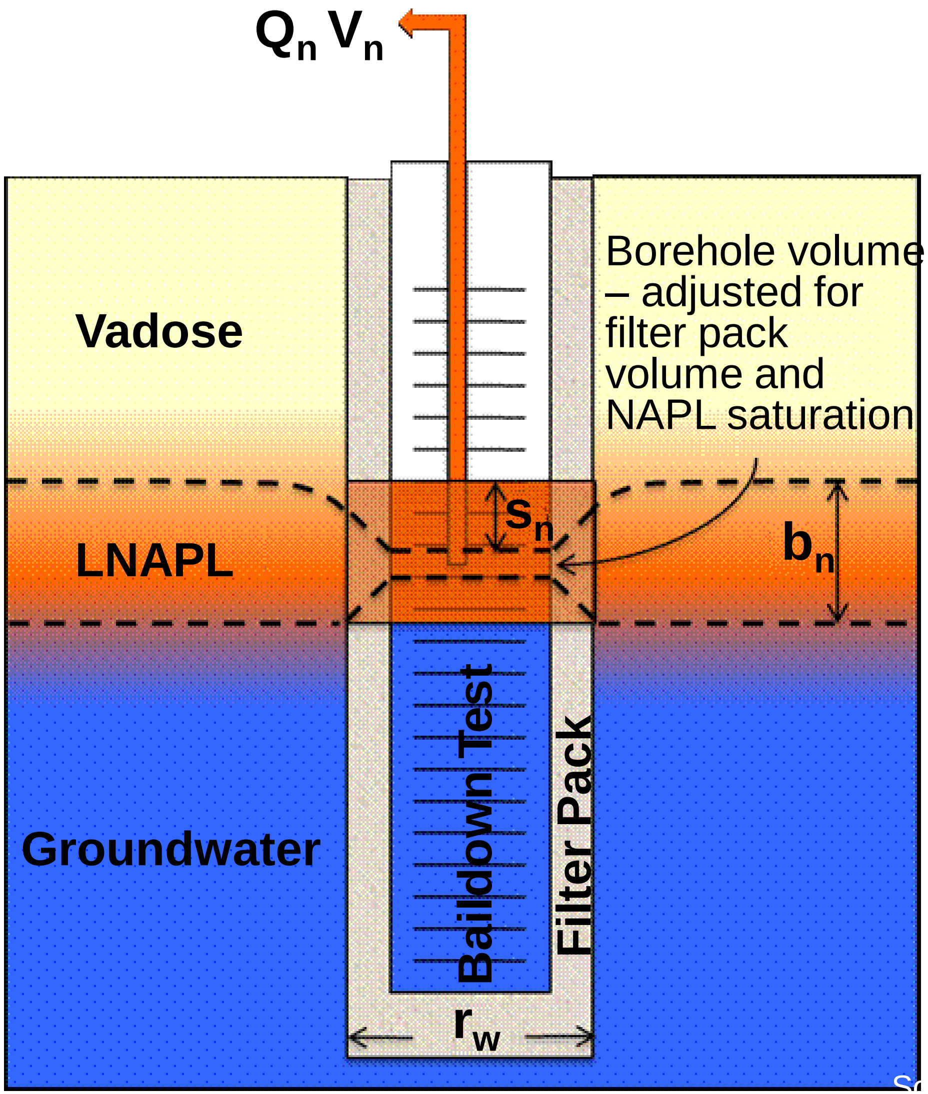
Short-Term Tests Methods

- LNAPL baildown test
  - Default method for determining T_n
  - Most common, relatively inexpensive, easy to conduct and analyze
  - Standard aquifer test software can analyze data
  - Yields T_n in the vicinity of test well
- LNAPL slug test
  - Analogous to baildown test
  - Not widely used
  - Yields T_n in the vicinity of test well

Source: ITRC LNAPL Course (ITRC)

Baildown Testing

LNAPL Transmissivity Measurement



- LNAPL thickness
  - >0.5 feet
- LNAPL conditions: confined, unconfined, perched
- Developed monitoring well
- Test method:
  - Remove borehole LNAPL (i.e. well plus sand pack)
  - Monitor LNAPL layer recovery
- Analytical options:
  - Huntley, 2000
  - Lundy and Zimmerman, 1996
  - ASTM, 2011 (updated 2013)
  - API spreadsheet; www.api.org search for LNAPL T_n Tool

Direct-Push (DP) based technologies:

Rapid, High-Resolution Assessment

Learning Objectives:

- Apply direct push-based assessment tools to characterize the source three-dimensional extent and hydrogeology

Source: ITRC LNAPL Course (ITRC)

Direct Push: Advantages/Disadvantages

- Revolutionize subsurface sampling and CSM/LCSM development:
  - Quick, flexible, low cost, high-resolution, adaptive screening methods; targeted sampling/monitoring; and produce little or no cuttings
- Two Modes of operation:
  - Cone tip with specialized tools for downhole measurement or sampling (no soil removed)
  - Dual tube arrangement for continuous soil sampling
- Direct-Push-based technologies: LIF, MIP, CPT, EC, Hydraulic profiling, etc.
- Disadvantages: limited depth (up to ~100’), unconsolidated materials

Direct Push: Soil Sampling

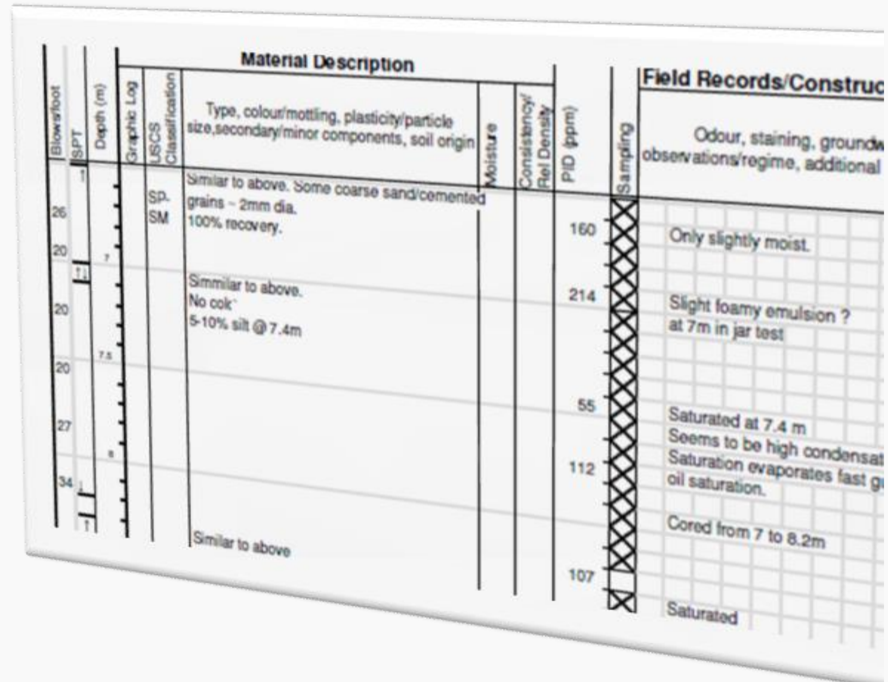
Indicator: Specialized Assessment Tools

Field Screening: PID/FID, Sudan Dye

Indicator: Specialized Assessment

Boring logs to characterize LNAPL source zone geometry

- Lateral and vertical extent
- Lithology, recovery, water content, stain, odor, OVA readings, Sudan dye



- Detailed soil boring logs through the source zone are key
  - Continuous cores

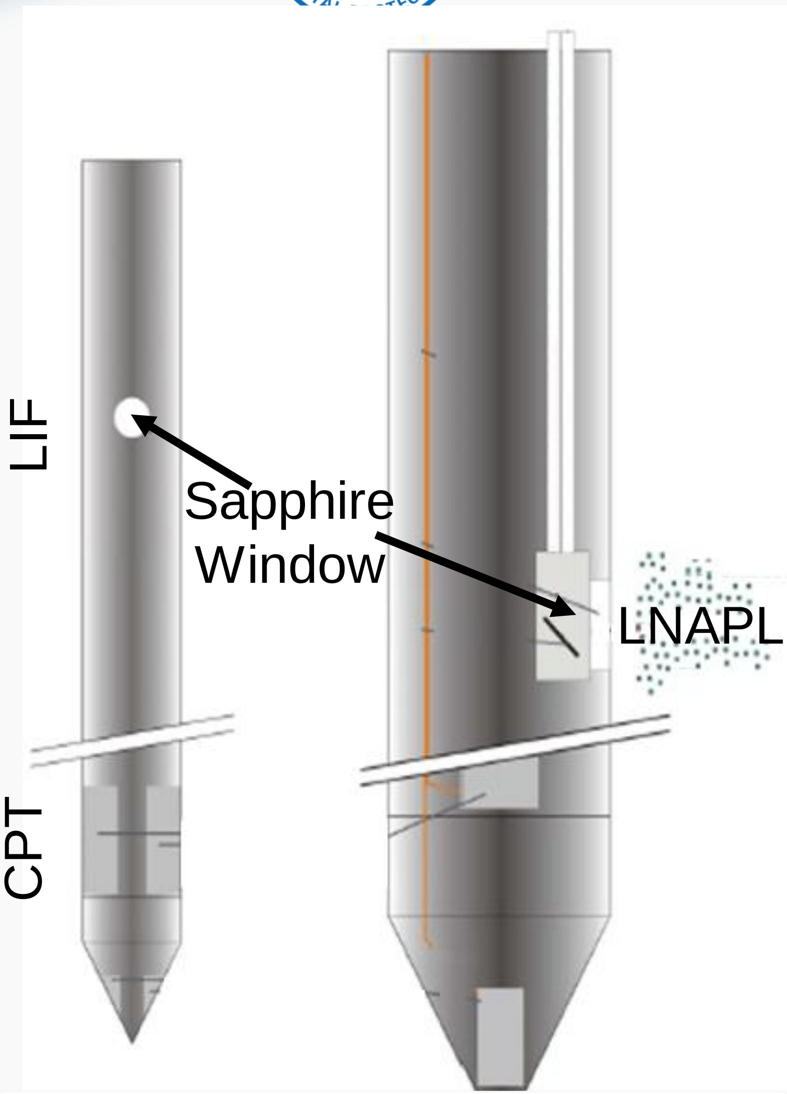
Direct–Push Based: Laser Induced Fluorescence (LIF) –LNAPL detection

- LIF: a method for real-time, in situ field screening of LNAPL
- The technology provides detailed, semiquantitative data
- LIF systems emit UV light that causes the PAHs in LNAPLs to fluoresce
- The intensity of the fluorescence is relative measure of amount of LNAPL present

Direct–Push Based: Laser Induced Fluorescence (LIF) –LNAPL detection

Indicator: Specialized Assessment

- Heavier LNAPLs have higher PAH content ((fluoresces more): #6> diesel>gasoline.
- LIF response inversely related to soil texture: > in sandy soils
- Used in conjunction with geotechnical sensors: Cone Penetrometer, (CPT)/Electrical Conductivity (EC)
  - Soil Texture
- High Vertical resolution: readings 1” apart

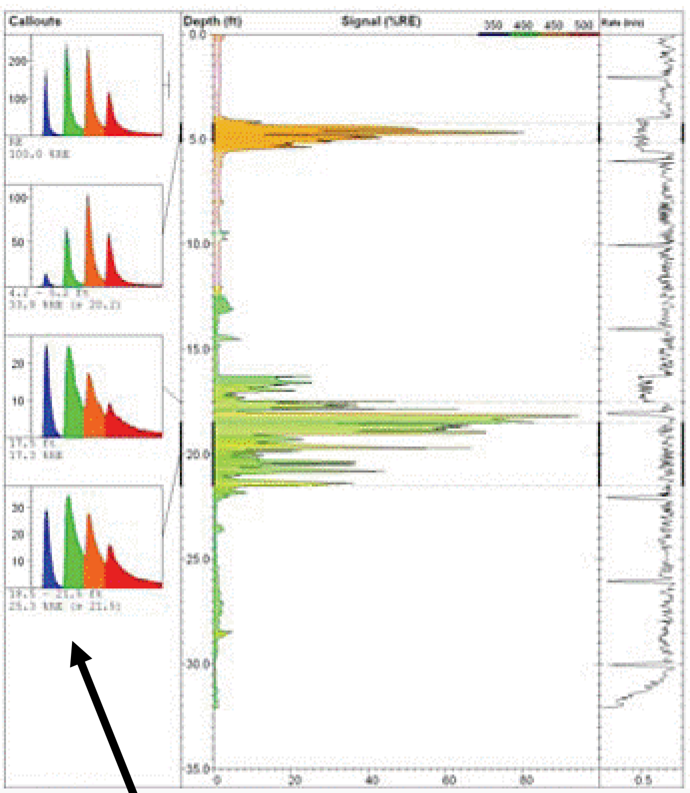


A variety of LIF technology vendors

Images from Fugro Promotional Material

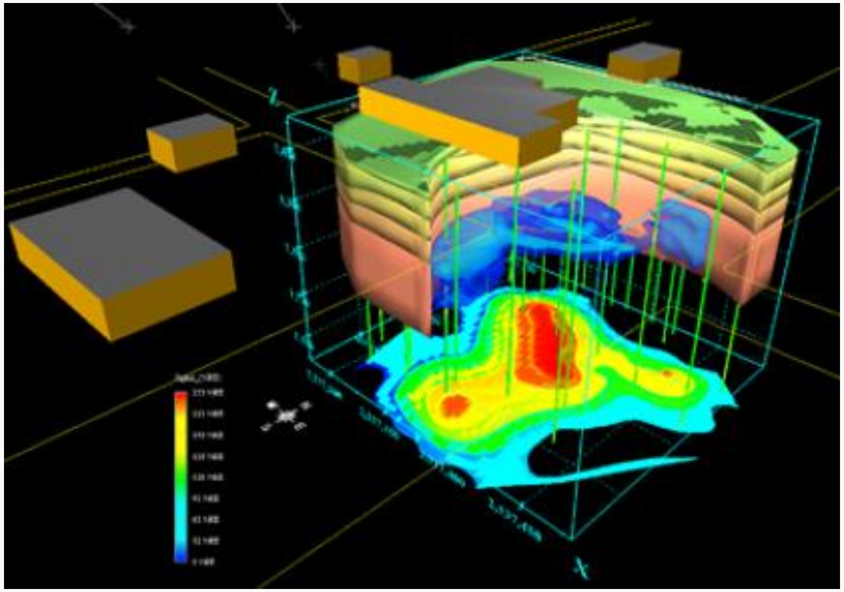
Direct Push: LIF cont'd

Indicator: Specialized Assessment



Waveform Indicates General Fuel Type

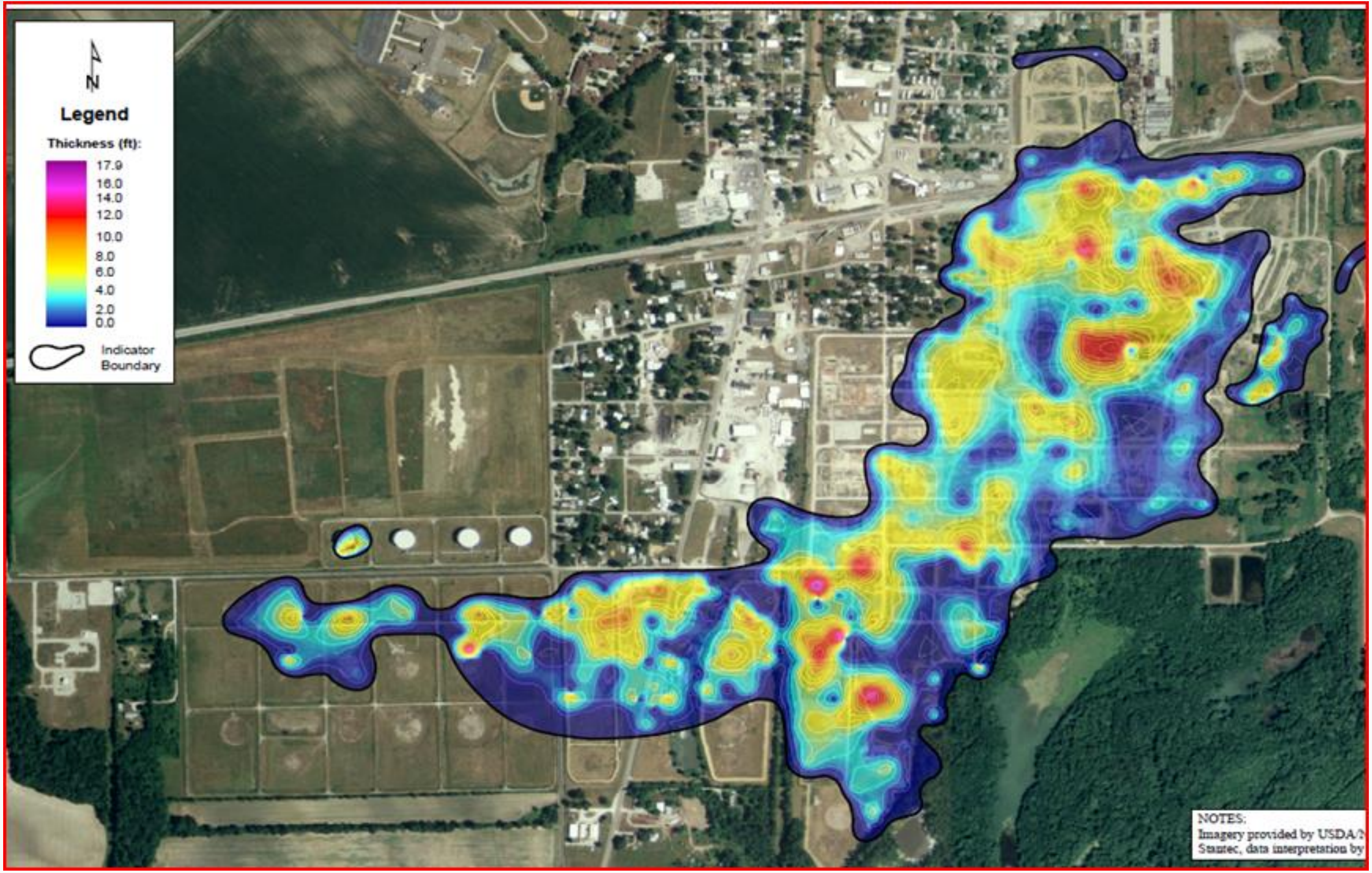
- Different LNAPL products and different soils fluoresce differently
- Typically used in conjunction with Cone Penetrometer Testing (CPT)



(courtesy Dakota Technologies)

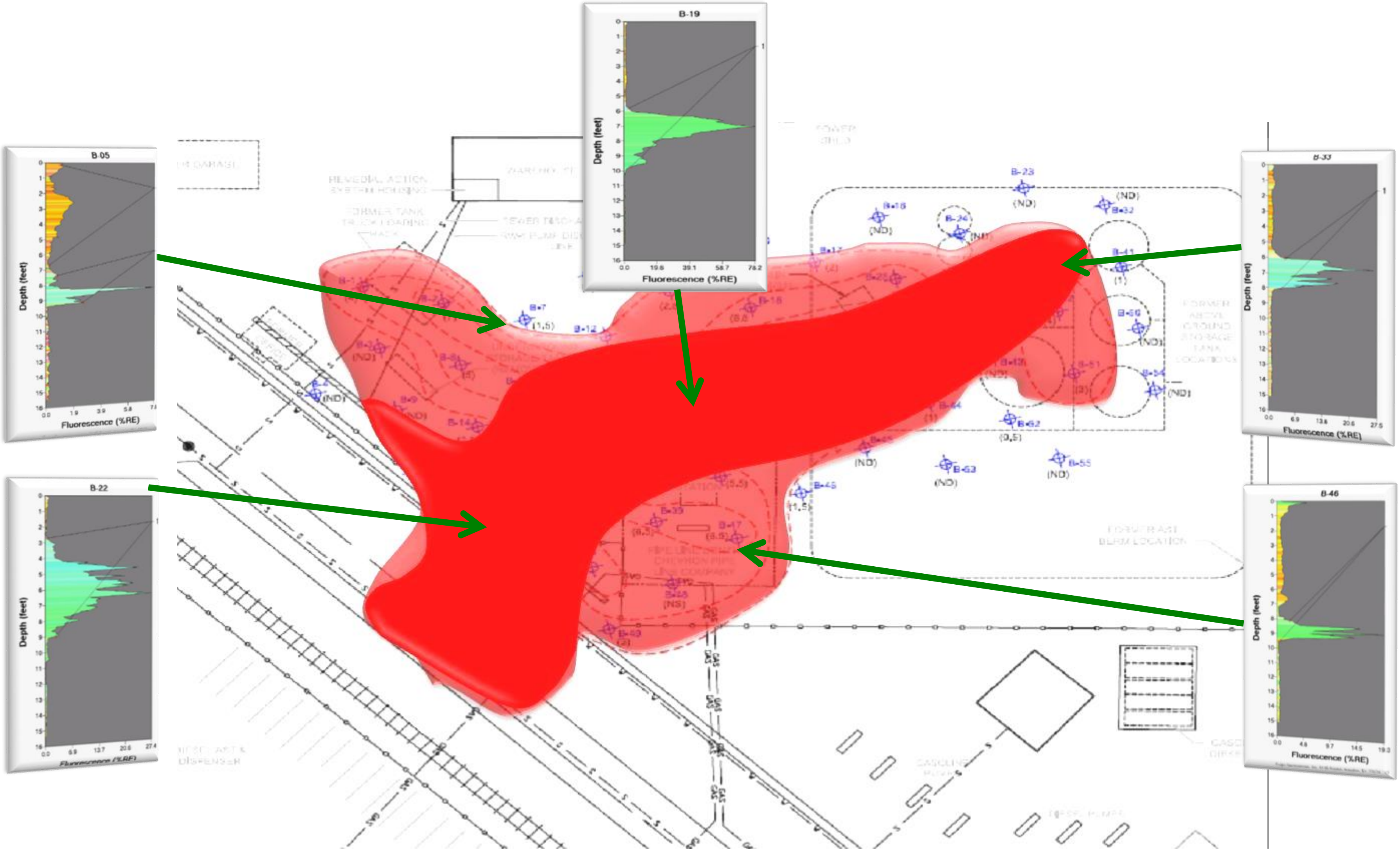
LIF Data: 2-D Visualization (Former Refinery)
Distribution of LNAPL Smear Zone Thickness

Indicator: Specialized Assessment



LNAPL *Lateral* Extent Can Be Greater Than That Inferred from In-Well LNAPL

Indicator: Specialized Assessment



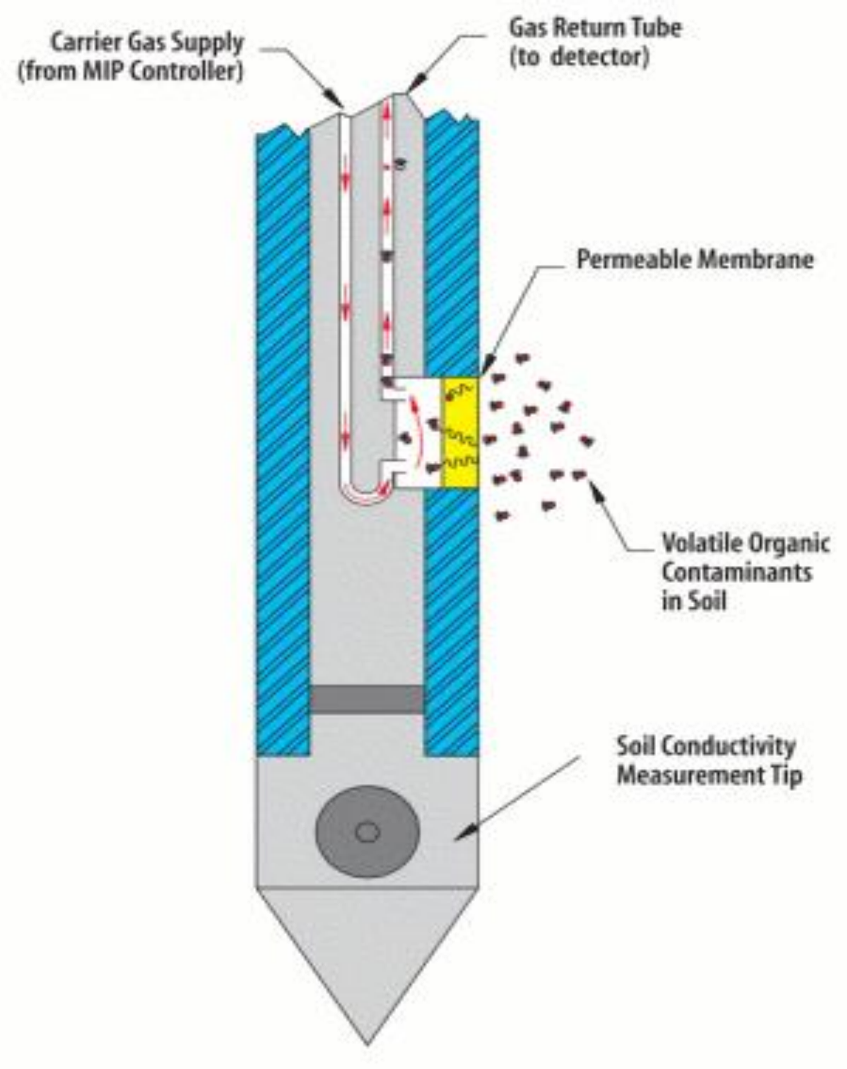
LNAPL observed by LIF

LNAPL observed in MWs

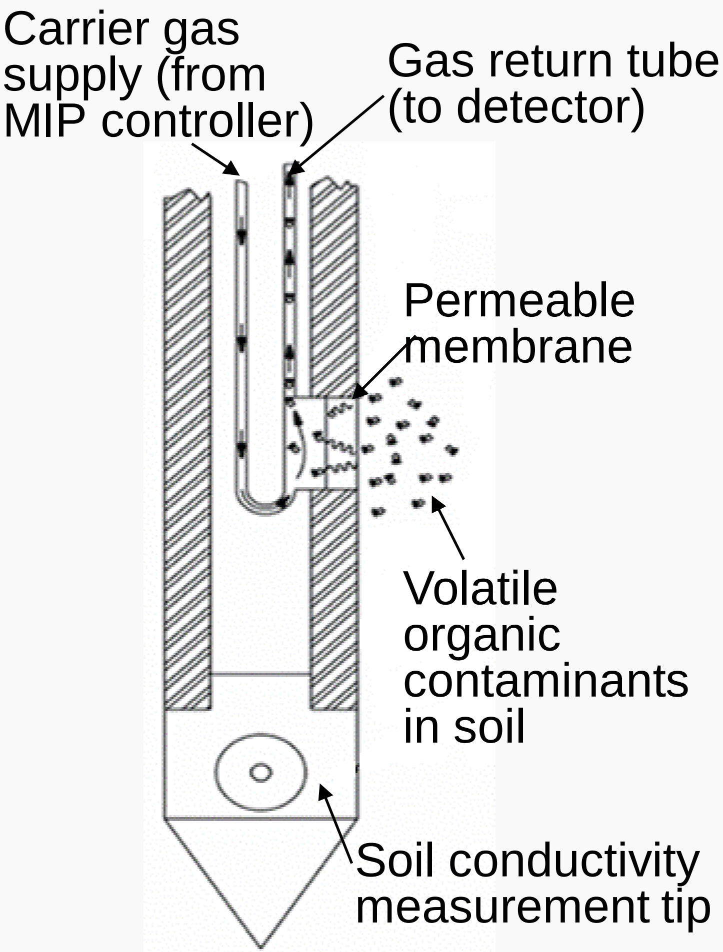
Direct–Push Based: Membrane Interface Probe (MIP)

