# Starting Soon: Hydrocarbons 101 Training

This event is being recorded; Event will be available On Demand after the event at the main training page

https://www.clu-in.org/conf/itrc/Hydrocarbons/

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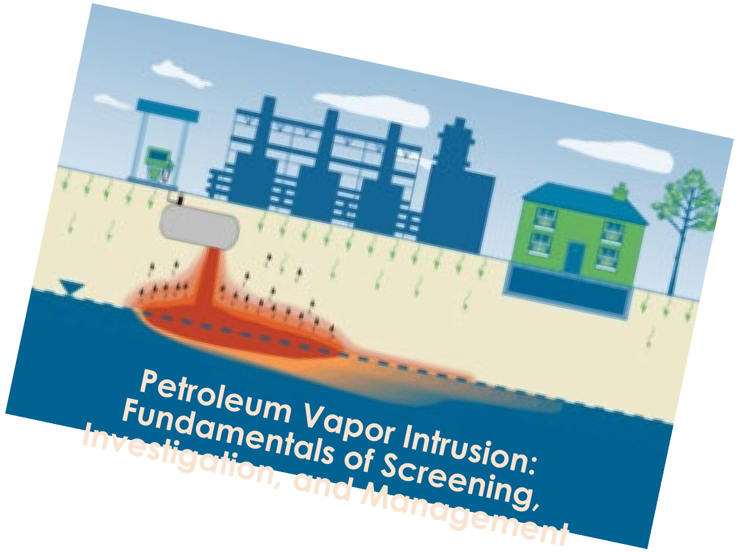
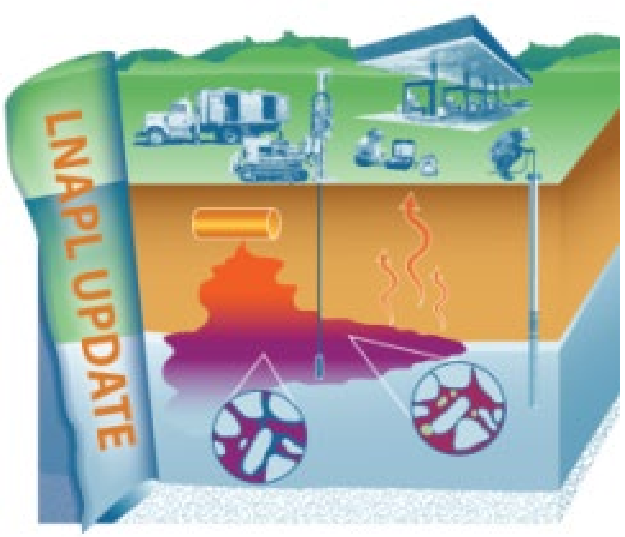
# ITRC: Introduction to Hydrocarbons



https://hyd-1.itrcweb.org/

Host Organization

ECOS

Network – 49 states, PR, DC

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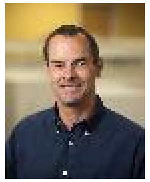

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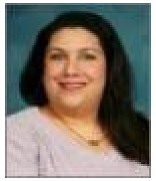

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Read Trainer Bios: https://www.clu-in.org/conf/itrc/Hydrocarbons/

# Key ITRC Petroleum Hydrocarbon Guidance

PVI (Petroleum Vapor Intrusion)

https://projects.itrcweb.org/PetroleumVI-Guidance/

LNAPL (Light Non-Aqueous Phase Liquids)

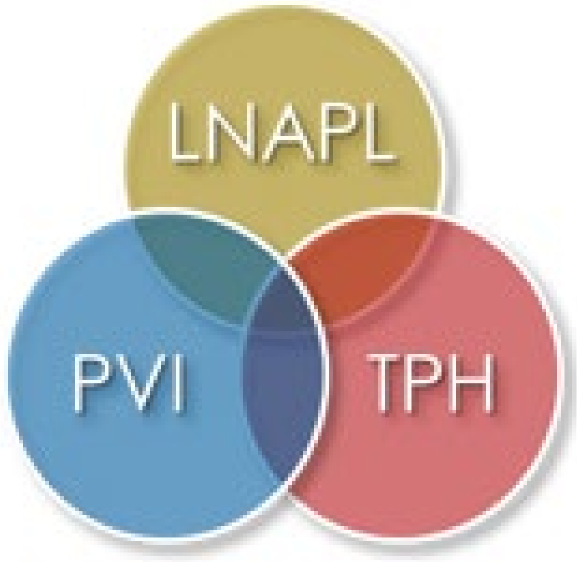
https://lnapl-3.itrcweb.org/

TPH (Total Petroleum Hydrocarbons)

https://tphrisk-1.itrcweb.org/

Hydrocarbons Sites (Effective Application of Guidance Documents)

https://hyd-1.itrcweb.org/



# Where Does This Training Apply?

All types of petroleum. Large or small sites.

# Course Training Goals

Overview of key issues to help identify and manage Total Petroleum Hydrocarbons (TPH), Light Non-Aqueous Phase Liquids (LNAPL), and Petroleum Vapor Intrusion (PVI) risks TOGETHER

Introduce what's contained in the ITRC petroleum hydrocarbon guidance documents and highlight where they overlap

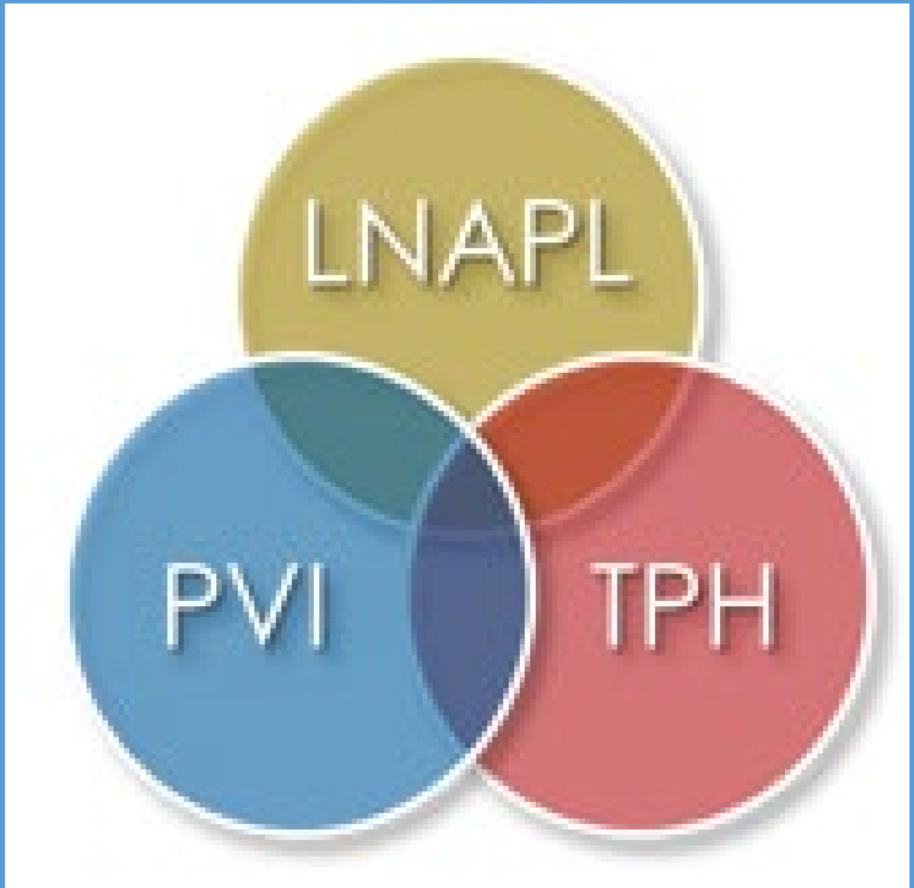
Present latest science to support best practices for site investigation (CSM development), risk management, and regulation development

Emphasize the importance of biodegradation in risk management decision making

# Course Outline

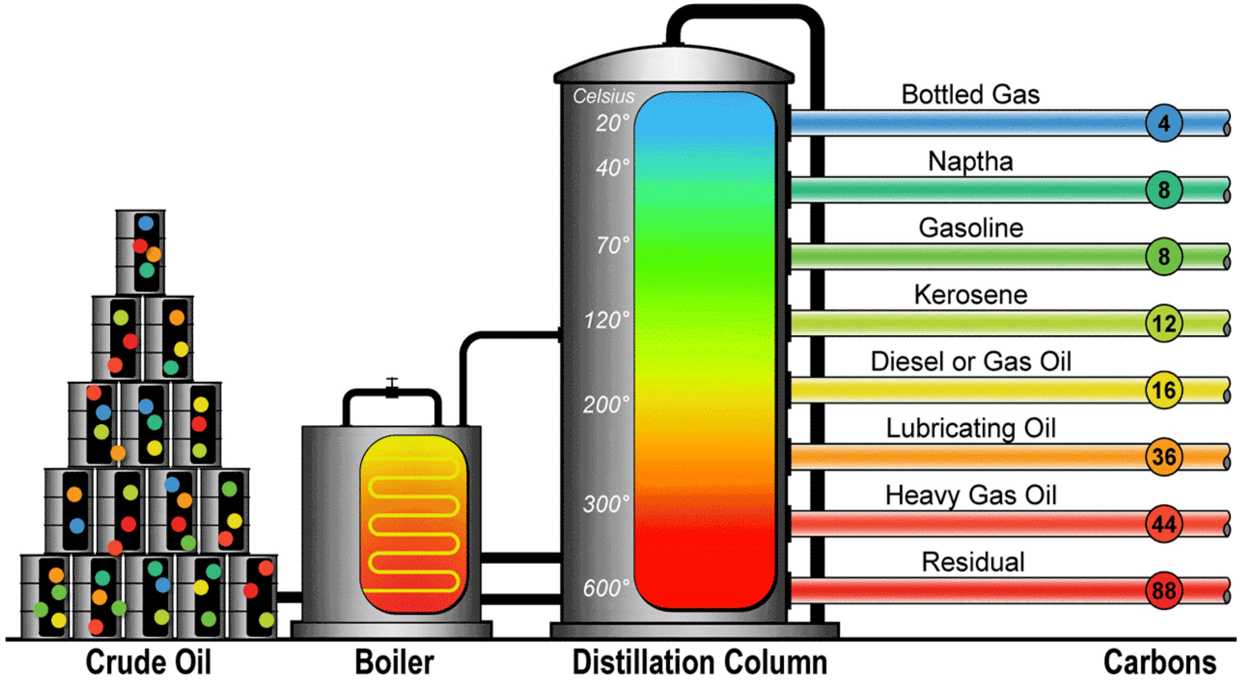
| Fundamentals of petroleum hydrocarbons | Building an integrated CSM | Identifying and managing the risks from petroleum hydrocarbons |
|---|---|---|
| Petroleum chemistry | What is a CSM… what is its purpose? | Defining LNAPL risks based on acute, saturation, composition, or aesthetic concerns |
| How are TPH, LNAPL, and PVI related? | When is a CSM complete? | |

# Fundamentals of Petroleum Hydrocarbons



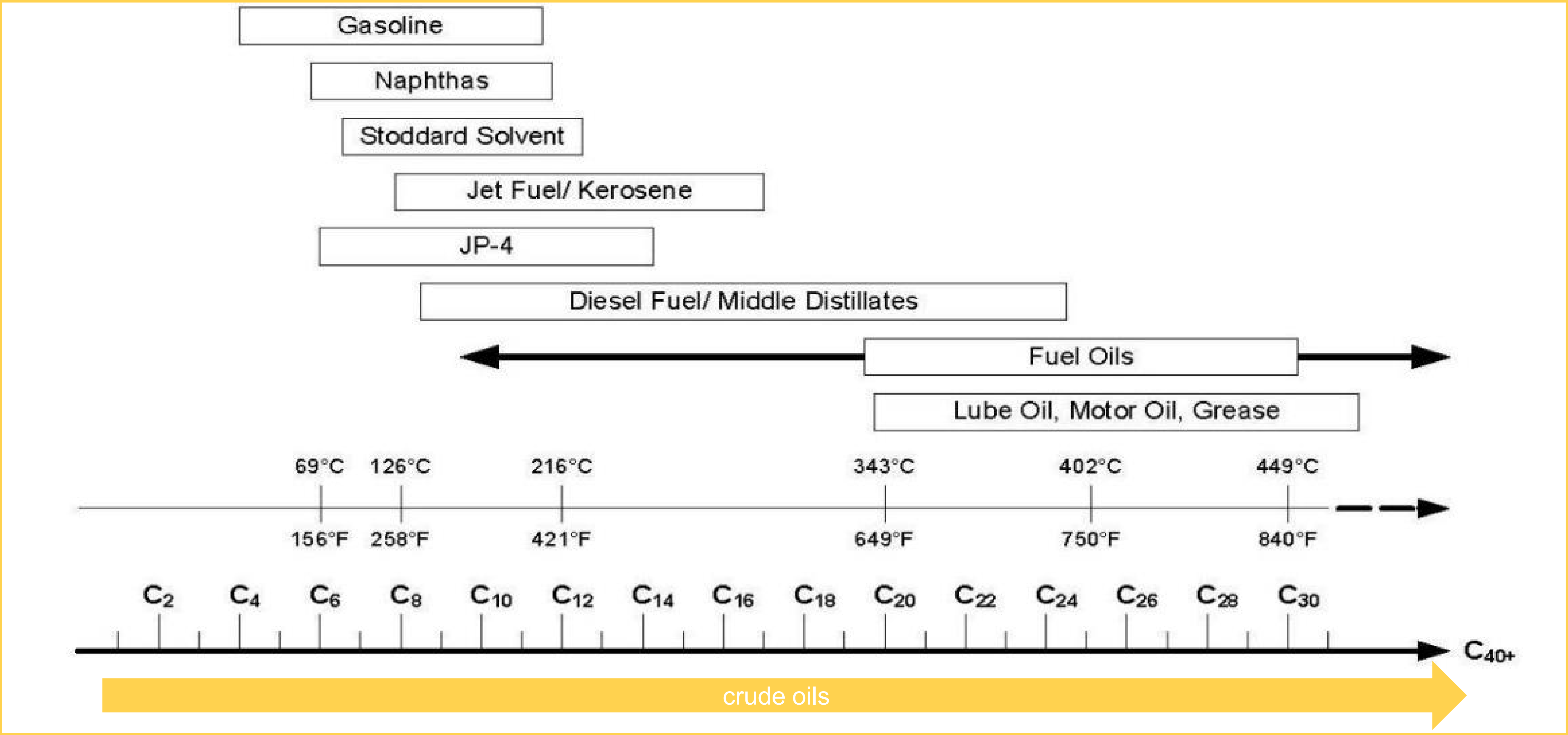
# The Chemistry of Petroleum Fuels

- Petroleum fuels (gasoline, motor oil, etc.) are distilled from the heating (refining) of crude oil
- Refined fuels contain 1000s of hydrocarbons and widely different compositions
- Petroleum and non-petroleum fuel composition are commonly quantified from TPH analyses
- TPH analyses measure petroleum hydrocarbons that are present in LNAPL, sorbed, dissolved, and vapor phases




Source: Haley & Aldrich

# Refined Fuels and Oils are Complex Mixtures




Source: TPH Criteria Working Group vol. 5 (1999)

# What is Light Non-Aqueous Phase Liquid (LNAPL)?

LNAPL is a fluid that has a density less than water and is immiscible with water

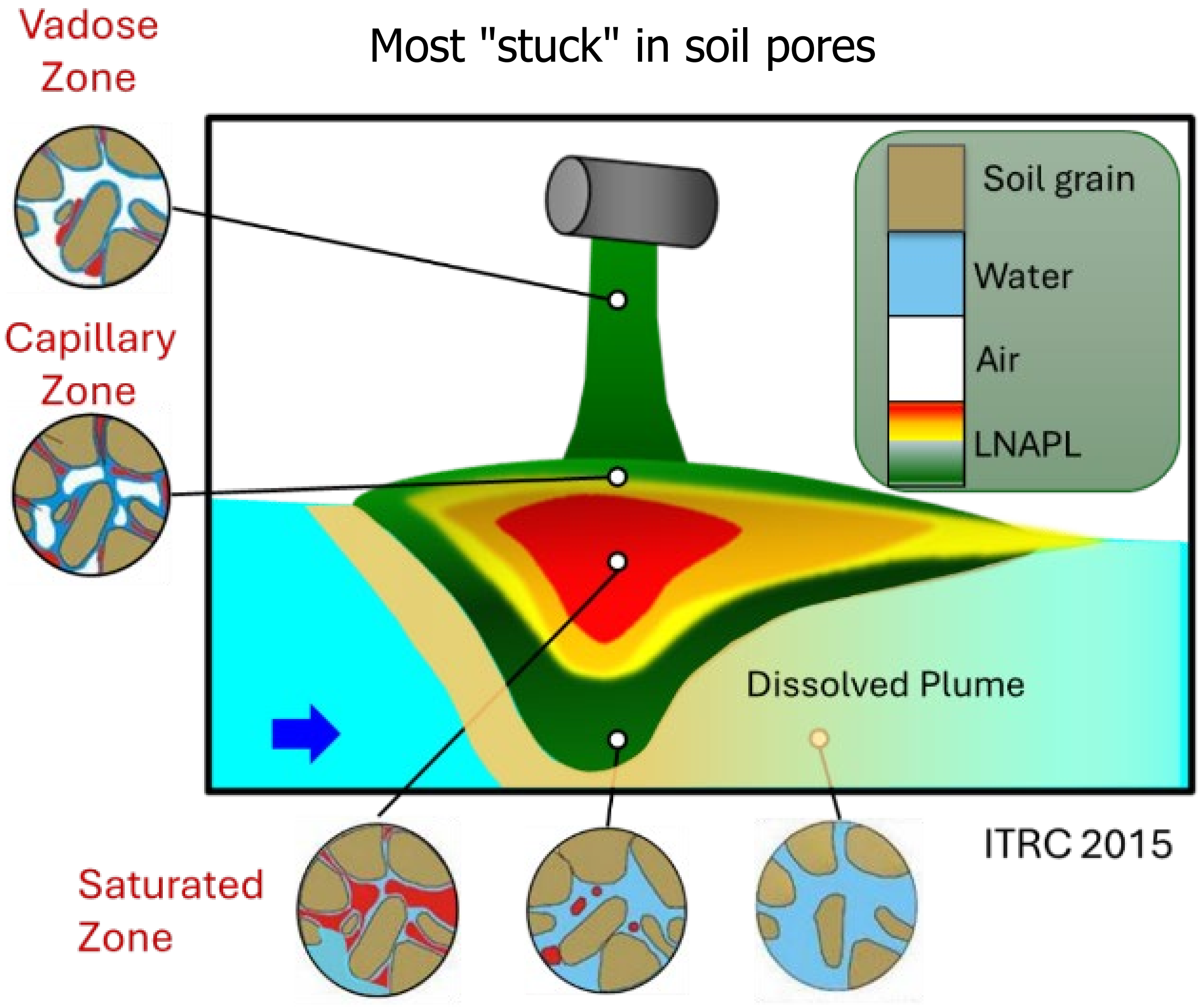
LNAPL can be difficult to assess and recover once released to the subsurface