Indicator: Specialized Assessment

- Semiquantitative measure of total VOCs
  - Heat up soil to 100 to 120 deg C
  - Vapors analyzed by GC detectors: PID, FID, ECD
  - Vapors: soil gas, LNAPL (DNAPL), soil, groundwater
  - Applied simultaneously with geotechnical sensors: CPT/EC



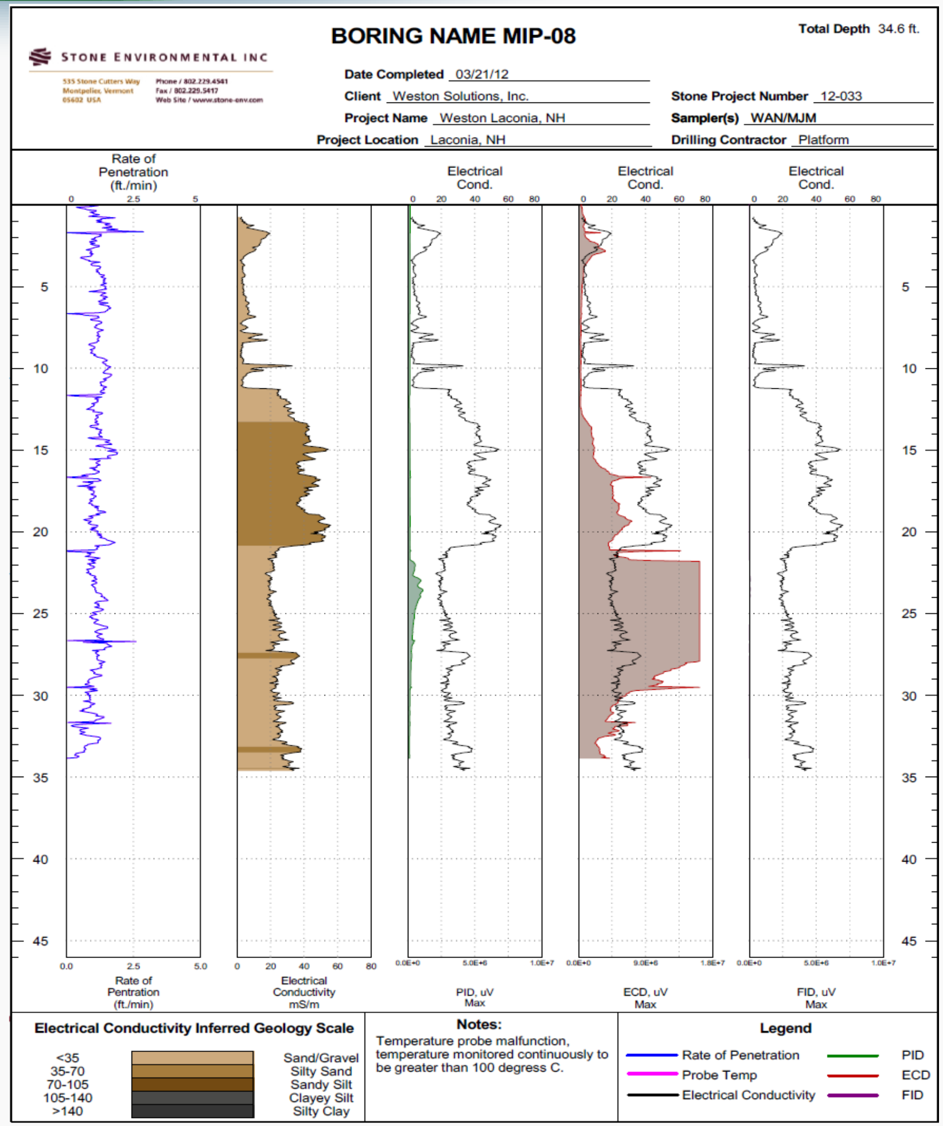
Membrane Interface Probe (MIP)



(image courtesy Geoprobe)

(Photo courtesy Geoprobe)

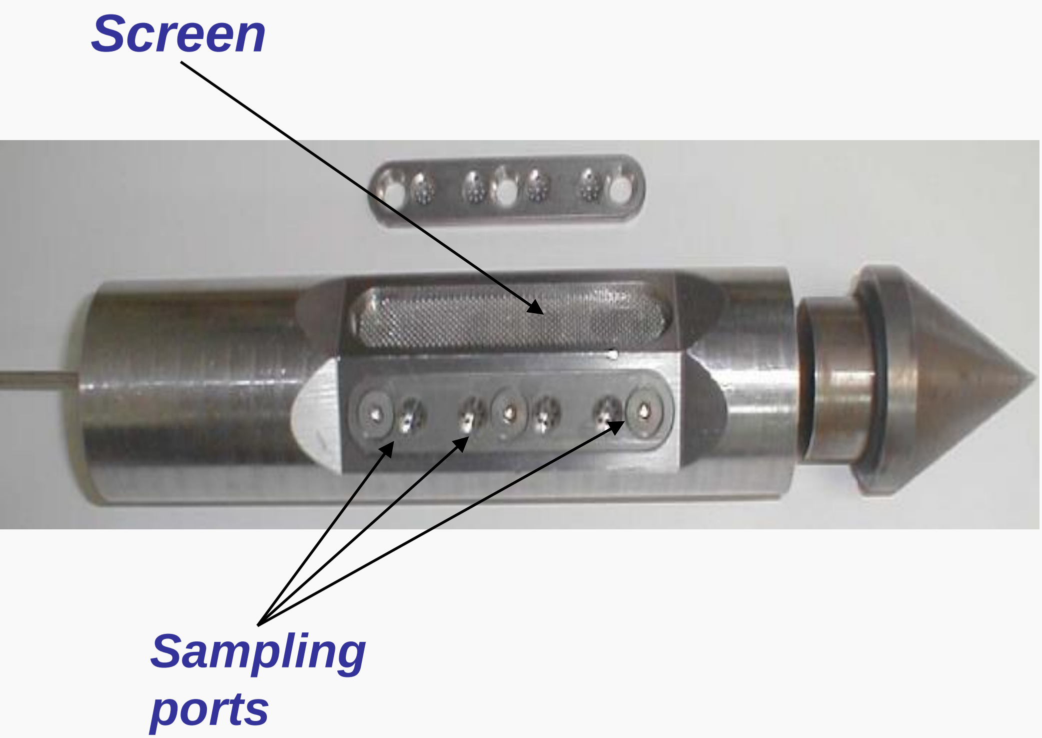
Example MIP Log



Direct–Push Based: Groundwater Profiling (GP)

- In addition to installing groundwater sampling wells (smaller wells with short, discrete screen intervals) direct push can be used for snap-shot, discrete, high-density groundwater profiling
  - Analyze samples for contaminant and water quality parameters
  - Delineate source, and dissolved plume
  - Optimize location and screen placement of permanent monitoring well network
- Disadvantage: samples may be turbid
  - an issue for organics

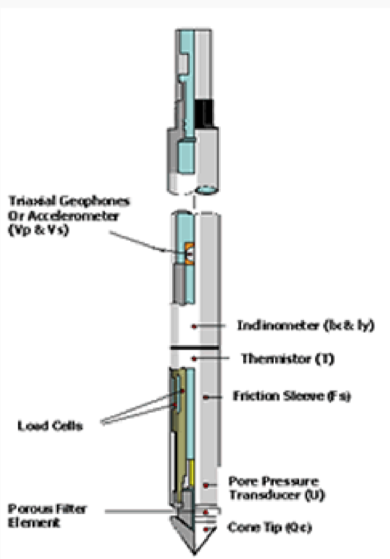
Groundwater Profiling (GP)



Waterloo Advanced Profiling System™ Courtesy Stone Environmental, Inc.

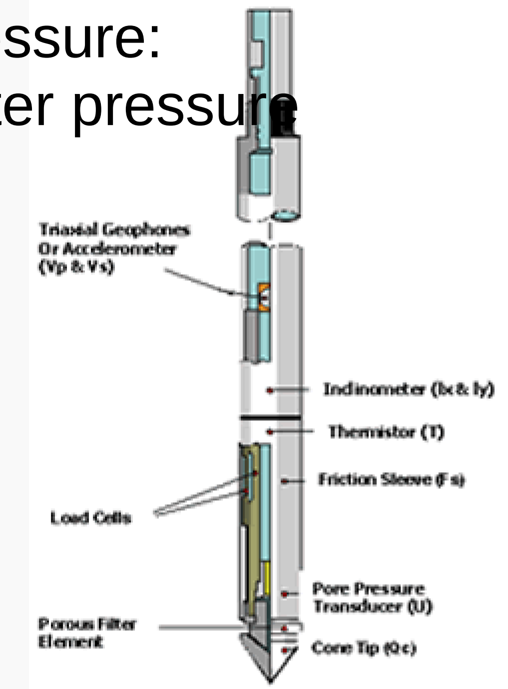
Direct–Push Based: Geotechnical Sensors

- Includes cone penetrometer (CPT) and Electric conductivity (EC) probes
- Measures lithology with depth, depth to groundwater, hydraulic conductivity, temperature, density, etc.

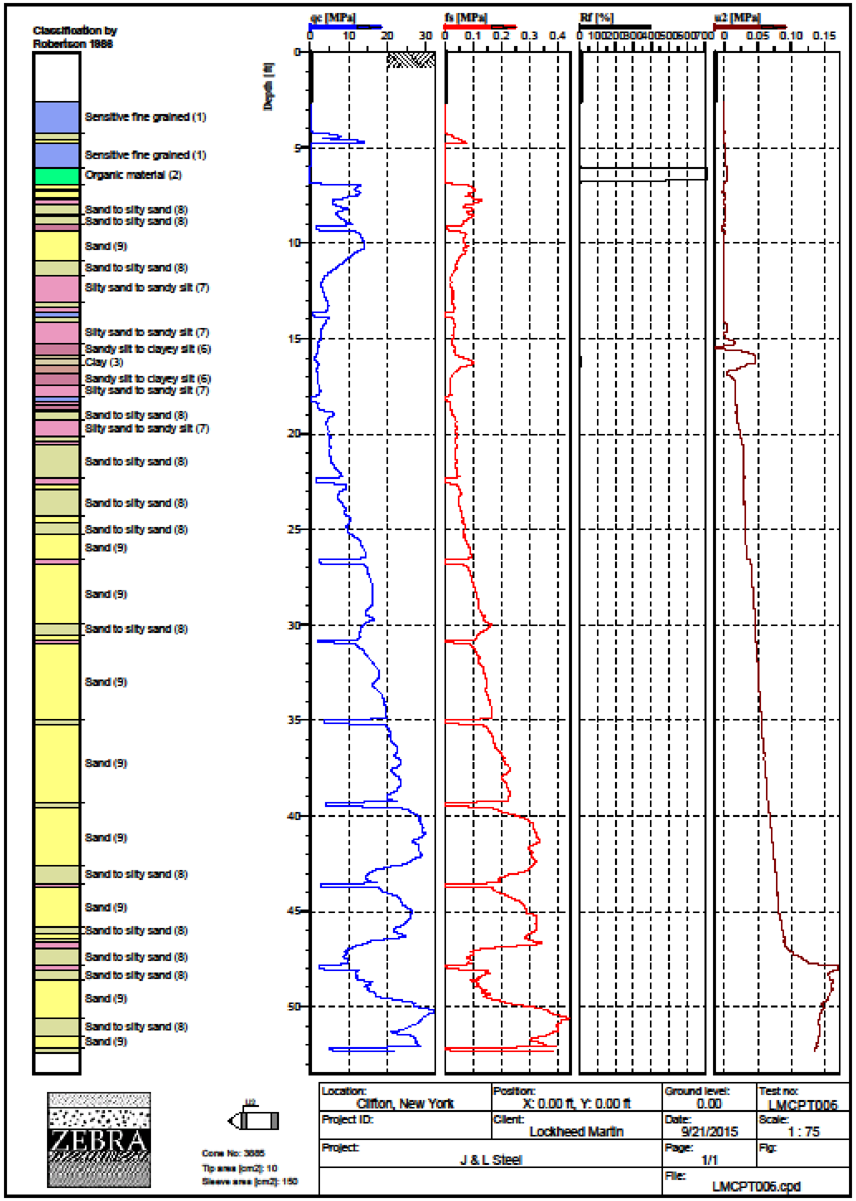


Cone Penetrometer (CPT)

- A number of sensors measurers various resistances along the device within the soil:
  - Cone tip: tip pressure
  - Sleeve: sleeve friction and adhesion
  - Pore pressure: pore water pressure



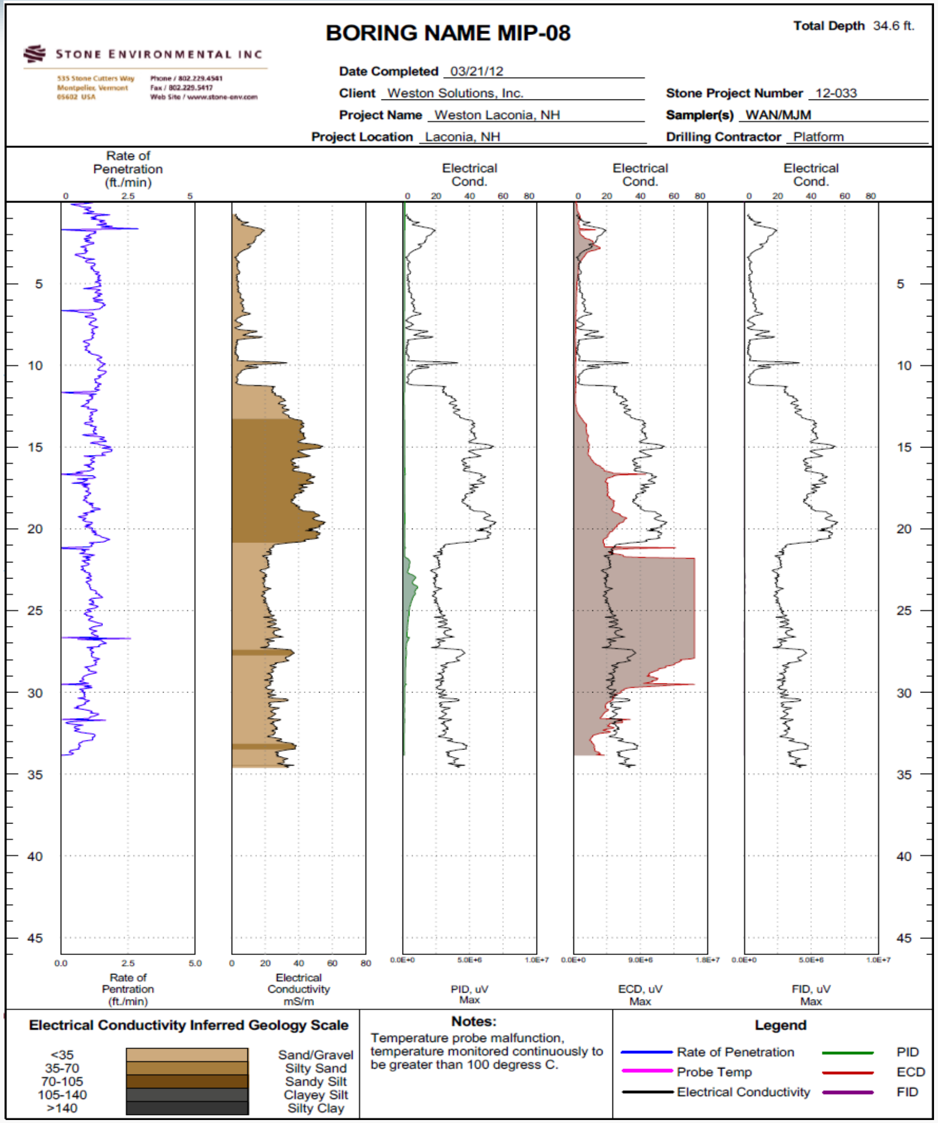
Example: CPT Log



Electrical conductivity(EC) Probe

- A pair of electrodes on the instrument surface passes current through the soil.
- A second pair of electrodes, also on the surface, measures the voltage drop.
- The combination of the current and the voltage drop gives the conductivity of the soil
- Clays tends to be more conductive than sands

Example EC Log



Direct-Push Based: Soil Gas Sampling / Monitoring

Direct Push can also be used for soil gas sampling/monitoring

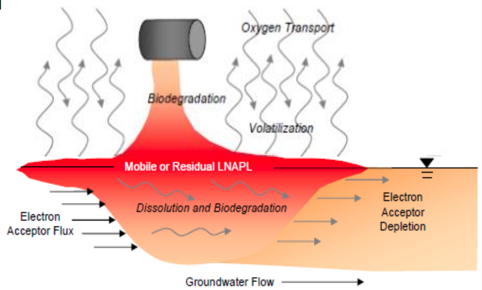
What Did We Learn?

Take Aways

- Transmissivity field measurement
- DP technologies for LCSM development
  - ✓ Quick, flexible, low cost, high-resolution, adaptive screening methods; targeted sampling/monitoring; and produce little or no cuttings
- Technologies: continuous coring, LIF, MIP, GP, and geotechnical sensors (CPT, and EC)
- DP methods for soil gas well installation, monitoring/sampling

Source: ITRC LNAPL Course (ITRC)

LNAPL Concerns, Objectives and Remdiation



LNAPL Concerns

↓

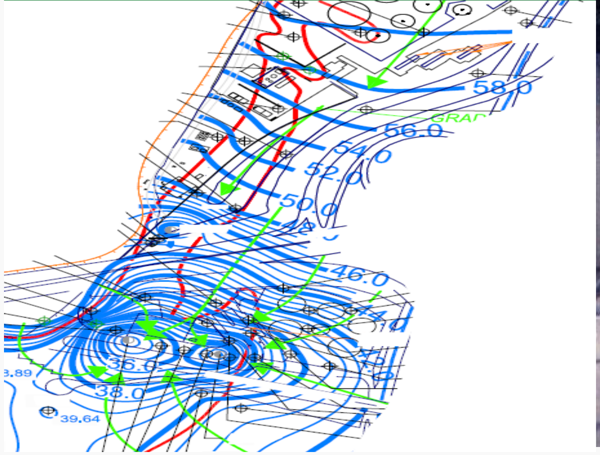
Removal Objectives

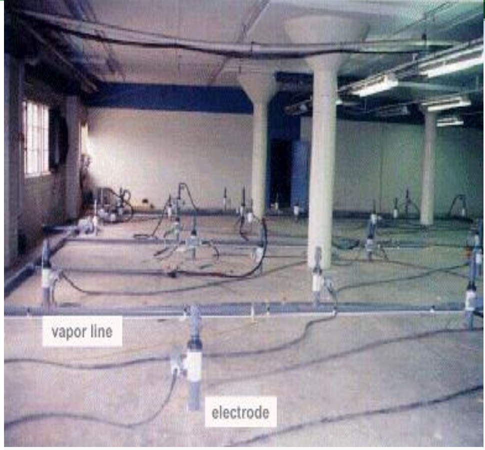
↓

Removal Goals

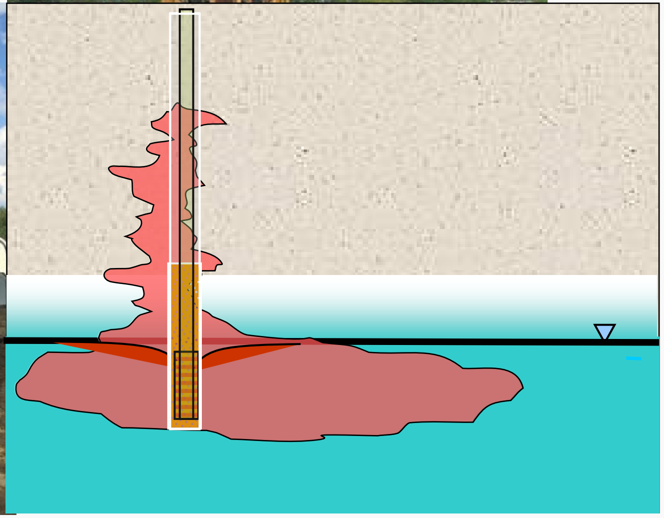
↓

Performance Metrics





LNAPL on

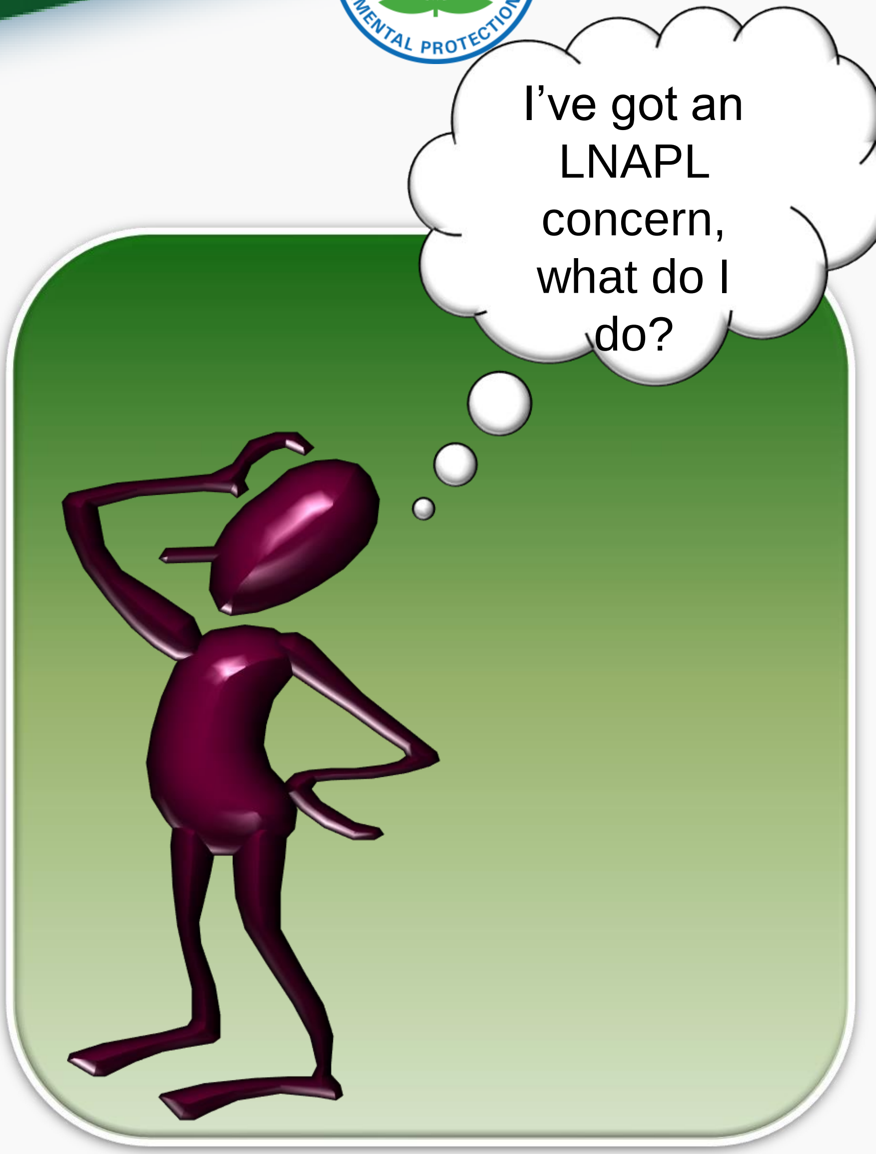


LNAPL Concerns/Risks and the Remedial Process

LNAPL Concerns and the Remedial Process

earning Objective:

Discuss the interrelations between LNAPL concerns, remedial objectives and how they drives remediation



Source: ITRC LNAPL Course (ITRC)

Drivers of LNAPL Remediation

LNAPL Concerns

↓

Removal Objectives

↓

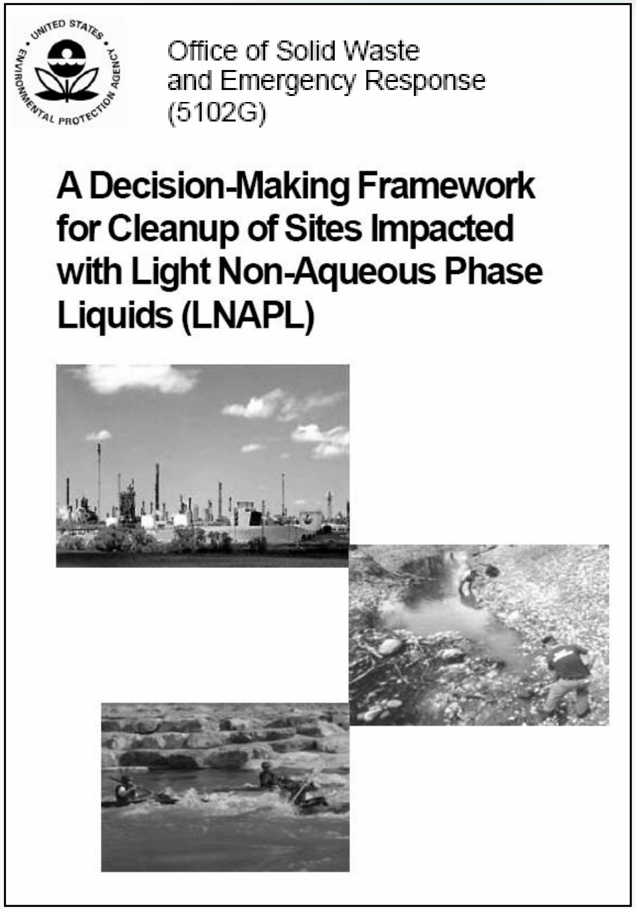
Removal Goals

↓

Performance Metrics

Source: ITRC LNAPL Course (ITRC)

EPA LNAPL Management Framework


Office of Solid Waste
and Emergency Response
(5102G)

A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (LNAPL)

EPA 542-R-04-011
March 2005

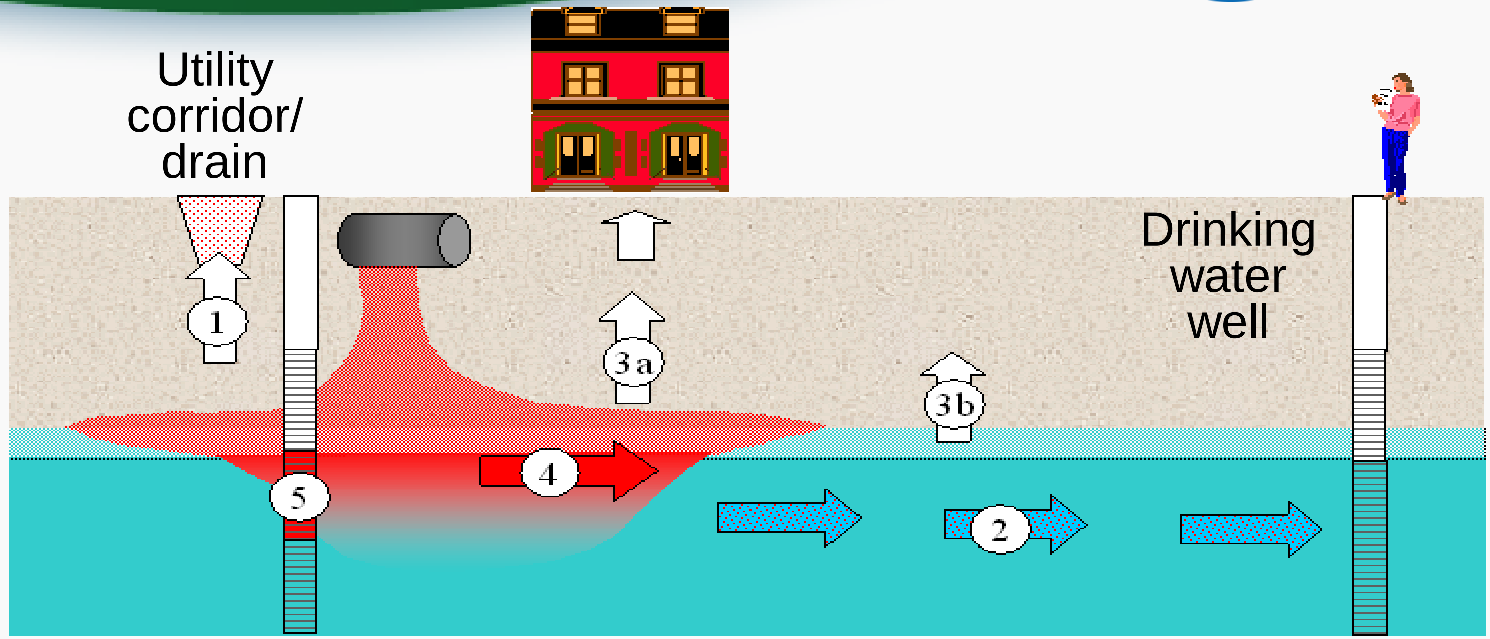
EPA LNAPL Management

- Review and revise LNAPL conceptual site model
- Develop a long-term vision and establish LNAPL goals
- Implement and monitor performance
- Evaluate progress

Source: ITRC LNAPL Course (ITRC)

LNAPL Concerns:
Saturation or Composition?

LNAPL Concerns



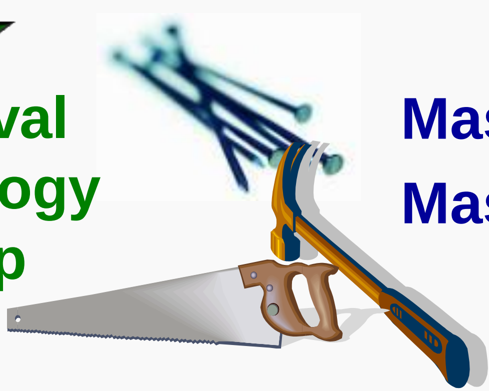
LNAPL Emergency Concerns	LNAPL Composition Concerns	LNAPL Saturation Concerns
(1) Fire (liquid) and/or explosive (vapors) hazards in subsurface utilities or basements. Direct liquid LNAPL migration to subsurface utilities or basements. Direct liquid LNAPL migration to surface water.	(2) Groundwater contaminated with TPH & BTEX. (3a) TPH & BTEX vapor intrusion from LNAPL body. (3b) TPH & BTEX in groundwater to soil gas.	(4) LNAPL migration off site. (5) LNAPL in a monitor well.

Source: ITRC LNAPL Course (ITRC)

Choose Removal Objectives based on your LNAPL Concerns

LNAPL Concerns

LNAPL Concern	LNAPL Saturation Concern	LNAPL Composition Concern
↓	↓	↓
LNAPL Removal Objective	Saturation Removal Objective	Composition Removal Objective
↓	↓	↓
Removal Technology Group	Mass Recovery Mass Control	Phase Change



Key Point: Select the right tool for the job!

Source: ITRC LNAPL Course (ITRC)

Saturation vs. Composition Objectives

Saturation and Composition

- Remove LNAPL mass
- Control LNAPL migration

LNAPL Saturation Objectives

- Reduce local concentrations
- Reduce toxicity
- Reduce constituent mass flux

LNAPL Composition Objectives

Contaminants in the Subsurface:
Source Zone Assessment and Remediation
National Research Council (2004)

Source: ITRC LNAPL Course (ITRC)

Match your LNAPL Concerns to Removal Objectives, Goals, and Performance Metrics

LNAPL Concerns

- <u>LNAPL Concern:</u>
  - What are your concerns?
- <u>LNAPL Removal Objective:</u>
  - Eliminate LNAPL concerns.
- <u>LNAPL Removal Goal:</u>
  - A measurable LNAPL remedial technology-specific endpoint selected to attain an LNAPL remedial objective
- <u>Performance Metric(s):</u>
  - Data that demonstrates progress towards remediation goal

Source: ITRC LNAPL Course (ITRC)

Examples of LNAPL Concerns

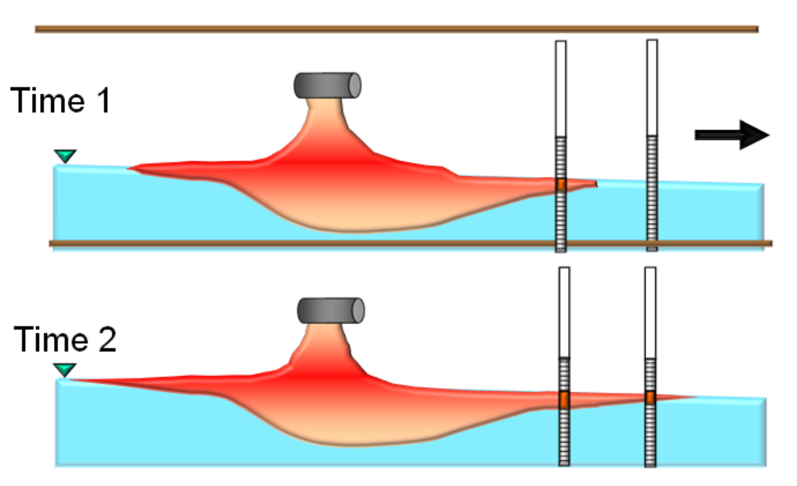
- Terminate LNAPL migration
- Reduce LNAPL saturation to the maximum extent practicable (MEP)
  - Above residual range
  - Within residual range
- Abate concentrations of concern
  - Groundwater
  - Soil vapor
- Abate aesthetic concern
  - LNAPL
  - Odor

Source: ITRC LNAPL Course (ITRC)

LNAPL Saturation Concern

LNAPL Concerns

- **LNAPL Saturation Concern:**
  - LNAPL migrating off site
- **LNAPL Removal Objective:**
  - Stop LNAPL migration
- **LNAPL Removal Goal:**
  - Remove sufficient LNAPL to reduce LNAPL saturation and LNAPL head
- **Performance Metric:**
  - LNAPL saturation: reduce satuarions on the leading edge of LNAPL body to preclude off-site migration



Source: ITRC LNAPL Course (ITRC)

LNAPL Composition Concern

- **<u>LNAPL Concern:</u>**
  - LNAPL is the source of a dissolved BTEX plume migrating off site
- **<u>LNAPL Removal Objective:</u>**
  - Remove BTEX from the LNAPL body
- **<u>LNAPL Removal Goal:</u>**
  - Selective strips volatile constituents (BTEX) from the LNAPL body using appropriate technology
- **<u>Performance Metric:</u>**
  - Reduce BTEX dissolved concentration below regulatory limit

Source: ITRC LNAPL Course (ITRC)

LNAPL Management Strategy

LNAPL Assessment/LCSM

What do you have?

Identify LNAPL Concerns and Set LNAPL Removal Objectives

What needs to be done?

Select Removal Technology to Achieve Remedial Objectives

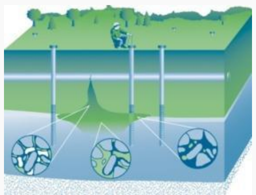
Install Removal Technology and Monitor Performance

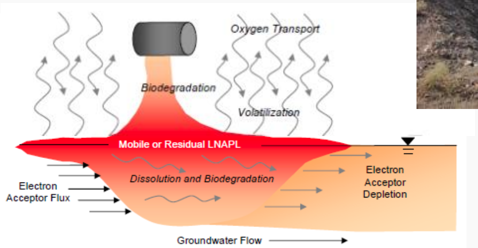
How to do it?

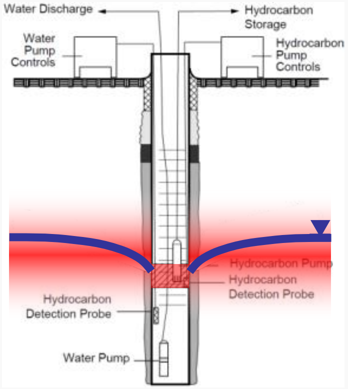
Source: ITRC LNAPL Course (ITRC)

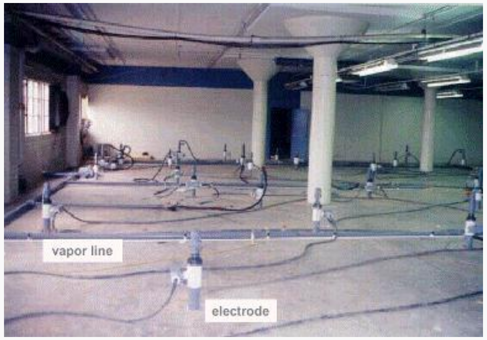
LNAPL Remediation: Technology Grouping

- Discuss why LNAPL Remediation Technologies are Group and relate the groups to clean-up objectives









Source: ITRC LNAPL Course (ITRC)

LNAPL Recovery Technology Groups

- **Learning Objective:** Understand:
  - What are technology groups,
  - Why they've been grouped, and
  - How site objectives influence the selection of a technology group

Source: ITRC LNAPL Course (ITRC)

Many Technologies Available

17 LNAPL technologies addressed

Technology Groups

Excavation

Physical containment Technologies

In-situ soil mixing

Air sparging/soil vapor extraction (AS/SVE)

LNAPL skimming

Bioslurping/EFR

Dual pump liquid extraction

Multi-phase extraction, dual pump

Multi-phase extraction, single pump

Recovery trench/Interceptor trench

Water/hot water flooding

- In situ chemical oxidation
- Radio frequency heating
- Three and six-phase electrical resistance heating
- Natural source zone depletion (NSZD)???
- Surfactant- enhanced subsurface remediation
- Cosolvent flushing
- Steam/hot-air injection

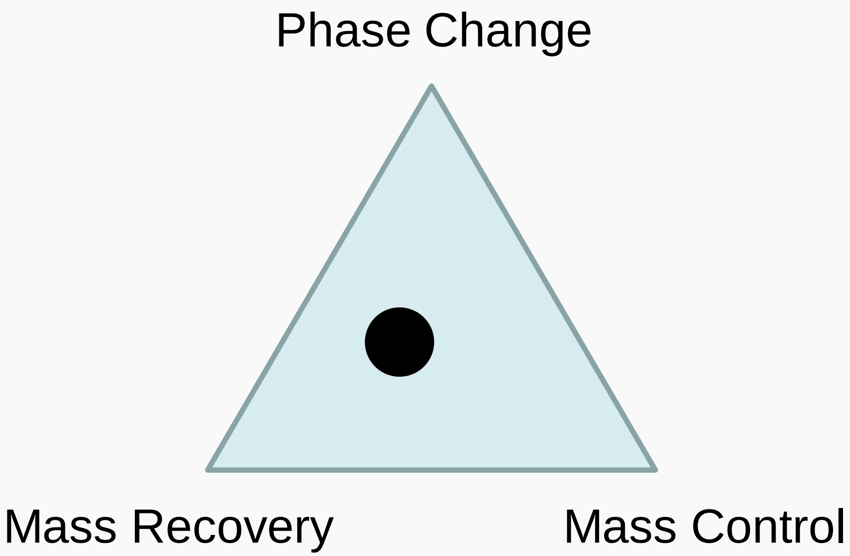
Key Point: Who ya gonna call?

Source: ITRC LNAPL Course (ITRC)

Technology Groups

Technology Groups

- Mass Control
- Mass Recovery
- Phase Change



Key Point: Simplify the selection of technology

Source: ITRC LNAPL Course (ITRC)

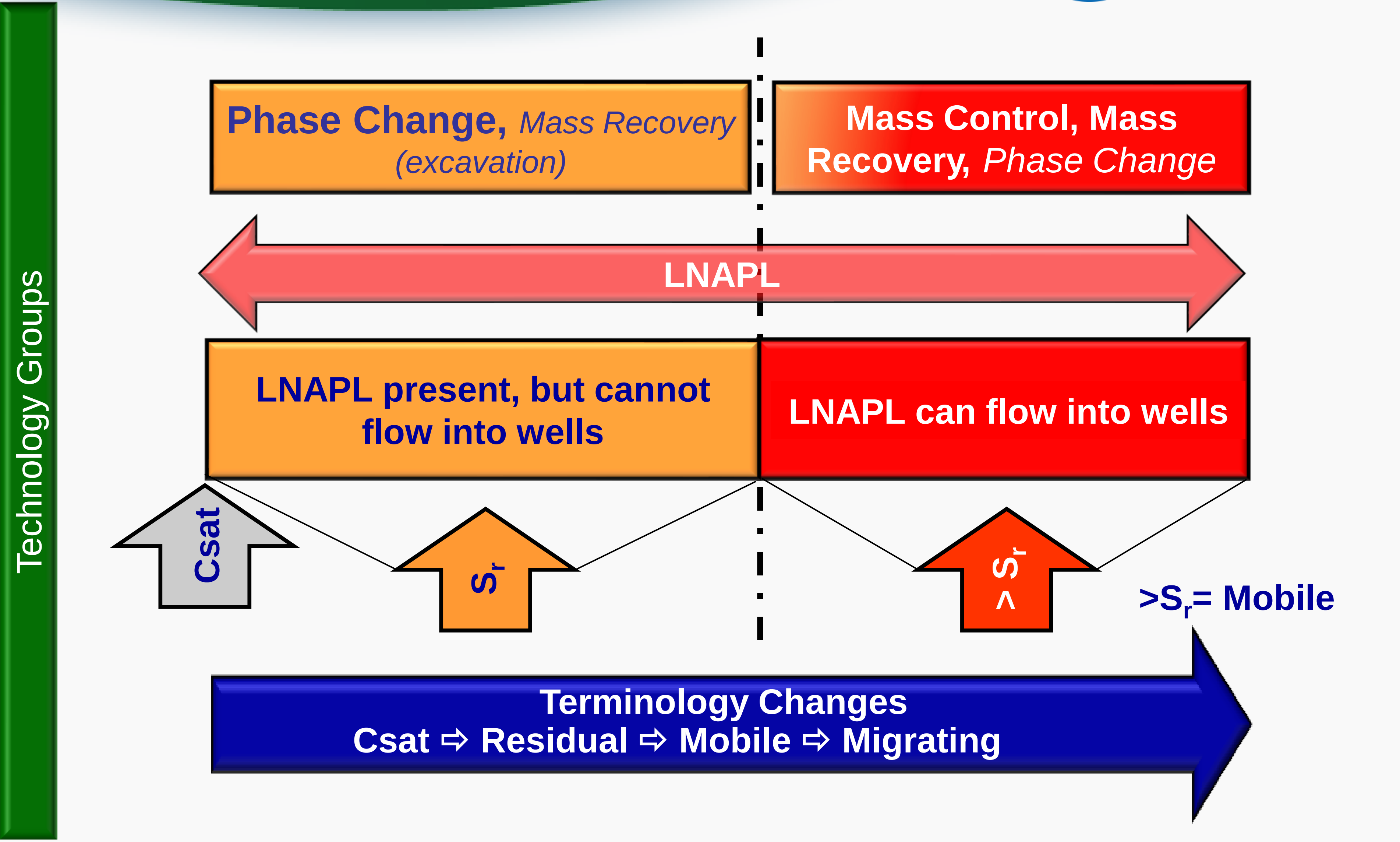
Linkage Between Removal Objectives and Technology Groups

Technology Groups

- "Containment objective" – LNAPL mass control
  - ***Stop*** LNAPL migration by containing LNAPL
- "Saturation objective" – LNAPL mass recovery
  - ***Reduce*** LNAPL saturation by recovering LNAPL
- "Composition objective" – LNAPL phase change
  - ***Change*** LNAPL characteristics by phase change

Source: ITRC LNAPL Course (ITRC)

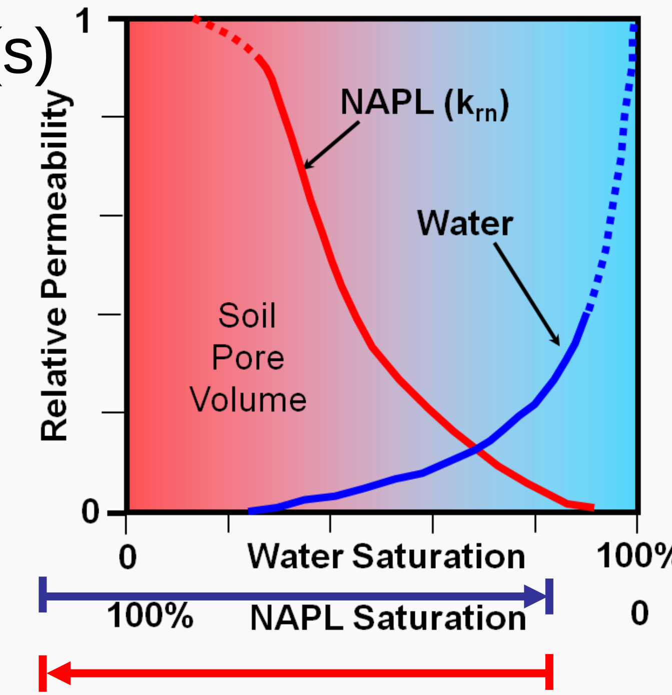
The Name Game & General Technology Group Applicability



Source: ITRC LNAPL Course (ITRC)

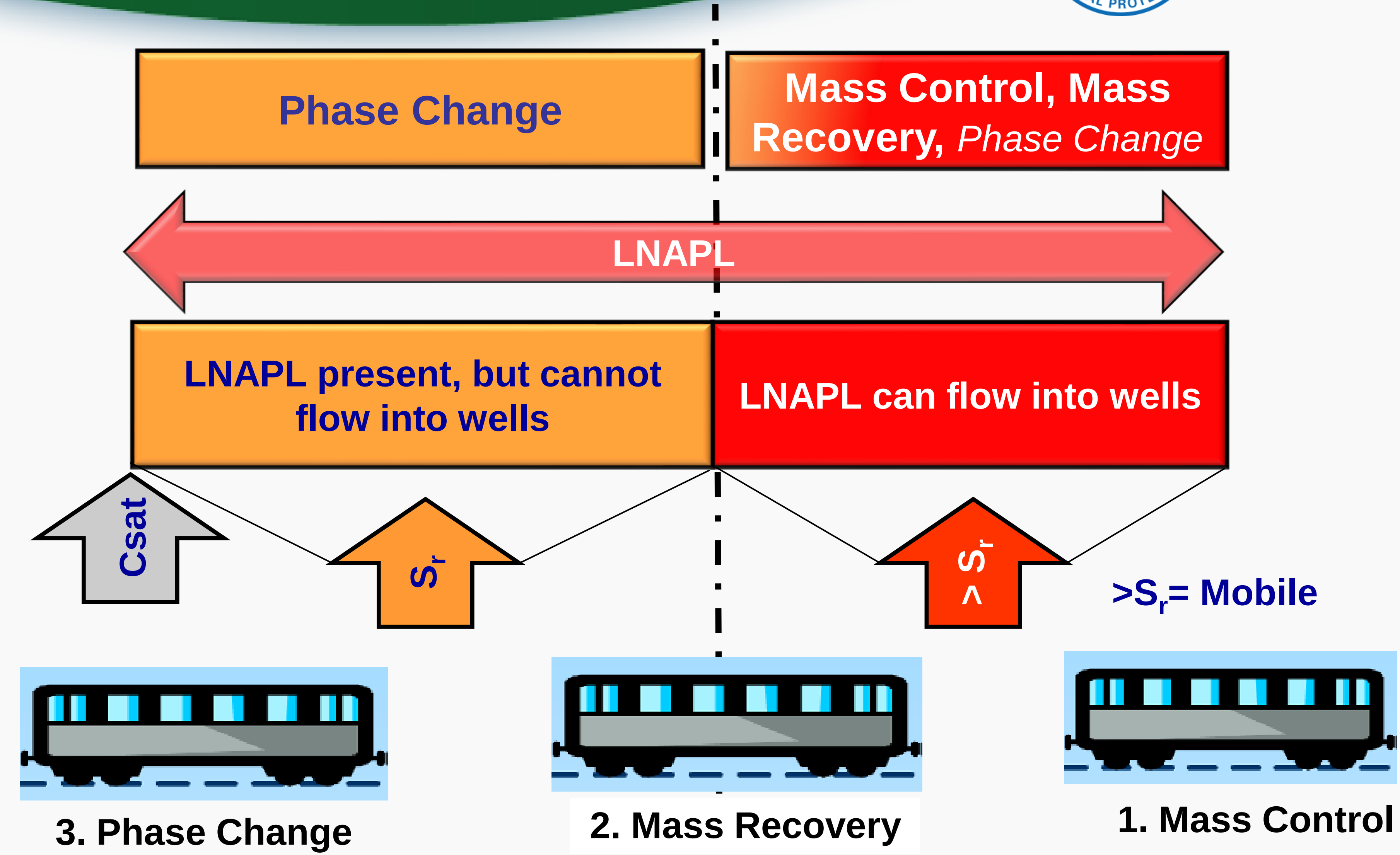
Choosing a Removal Technology

- The whole process is driven by your LCSM,
  - You know if the LNAPL is migrating
  - You know what is recoverable (hydraulically)
  - You know what LNAPL composition fraction to target
  - You have defined your objective(s) based on your concerns
- What physical property will a technology manipulate?
  - Migration potential (saturation)
  - Mobile LNAPL (saturation)
  - Composition



Source: ITRC LNAPL Course (ITRC)

Sequenced Technology Deployment - “Treatment Train”



Source: ITRC LNAPL Course (ITRC)

Treatment Train

Good

- Based on a sound/robust LCSM
- When planned with goals & metrics for transition
- Orderly implementation

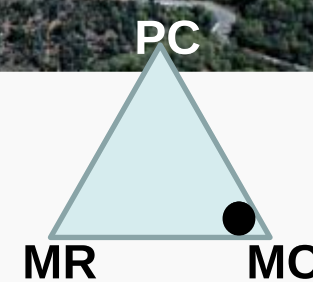
Bad

- Based on unsound LCSM
- Unplanned, lacking specific goals and metrics for transition
- “Throwing” more technologies at the problem

Source: ITRC LNAPL Course (ITRC)

Dam the LNAPL!