LNAPL contains >99% of the hydrocarbon source mass and often acts as a long-term source of vapor, groundwater, and soil contamination

# How Petroleum Exists in the Environment

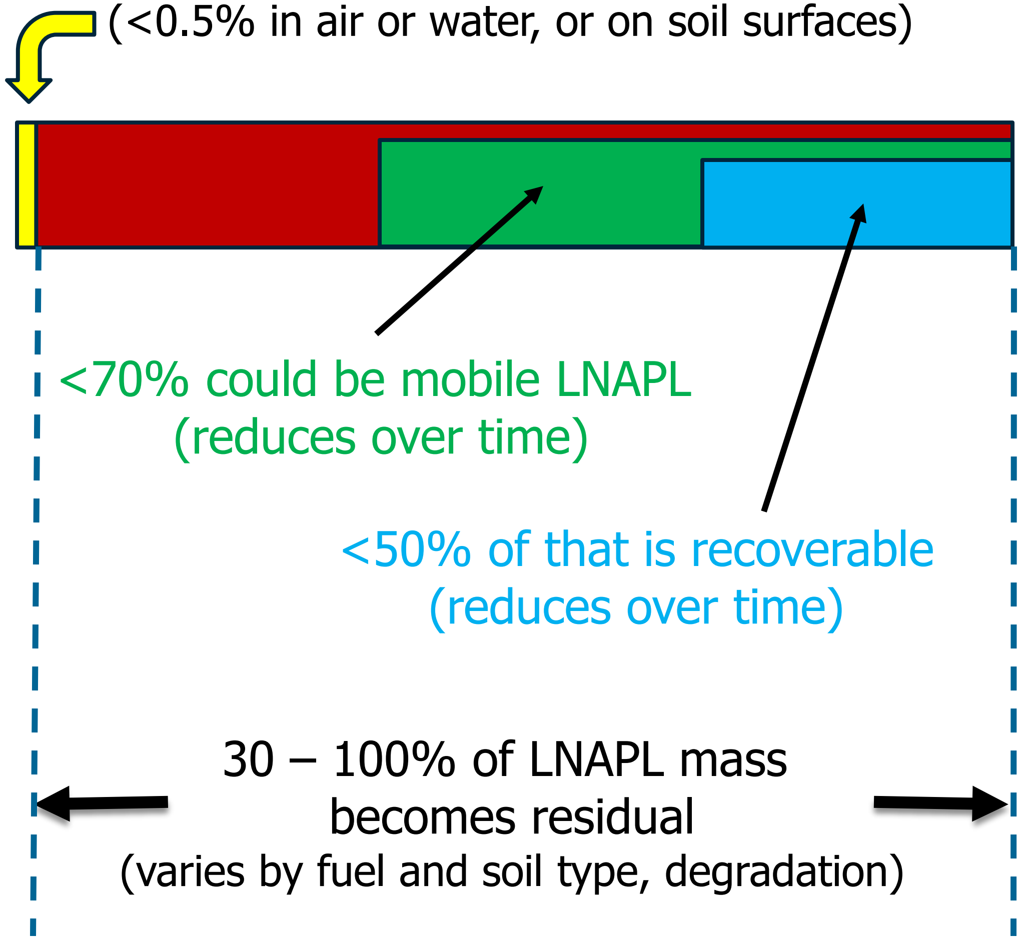
## LNAPL Location

Most "stuck" in soil pores




## LNAPL Partitioning

~99% of mass remains LNAPL!

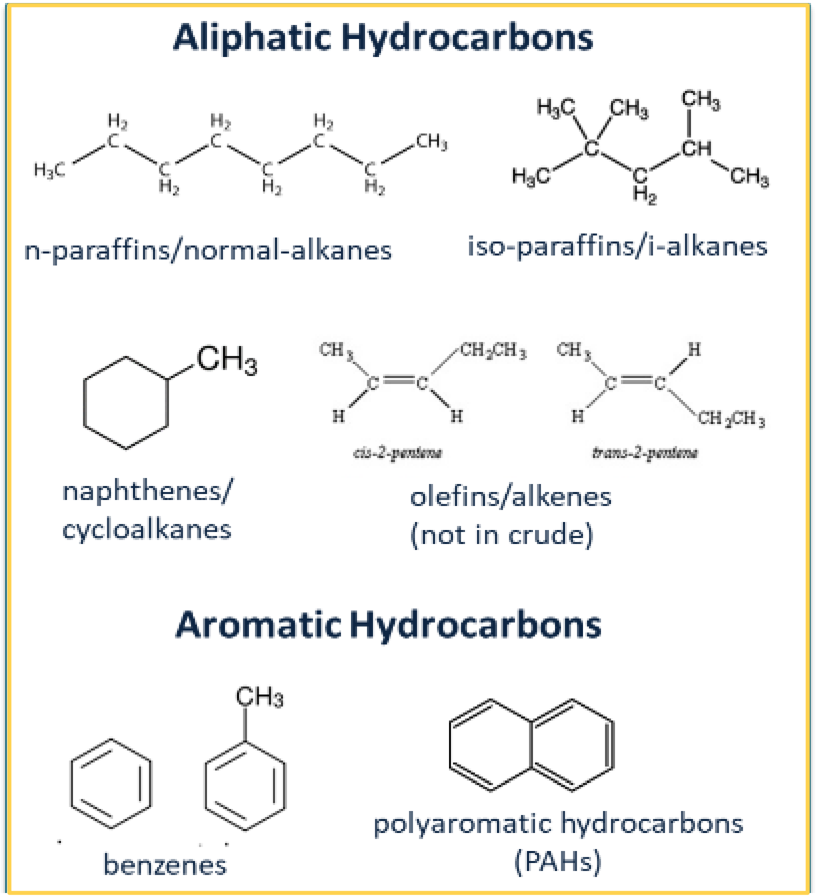


# What is TPH (Total Petroleum Hydrocarbons)?

TPH is present in soil gas, pore water, sorbed phase, and LNAPL related to:

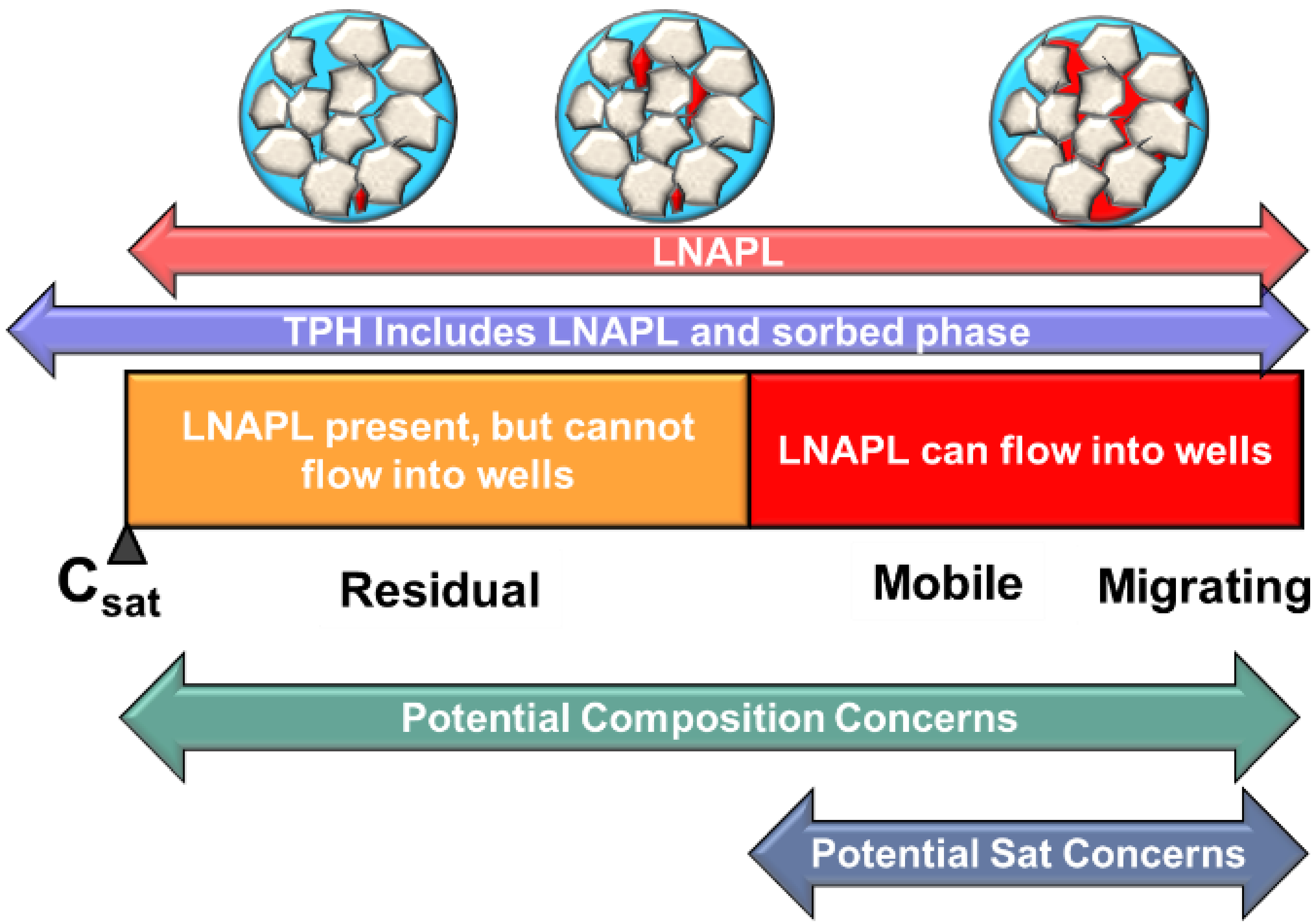
- Original LNAPL release
- LNAPL after weathering
- Hydrocarbons dissolving (leaching) from the parent
- LNAPL into porewater, groundwater, or surface water
- Hydrocarbons volatilizing from the parent LNAPL, groundwater, or pore water to soil vapor

TPH can be fractionated to understand aliphatic and aromatic classes for different carbon ranges




Source: ITRC TPHRisk-1 Figure 4-3

# TPH Versus LNAPL (Migrating, Mobile, and Residual)

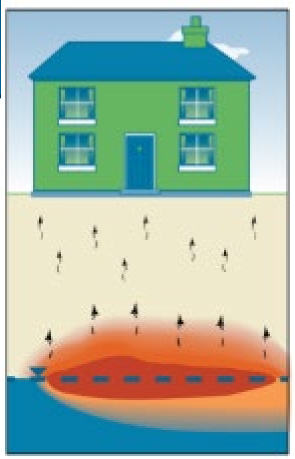



$TPH > C_{sat} \Rightarrow LNAPL$

$C_{sat}$ is a TPH concentration threshold that indicates when residual LNAPL is potentially present in soil (effective aqueous solubility & vapor pressure limits)

$C_{sat}$ varies with fuel type (gasoline, diesel) & soil type (sand, silt, clay)

# What is Petroleum Vapor Intrusion (PVI)?



Migration of vapors from petroleum-related contaminants from the subsurface into overlying buildings, causing a potential public health concern

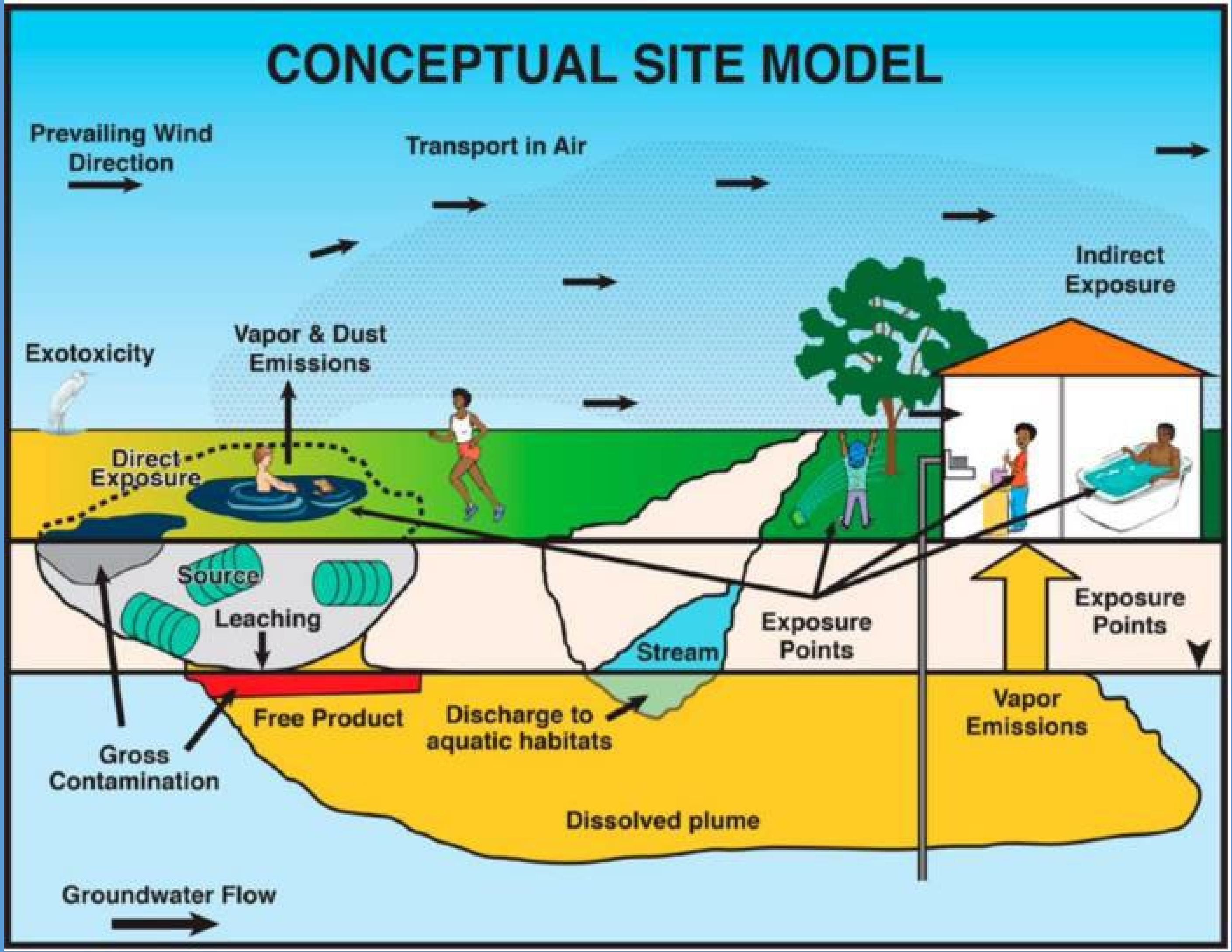
Often a key risk driver at petroleum release sites, driving environmental clean-up

Strongly influenced by source type (fuel type, LNAPL vs. dissolved phase)

Differs from chlorinated vapor intrusion (CVI)

- petroleum vapors are highly susceptible to biodegradation
- can create certain acute risks (explosion hazards) from the production of methane during biodegradation

# Building an Integrated Conceptual Site Model (CSM)

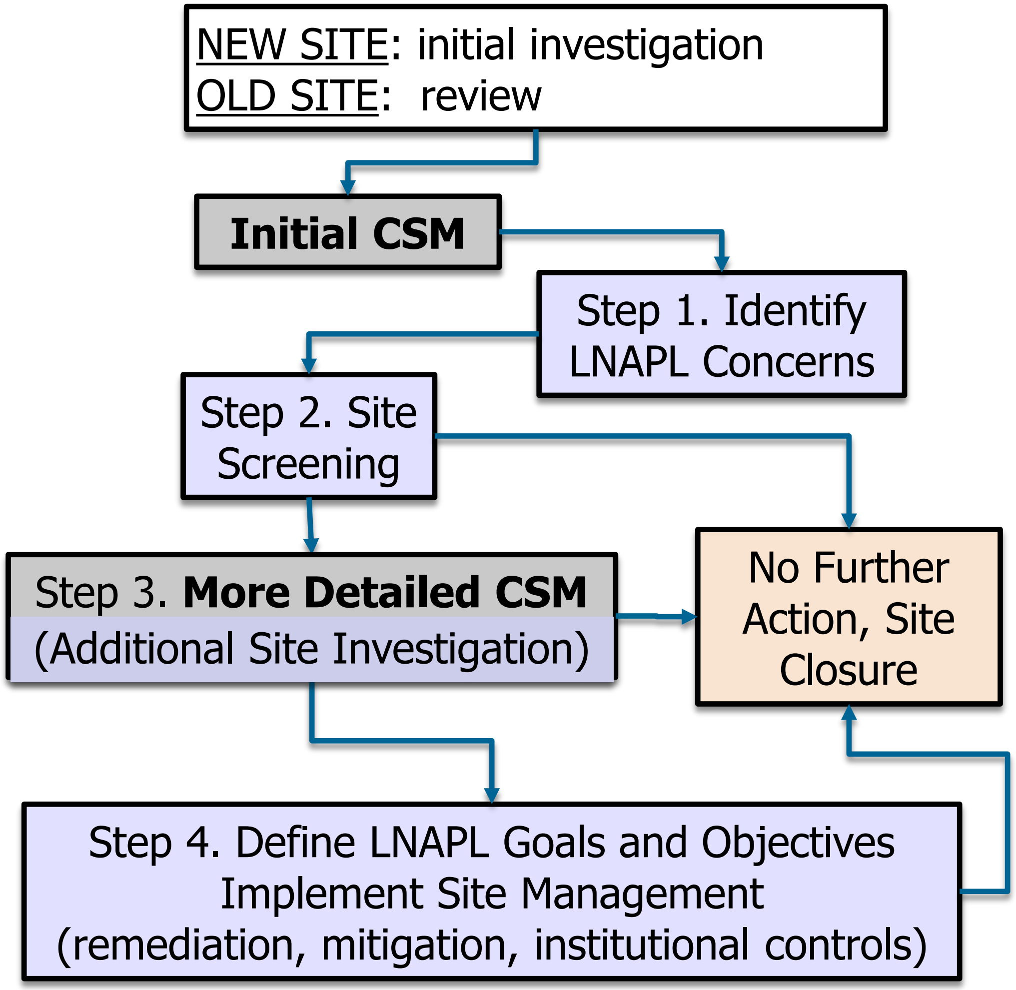



ITRC TPHRisk-1 Figure 5-1. Conceptual site model (visual depiction) showing the migration pathways of petroleum from source to receptors.