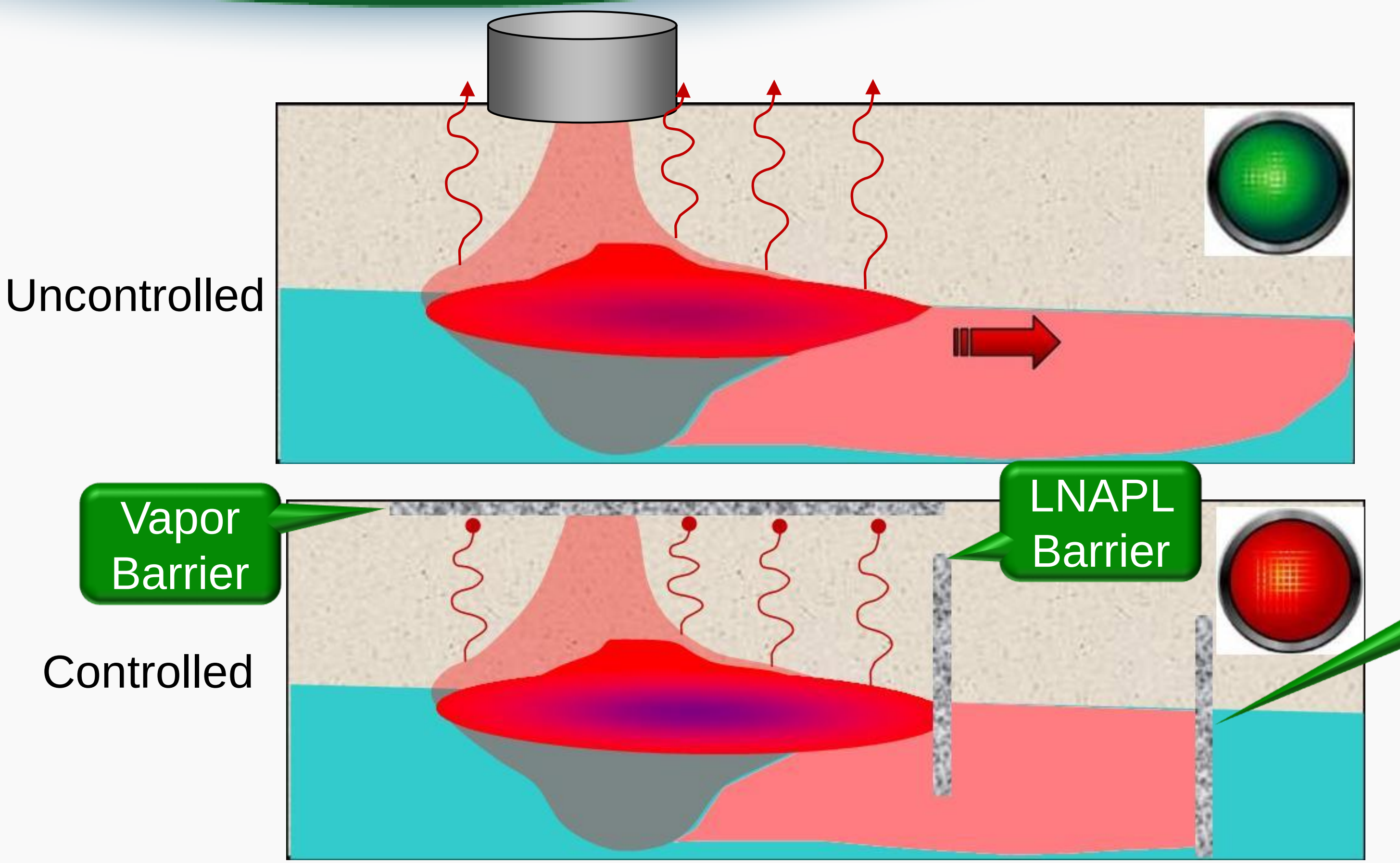
LNAPL Mass Control Concept

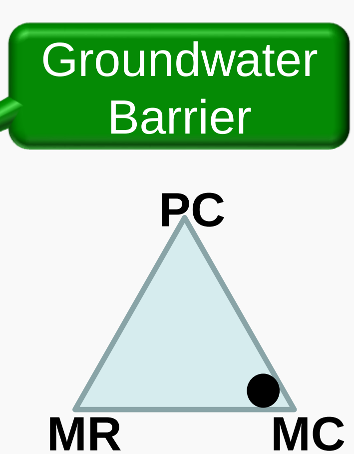


Source: ITRC LNAPL Course (ITRC)

Think Barriers

LNAPL Mass Control Concept





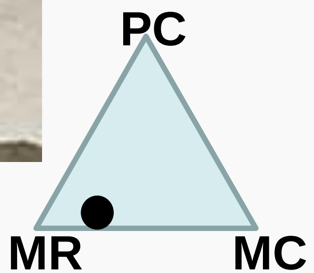
Key Point: Mass control technologies block LNAPL migration in soil/groundwater and/or surface discharge

Source: ITRC LNAPL Course (ITRC)

LNAPL Mass Recovery

LNAPL Mass Recovery Concept

Think removal as bulk liquid…



Source: ITRC LNAPL Course (ITRC)

Saturation Objective

LNAPL Mass Recovery Concept

LNAPL Concern	LNAPL Remedial Objective	Remediation Goals
Migration or Mobility	Saturation Objective	• Reduce LNAPL Mobility • Recover LNAPL to Maximum Extent Practicable

Key Point: Reduce mobility and potential for migration by reducing LNAPL saturation through mass recovery

Source: ITRC LNAPL Course (ITRC)

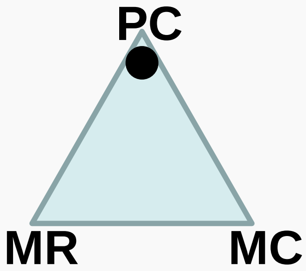
LNAPL Saturation

- Reduce LNAPL saturation by bulk LNAPL mass removal via fluid flow recovery or excavation
- LNAPL fluid factors to manipulate:
  - LNAPL gradient (*remember Darcy's Law**) – skimming, dual pump liquid extraction, water flood, vacuum enhanced fluid recovery
  - LNAPL viscosity (*remember LNAPL conductivity**) – heating, hot water flood
  - Interfacial tension (*remember capillary pressure**) – surfactant/cosolvent flushing

Source: ITRC LNAPL Course (ITRC)

LNAPL Phase Change

LNAPL Phase Change



Source: ITRC LNAPL Course (ITRC)

Composition Objective

LNAPL Phase Change

LNAPL Concern	LNAPL Remedial Objective	Remediation Goals
Risk via Vapors or Dissolved Plume	**Composition Objective**	• **Deplete volatile (vapor pressure) or soluble constituents in LNAPL (Raoult's Law)**

Key Point: Reduce soil vapor or groundwater risk by removing risk-driving constituent(s) from LNAPL

Source: ITRC LNAPL Course (ITRC)

LNAPL Composition Objective

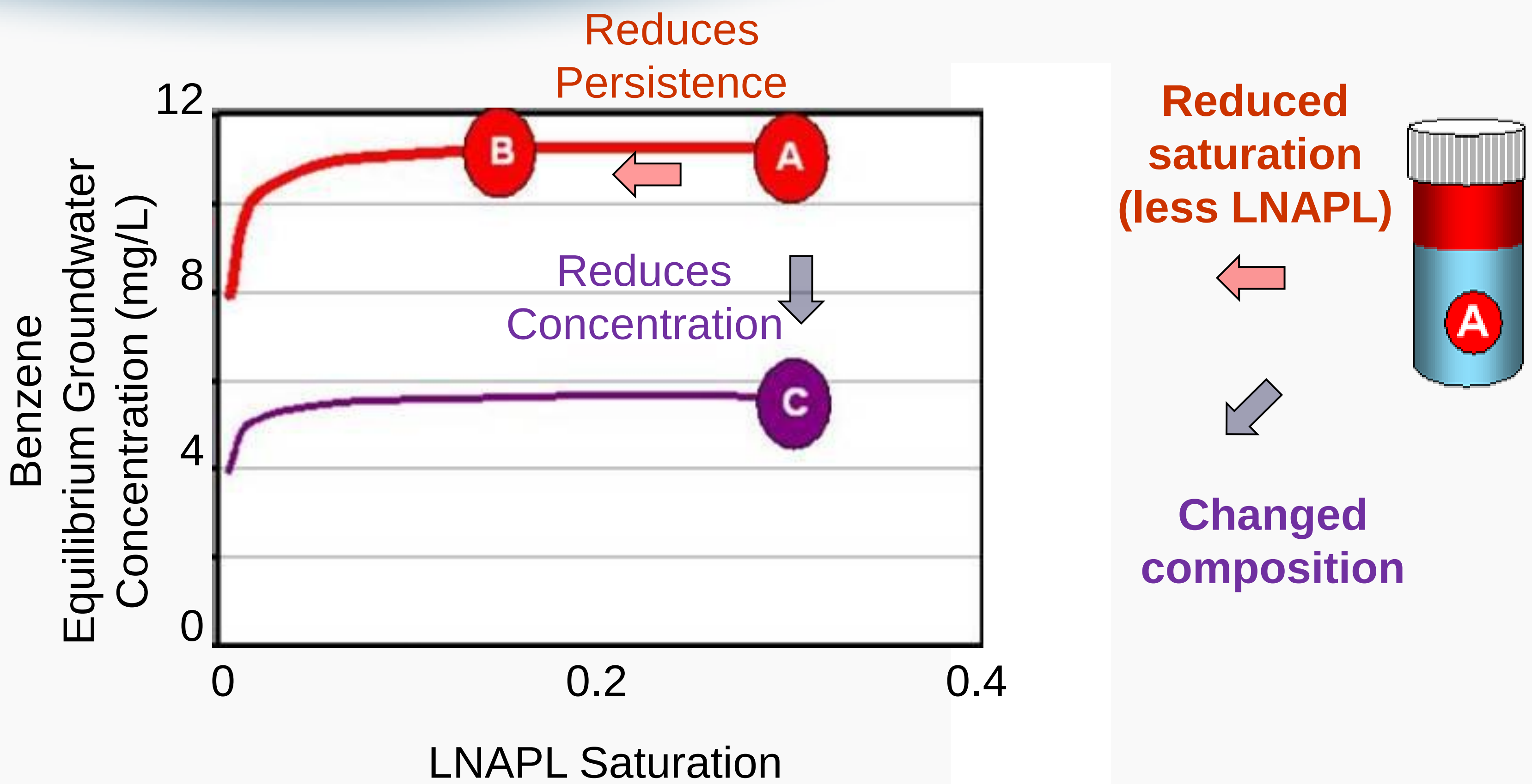
LNAPL Phase Change

- Modified by increasing rates of volatilization and dissolution from LNAPL body – phase change from LNAPL to vapor phase or LNAPL to dissolved phase
- Example technologies
  - Soil vapor extraction, or in combination:
    - Air sparging
    - Heating
    - Steam injection
  - Enhanced aerobic biodegradation
  - Enhanced anaerobic biodegradation
  - In-situ chemical oxidation

Source: ITRC LNAPL Course (ITRC)

Contrast Between Composition And Saturation Objectives

Saturation vs Composition

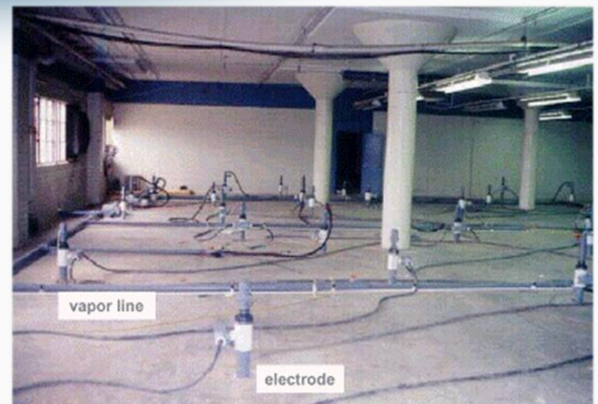


Key Point: Abatement of dissolved or vapor concentration is dependent on change in composition (mole fraction) and not saturation (unless almost all LNAPL is removed)

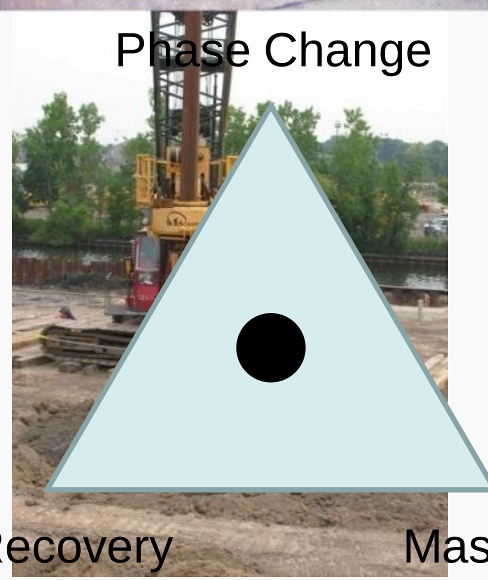
Source: ITRC LNAPL Course (ITRC)

Technology Grouping Overlap

Remediation Technology Group

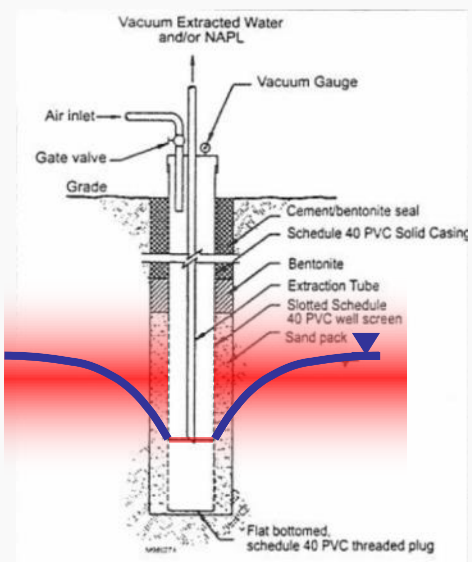


Phase Change



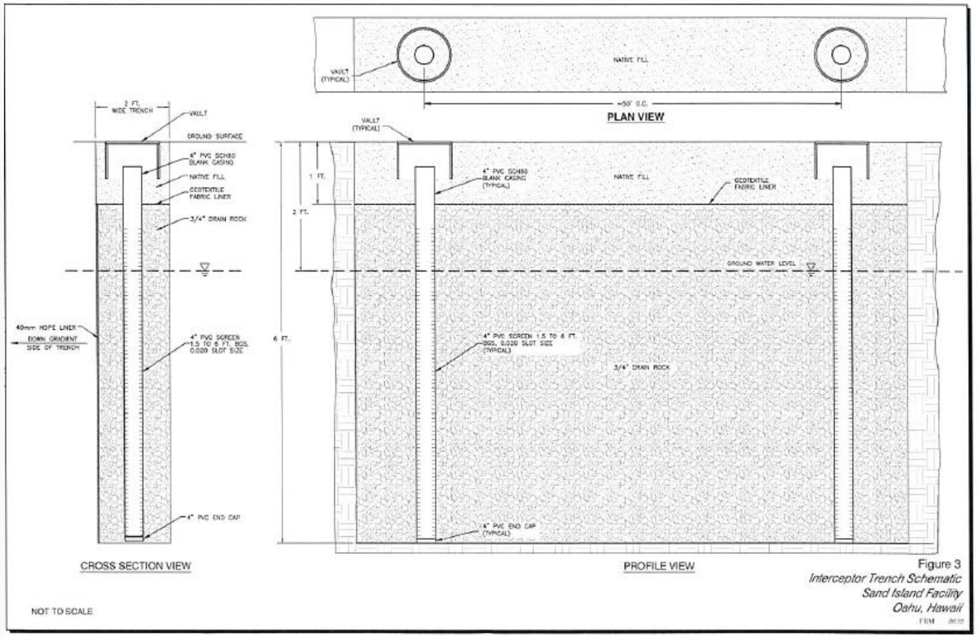
Mass Recovery

Mass Control



Source: ITRC LNAPL Course (ITRC)

LNAPL Mass Control Technologies



- **Mass Control**
- **Mass Recovery**
- **Phase Change**

Source: ITRC LNAPL Course (ITRC)

LNAPL Mass Control

Learning Objectives:

- Understand the differences between individual mass control technologies and how to measure (demonstrate) their success

Source: ITRC LNAPL Course (ITRC)

Mass Control Technologies

LNAPL Mass Control

- Physical containment
- Hydraulic containment
- Solification/stabilization

Source: ITRC LNAPL Course (ITRC)

Physical Containment

LNAPL Mass Control

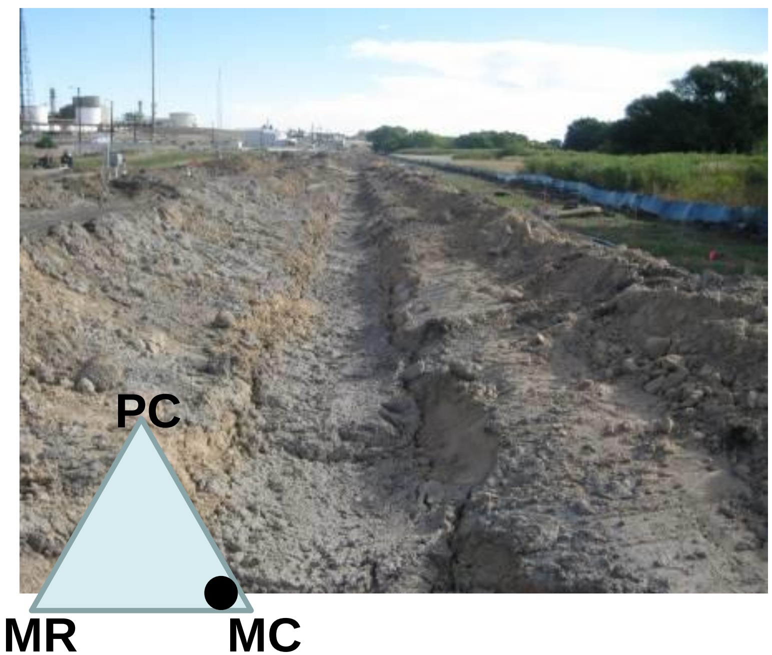
- Barrier wall; Vapor barrier/cap

Advantages

- Short time frame to implement

Disadvantages

- Long time frame to maintain
- Large carbon footprint (wall)



- Design Considerations
  - Grain size distribution
  - Depth below grade, access
  - Depth to water table and zone of fluctuation
  - Keyed or hanging: integrity of keyed material
  - compatibility of subsurface with slurry

Physical Containment: Interceptor Trench

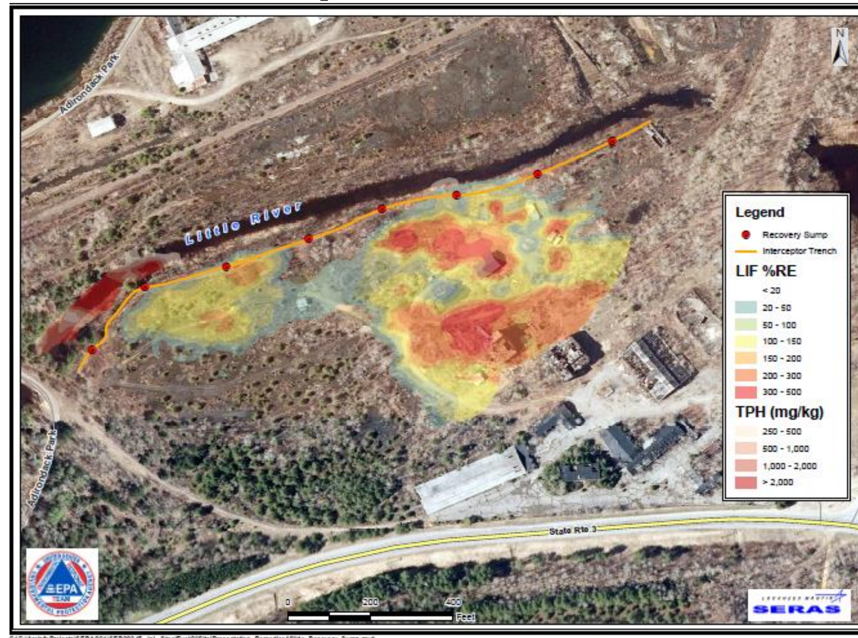
LNAPL Mass Control

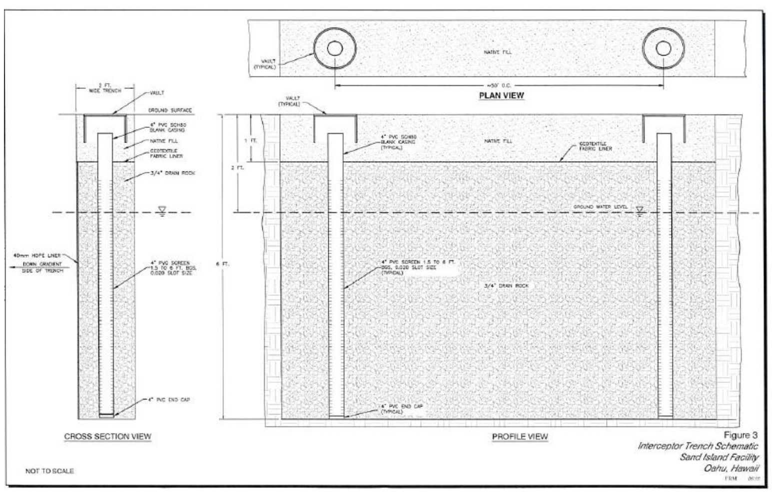
Advantages

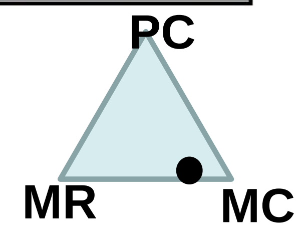
- Short time frame to implement
- Intercepts oil producing zones
- Capillary barrier to oil migration, however water can move through trench

Disadvantages

- Depth constrained
- Source not addressed source: long monitoring time







- Engineering
  - Perpendicular to Groundwater flow
  - Geometry of trench
  - Depth to water table and fluctuation zone
  - Coarse Aggregate within Trench
  - Spacing of monitoring/recovery sumps

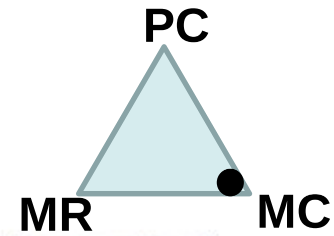
Trenching : Require Shoring/Specialized Heavy Equipment

Trenching : Heavy Equipment with Sspecialized Tools

You Never Know What You May Unearth

Physical Containment: Permeable Adsorptive Barrier (PAB)

LNAPL Mass Control



- ✓ High permeability materials, consisting of mixture of sand and organoclay (~25-50%) are emplaced perpendicular to groundwater flow

- ✓ Groundwater and LNAPL flow into barrier, but the organoclay traps the LNAPL

Advantages

- Short time frame to implement
- Intercepts migrating oil
- Capillary barrier to oil migration, however water can move through trench

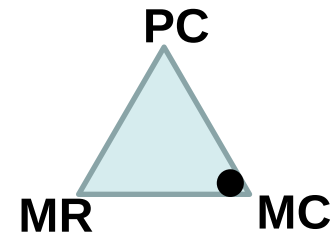
Disadvantages

- Depth constrained
- Long time monitoring
- Source not addressed source: long monitoring time

- Engineering
  - Perpendicular to Groundwater flow
  - Geometry of trench
  - Depth to water table and fluctuation zone
  - Coarser aggregate within trench than neighboring soil
  - Spacing of monitoring/recovery sumps

Physical Containment: Capillary Barriers

LNAPL Mass Control



- ✓ High LNAPL pore entry pressure materials are emplaced perpendicular to groundwater flow
- ✓ High pore entry pressure precludes LNAPL for entering, however, groundwater flows through

Advantages

- Short time frame to implement
- Intercepts migrating oil
- Capillary barrier to oil migration, however water can move through trench

Disadvantages

- Depth constrained
- Could cause mounding diverting groundwater flow
- Source not addressed source: long monitoring time

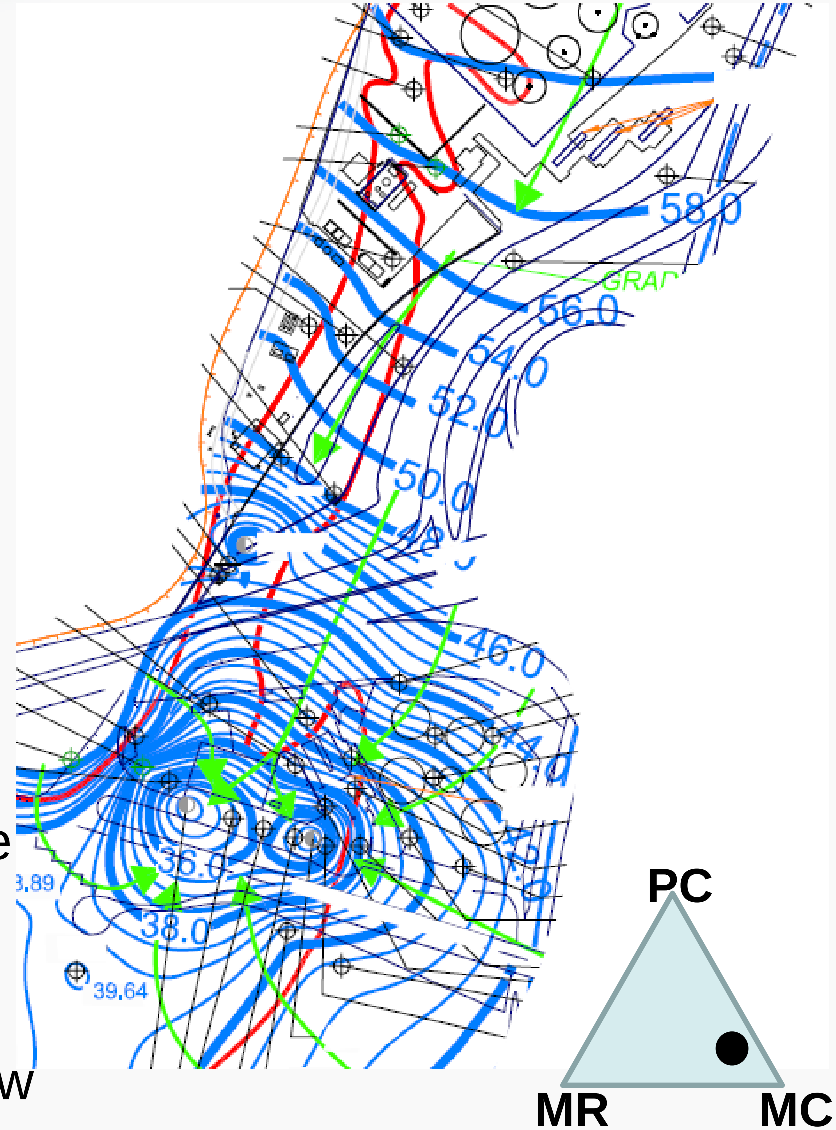
➢ Engineering

- Perpendicular to Groundwater flow
- Geometry of trench
- Depth to water table and fluctuation zone
- Coarser aggregate within trench than neighboring soil
- Spacing of monitoring/recovery sumps

Hydraulic Containment

LNAPL Mass Control

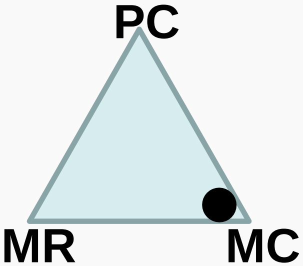
- Isolates LNAPL as a source to vapor or groundwater
- Approaches
  - Groundwater pump and treat
  - Venting/subslab depressurization (SVE to intercept vapor)
- Advantages
  - Short time frame to implement
- Disadvantages
  - Long time frame of maintenance
- Engineering
  - Radius of capture
  - Depressurization: prevents inflow of contaminated air into buildings



Source: ITRC LNAPL Course (ITRC)

In-Situ Soil Mixing: Solidification/Stabilization

- Isolates LNAPL as a source to vapor or groundwater
- Additives to stabilize LNAPL
- Advantages
  - Short time frame to implement
  - LNAPL left in place
- Disadvantages
  - High energy requirements (carbon footprint)
  - Disruptive to other site activities
- Engineering
  - Soil type
  - Additive compatibility with LNAPL



Source: ITRC LNAPL Course (ITRC)

Metrics For Mass Control Performance

LNAPL Mass Control

- No first LNAPL occurrence downgradient of barrier
  - Absence of LNAPL in sentinel wells
  - Absence of surface water LNAPL discharge(s)

- Reduced dissolved-phase concentrations downgradient of barrier

Source: ITRC LNAPL Course (ITRC)

LNAPL Mass Recovery Technologies

- Mass Control
- **Mass Recovery**
- Phase Change

Source: ITRC LNAPL Course (ITRC)

Mass Recovery Technologies

LNAPL Mass Recovery

Learning Objectives:

- Know the differences between mass recovery technologies
- Know the differences between the various simple hydraulic recovery methods

Source: ITRC LNAPL Course (ITRC)

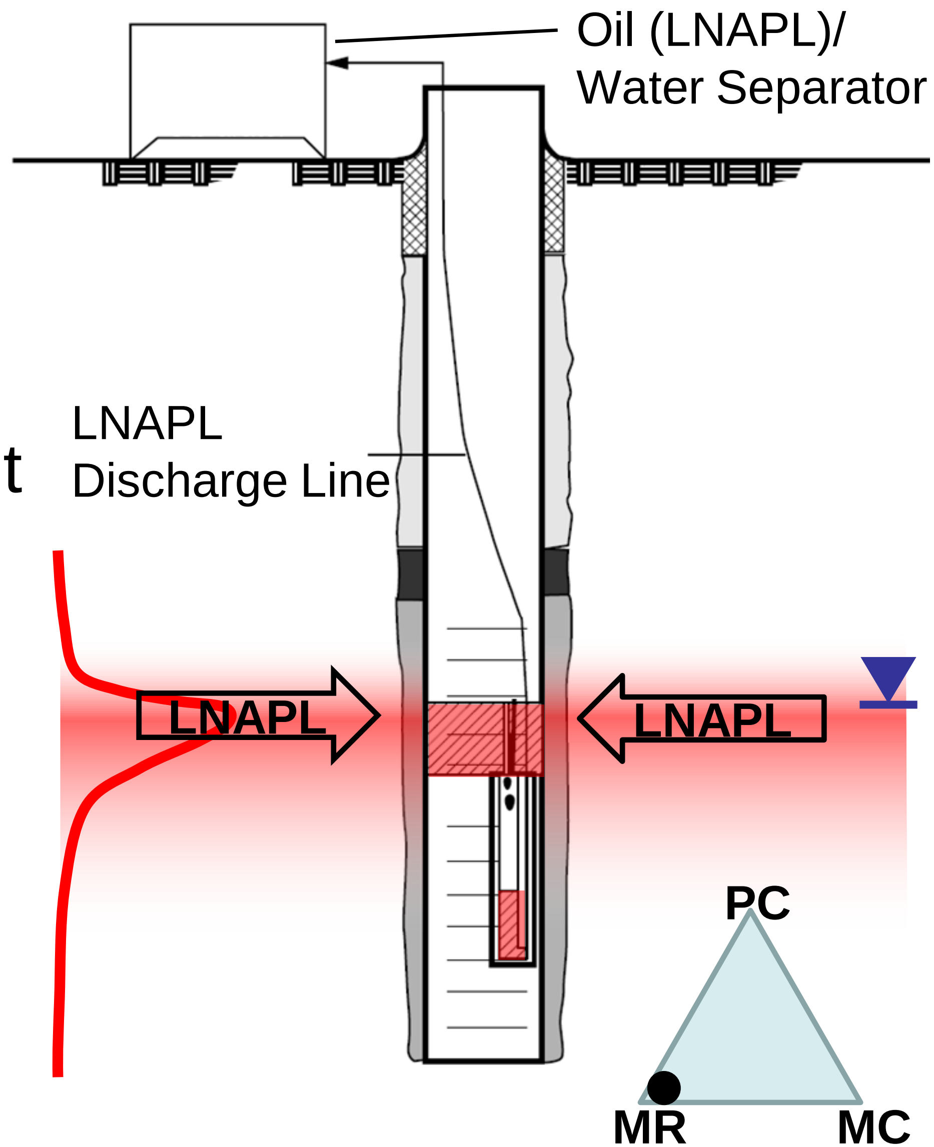
Mass Recovery Technologies

- (Simple) Hydraulic Recovery
  - Skimming
  - Dual-pump liquid extraction (DPLE)
  - Bioslurping/enhanced fluid recovery (EFR)
  - Multiphase extraction (MPE) – single pump
  - Multiphase extraction (MPE) – dual pump
  - Recovery Trenches
  - Excavation
- Enhanced Hydraulic Recovery
  - (Hot) Water flooding
  - Surfactant-enhanced subsurface remediation (SESR)
  - Cosolvent flushing

Source: ITRC LNAPL Course (ITRC)

Skimming

- Recover only LNAPL (incidental water)
- Induce LNAPL flow to well by creating gradient in LNAPL only
- Applicable to broad range of geologic conditions
- Applicable to broad range of LNAPL types

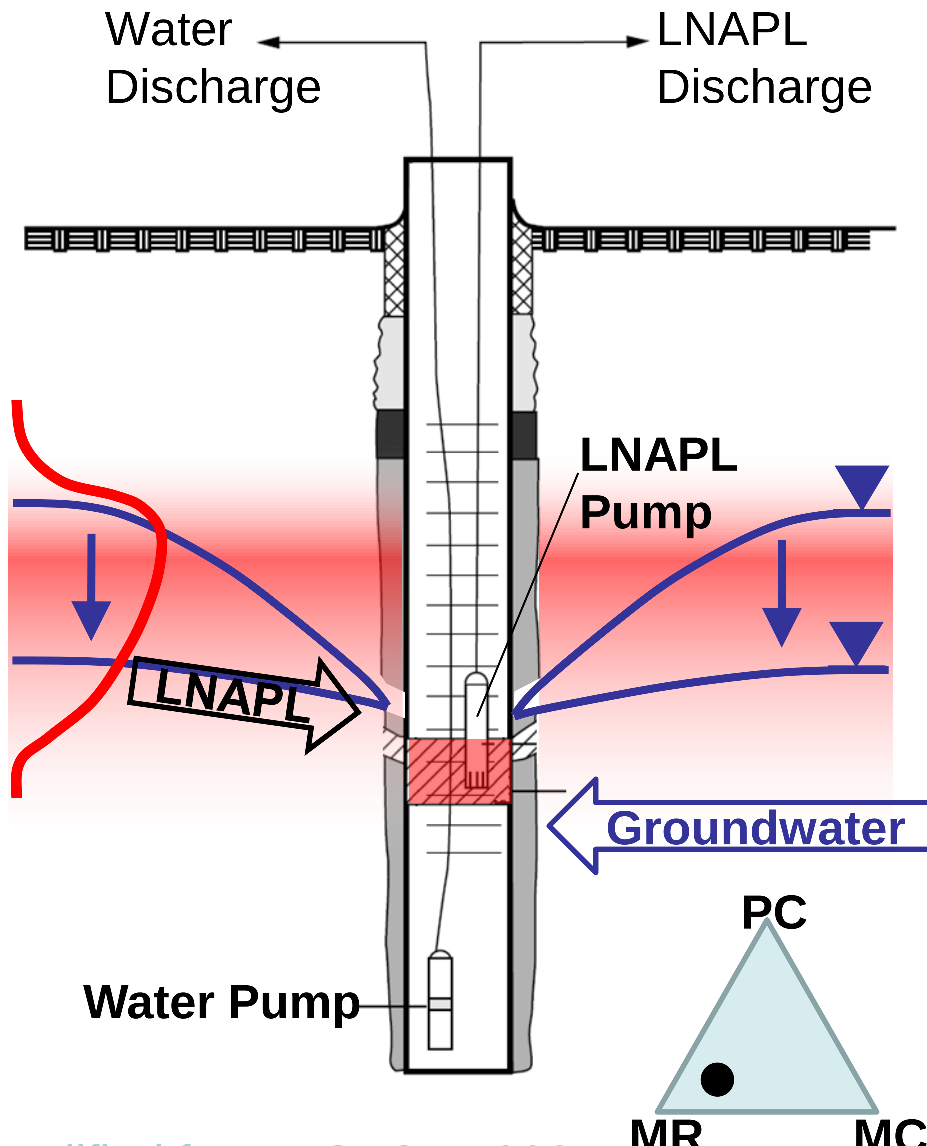


Modified from USACE 1999

Dual-Pump Liquid Extraction (DPLE)

LNAPL Mass Recovery

- Extract LNAPL and groundwater
- Induce LNAPL flow into extraction well by creating gradients in LNAPL and groundwater
- Expose Submerged LNAPL
- Control water table fluctuations
- Applicable to range of geologic conditions
- Applicable to broad range of LNAPL types
- Not applicable to perched LNAPL

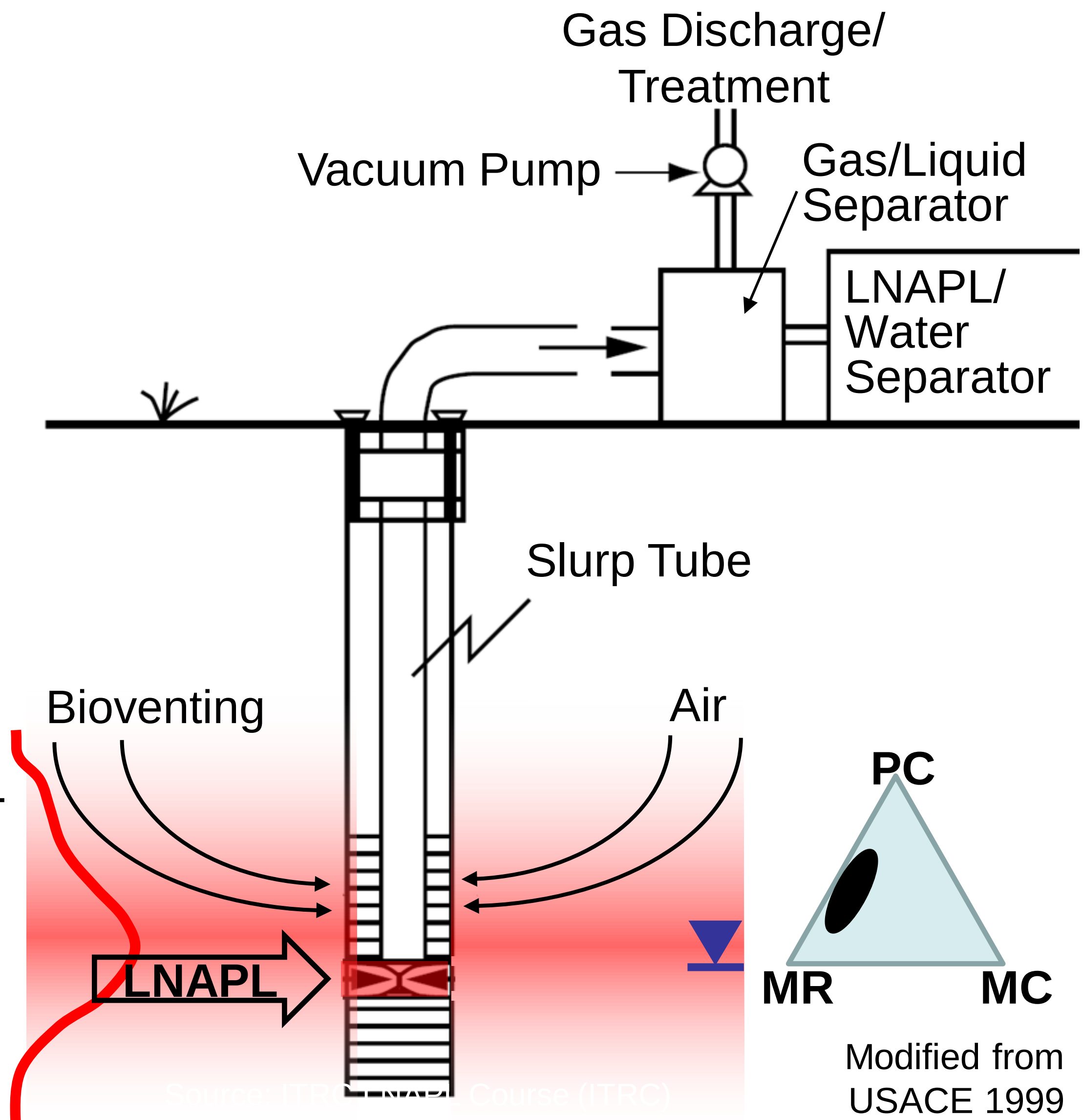


Modified from USACE 1999

Bioslurping / Enhanced Fluid Recovery (EFR)

LNAPL Mass Recovery

- Extract LNAPL and vapor (vapor enhanced fluid recovery)
- Induce LNAPL flow into extraction well by creating gradients in LNAPL and soil vapor
- Increase aerobic biodegradation
- Better suited to higher conductivity soils LNAPL
- Not suited to confined or submerged LNAPL

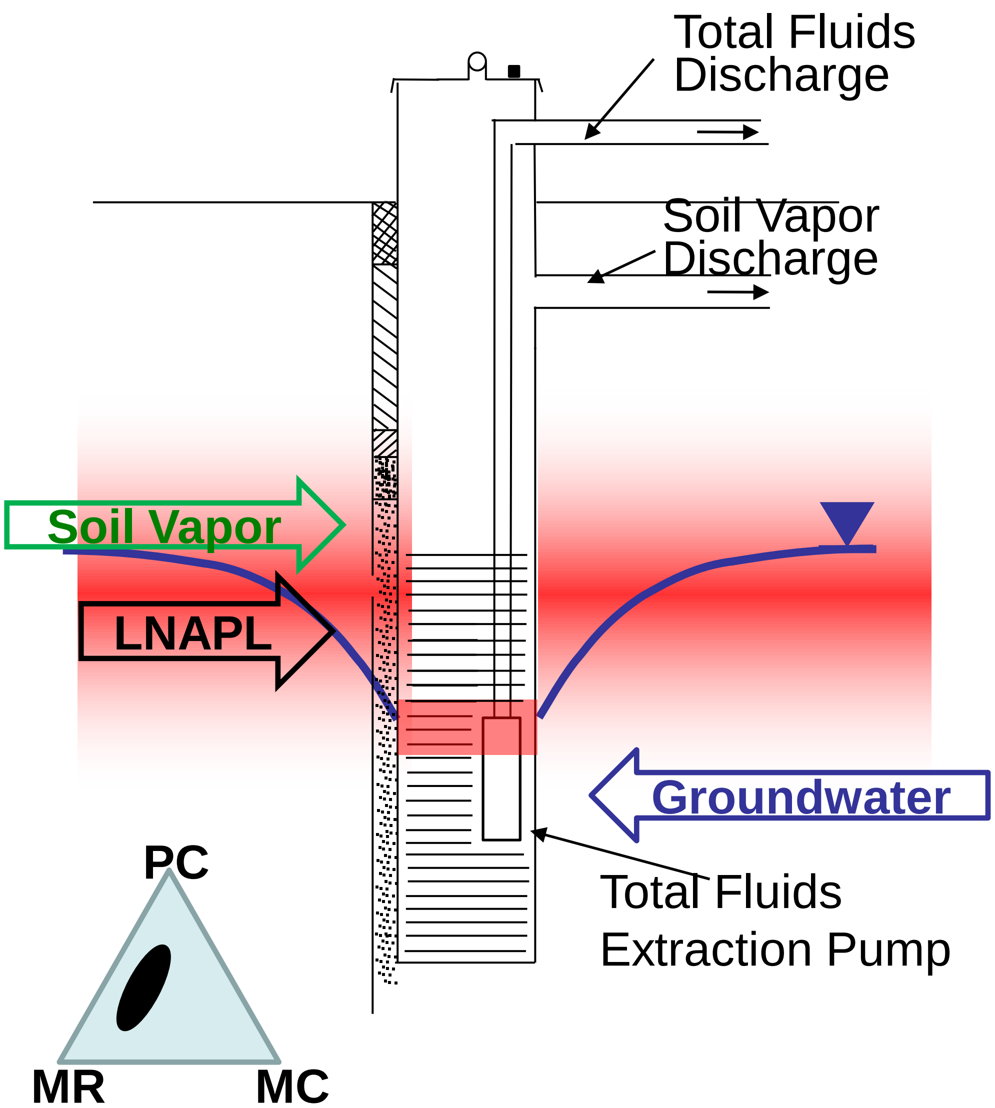


Modified from USACE 1999

MPE – Single Pump

LNAPL Mass Recovery

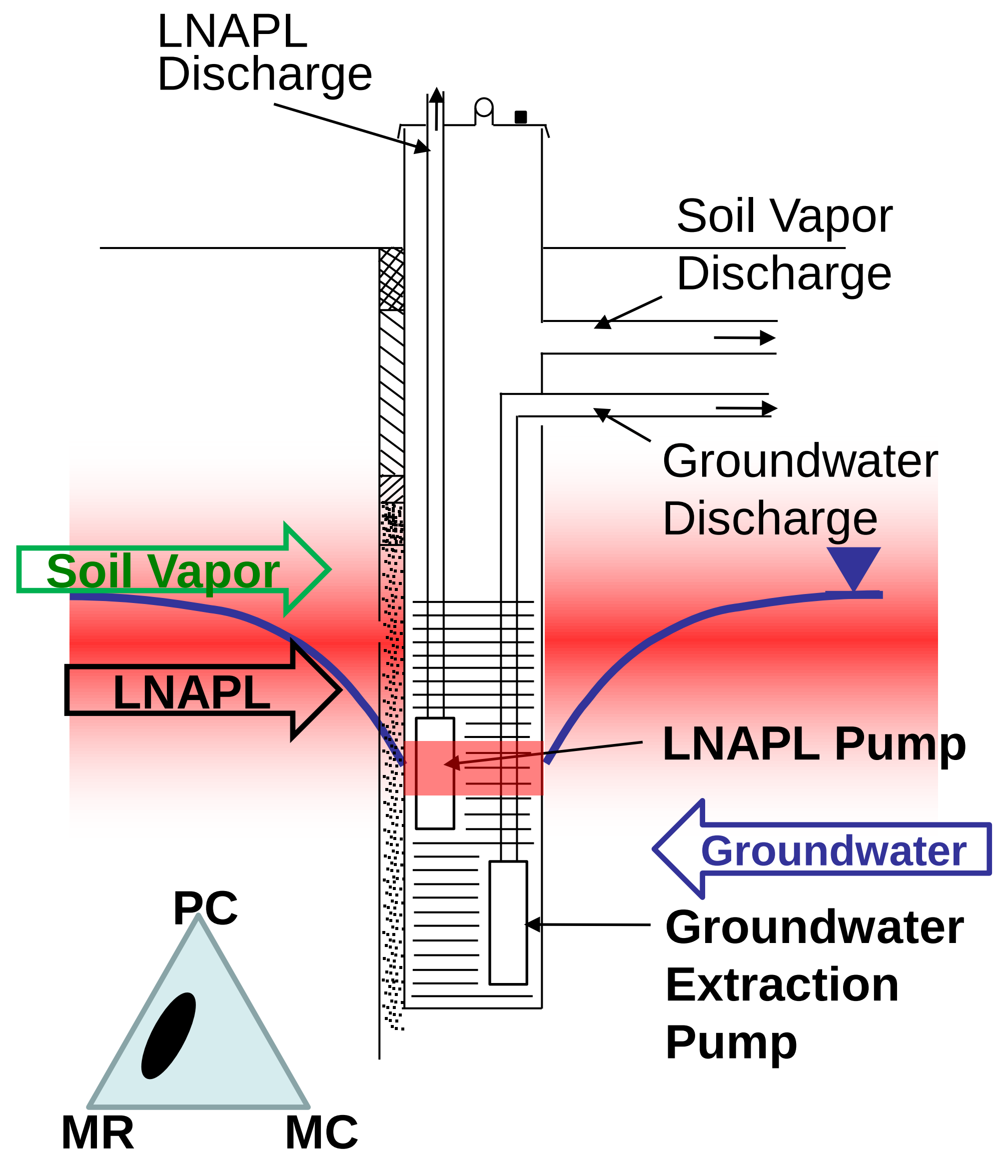
- Extract LNAPL, groundwater, and vapor
- Induce LNAPL flow into extraction well by creating gradients in LNAPL, groundwater, and soil vapor
- Typically, Higher Vacuum
- Better suited to lower conductivity soils LNAPL



MPE – Dual Pump

LNAPL Mass Recovery

- Extract LNAPL, groundwater, and vapor
- Induce LNAPL flow into extraction well by creating gradients in LNAPL, groundwater, and soil vapor
- Better suited to higher conductivity soils LNAPL



Recovery Trenches

LNAPL Mass Recovery

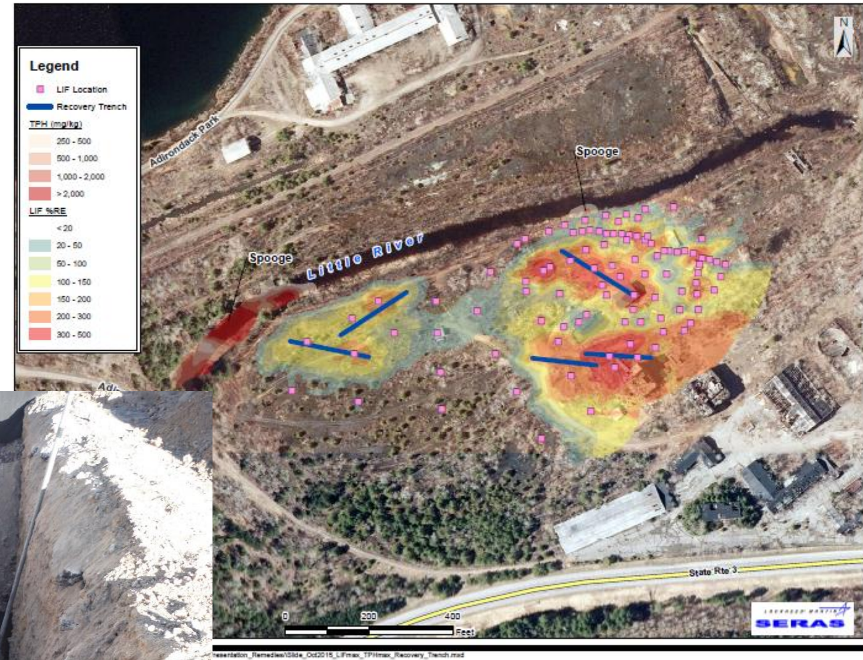
Like interceptor trenches except, goal is mass removal
- ✓ shorter trench segments

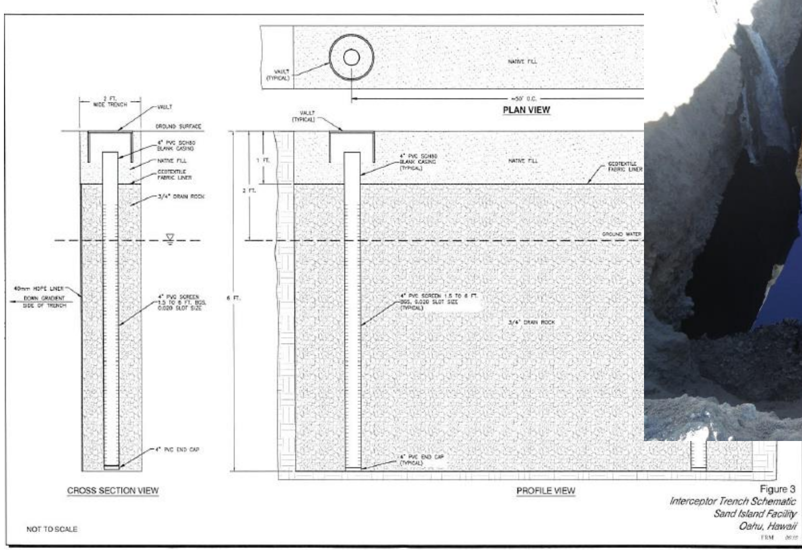
Advantages

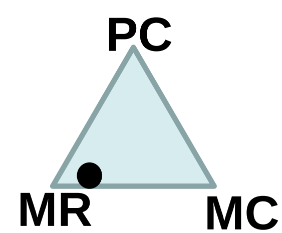
- Short time frame to implement
- Intercepts oil producing zones

Disadvantages

- Depth constrained
- Leaves residual LNAPL







g factors
- ry of trenches
-) water table and fluctuation zone
- aggregate within Trench
- Spacing of sumps for hydraulic recovery/monitoring

Hydraulic Recovery Technology Pros

Technology	Advantage
Skimming	• LNAPL-only waste stream • Lowest per-well cost
DPLE	• Increased radius of capture (ROC) • Shorter time frame than skimming
EFR/Bioslurp	• In-situ biodegradation • Low per-well cost
MPE (Single Pump)	• Largest ROC • Shortest time frame
MPE (Dual Pump)	• Largest ROC / Shortest time frame • Separate waste streams simplifies treatment

Source: ITRC LNAPL Course (ITRC)

Hydraulic Recovery Technology Cons

LNAPL Mass Recovery

Technology	Disadvantage
Skimming	• Smallest radius of capture (ROC) • Longest time frame
DPLE	• Recovered water or combined water/LNAPL disposal
EFR/Bioslurp	• Single LNAPL/vapor/water waste stream • Long time frame; limited depth
MPE (Single Pump)	• Treatment of single fluid waste stream; limited depth
MPE (Dual Pump)	• Highest per-well cost; limited depth

Source: ITRC LNAPL Course (ITRC)

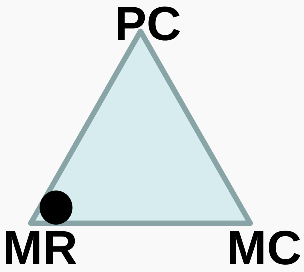
Hydraulic Recovery Technologies Engineering Considerations

Technology	Parameters for Design
Skimming	• LNAPL ROC
DPLE	• Groundwater flow vs. drawdown and capture zone
EFR/Bioslurp	• Vacuum radius of influence (ROI), aeration and pore volume exchange
MPE (Single Pump)	• Vacuum ROI • Groundwater flow vs. drawdown and ROC • Depth to LNAPL
MPE (Dual Pump)	• Vacuum ROI • Groundwater flow vs. drawdown and ROC • Depth to LNAPL