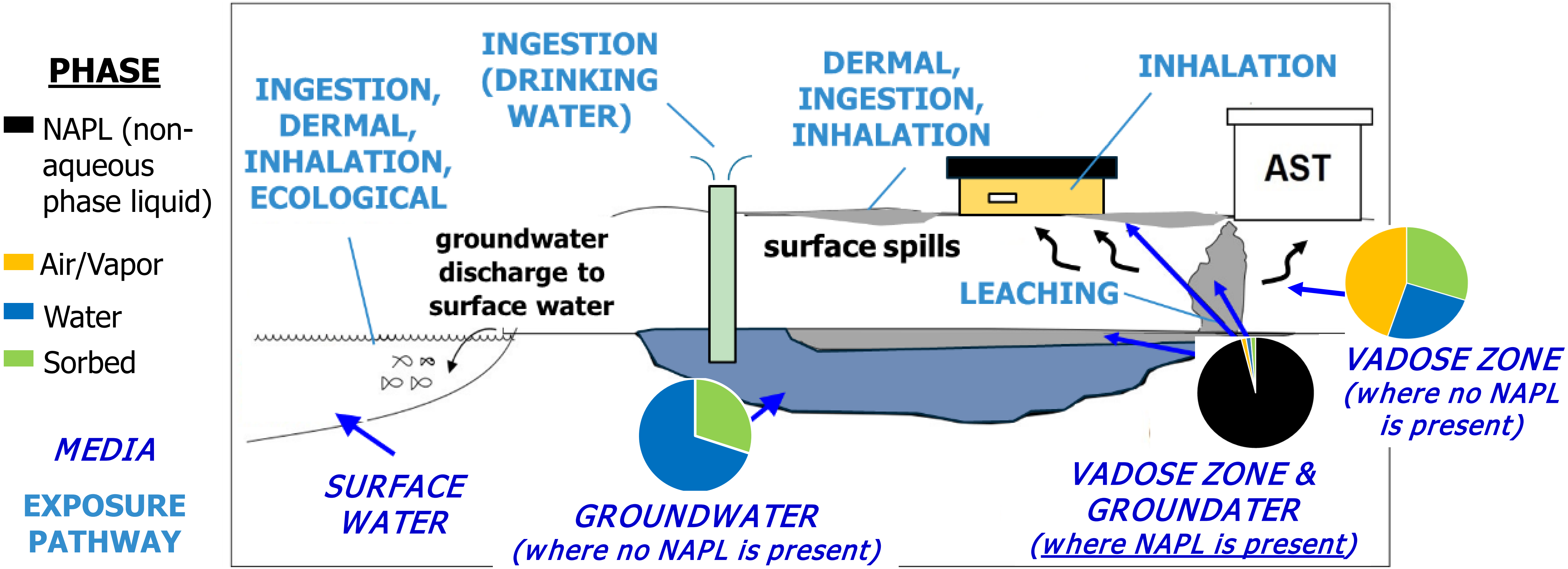
# What Is a CSM and What's It's Purpose?

- A CSM is used to:
  - ✓ identify potential sources, pathways, receptors, for current and reasonably anticipated future site conditions
  - ✓ define LNAPL concerns, goals, and objectives
  - ✓ support decision making (site screening, further data collection, risk management)

- A CSM (presented as text with supporting diagrams) is constantly updated with new site information (development and application are an iterative process)



# CSM: General Petroleum Hydrocarbon Distribution and Exposure Pathways




Source: modified from HIDOH Case Study #1, Figure 1-3 (HIDOH 2018)

hydrocarbon distributions in groundwater and the vadose zone will vary depending on hydrocarbon

# ITRC's Hydrocarbons CSM Development Checklist

## ITRC Petroleum Risk Evaluation Checklist

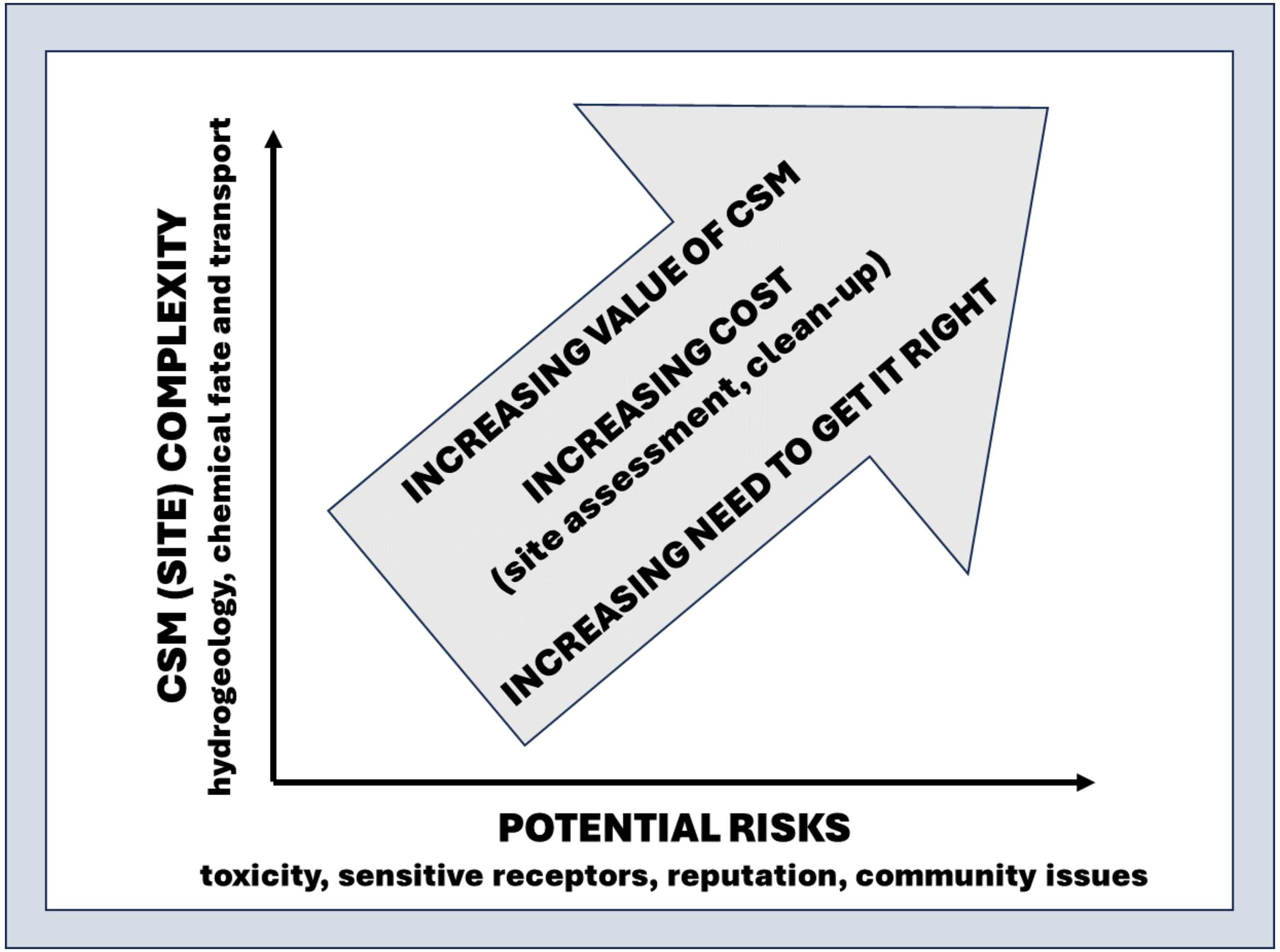
| *Screening Questions* | *References* (all PVI references can be accessed through links on page 12 of the Tech Reg) | *Applicable to Scenario? (Y/N)* | *Notes* |
| --- | --- | --- | --- |
| **STEP 1: Emergency Response/Initial Investigation** *(LNAPL: does not address emergency responses)* | | | |
| Was emergency response required? | PVI Figure 1-1<br>TPH Section 2.4<br>TPH Section 9.2 | | maintain surveillance of any location where an exposure has already occurred (identifies preferential migration pathways) |
| **STEP 2: Site Characterization to create the Conceptual Site Model** | | | |
| How to create an Initial Conceptual Site Model. | LNAPL Section 4 - 4.3<br>TPH Section 5<br>PVI Section 2.3 | | |
| Where is the release source location?<br>Is there an ongoing release of LNAPL? | TPH Table 5-1<br>LNAPL Section 3.2.1<br>PVI Section 3.1.4 | | |
| **Site Type** - Classify site as either:<br>• Petroleum UST/AST Site: Petroleum UST/AST sites generally include: a) facilities used for vehicle fueling (e.g., gas stations, municipal fleet yards, bus terminals, fire stations, etc.) and b) commercial/home heating oil tanks. Fuels and oils at these sites are typically stored in USTs, but could be stored in similarly sized ASTs.<br>• Petroleum Industrial Site: Includes: a) bulk fuel terminals, b) refineries, c) exploration and production sites, d) crude oil and product pipelines, and e) former manufactured gas plants. | PVI Section 2.5<br>PVI Table 2-2<br>PVI Section 3.1.1<br>PVI Appendix E | | |

https://hyd-1.itrcweb.org/petroleum-risk-evaluation-checklist/

# Not All CSMs Are Created Equal

- The CSM should be tailored to site conditions and identifying and managing potential risks

- Sites with complex hydrogeology and/or high technical or reputational risks require a more detailed CSM!

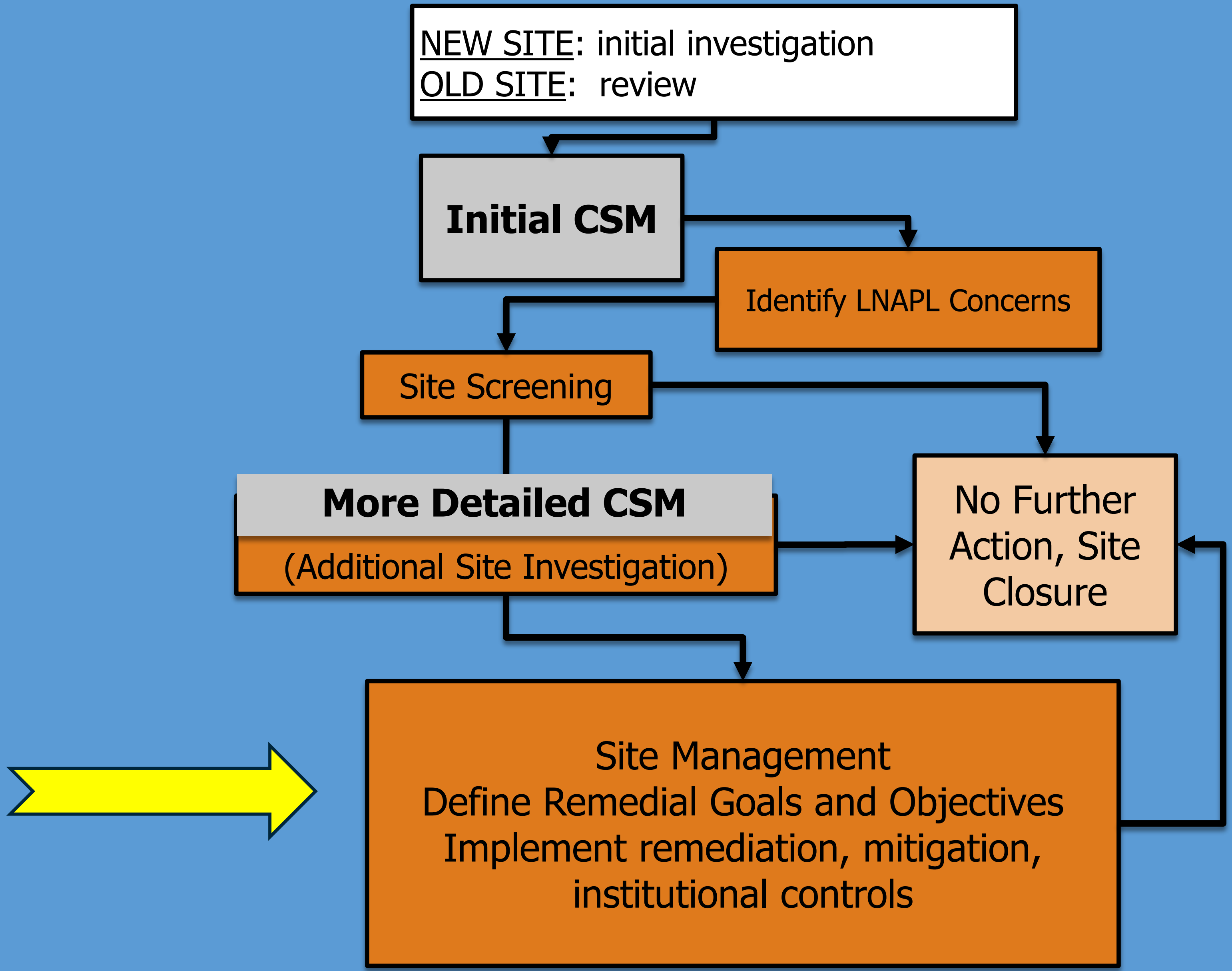


# When is the CSM Complete?

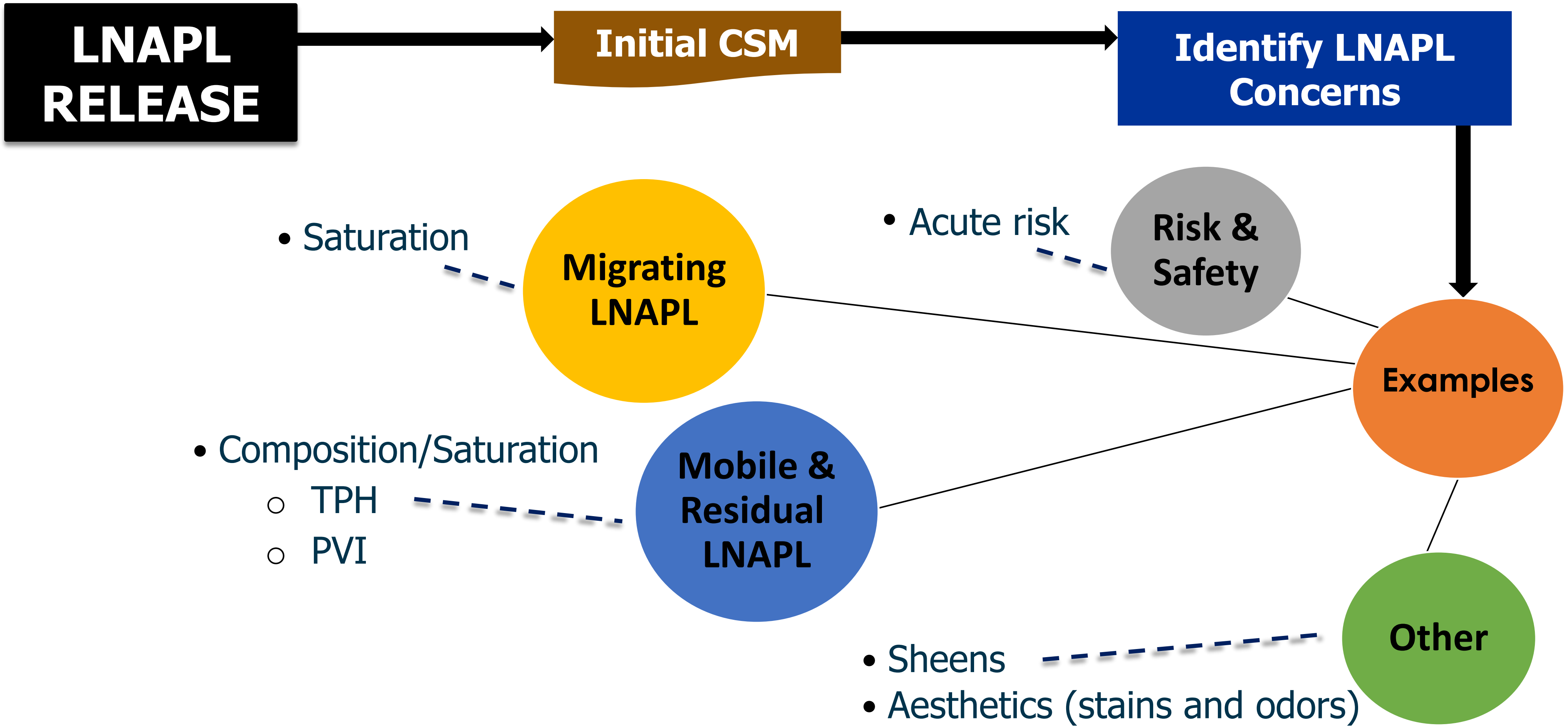
| Have relevant sources, pathways, and current/future receptors been identified? | Is the information sufficient to bound uncertainties related to changes in site conditions (e.g., spatiotemporal variability in constituent concentrations, changes in land use)* | Is the information sufficient to support the identification of LNAPL goals, concerns and objectives (described in next section)? |
|---|---|---|

* **greater uncertainty may be ok at low-risk sites (e.g., urban gas station with no drinking water wells)**

# Identifying & Managing Risks from Petroleum Hydrocarbons



# Identifying LNAPL Concerns (4 Types)




**GENERAL TIERED ASSESSMENT**

1) Identify acute risks
2) Identify and address Migrating LNAPL
3) Identify and address risks from Mobile and Residual LNAPL (TPH, PVI, sheens, aesthetics)

# Terminology

## Remedial Concern

LNAPL condition or potential condition:

- additional LNAPL migration (saturation concern)
- safety or health/environment risk (composition concern)
- seep, sheen, stain, odor (aesthetic/other concern)