Source: ITRC LNAPL Course (ITRC)

Excavation

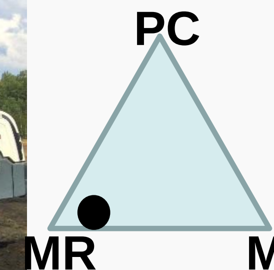
- High removal efficiency for residual LNAPL, or heavier ends in tight soils
  - Mobile LNAPL readily drains from coarse soil
  - May have to combine the recover LNAPL that drains
- Not well suited to coarse soils with mobile oil
- Depth and bedrock constrained



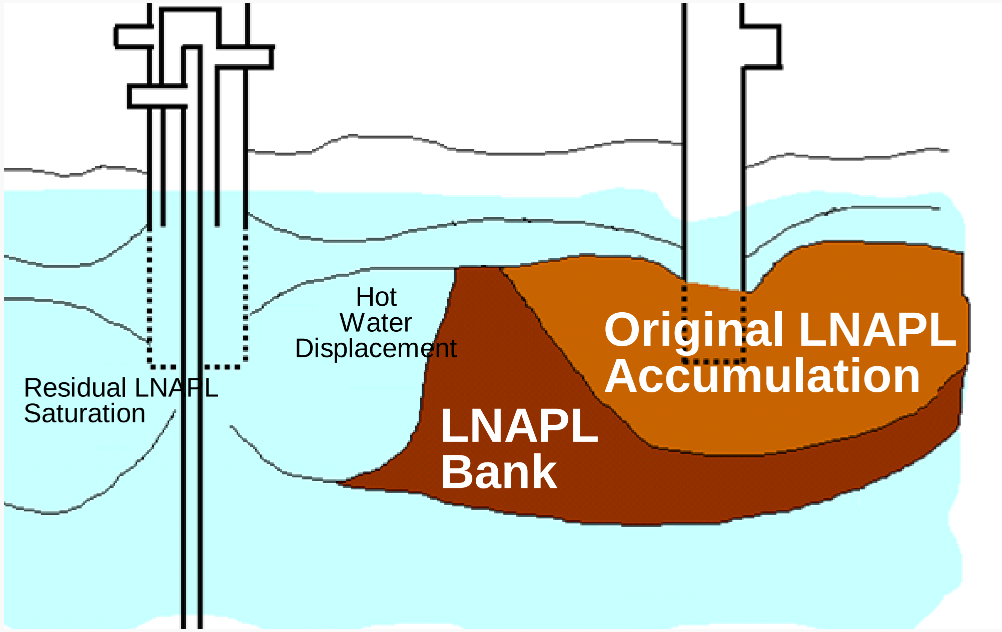
Excavation

LNAPL Mass Recovery

- **Advantages**
  - Short time frame
- **Disadvantages**
  - Access restrictions
  - Sustainability
  - Secondary technology may be needed to recover drained oil
  - Move oil to new location
  - Expensive
- **Engineering**
  - LNAPL zone depth interval
  - Depth to water



Enhanced Mass Recovery Technologies with Phase Change



Source: ITRC LNAPL Course (ITRC)

Learning Objectives:

- Understand there are more aggressive mass recovery methods and what they can accomplish

Source: ITRC LNAPL Course (ITRC)

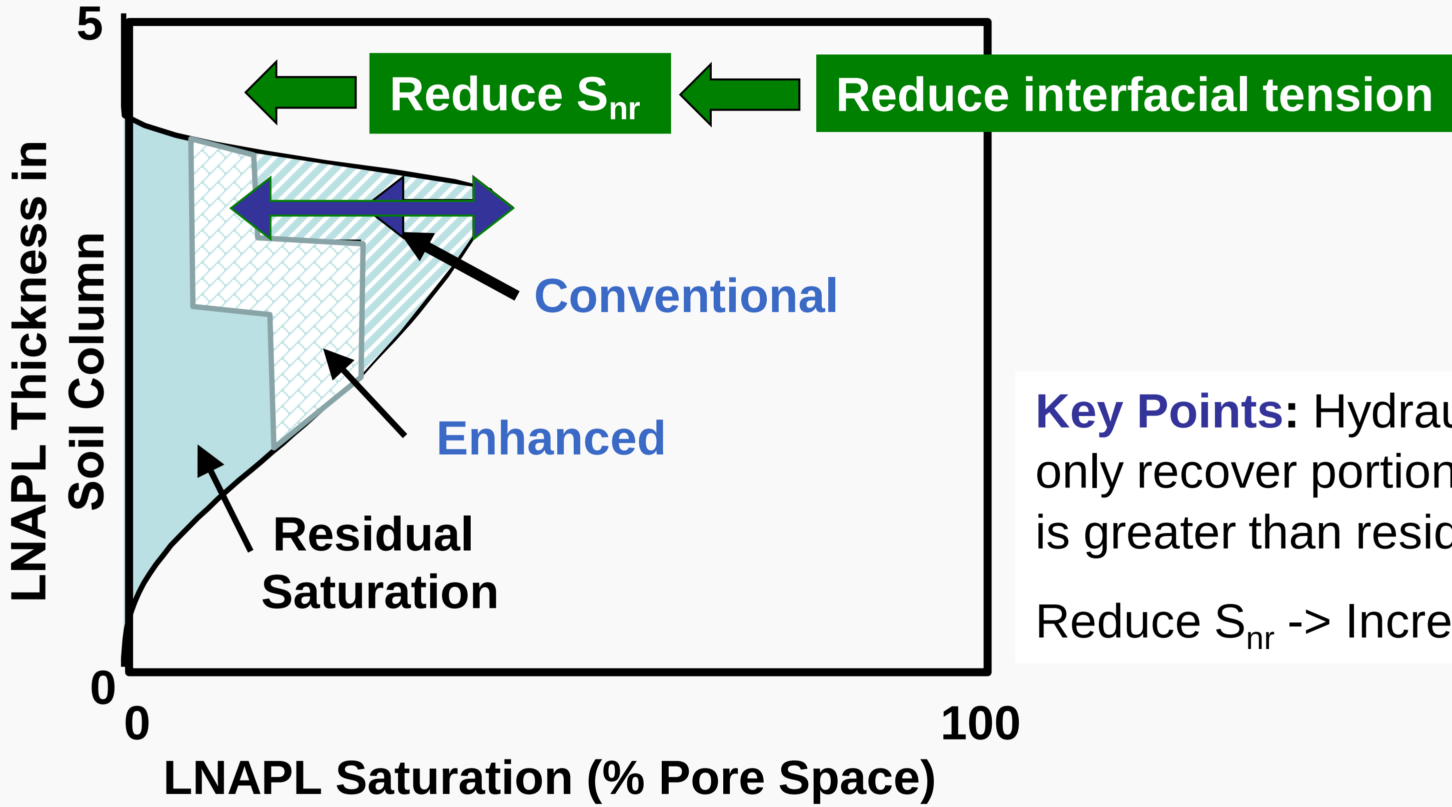
Enhanced Mass Recovery Technologies

- (Simple) Hydraulic recovery
  - Skimming
  - Dual-pump liquid extraction (DPLE)
  - Multiphase extraction (MPE) – single pump
  - Multiphase extraction (MPE) – dual pump
  - Bioslurping / enhanced fluid recovery (EFR)
- Enhanced hydraulic recovery
  - (Hot) Water flooding
  - Surfactant-enhanced subsurface remediation (SESR)
  - Cosolvent flushing

Source: ITRC LNAPL Course (ITRC)

Enhanced LNAPL Mass Recovery

Review – Potentially Mobile Fraction of the LNAPL



Key Points: Hydraulic methods will only recover portion of LNAPL that is greater than residual saturation.

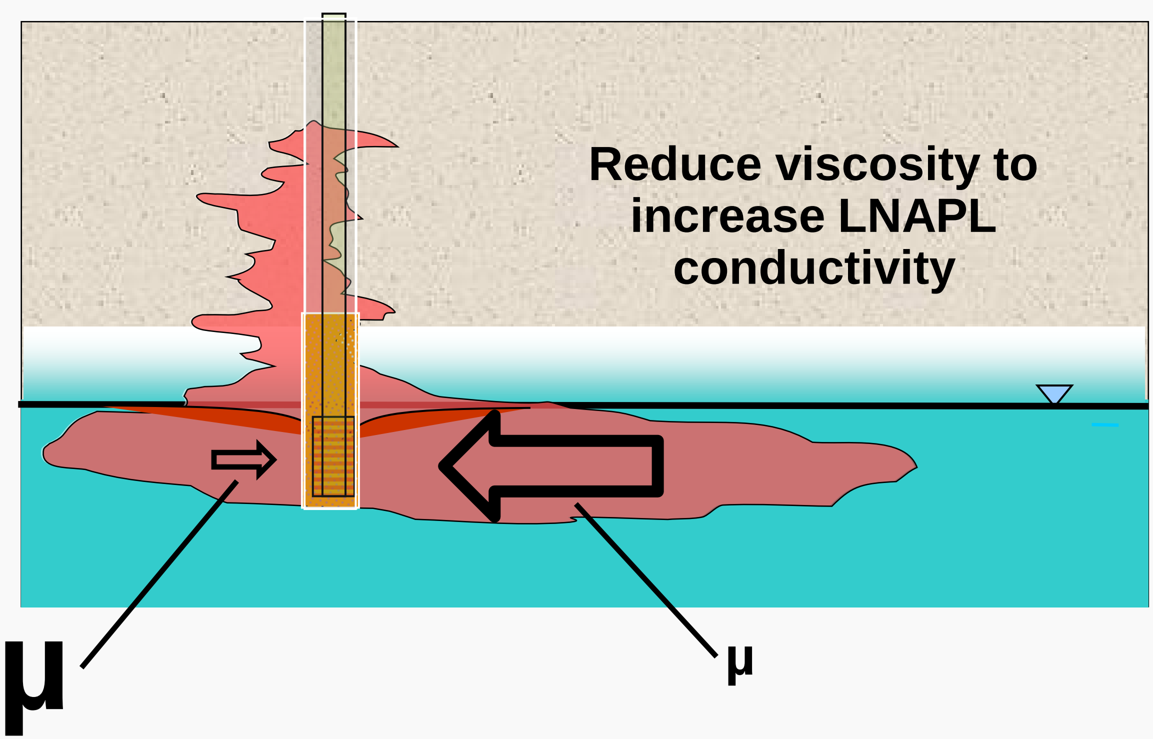
Reduce S_{nr} -> Increase Recovery

Source: ITRC LNAPL Course (ITRC)

Enhanced LNAPL Mass Recovery

Review – LNAPL hydraulic conductivity

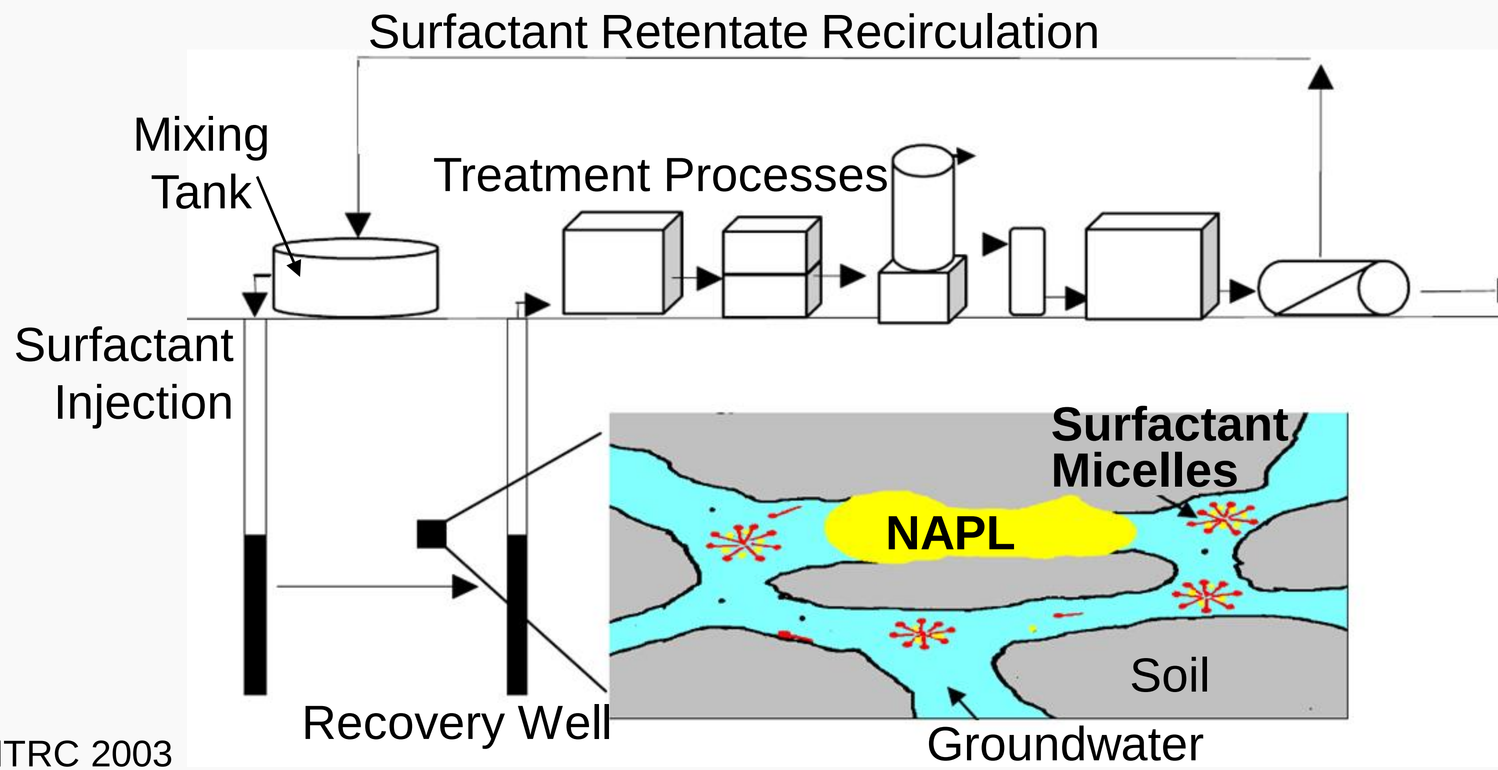
$$K_n = \frac{\rho_n \cdot g \cdot k \cdot k_{rn}}{\mu_n}$$



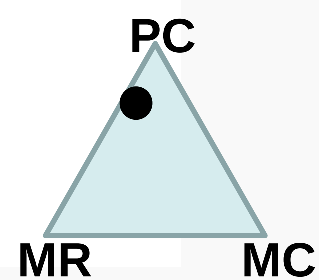
Source: ITRC LNAPL Course (ITRC)

Surfactant Enhanced Subsurface Remediation (SESR)

- Increase solubility of contaminants (primarily)
- Decreases LNAPL-water interfacial tension
  - Increases mobility and recoverability
  - Reduces residual saturation
- Recirculation or push-pull



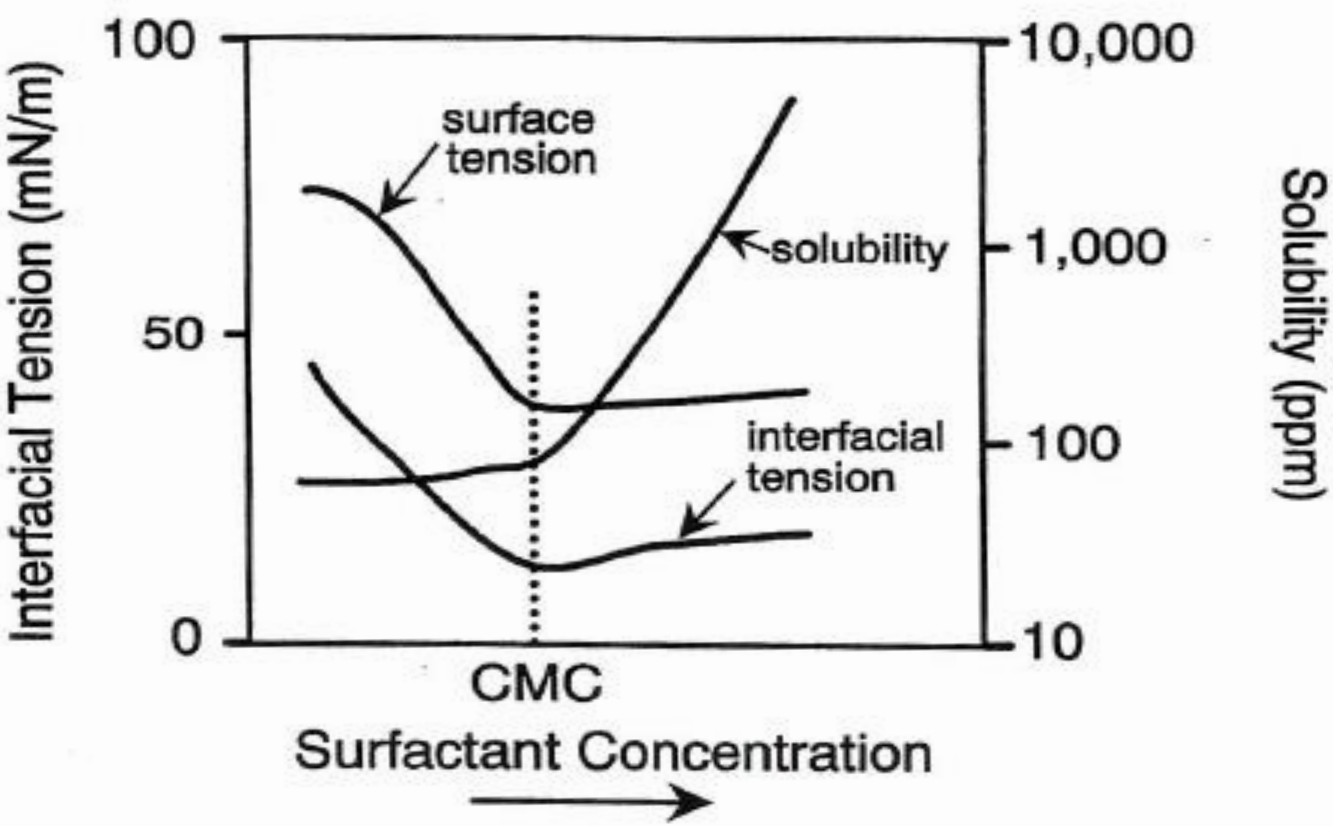
ITRC 2003



Source: ITRC LNAPL Course (ITRC)

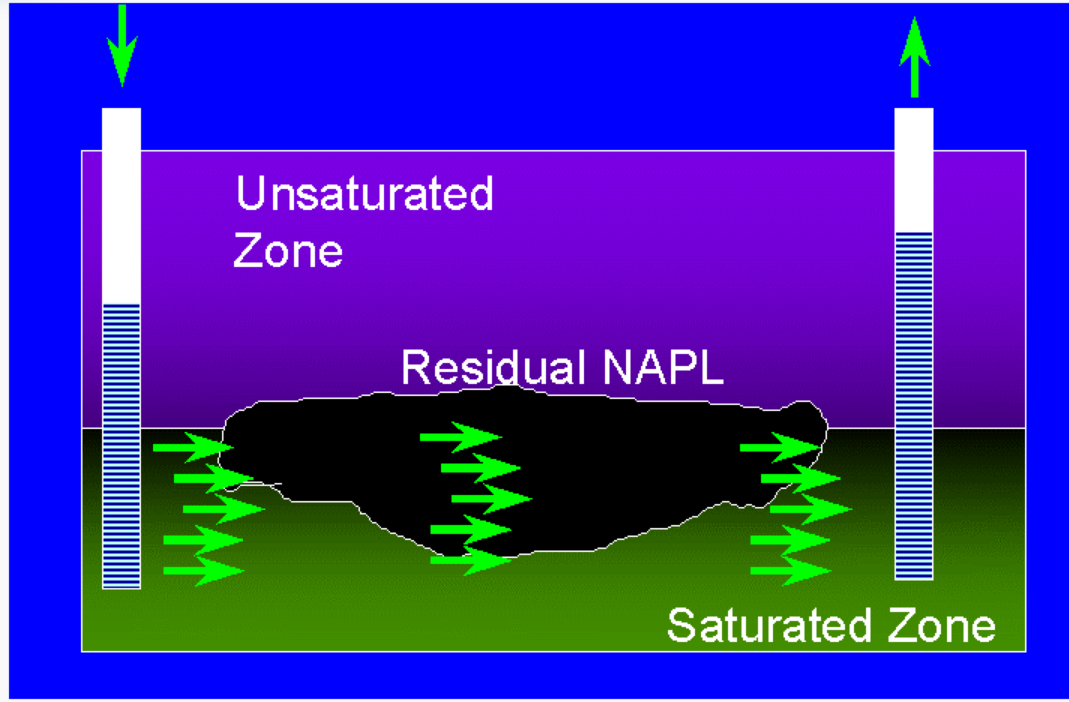
Major Surfactant Impact: Solubility

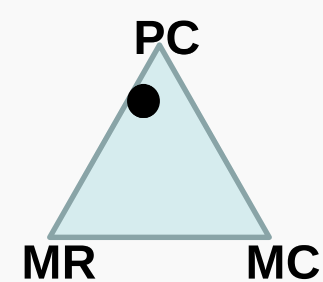
SURFACTANT ENHANCED SOLUBILIZATION



Cosolvent Flushing

- Example alcohols
- Increases LNAPL solubility
  - Increases mass recovered in aqueous phase
  - Reduces residual saturation
- Decreases LNAPL-water interfacial tension (secondary)
  - Increases mobility and recoverability
  - Reduces residual saturation
- Recirculation or push-pull

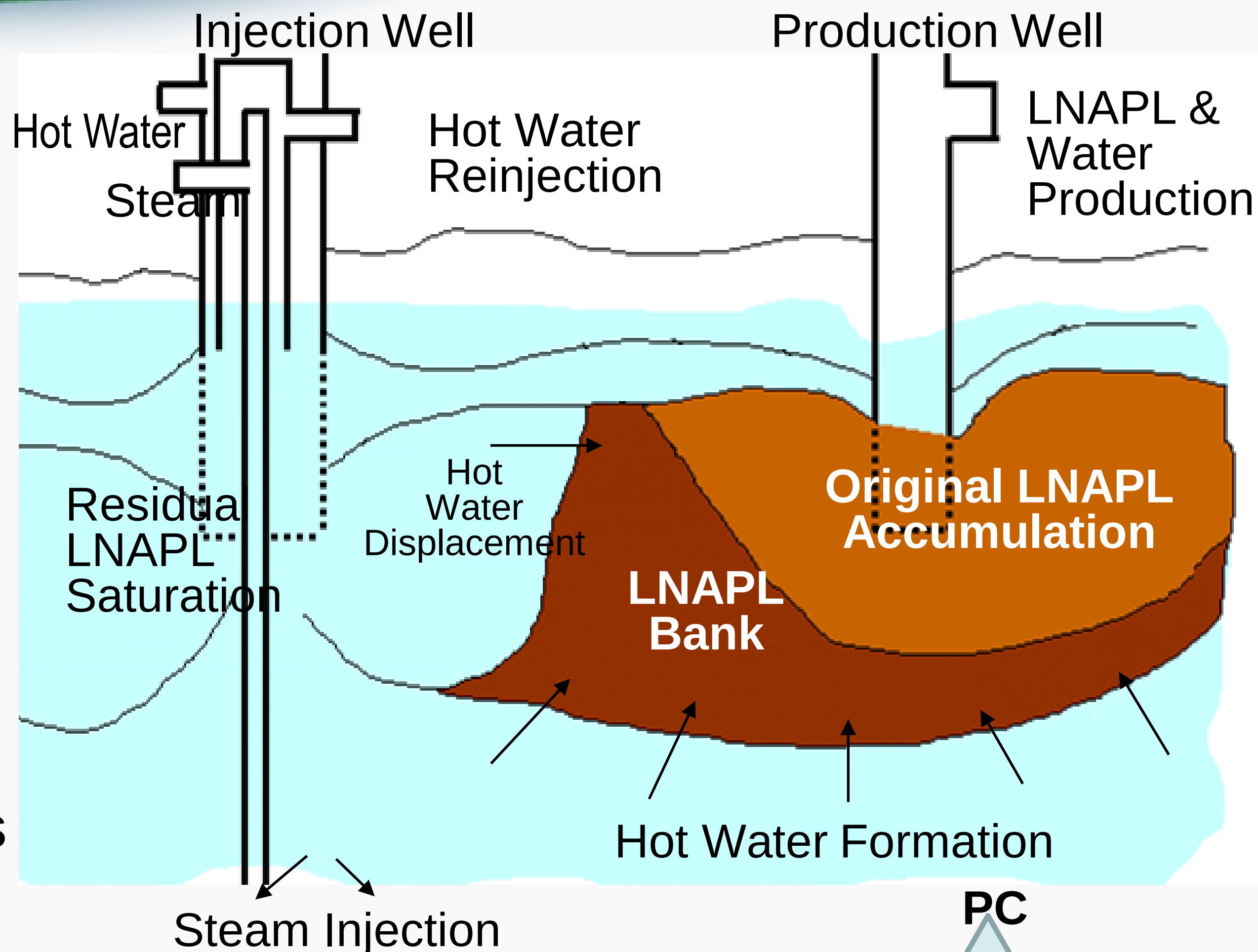


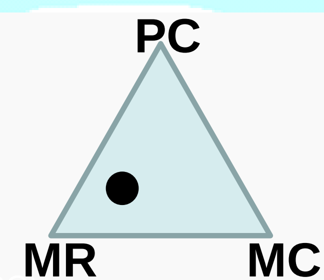


Source: ITRC LNAPL Course (ITRC)

Hot Water Flooding

- Increases groundwater gradient across LNAPL
- Decreases LNAPL viscosity (hot)
- Applied with recirculation
- Most benefit in moderate permeability soils
- Most benefit to more viscous LNAPL (hot)



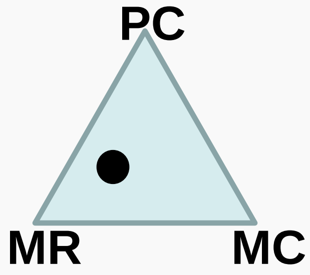


Source: ITRC LNAPL Course (ITRC)

(Hot) Water Flooding

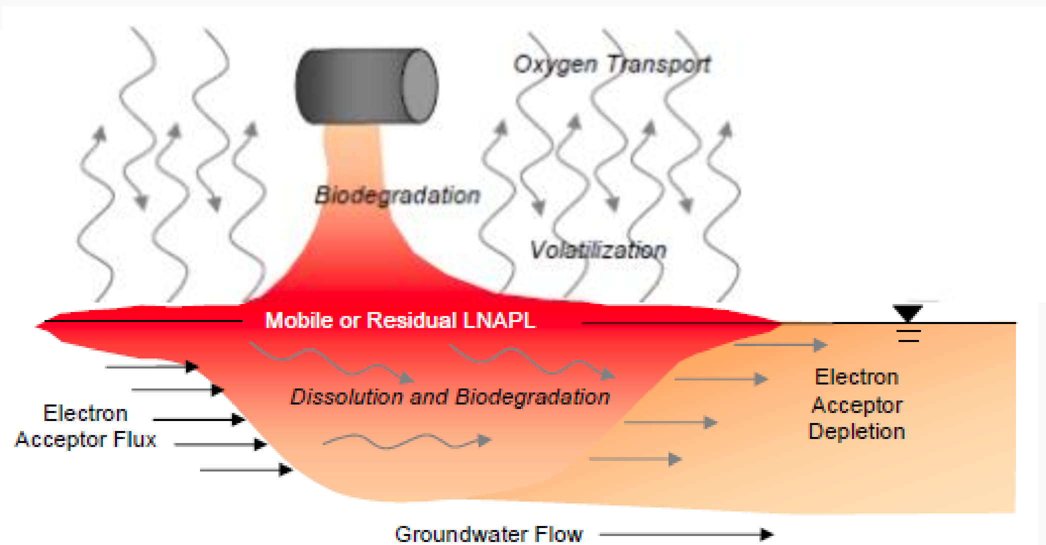
Enhanced LNAPL Mass Recovery

- Advantages
  - Shorter time frame
  - Reduced residual saturation (hot)
- Disadvantages
  - Sustainability (hot)
  - Safety (hot)
- Engineering
  - LNAPL fluid properties
  - Groundwater and LNAPL ROC



Source: ITRC LNAPL Course (ITRC)

Phase Change Technologies



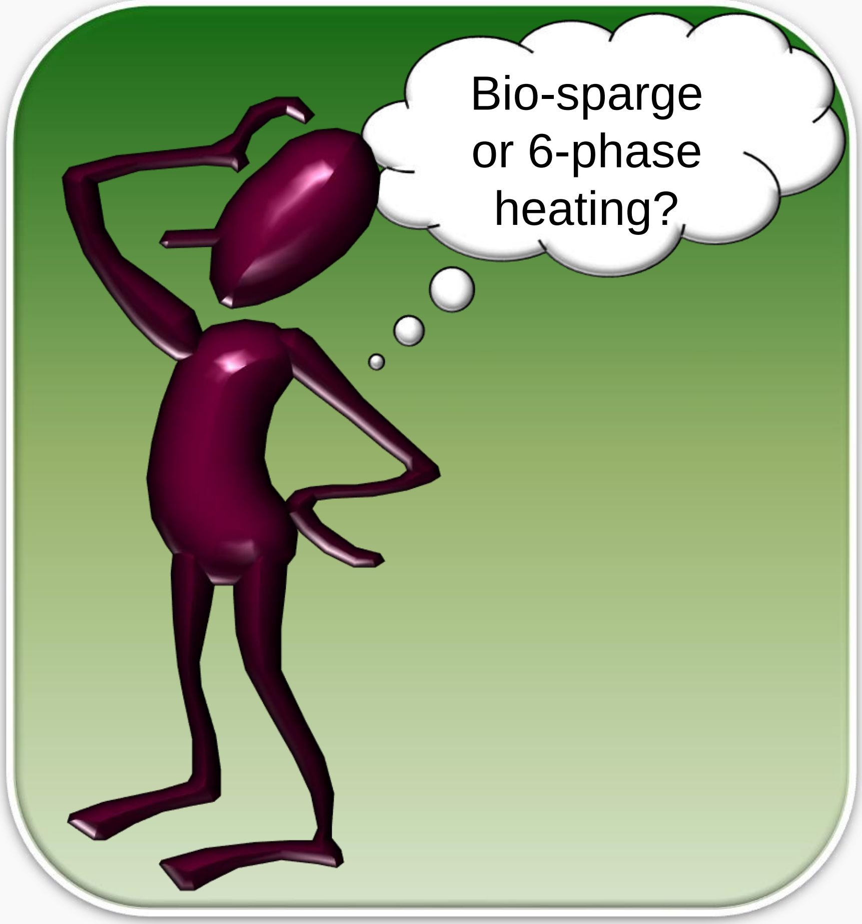
- Mass Control
- Mass Recovery
- **Phase Change**

Source: ITRC LNAPL Course (ITRC)

Phase Change Technologies

Learning Objectives:

- Review types of technologies that exploit phase change, their differences, and when to apply aggressive phase change technologies



Source: ITRC LNAPL Course (ITRC)

Phase Change Technologies

LNAPL Phase Change

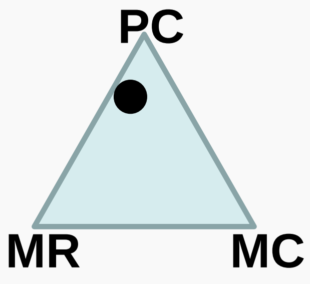
- Ambient
  - Soil Vapor Extraction (SVE)
  - Air Sparge (AS) / Soil Vapor Extraction (SVE)
  - Ground Water Circulating Well with In-Well Stripping/SVE
  - *MPE / EFR (primarily mass recovery)*
- Enhanced
  - Steam / Hot-Air
  - Radio Frequency Heating (RFH)
  - 3- and 6-Phase (Electrical Resistance) Heating (ERH)
  - In-Situ Chemical Oxidation (ISCO)
  - *Cosolvent Flushing (primarily mass recovery)*
  - *SESR (primarily mass recovery)*

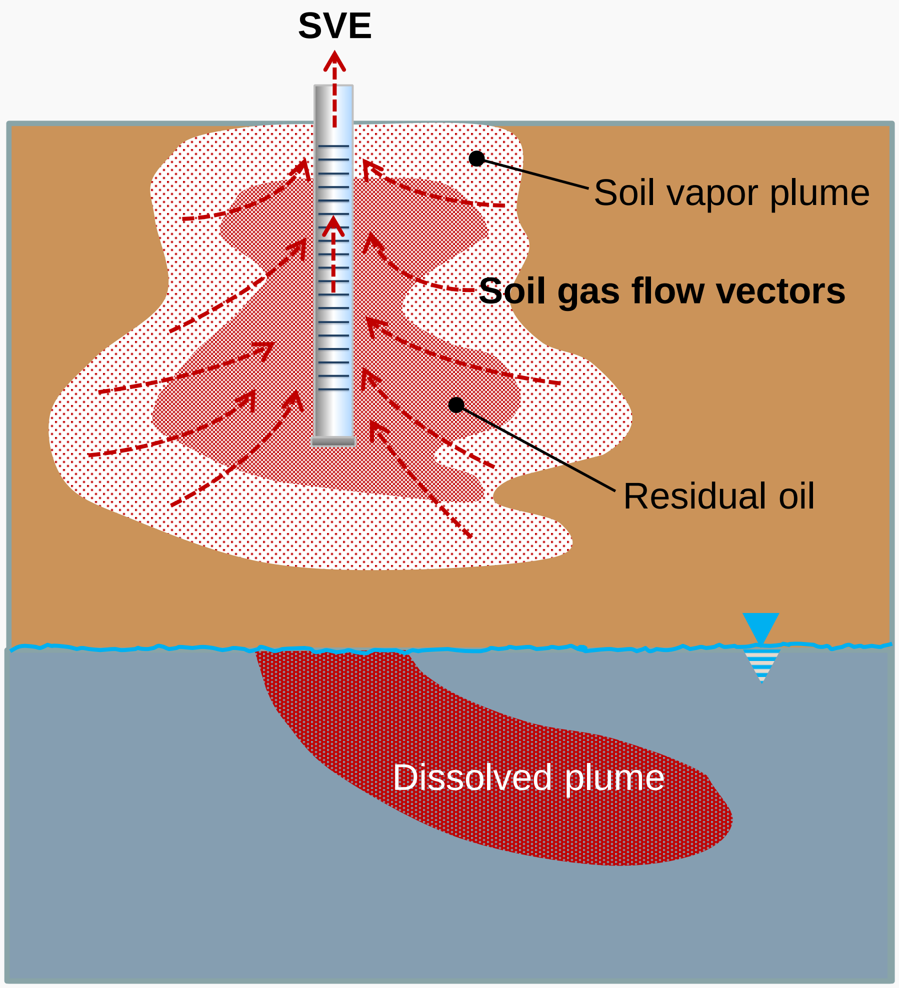
Source: ITRC LNAPL Course (ITRC)

Soil Vapor Extraction (SVE)

LNAPL Phase Change

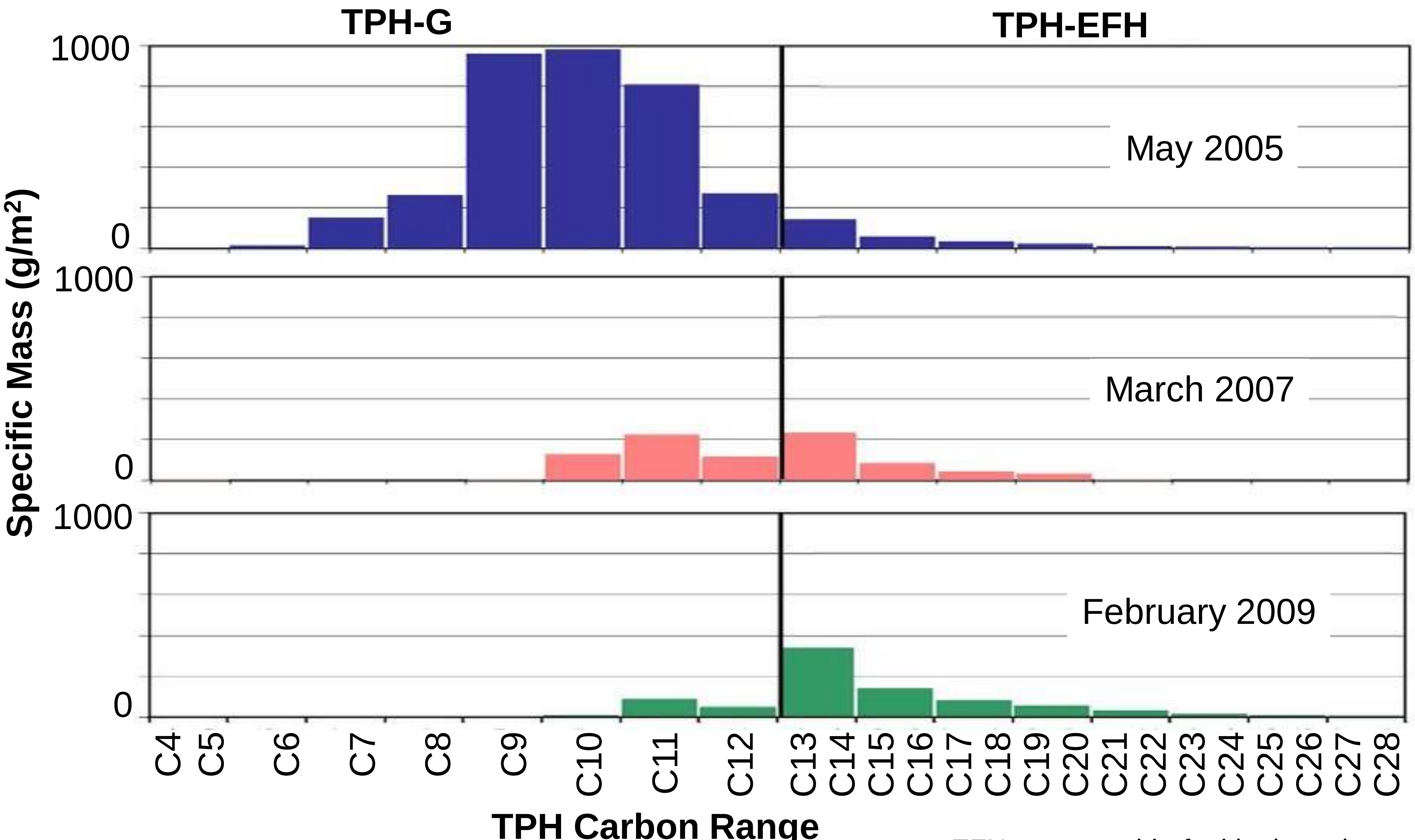
- Treats volatile LNAPL vadose zone compounds
- Short implementation time
- Short clean up time
- Promotes Aerobic Biodegradation
- More effective in higher K soils with low heterogeneity





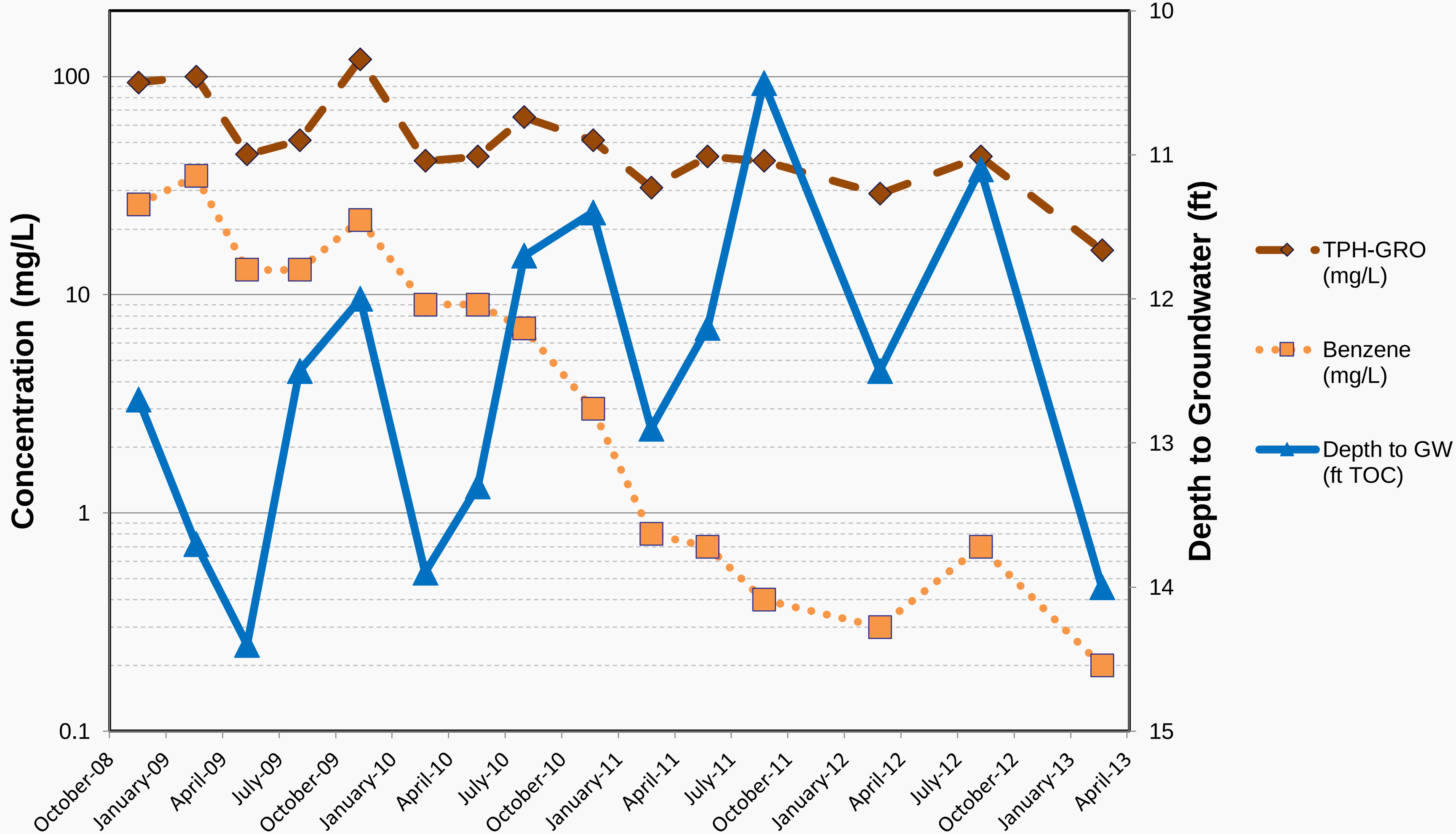
Result of Soil Vapor Extraction (SVE) Remediation

Composition Objective Illustrated



EFH – extractable fuel hydrocarbons

Reduction in Groundwater Benzene Concentrations due to SVE at site

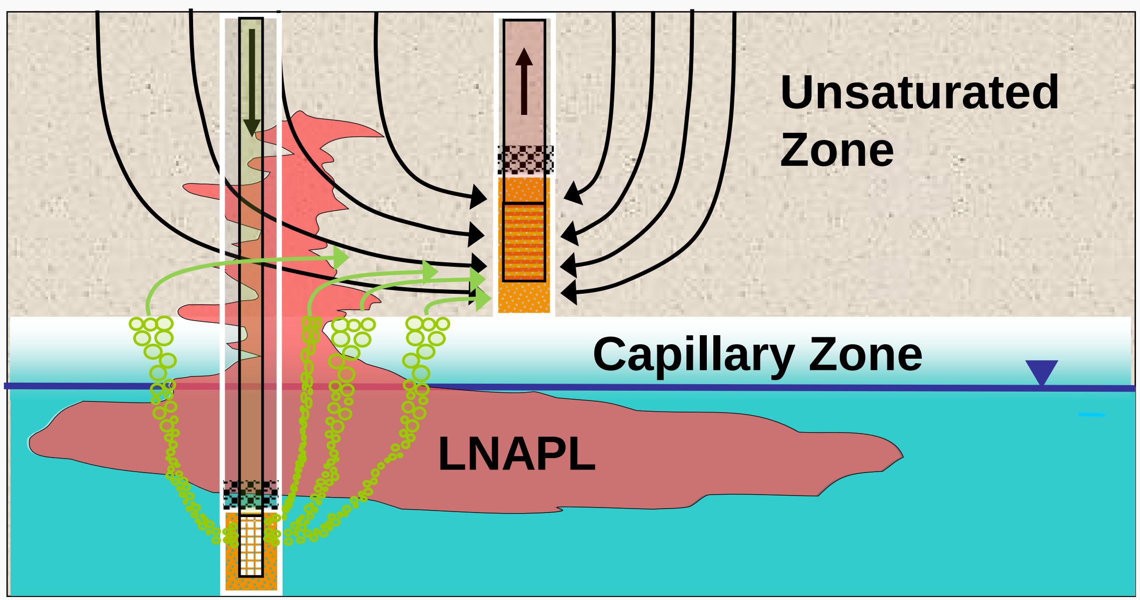


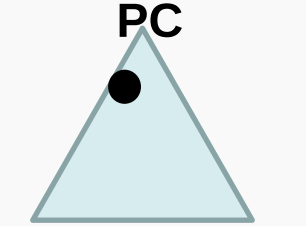
Source: ITRC LNAPL Course (ITRC)

Air Sparging/Soil Vapor Extraction (AS/SVE)

LNAPL Phase Change

- Treats Volatilize LNAPL compounds
- Promotes Aerobic Biodegradation
- Treats both LNAPL both in vadose and saturated zones
- More effective in higher K soils with low heterogeneity



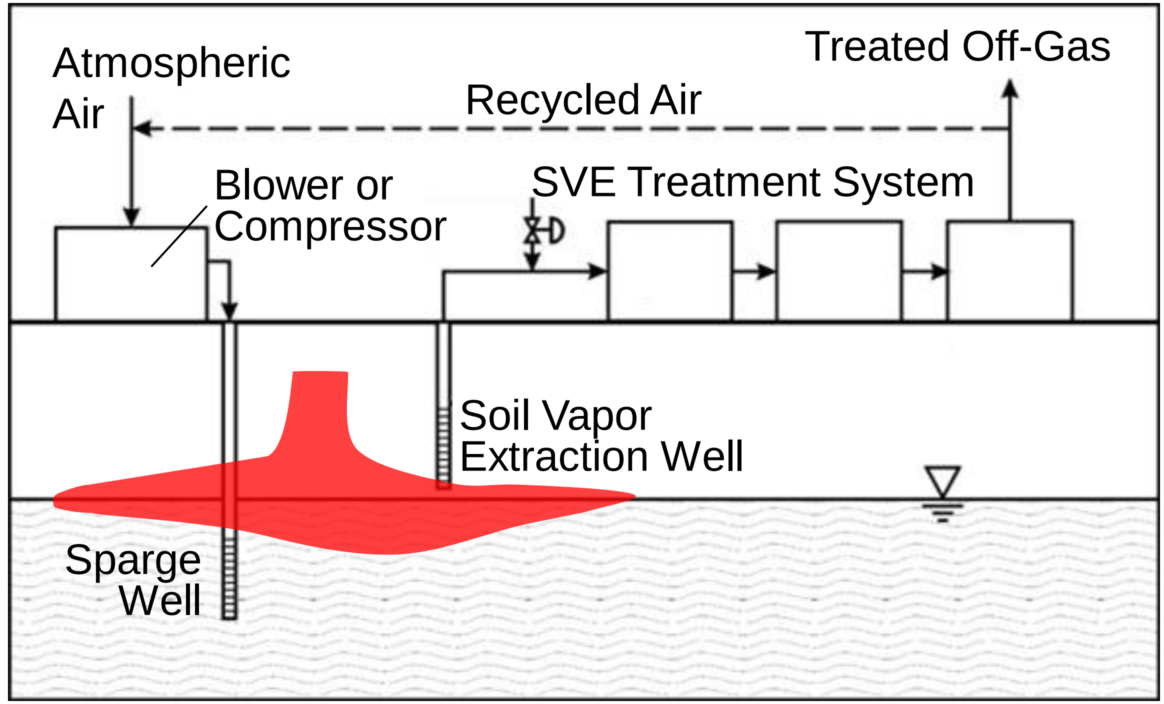


Source: ITRC LNAPL Course (ITRC)

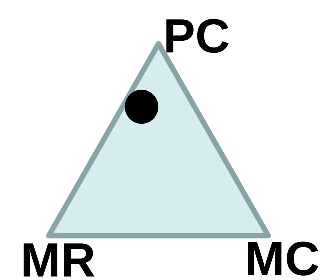
Air Sparging/Soil Vapor Extraction (AS/SVE)

LNAPL Phase Change

- Advantages:
  - Few site restrictions
  - Scalable
  - Moderate time frame
- Disadvantages:
  - Less effective for low volatility LNAPL
  - Moderate to high carbon footprint



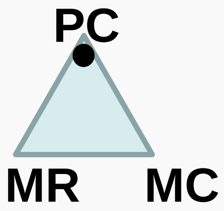
- Engineering Consideration:
  - Air entry pressure for sparging
  - AS and SVE ROI and radius of sweep
  - Flow vs. vacuum (SVE) and pressure (AS)
  - LNAPL composition and volatility

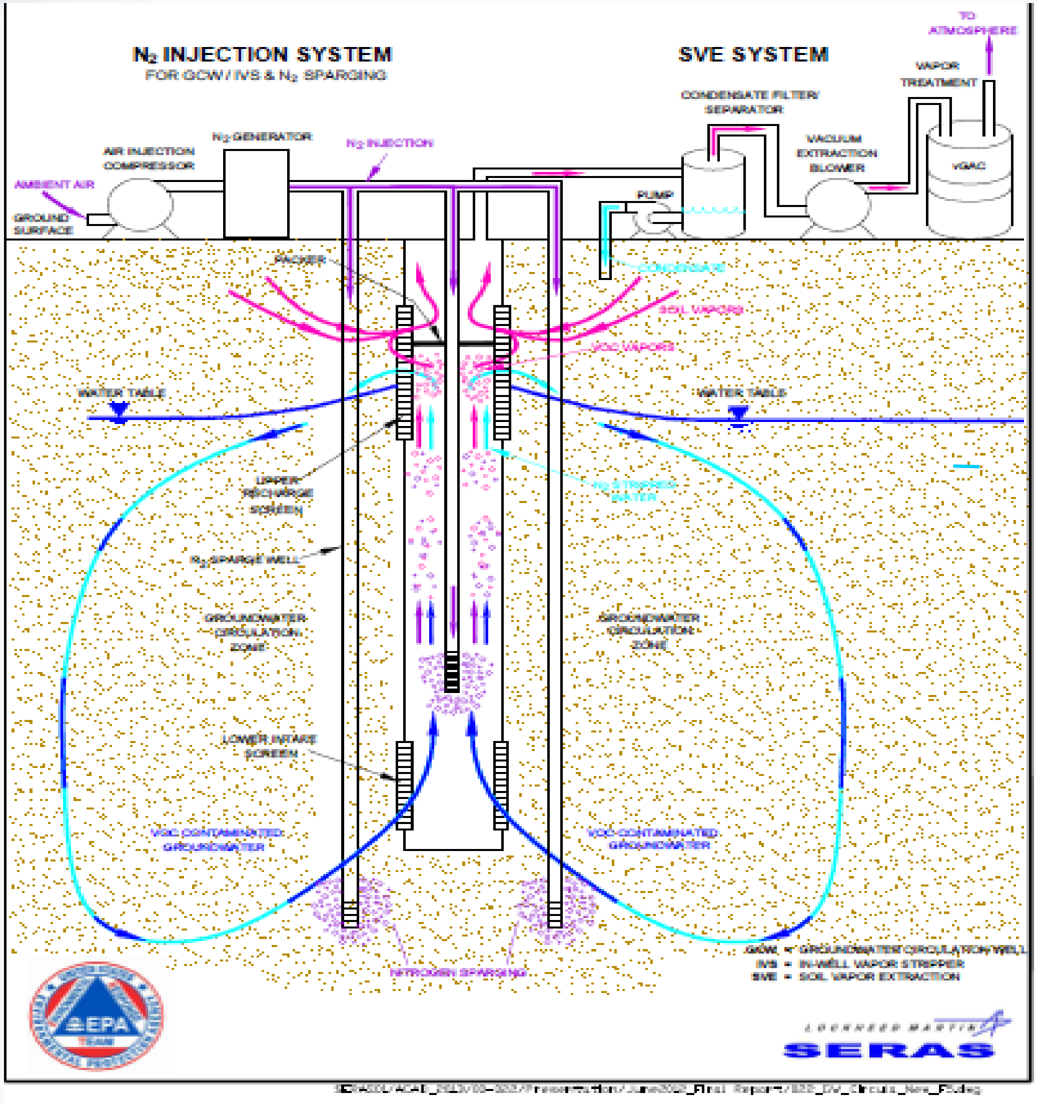


Vertical Groundwater Circulation with in-well Stripping (GCWIS)/SVE

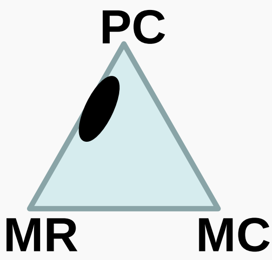
LNAPL Phase Change

- Treats volatile LNAPL compounds
- Treat vadose/saturated zones
- Short implementation time
- Short clean up time
- Promotes Aerobic Biodegradation
- More effective in higher K soils with low heterogeneity