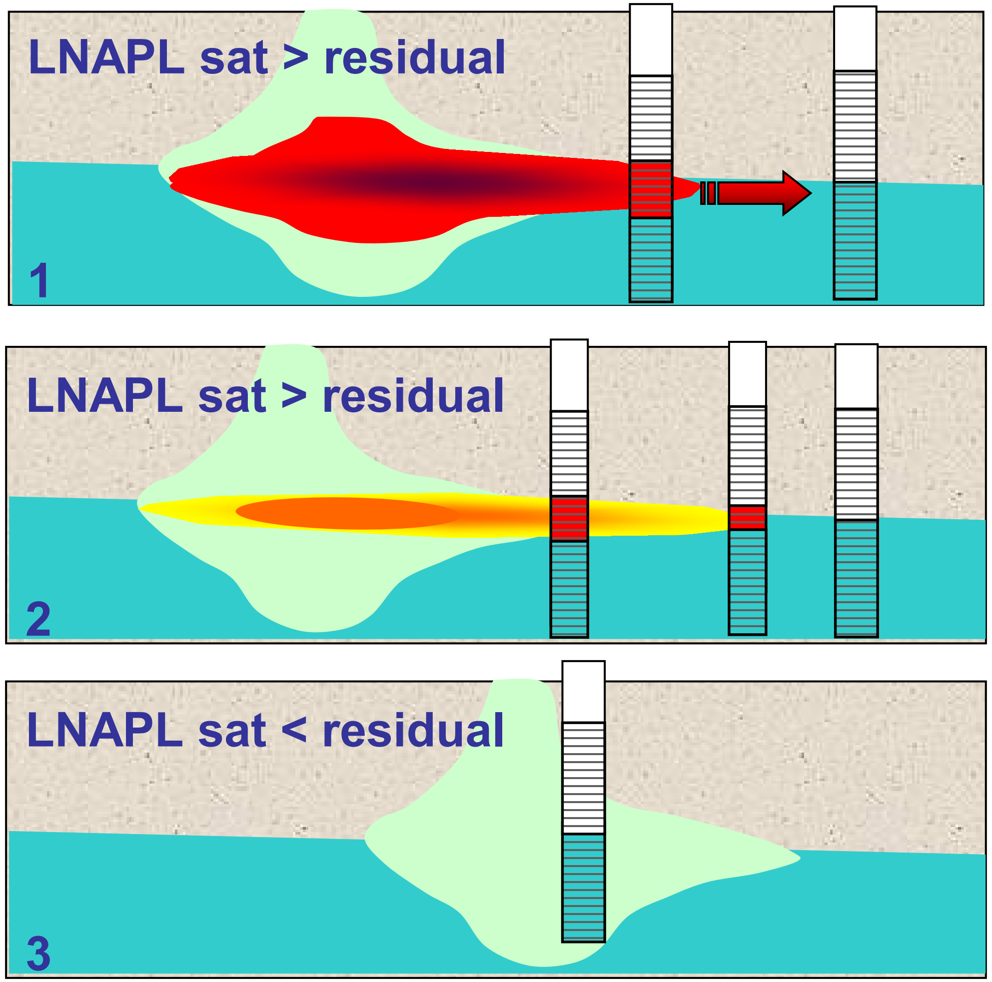
## Remedial Goals

Desired LNAPL outcome of remediation (e.g., reduce COC concentrations to below clean-up levels)

## Remedial Objectives

Describes how the goal will be accomplished and must be linked to the technology(ies) to be used (e.g., target volatiles COCs using soil vapor extraction - SVE)

# Concerns Differ Based on General LNAPL Scenario




Condition: LNAPL in wells, <u>migrating</u>
Concern: LNAPL <u>saturation</u>

**Migrating LNAPL**

Condition: LNAPL in wells, <u>mobile</u>
Concern: LNAPL <u>composition, saturation</u>

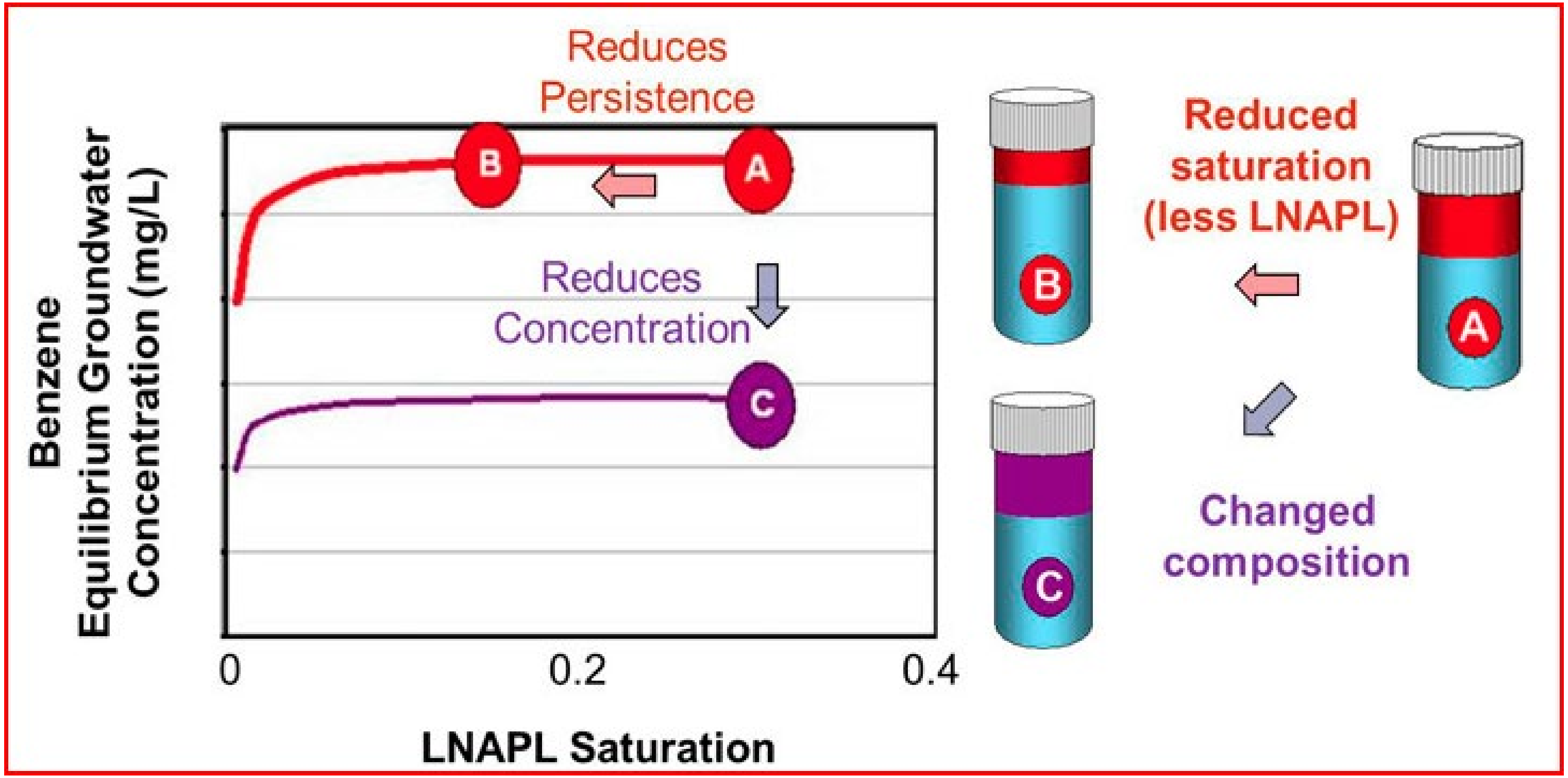
**Mobile LNAPL**

Condition: No LNAPL in wells, residual
Concern: LNAPL <u>composition</u>

**Residual LNAPL**

Image: ITRC LNAPL-3 Figure 3-8.

# Contrast Between Saturation and Composition Goals




Reducing LNAPL saturation will not affect composition (chemical concentrations in groundwater or soil gas) unless virtually all LNAPL is removed!!

Image: ITRC LNAPL-3 Figure 3-5.

# Key Message 1

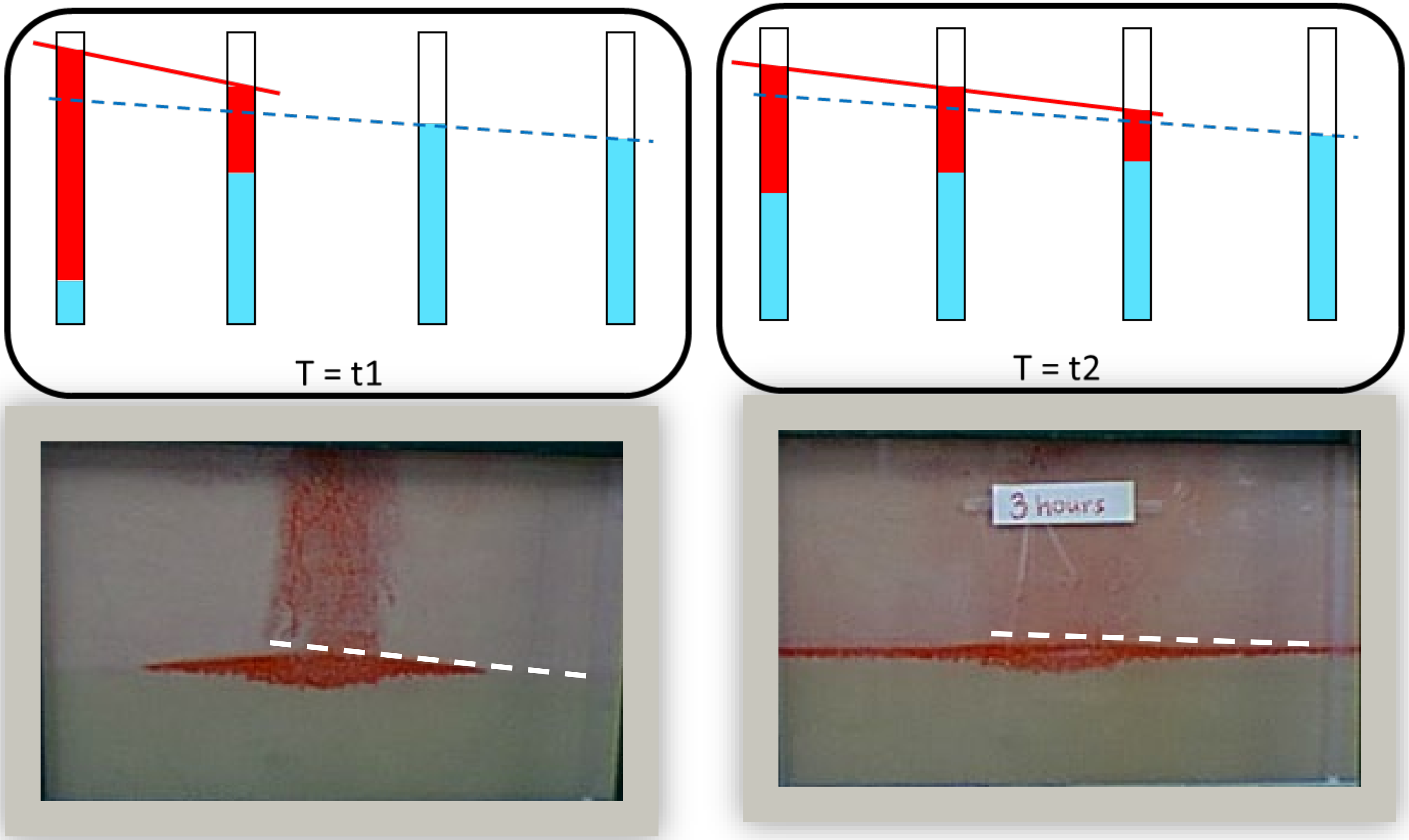
LNAPL bodies typically stabilize quickly.

Mobile LNAPL in wells does not mean that the LNAPL body is migrating

Additional Information: LNAPL-3: Section 3.2

# LNAPL Gradient: Finite Releases Flatten Over Time

**Migrating LNAPL**



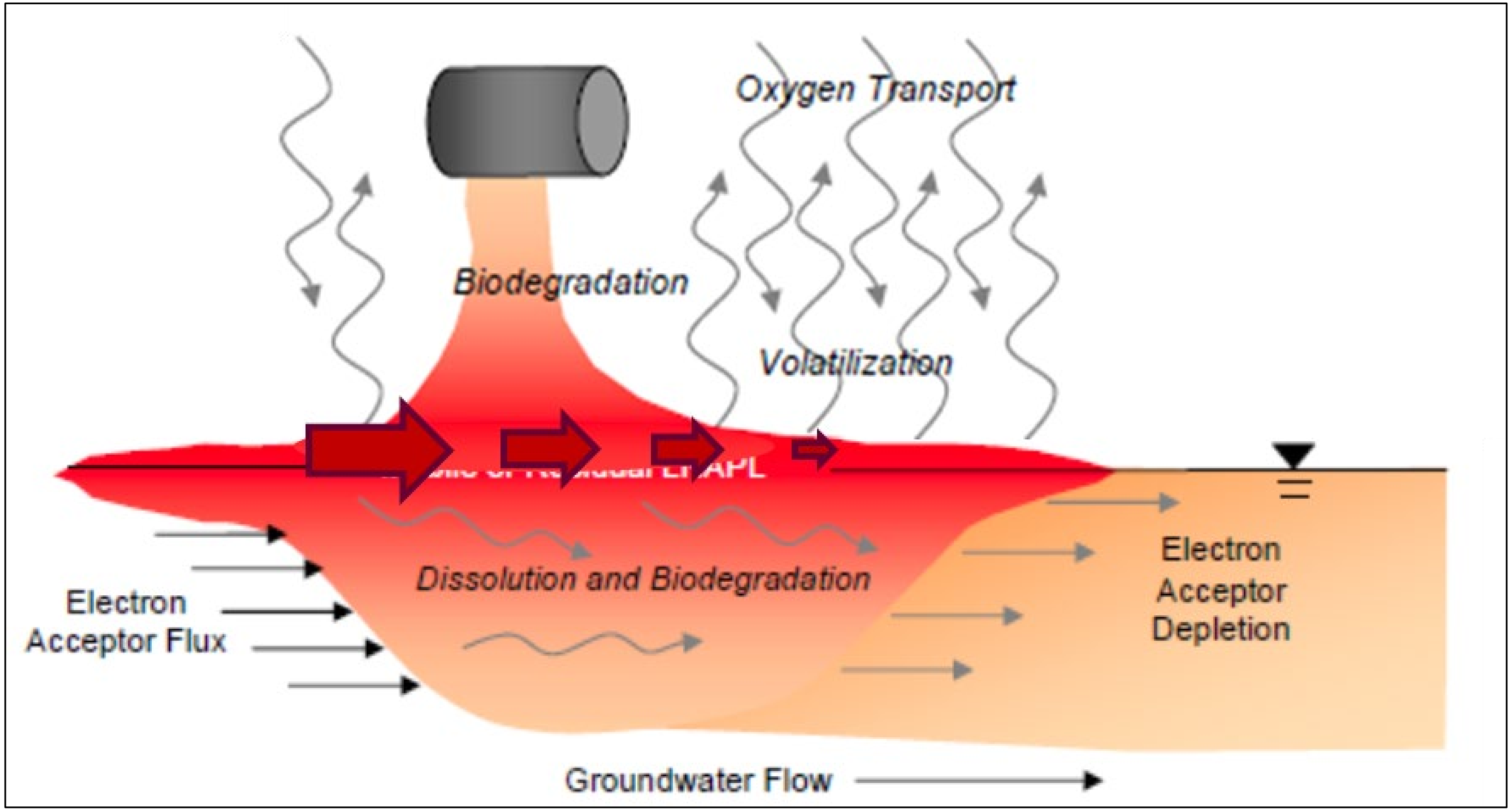

- 30-60% of the pore volume occupied by LNAPL will remain as residual
- Finite release means finite extent
- Abating the release promotes stability

Image: ITRC LNAPL-3 Training

Additional Information: LNAPL-3: Section 3.2.1

# LNAPL Body Stability

**Migrating LNAPL**




Plume stability occurs when the perimeter of the plume attains sufficient size or location such that attenuation mechanisms equal or exceed the mass flux at that boundary

Image: ITRC LNAPL-1 Figure 1-1. Example LNAPL Source Zone

Additional Information: LNAPL-3: Section 3.3

# What We Have Observed at LNAPL Sites

Migrating LNAPL

Mobile LNAPL

LNAPL can initially spread at rates higher than the groundwater flow rate due to large LNAPL hydraulic heads at time of release

LNAPL can spread opposite to the direction of the groundwater gradient (radial spreading)

After LNAPL release is abated, the petroleum hydrocarbon mass becomes finite and the LNAPL body becomes stable. Stability is generally achieved within a short period of time (<5 years)



Additional Information: LNAPL-3: Section 3.2

# Evidence To Demonstrate LNAPL Is Not Migrating

**Migrating LNAPL**

**Mobile LNAPL**

Stable/decreasing LNAPL footprint (areal distribution or thickness of LNAPL in monitoring wells over time that accounts for seasonal changes in water-table elevation)

Stable/decreasing COC concentrations and plume lengths over time

Low LNAPL transmissivities (such as less than 0.8 $ft^2/d$) when not adjacent to a surface water body (ITRC, 2018)

Residual LNAPL observed beyond the footprint of mobile LNAPL

LNAPL thickness (in MW) exceeds a critical thickness for migration (LNAPL and soil type dependent unconfined conditions only)

*Society of Brownfield Risk Assessment - SOBRA, 2023*



From WK78667 Draft ASTM Guide for Advancing Stalled Corrective Action Sites Toward Site Closure

# Questions

# Key Message 2

Apparent LNAPL thicknesses in wells is affected by water table fluctuations and the LNAPL hydrogeologic condition.

Additional Information: LNAPL-3: Sections 3.1, 3.4, and 3.5

# Thickness of Mobile LNAPL ≠ Thickness in Formation

Mobile & Residual LNAPL

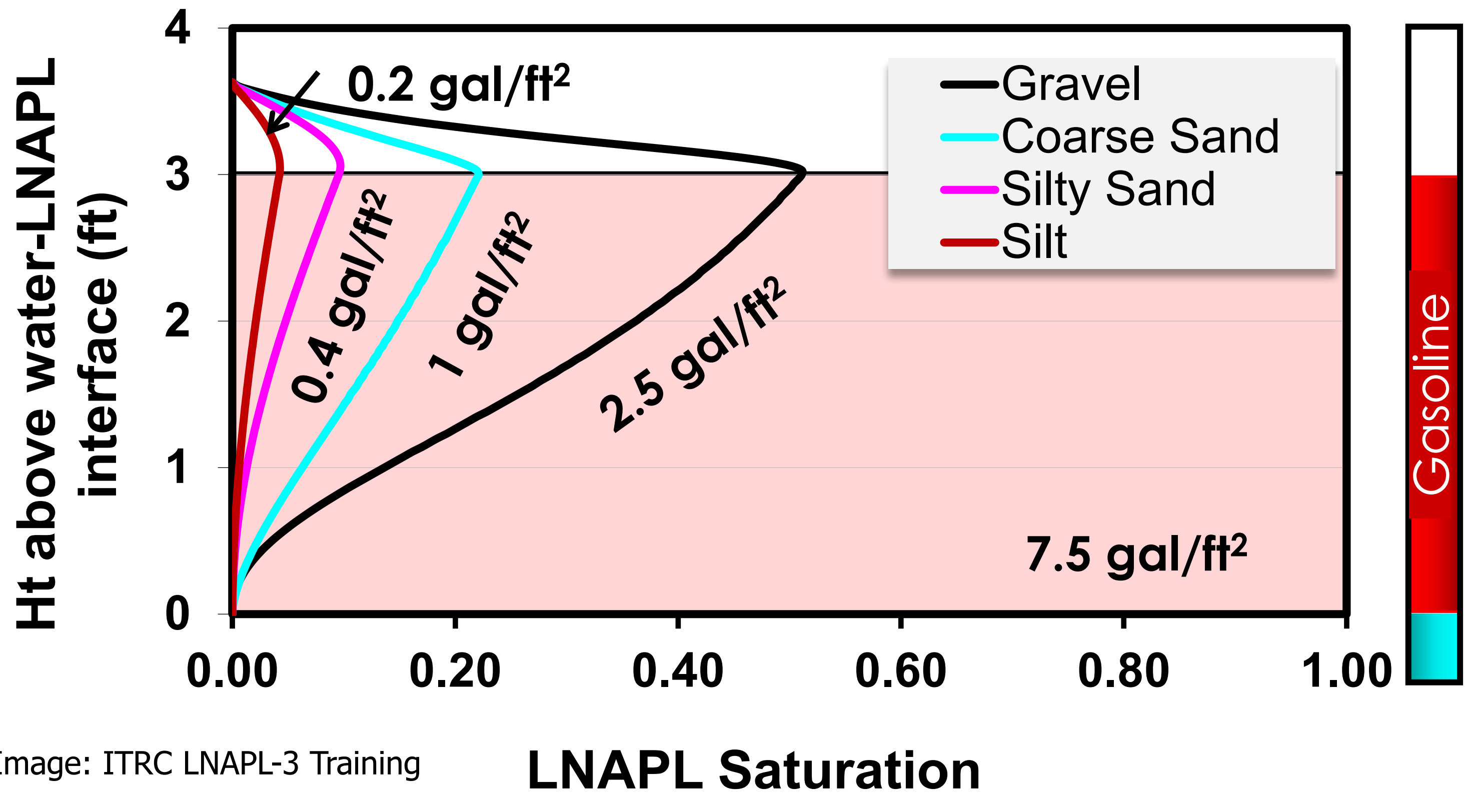



Image: ITRC LNAPL-3 Training

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

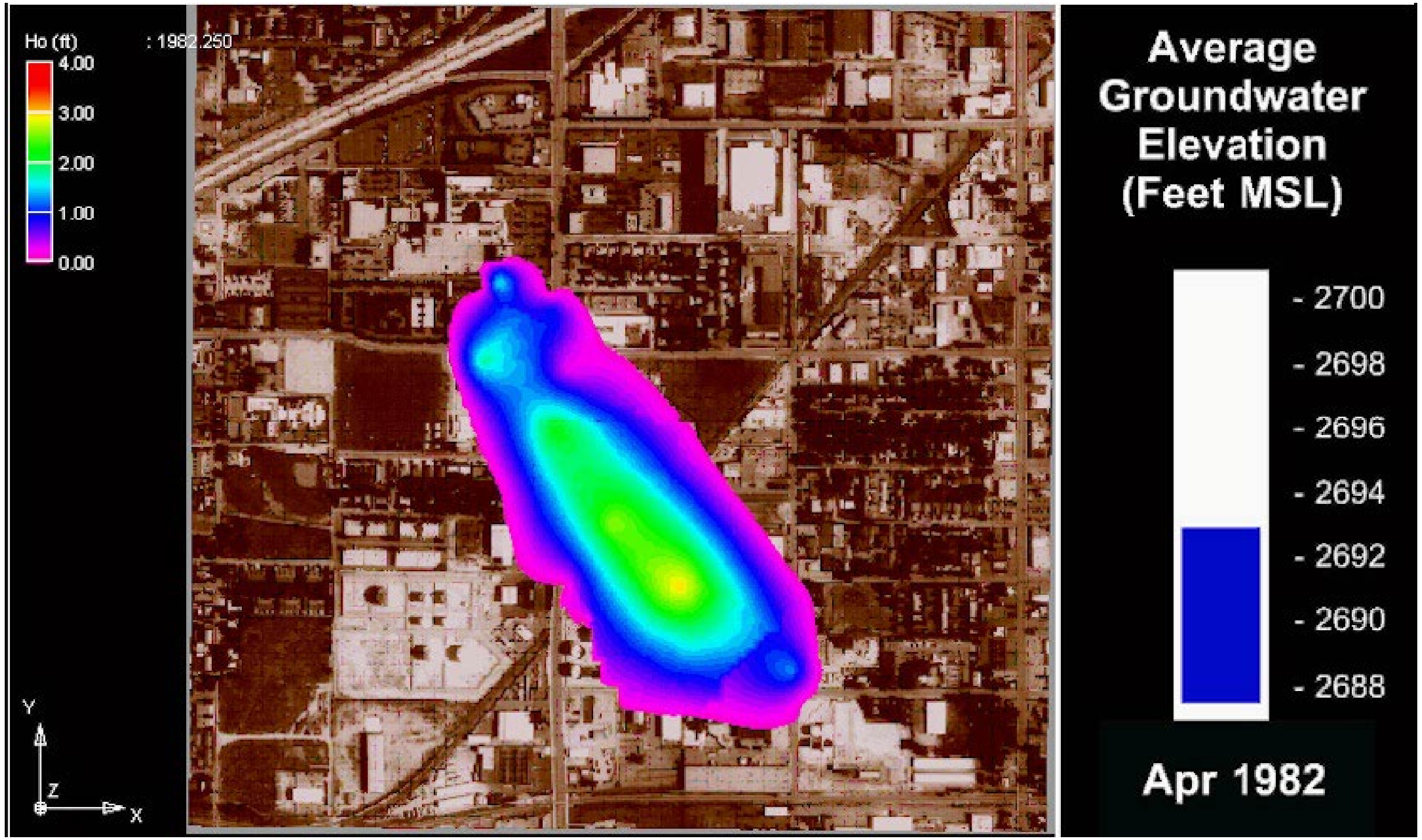
Thickness of Mobile LNAPL ≠ Thickness in Formation
(Vertical Distribution is a Shark Fin, Not a Pancake)

# Fluctuations in Groundwater Levels

**Migrating LNAPL**

**Mobile LNAPL**

Gauged LNAPL Thickness in MWs Over Time (Refinery)



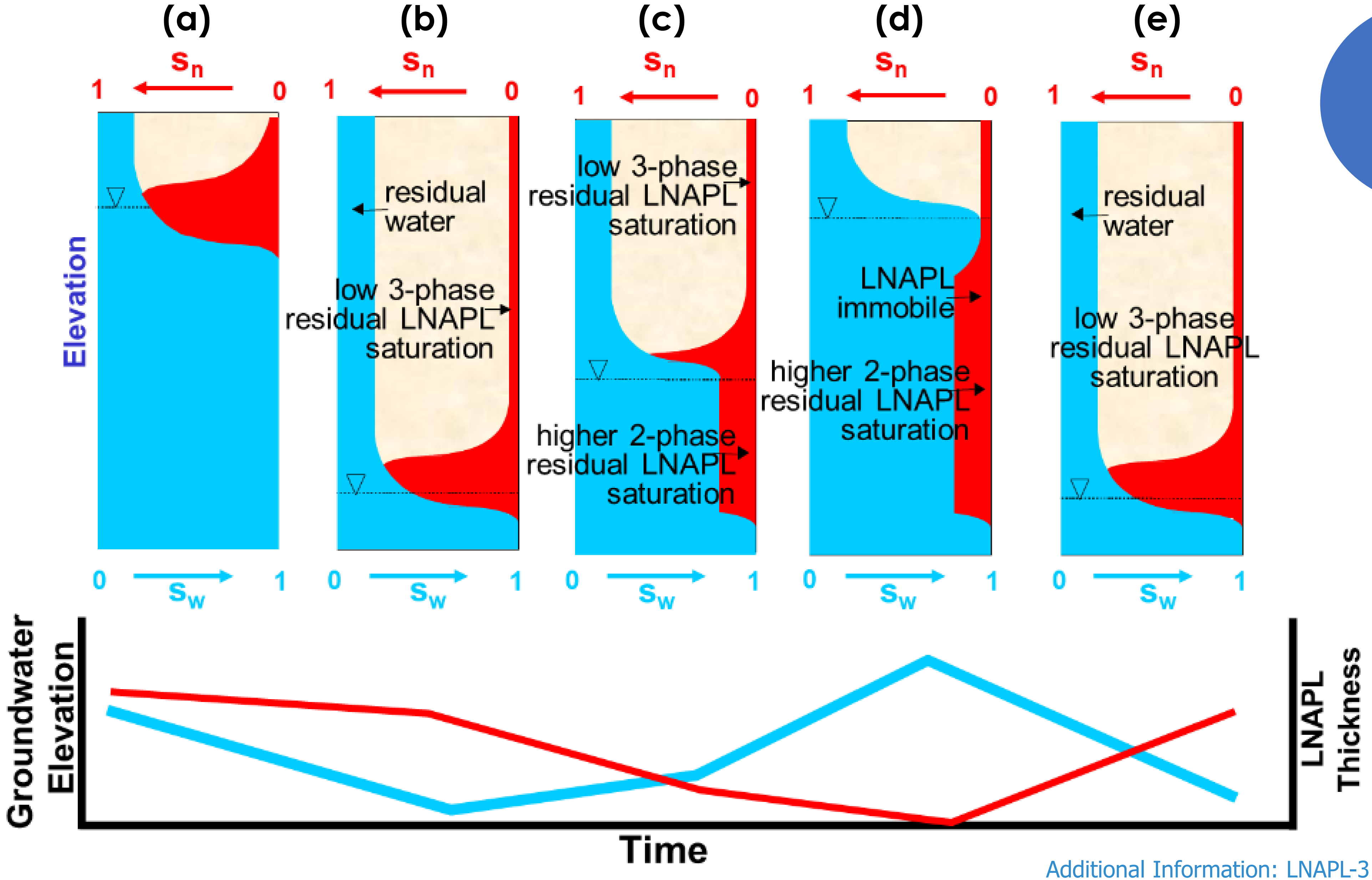

From API Interactive NAPL Guide, 2004

Fluctuations in GW Levels Can Make LNAPL Appear to Be Migrating When It Is Not



Additional Information: LNAPL-3: Section 3.5/Figure 3-9

# LNAPL Thickness Change with Water Table Fluctuation




Mobile LNAPL

After ITRC 2012

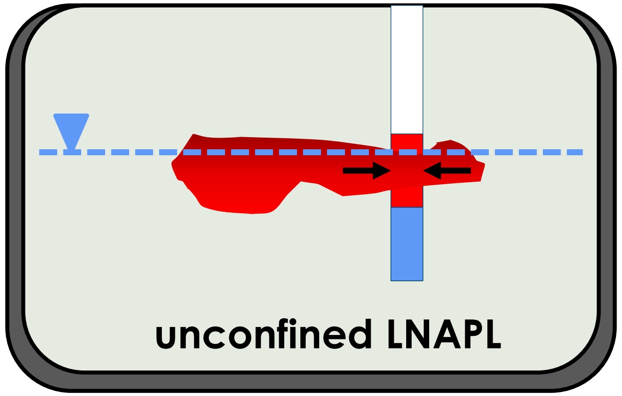


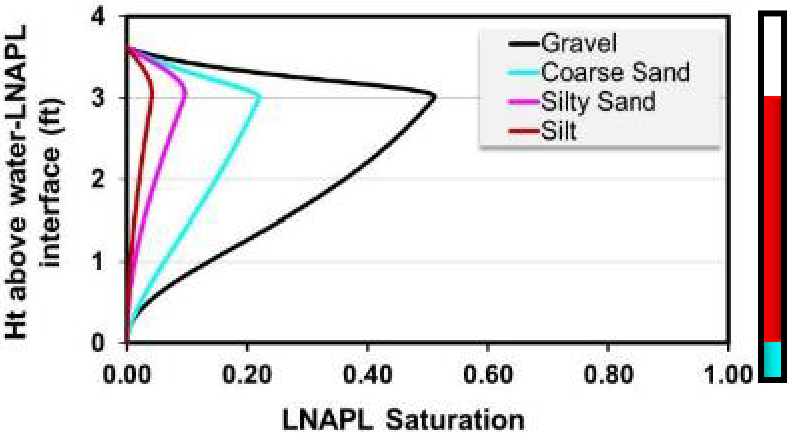
Additional Information: LNAPL-3: Section 3.2.3

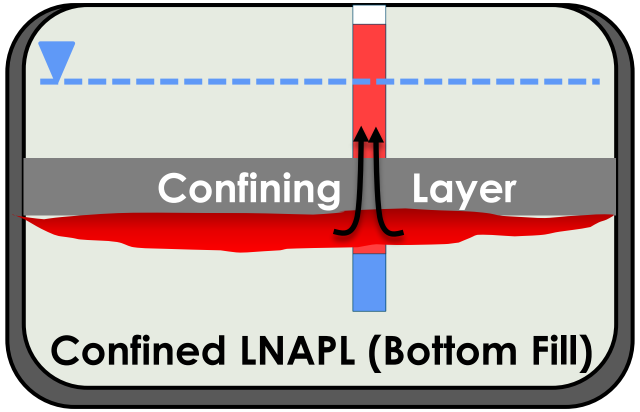
# Apparent LNAPL Thickness

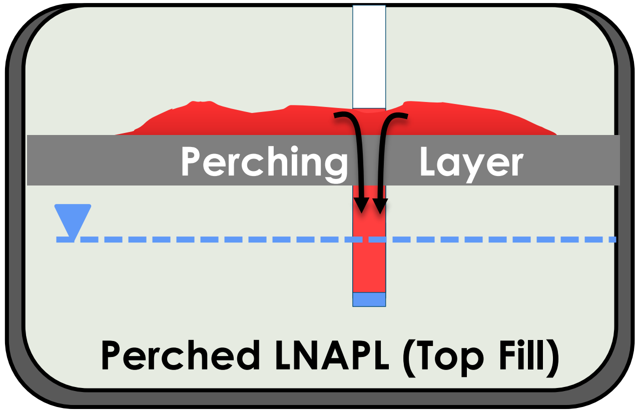
Apparent LNAPL Thickness Is Not a Good Indicator of LNAPL Thickness in Formation

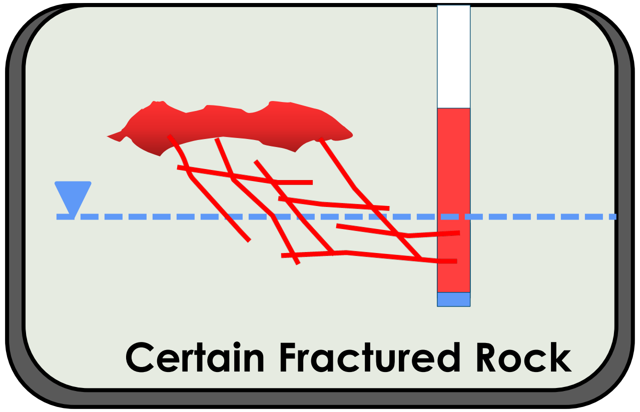
**Mobile LNAPL**






Additional Information: LNAPL-3: Section 3.4

# Key Message 3

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

Additional Information: LNAPL-3: Sections 3.1 and 3.5

# Identification of Residual LNAPL is Critical For PVI Screening and Risk Assessment

Residual LNAPL sources represent similar PVI risks as mobile or migrating LNAPL sources and can be difficult to identify