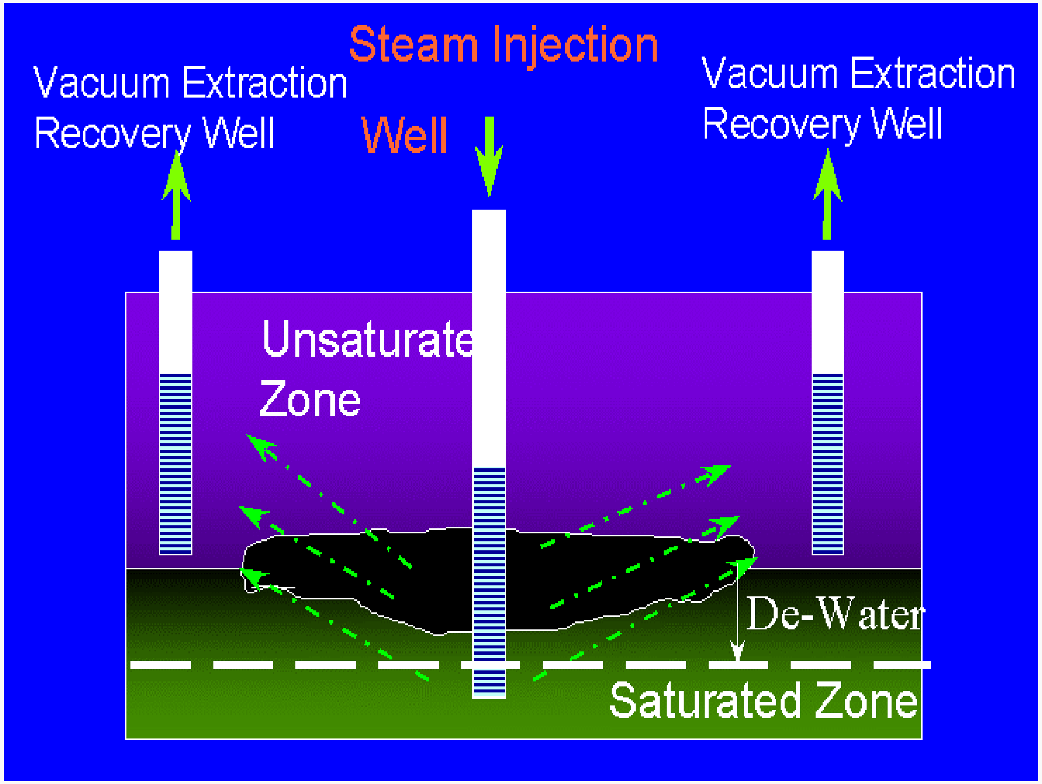




In-Situ Heating Technologies



- Technologies
  - **Steam/Hot Air Injection**
  - Radio-Frequency Heating
  - Electrical Resistance Heating
- Increases LNAPL volatility
- SVE for recovery of volatilized LNAPL
- Reduces LNAPL viscosity
- Hydraulic recovery of mobilized LNAPL
- Applicable most LNAPL
- Better in low groundwater velocity settings (<heat loss)

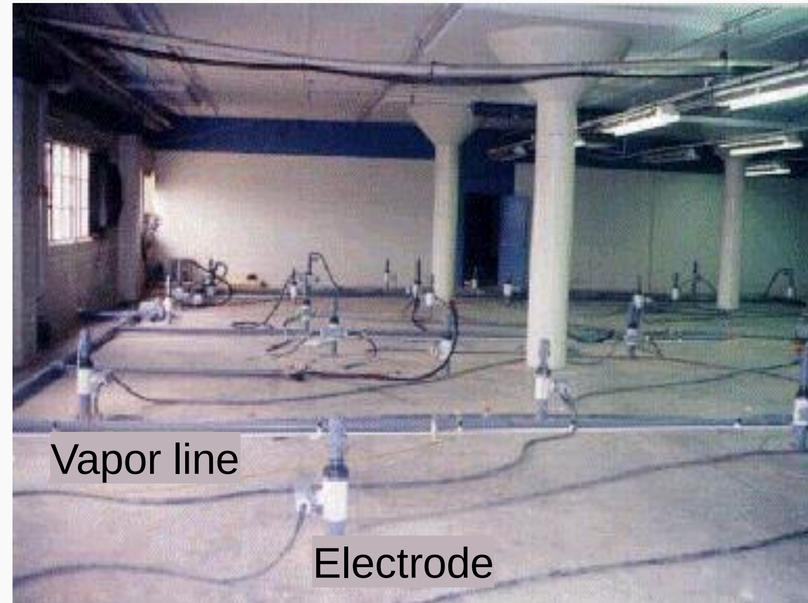


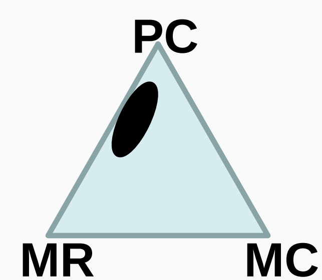
Source: ITRC LNAPL Course (ITRC)

Heating/SVE Technologies

LNAPL Phase Change

- Steam / Hot Air Injection Condensation front hydraulically drives LNAPL
  - Applicable to higher permeability soils
- Radio Frequency Heating
- Electrical Resistance Heating
  - Applicable to lower permeability soils



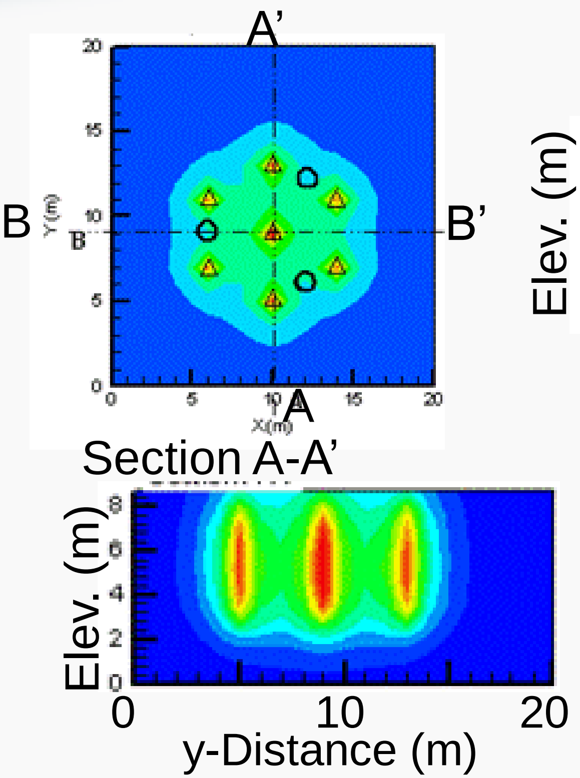


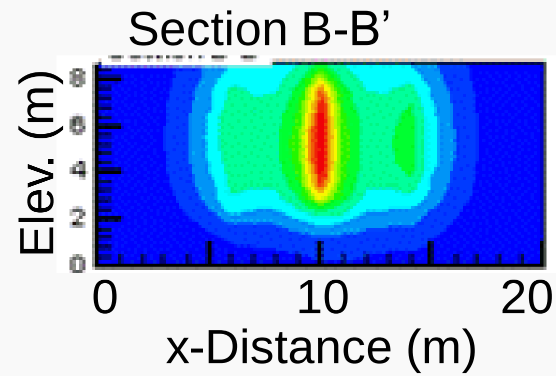
Source: ITRC LNAPL Course (ITRC)

Electrical Resistance Heating

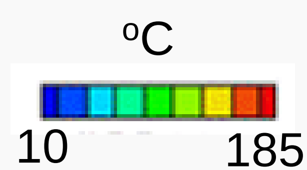
LNAPL Phase Change

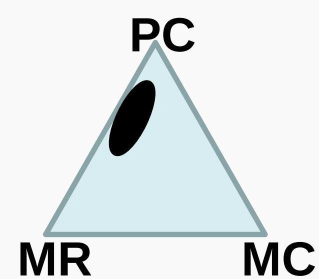
- Advantages
  - Short time frame
  - Very efficient on low K soils
  - Eliminate volatile/semivolatile compounds
  - reduce some LNAPL low saturations
  - Treats both saturated and vadose zones
- Disadvantages
  - Safety – high temperatures and pressures, electricity
  - Site restrictions due to amount of infrastructure
  - High energy requirement (carbon footprint)
- Engineering
  - SVE and hydraulic recovery well ROI
  - LNAPL chemical and fluid properties





CompFlow Simulation Extraction with heating, 130 days
Source I. Hers, Golder



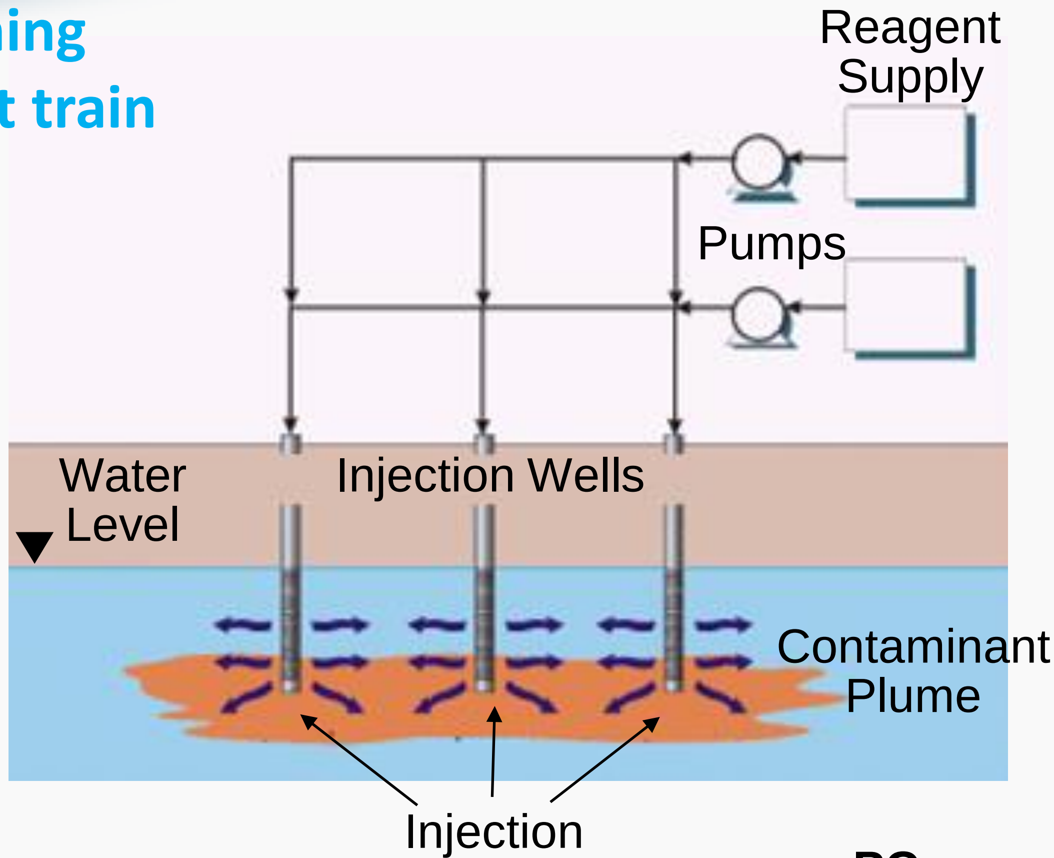


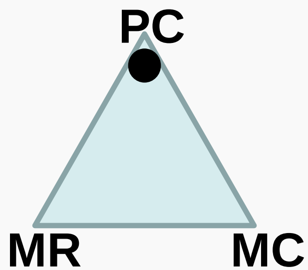
In-Situ Chemical Oxidation

LNAPL Phase Change

Typically applied as a polishing technology in the treatment train

- Destroys dissolved phase contaminants
- Increases LNAPL dissolution rate
- Applicable to residual LNAPL in high permeability soils relatively homogeneous
- Oxidants Fenton's Reagent, Persulfate, Ozone, Hydrogen Peroxide, and Permanganate



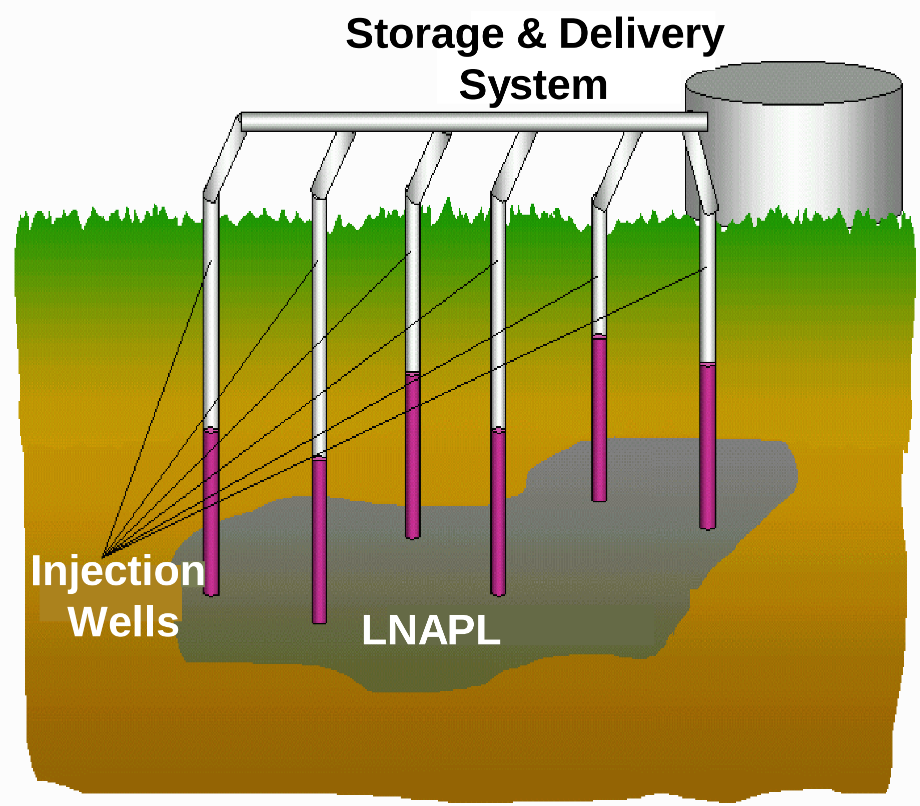


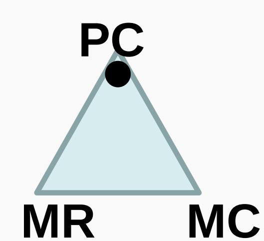
Source: ITRC LNAPL Course (ITRC)

In-Situ Chemical Oxidation

LNAPL Phase Change

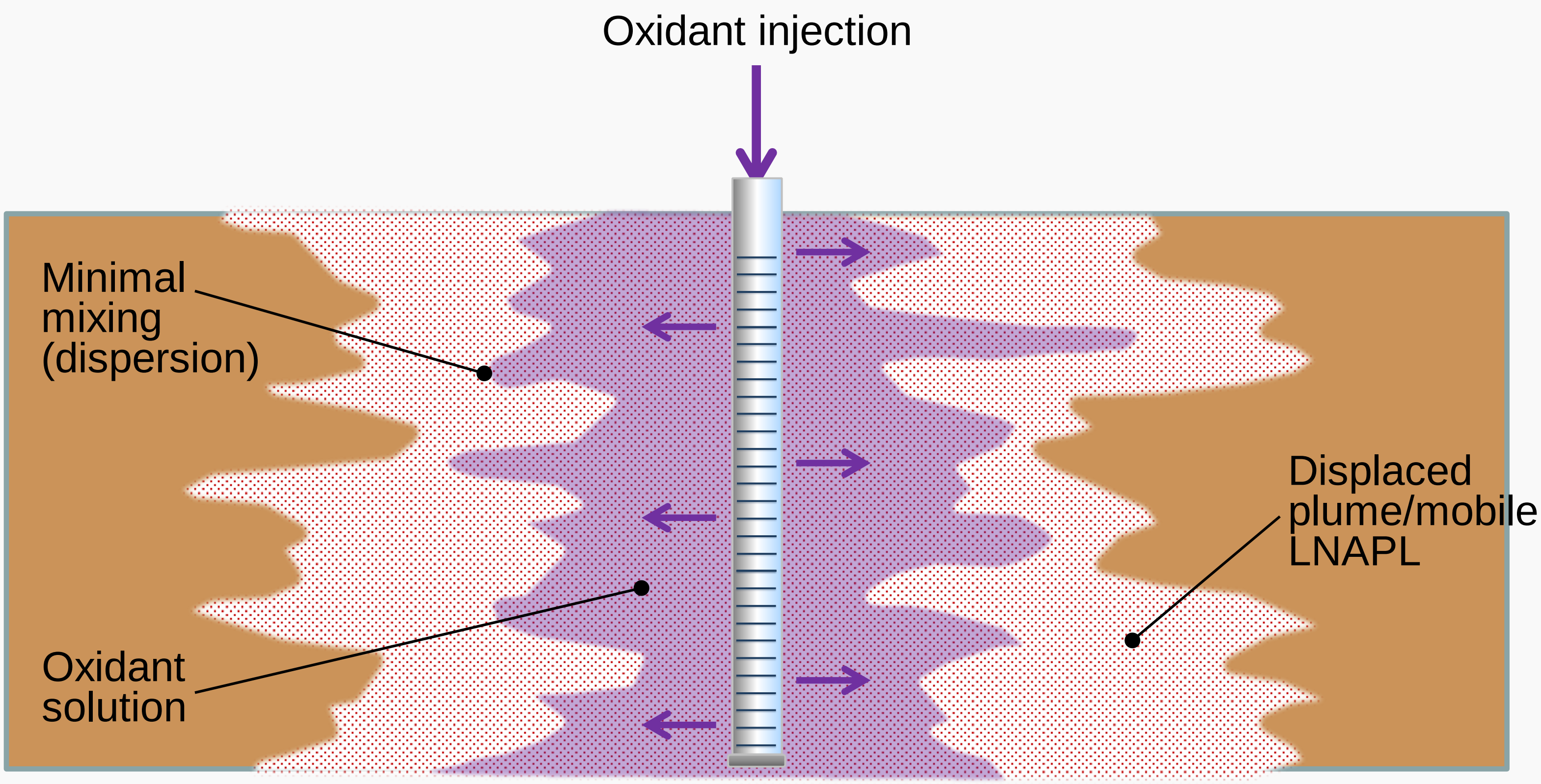
- Advantages
  - Short time frame
- Disadvantages
  - Safety – reactive chemical handling
  - Soil not a good mixing zone
  - Displaces plume and mobile LNAPL/dissolved contaminants
  - Contaminant rebound
  - Repeated treatment
- Implementation concerns
  - Match oxidant to LNAPL constituents
  - Injection ROI and volumes
  - Soil plus LNAPL oxidant demand



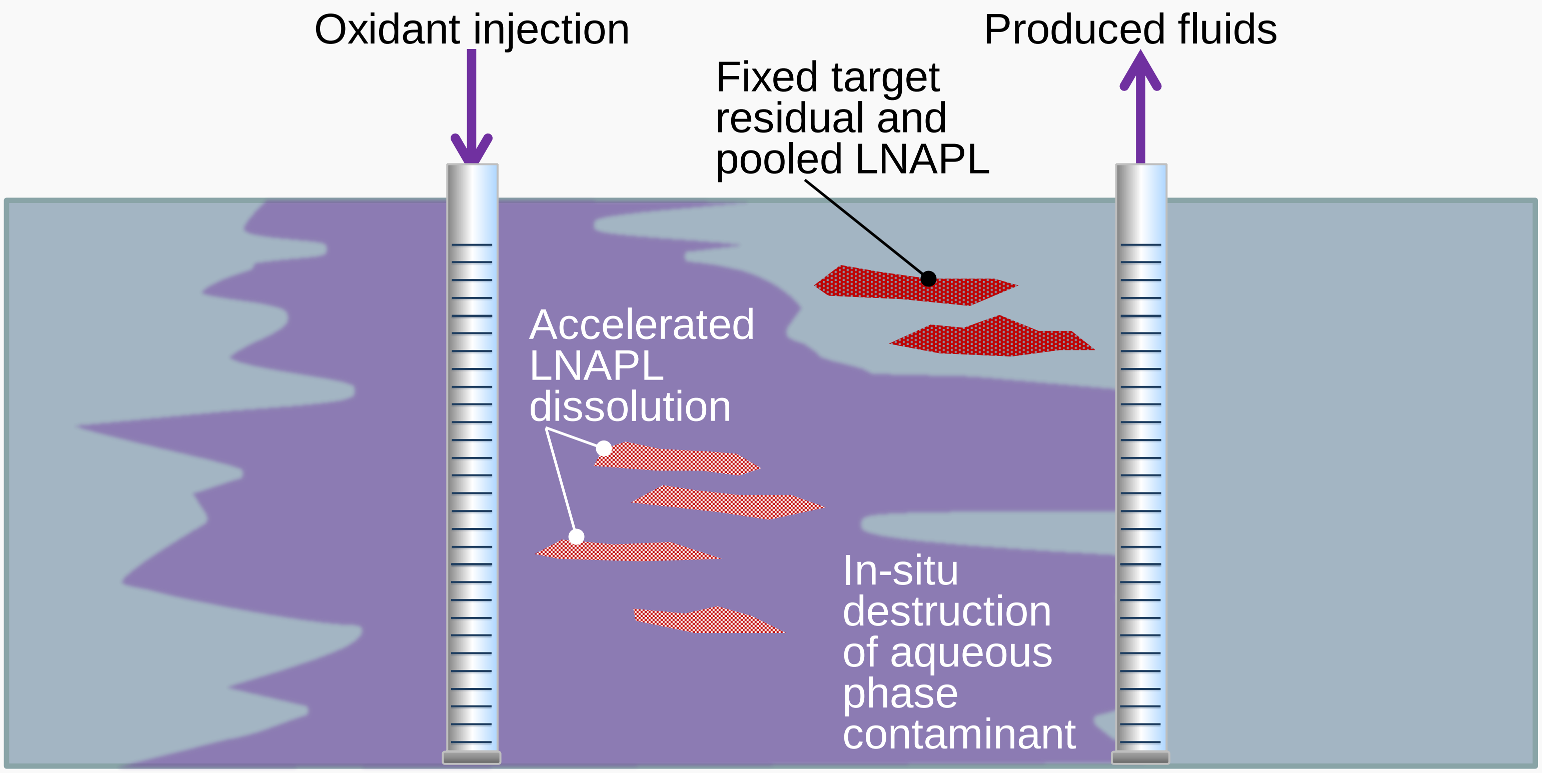


Source: ITRC LNAPL Course (ITRC)

The subsurface is not a good mixing reservoir!



Target should be immobile LNAPL



Metrics for Phase Change Technologies

- Concentrations of targets of phase change (COCs), e.g., BTEX, MTBE, or Concentrations of analytes representative of targets, e.g., TPH-GRO vs. TPH-DRO
  - Groundwater
  - Soil vapor
  - LNAPL (soil)
  - In extraction stream, e.g., soil vapor treatment system influent

Source: ITRC LNAPL Course (ITRC)

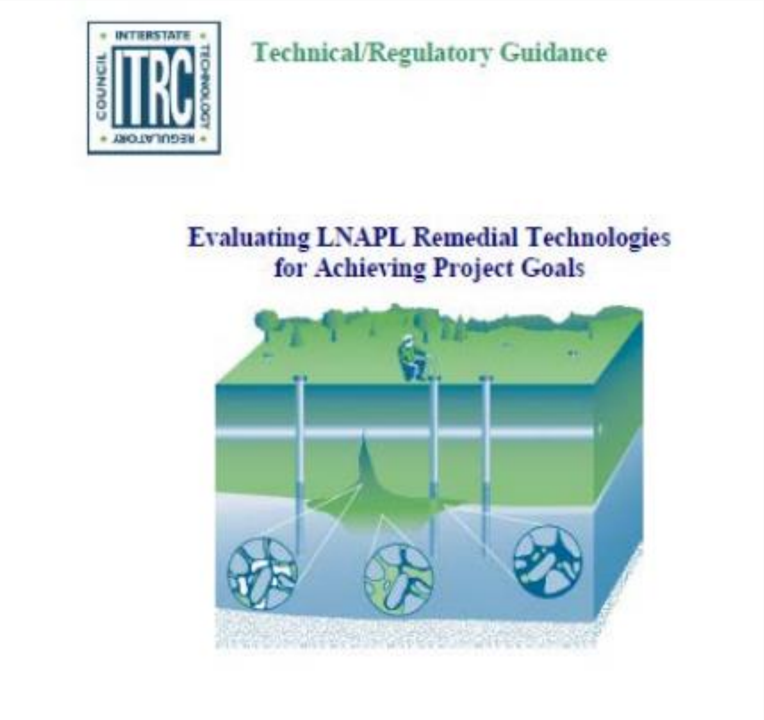
Summary and Review

- Group LNAPL Remedial Technologies
  - Physics and Chemistry of Action
  - Attainable Remedial Objectives
- Remedial Technology Groups
  - Mass Control
  - Mass Recovery
  - Phase Change
- Technology Group Overlap
- Basic and Enhanced Technologies

Source: ITRC LNAPL Course (ITRC)

ITRC Regulatory Guidance

Great Resource!!



Follow-Up

Additional training is available at: Interstate Technology and Regulatory Council https://itrcweb.org/home

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