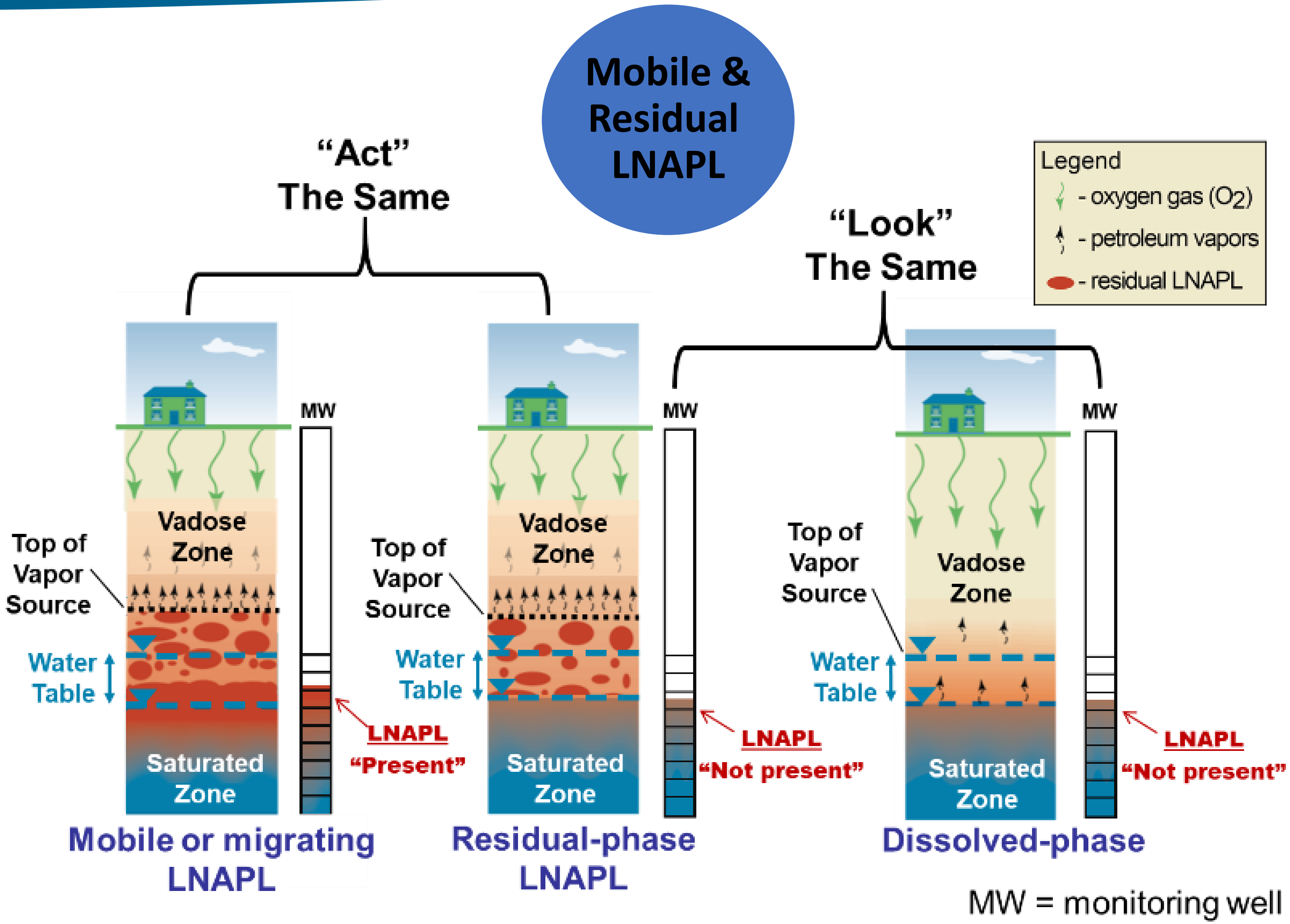



Image: ITRC PVI Training

# Potential Indicators of Residual LNAPL (mainly gasoline)

**Residual LNAPL**

| Indicator | Comments |
| --- | --- |
| **Groundwater** | |
| • benzene: > 1 - 5 mg/L<br>• $TPH_{(gasoline)}$: > 30 mg/L<br>• BTEX: > 20 mg/L<br>• current or historical presence of LNAPL (including sheens) | • no specific hydrocarbon concentration in groundwater that defines all LNAPL types because:<br>- varying product types<br>- degrees of weathering |
| **Soil** | |
| • current or historical positive shake test results<br>• benzene > 10 mg/kg<br>• **ITRC**: TPHg > 250 - 500 mg/kg; **US EPA OUST:** TPHg > 100 (fresh); $TPH_D$ > 250 (weathered, diesel)<br>• ultraviolet light (UV) or laser-induced fluorescence (LIF) response in LNAPL range<br>• PID or FID readings > 500 ppm<br>• Soil Gas Readings Low ($O_2$), High ($CO_2$, $CH_4$, Aliphatics) | • **use of TPH soil concentrations as LNAPL indicators should be exercised with caution**:<br>- can be affected by the presence of soil organic matter<br>- TPH soil concentrations are not well correlated with TPH or $O_2$ soil gas concentrations |
| **Location relative to UST system (e.g., tank, dispenser, pipework) or AST** | |
| • adjacent (e.g., < 20 feet) from a known or suspected LNAPL release or petroleum UST/AST equipment | • probability of encountering LNAPL increases closer to release location |

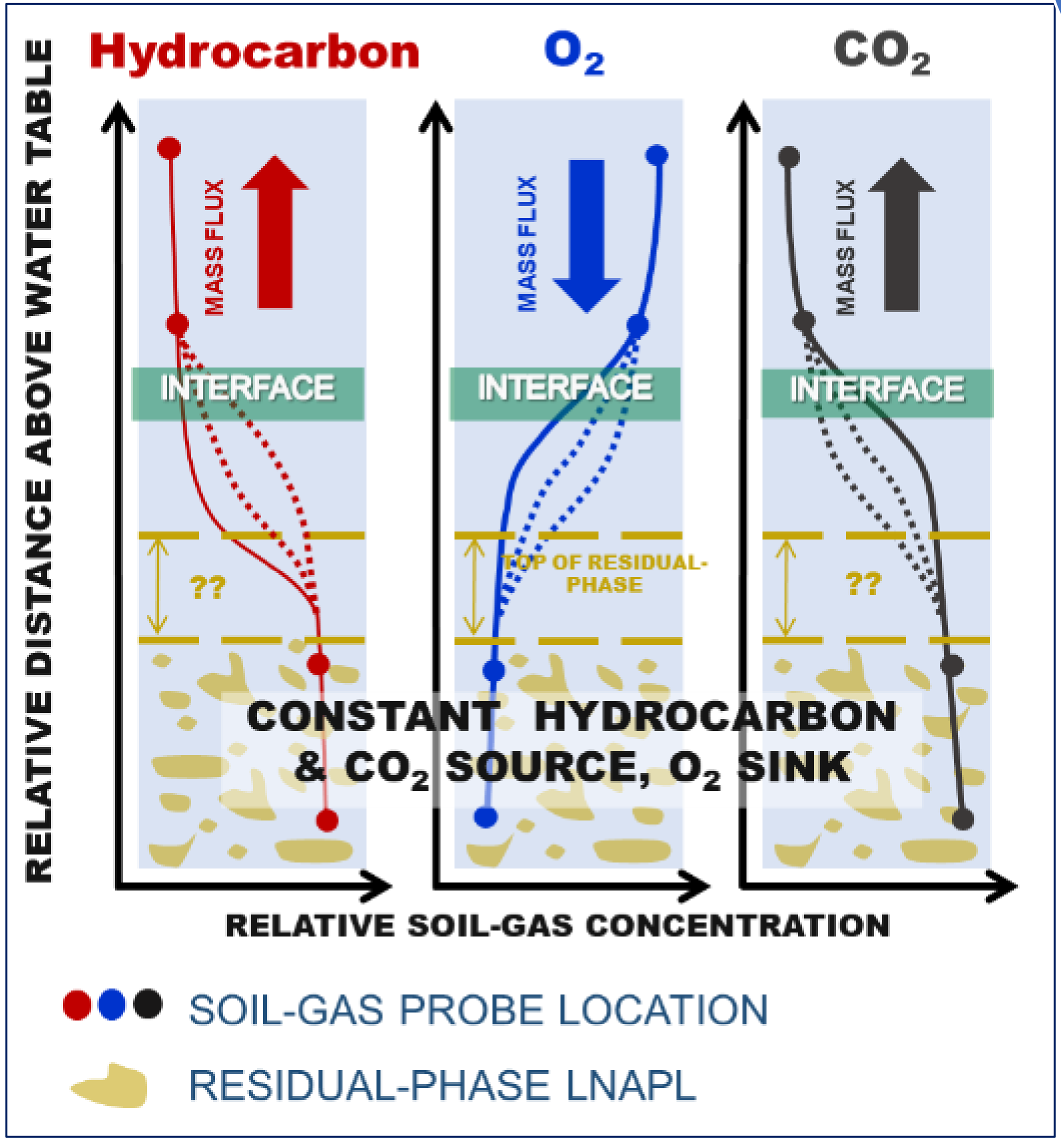
Table 3-1 ITRC PVI Guidance - https://projects.itrcweb.org/PetroleumVI-Guidance/

# Other General Indicators of Residual LNAPL

Residual LNAPL

## Soil gas indicators include:

- Oxygen ($O_2$) < 5% vol/vol
- Carbon dioxide ($CO_2$) > 15% v/v
- Methane > 1% v/v
- Benzene > 1,000 mg/m$^3$
- Hexane > 100,000 mg/m$^3$
- $C_5 - C_8$ aliphatics > 100,000 mg/m$^3$
- $C_9 - C_{12}$ aliphatics > 10,000 mg/m$^3$



# LNAPL Characterization Tools

Migrating LNAPL

Mobile & Residual LNAPL

| Data Need | Description | Examples | References |
|---|---|---|---|
| LNAPL Delineation | Presence | LIF (UVOST/OIP), soil borings (visual, PID, shake tests, dye tests), soil concentrations, dissolved-phase concentrations, soil vapor (VOCs and/or biogenic gases) | LNAPL-3: Table 3-2 |
| | Mobile | Monitoring wells, core LNAPL saturations | LNAPL-3: Section 3.5 |
| LNAPL Properties | Chemical | Site history, gas chromatography, biomarkers, distillation, PIANO | LNAPL-3: Table 4-2 |
| | Physical | Density, viscosity, interfacial tension | LNAPL-3: Table 4-2 |
| LNAPL Hydrogeologic Condition | Unconfined, confined, or perched | Hydrographs, diagnostic gauge plots | LNAPL-3: Section 3.4 |
| LNAPL Stability | Apply multiple lines of evidence | Release date, mobile LNAPL extent, dissolved and/or vapor footprint, hydrographs, | LNAPL-3: Table 4-1 |
| LNAPL Recoverability | LNAPL transmissivity | Baildown, manual skimming, LNAPL recovery system evaluations | LNAPL-3: Appendix C, Section 2 |
| Natural Biodegradation Processes | NSZD | Gradient, $CO_2$ flux, temperature methods, LNAPL composition, polar metabolites | LNAPL-3: Appendix B, Section 4 |

ITRC DNAPL Site Characterization and Tools Selection Worksheet.

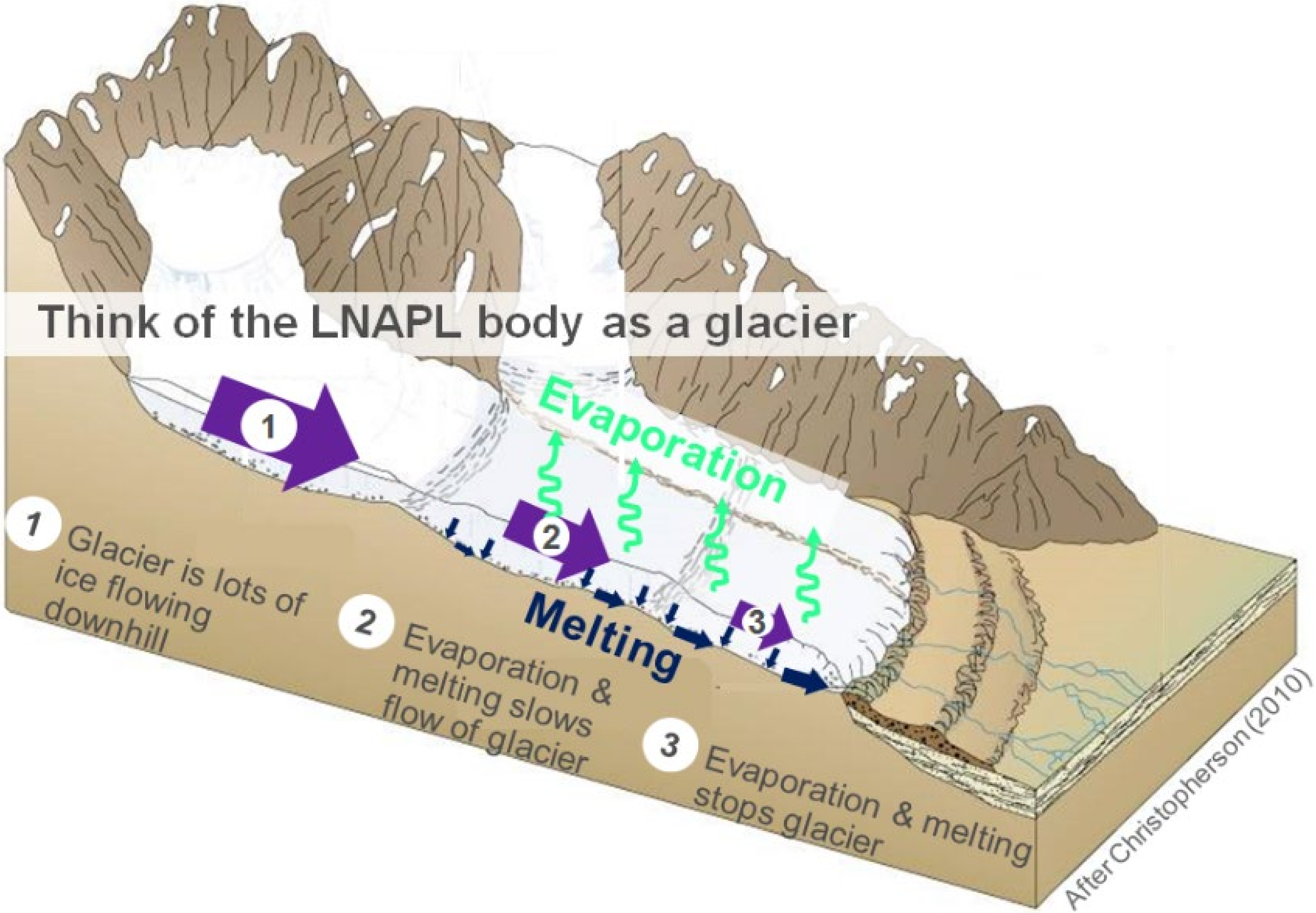
LIF: Laser Induced Fluorescence
UVOST: Ultraviolet Optical Screening Tool
OIP: Optical Image Profiler

PID: Photoionization Detector
PIANO: n-Paraffins (P), Iso-paraffins (I), Aromatics (A), Naphthenes (N) and Olefins (O)

# Key Message 4

Biodegradation helps LNAPL bodies and groundwater plumes stabilize and/or shrink

# Biodegradation Is the Ultimate Contributor to LNAPL Stability



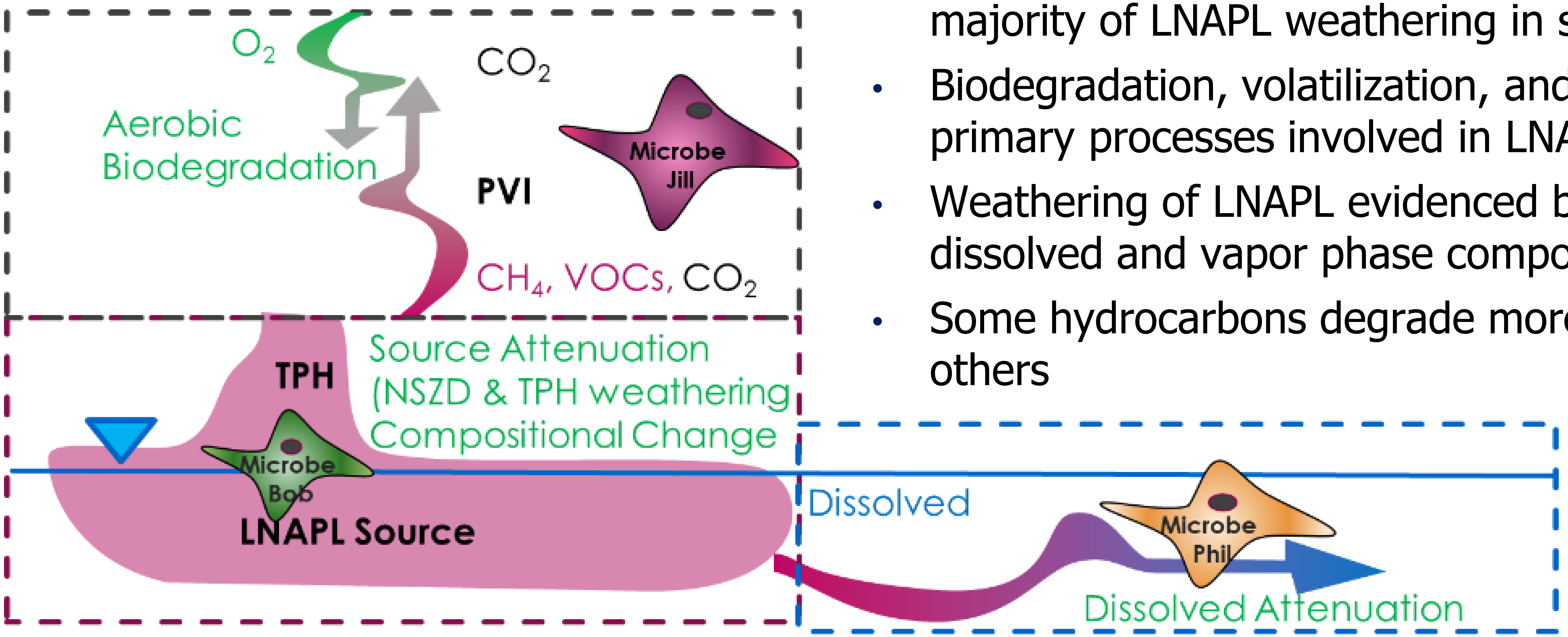

Mobile & Residual LNAPL

Migrating LNAPL

# Biodegradation Is A Primary Contributor to LNAPL Stability

Migrating LNAPL

Hydrocarbons degrade faster in the presence of oxygen (aerobic conditions) than without it (anaerobic conditions)



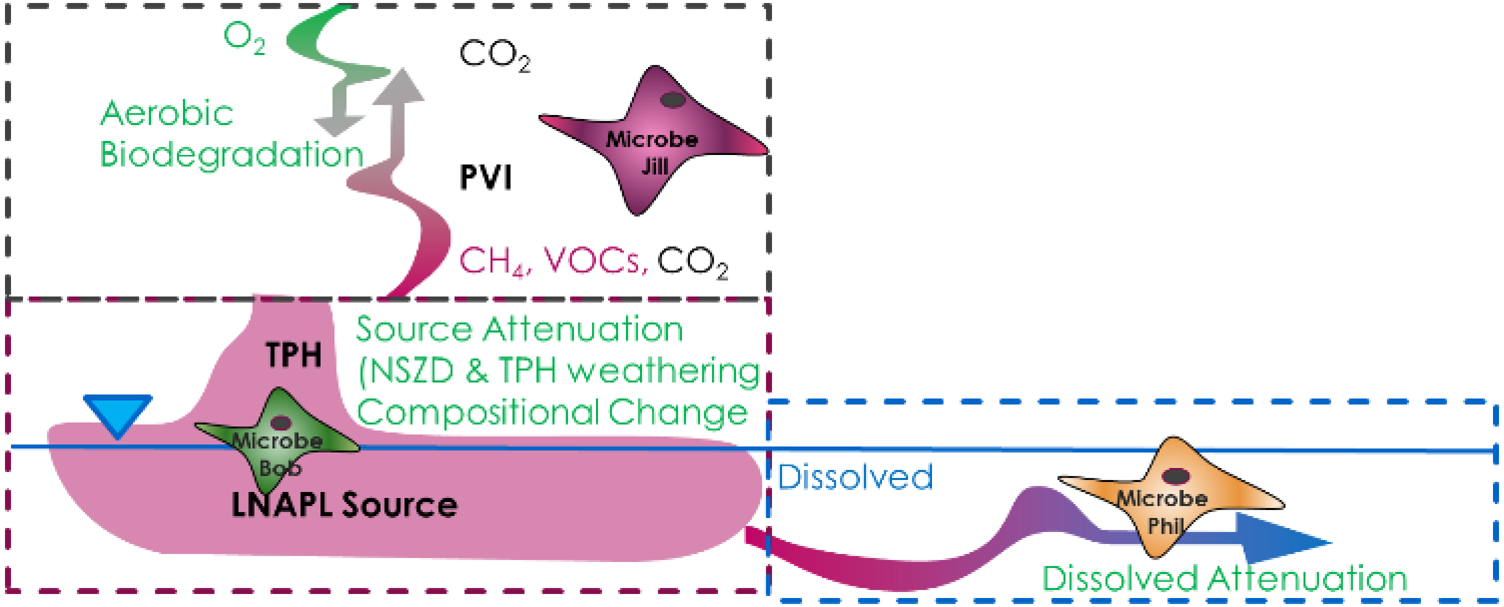

- Anerobic processes are important (account for majority of LNAPL weathering in saturated zone)
- Biodegradation, volatilization, and dissolution are primary processes involved in LNAPL weathering
- Weathering of LNAPL evidenced by changes in dissolved and vapor phase composition
- Some hydrocarbons degrade more quickly than others

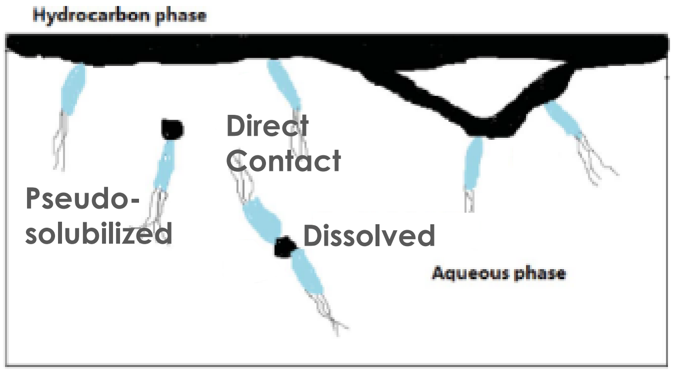
https://www.itrcweb.org/guidancedocuments/lnapl-1.pdf

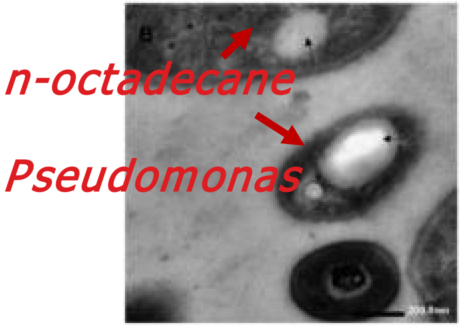
# Biodegradation Is a Primary Contributor to LNAPL Stability

Migrating LNAPL

- Microbes that degrade hydrocarbons are ubiquitous
- Biodegradation occurs in the saturated and vadose zones in:
  - LNAPL – using enzyme surfactants
  - Aqueous phase -- primary location where bacteria reside



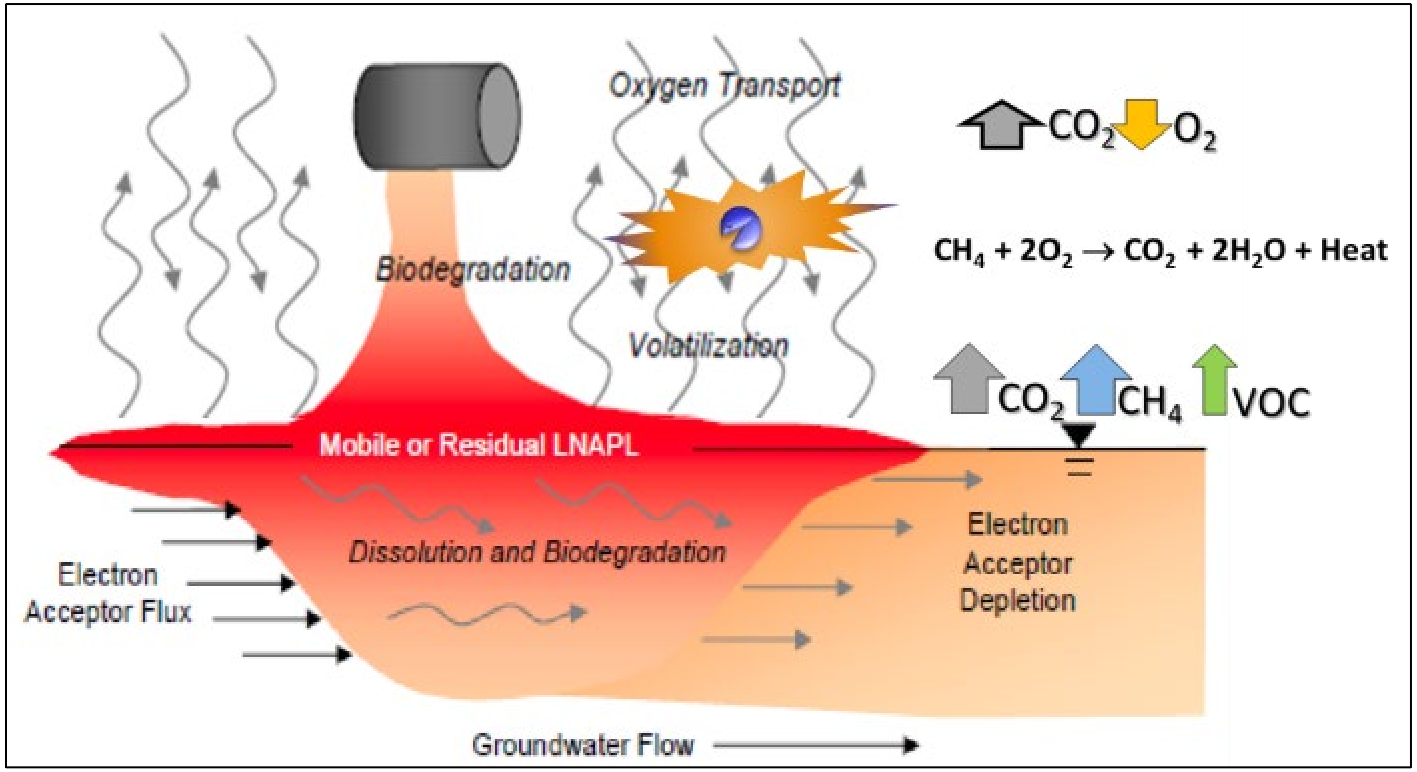




Hua et al., 2014

# Primary NSZD Processes

Migrating LNAPL

Mobile & Residual LNAPL




ITRC LNAPL-1 Figure 1-1. Example LNAPL Source Zone

Methane oxidation and aerobic biodegradation in the vadose zone account for >99% of LNAPL mass loss

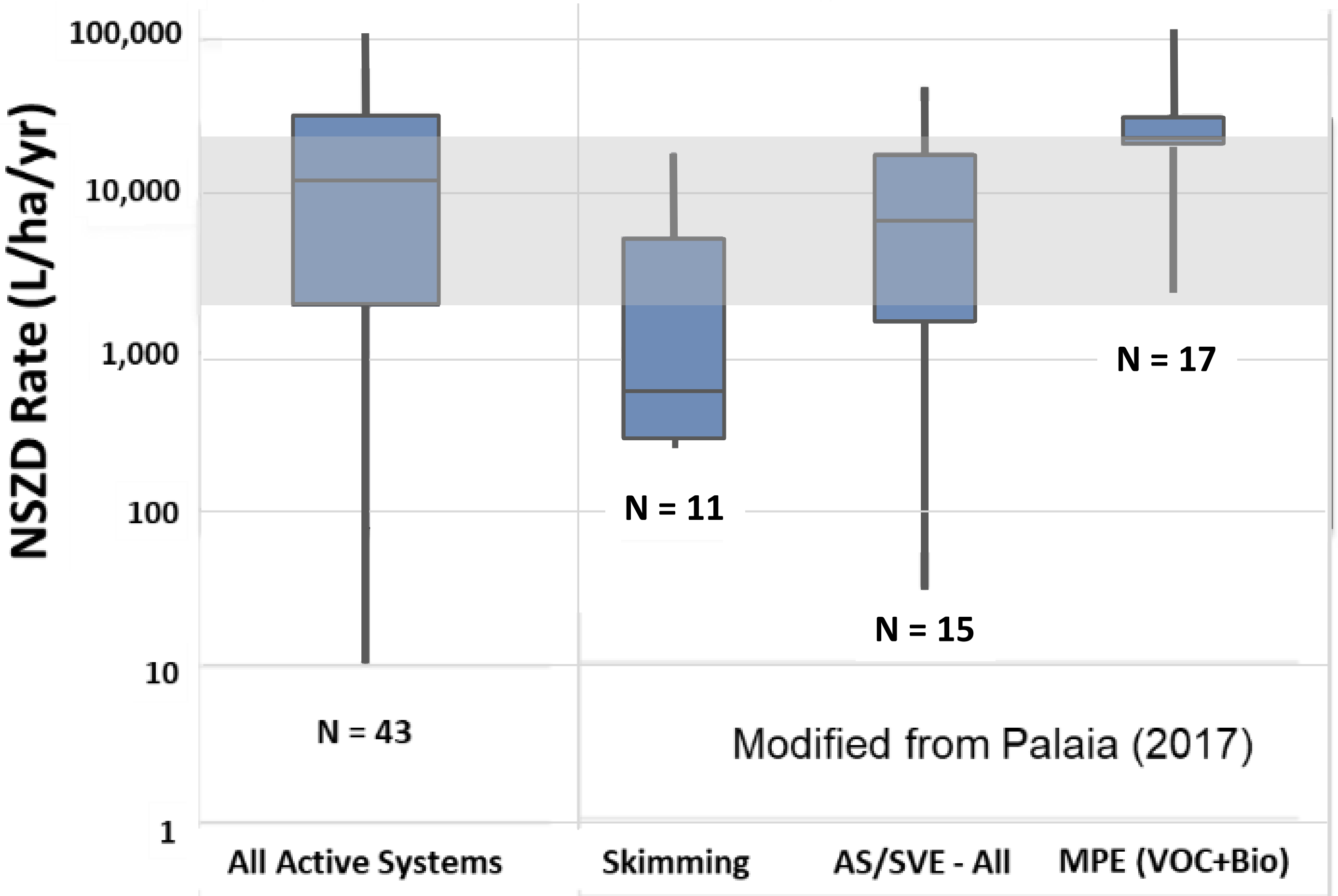
- Primary saturated-zone and LNAPL processes include:
  - Anaerobic biodegradation
  - Degassing and ebullition
  - Direct outgassing from microbes in contact with LNAPL
  - Dissolution
  - Volatilization
- Primary vadose-zone processes include:
  - Methane ($CH_4$) oxidation (involving oxygen – $O_2$) to carbon dioxide ($CO_2$)
  - Aerobic biodegradation of VOCs

# NSZD Rates Can Compete with Certain Engineered Remediation Systems

**Migrating LNAPL**

**Mobile & Residual LNAPL**

Important to factor in NSZD rate into remedial decision making to minimize unnecessary remediation




Kulkarni et al., 2022
Site Average NSZD Rates: various methods (40 LNAPL sites)

90% > 1600 L/ha/yr (170 gal/acre/yr)

# NSZD in Context with CSM and Remedial Decision Making

**NSZD – An important part of the petroleum NAPL CSM**

- Refine the CSM with quantification of bulk petroleum NAPL and/or chemical constituent loss rates
- Determine whether NSZD is sufficient to address risk/concerns
- Determine the NAPL footprint using vadose zone indicators of biodegradation
- Compare NSZD to historical or potential future remedial activities
- Support estimates of source zone remedial timeframes
- Assess NAPL stability through application of a mass balance of NSZD mass losses and measured mobile NAPL flux

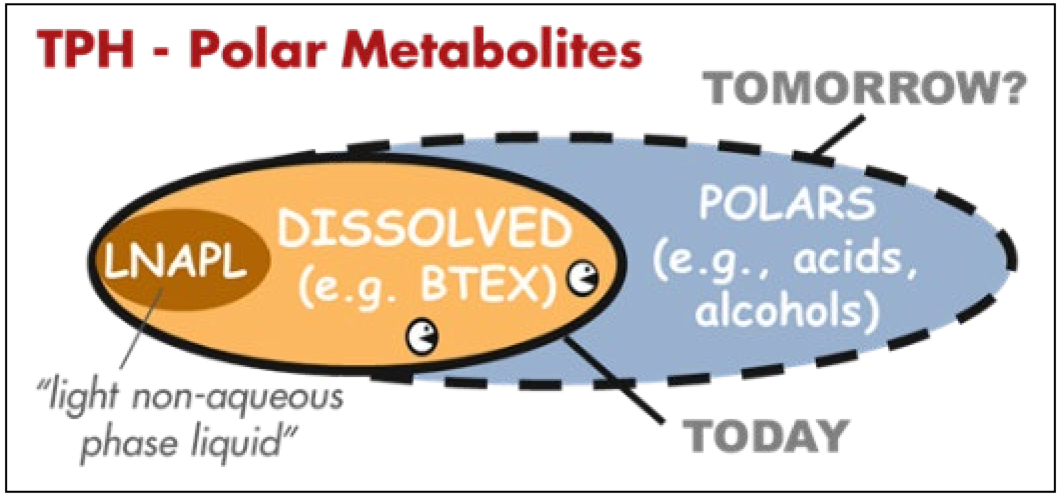
**Migrating LNAPL**

**Mobile & Residual LNAPL**

# Hydrocarbon Biodegradation Can Lead to Formation of Polar Metabolites

Mobile & Residual LNAPL

- Intermediate (anaerobic) biodegradation products
- Challenge assessing risk because of limited toxicity information for individual metabolites and mixtures
- Different properties from HCs
  - $O_2$
  - Polar
  - More soluble / mobile




**TPH-gas plume lengths (Shih 2004)**

- **Median: 220 feet**
- **Max: ~600 feet**

**Solubility of n-Hexane vs Metabolites**

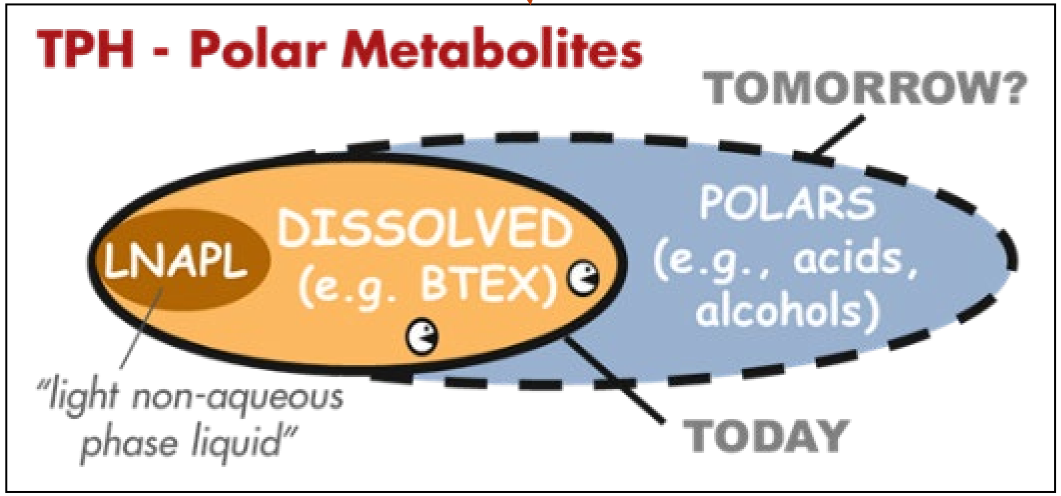
| Chemical | Formula | Boiling Point (°C) | Solubility (µg/L) |
|---|---|---|---|
| n-Hexane | $C_6H_{14}$ | 69 | 9.5E+03 |
| 2-Hexanone | $C_6H_{12}O_1$ | 128 | 7.7E+06 |
| Hexanoic Acid | $C_6H_{12}O_2$ | 205 | 5.8E+06 |

# How Can You Identify Polar Metabolites?

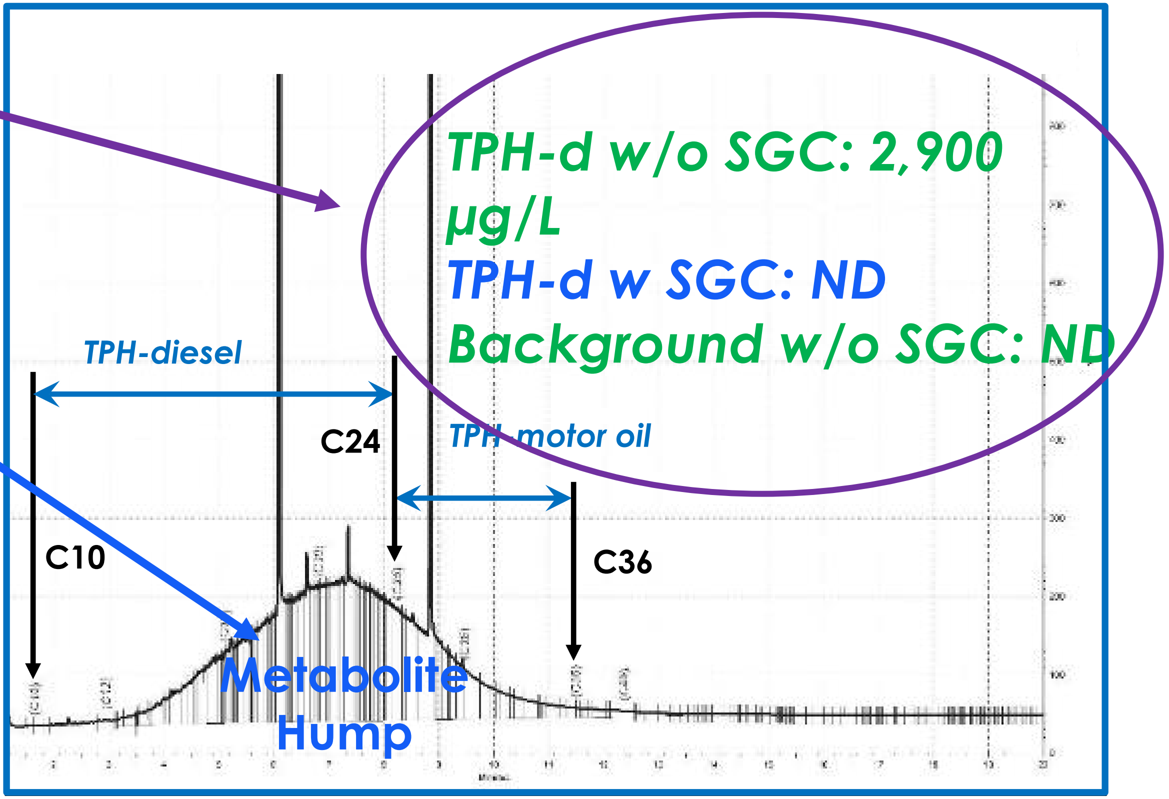
Mobile & Residual LNAPL

Identify metabolites using:

- Analysis w/ & w/out SGC
- Chromatogram pattern
- Conceptual site model (e.g., more mobile/soluble)




## Metabolites detected as TPH when silica gel cleanup (SGC) not used



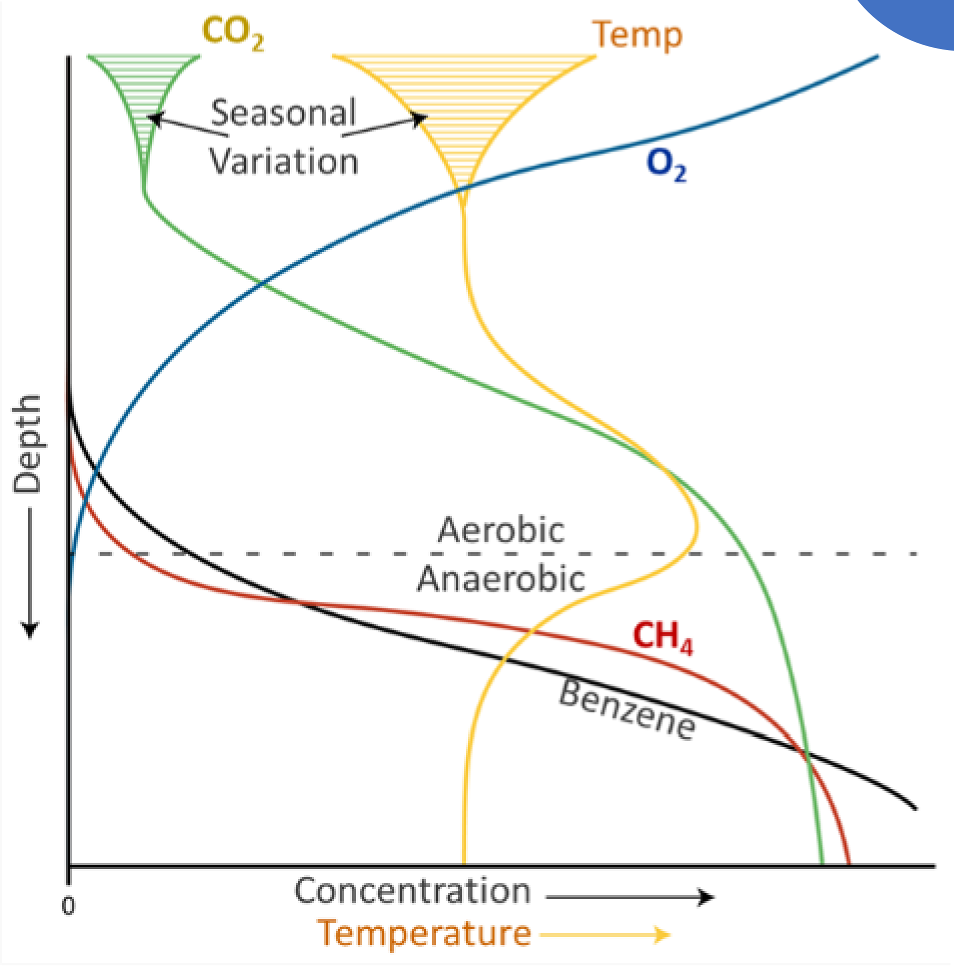

ITRC TPHRisk-1: Figure A5-5
(data from CA site)

# Biodegradation is Also a Key Process Limiting PVI

**Mobile & Residual LNAPL**

- Hydrocarbons (and methane) attenuate rapidly in the presence of $O_2$

- At some distance above the source, rates of biodegradation for most COCs exceeds rates of upward migration by physical processes (e.g., diffusion)
  - ✓ Aerobic: utilize $O_2$, produce $CO_2$ and $H_2O$
  - ✓ Anaerobic: utilize $CO_2$ and $H_2$, produce $CH_4$
  - ✓ Produce heat
  - ✓ Acclimate/adapt relatively quickly



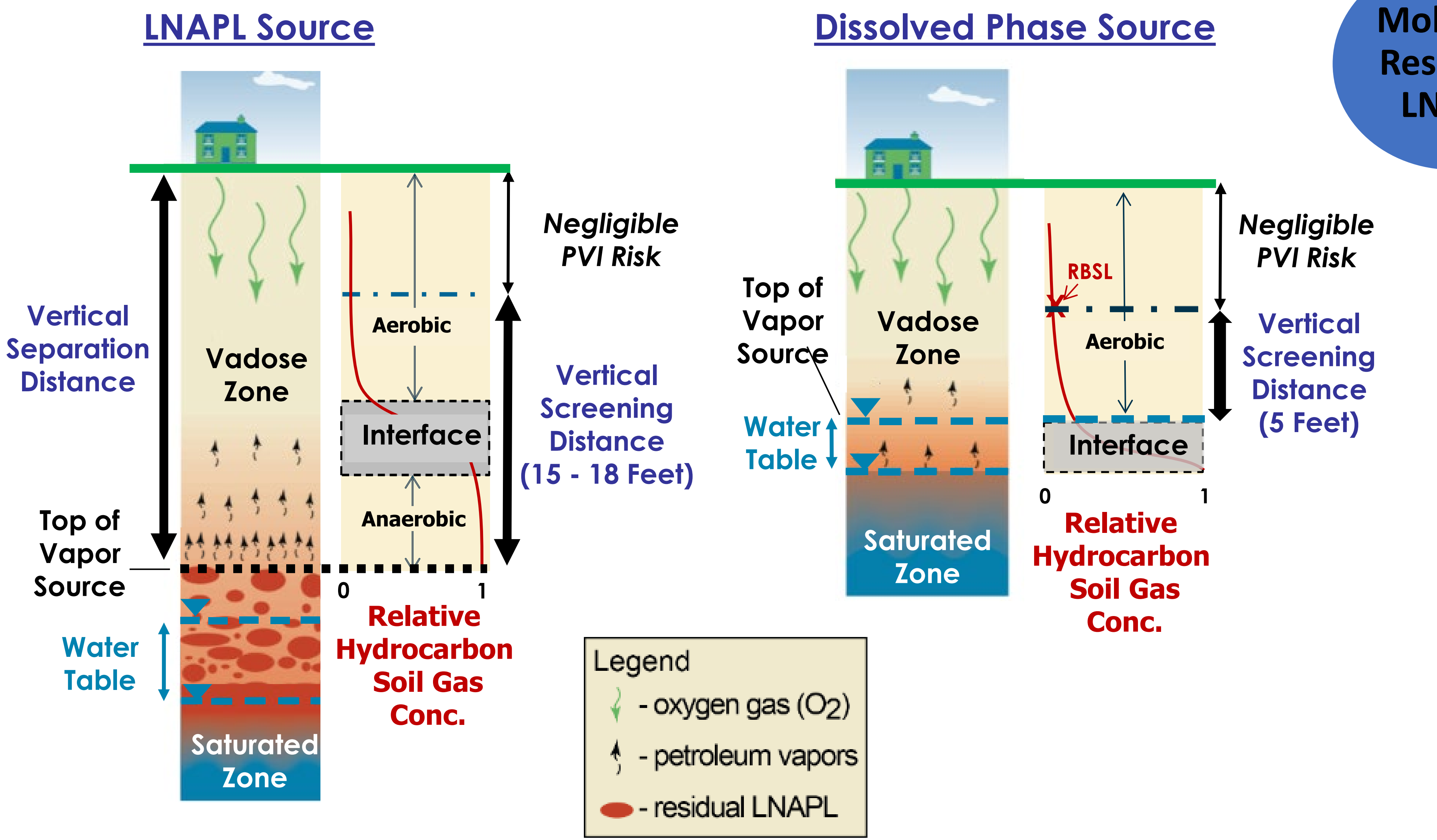

Source: G.T. Ririe, 2013

# Key Message 5

**PVI IS PRIMARILY ASSOCIATED WITH LNAPL SOURCES: SOURCE TYPE MATTERS**

# Site Screening Is Important for PVI: Vertical Screening Distance Concept

Source Type Matters !!




Mobile & Residual LNAPL

Image: ITRC PVI Training

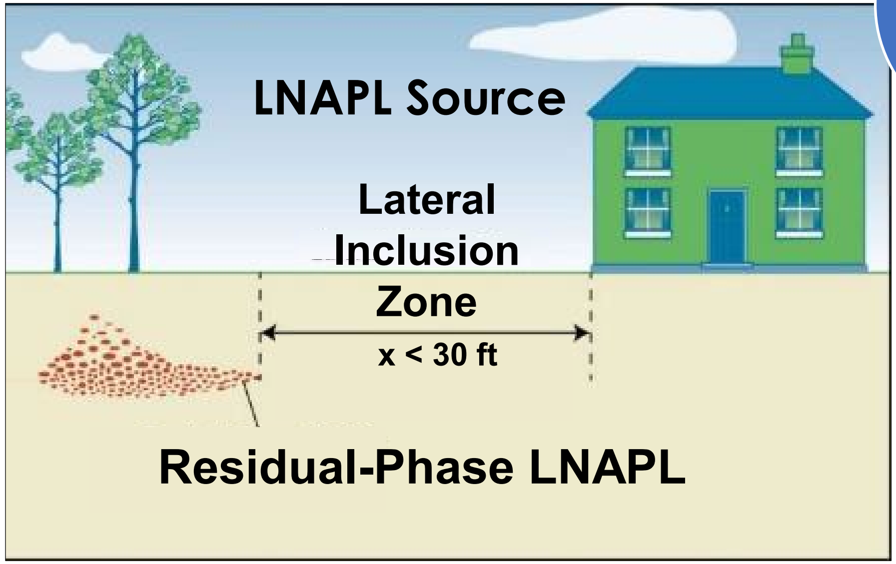
# Which Buildings Screen In – Lateral Inclusion Zone

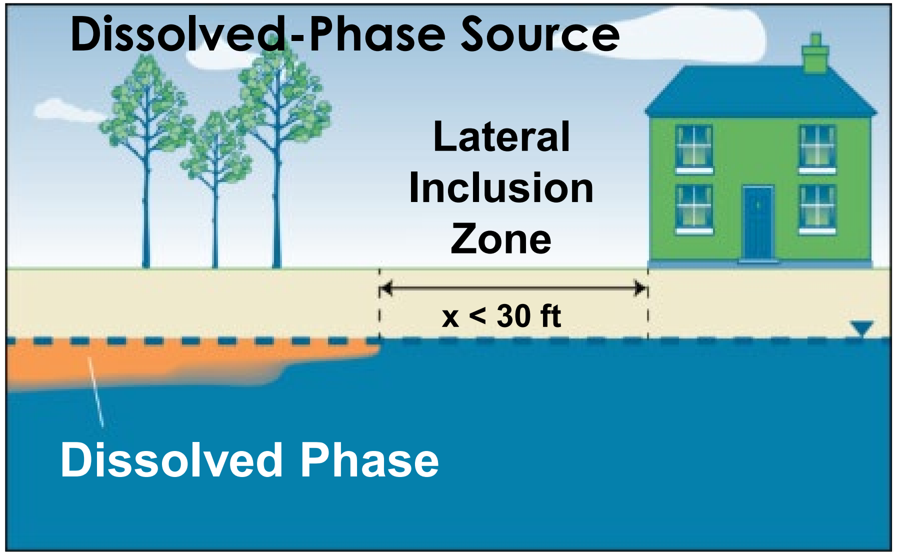
Mobile & Residual LNAPL

## Which buildings get screened in & which screening distance to apply?

30 feet* from ***edge*** of PVI source to building unless site data prove otherwise

*30 feet is conservative given that lateral screening distances should be roughly the same as the vertical screening distances of 5 and 15 ft



# Screening Distances Do Not Apply to Certain Buildings If Precluding Factors Are Present

Mobile & Residual LNAPL

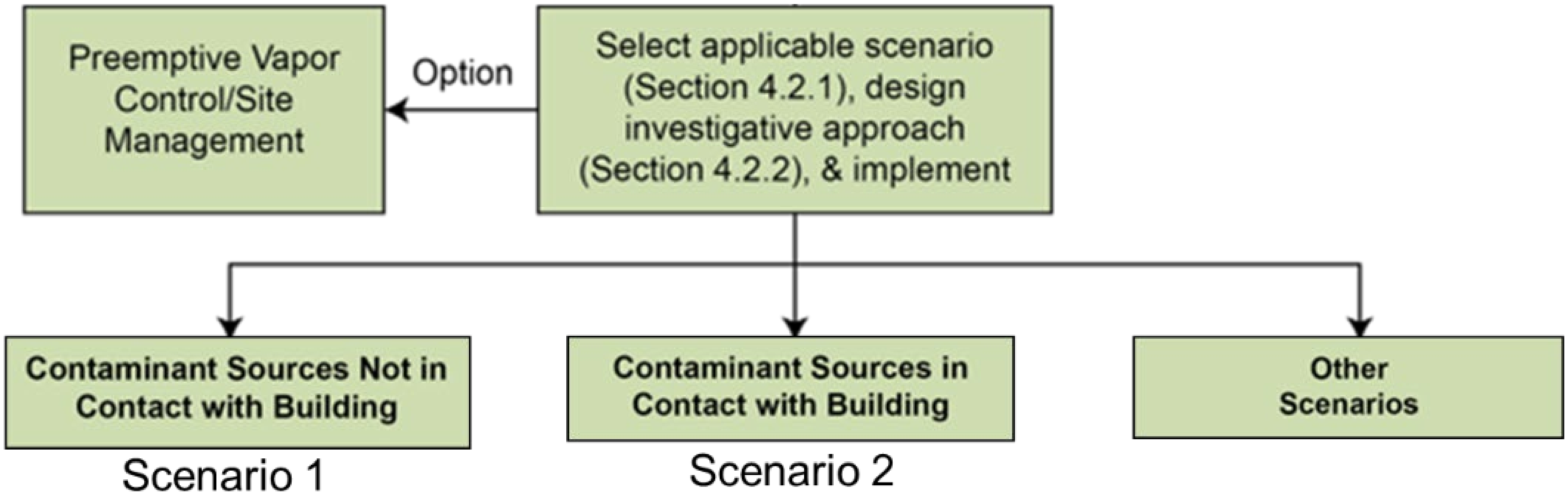
<u>Definition</u>: Site-specific conditions which preclude (prevent) the application of site screening

- ✓ Preferential pathways (e.g., utilities, conduits, fractured rock connecting vapor source to building)
- ✓ Certain fuel types (e.g., gasoline containing lead scavengers or > 10% ethanol by volume)
- ✓ Expanding/advancing plume with potential to migrate below buildings or enter the "lateral inclusion zone"
- ✓ Certain soil types (arid soils or soils with very high organic matter content)

*US EPA (2015) also lists certain building types with large foundations > 66 feet on each side

# For Buildings That Do Not Screen Out for PVI: Soil Gas → Subslab Vapor → Indoor Air

Mobile & Residual LNAPL

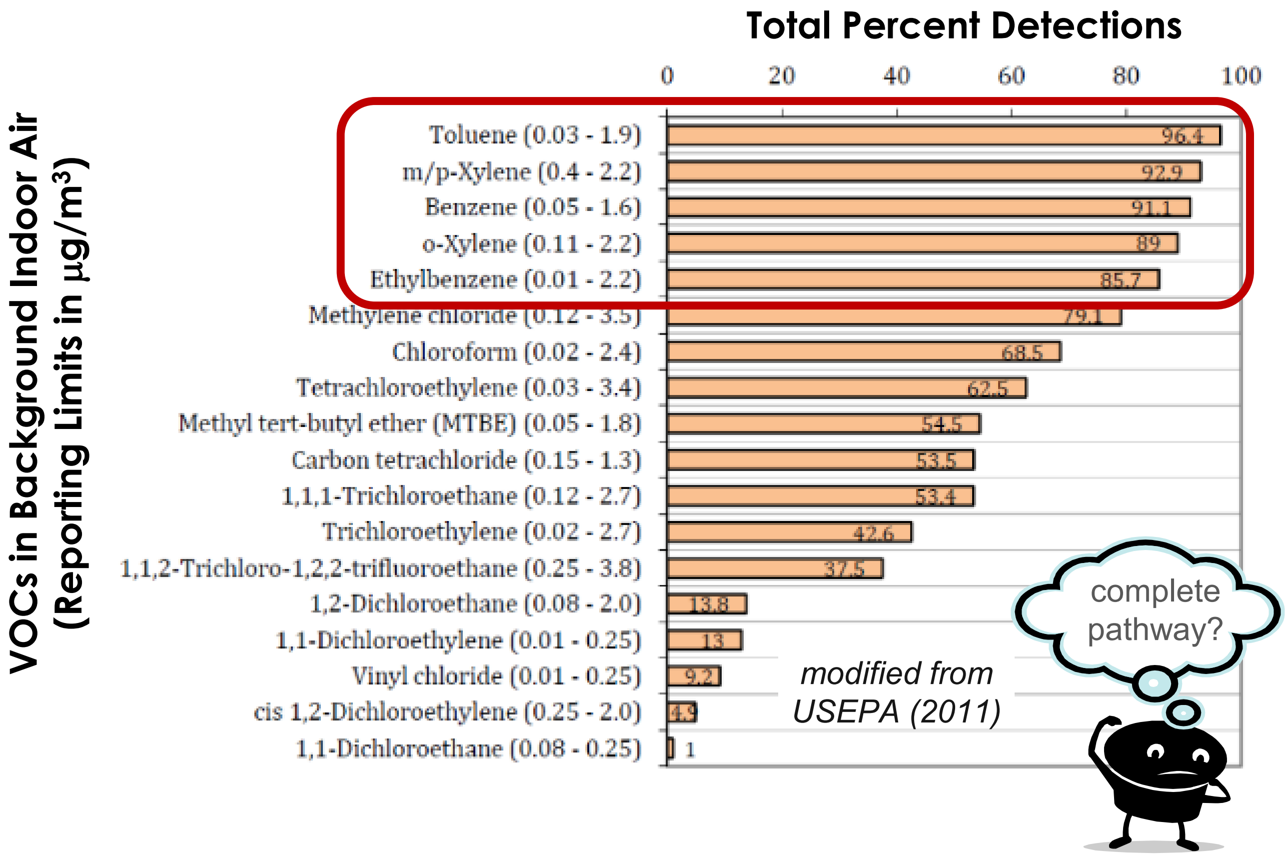


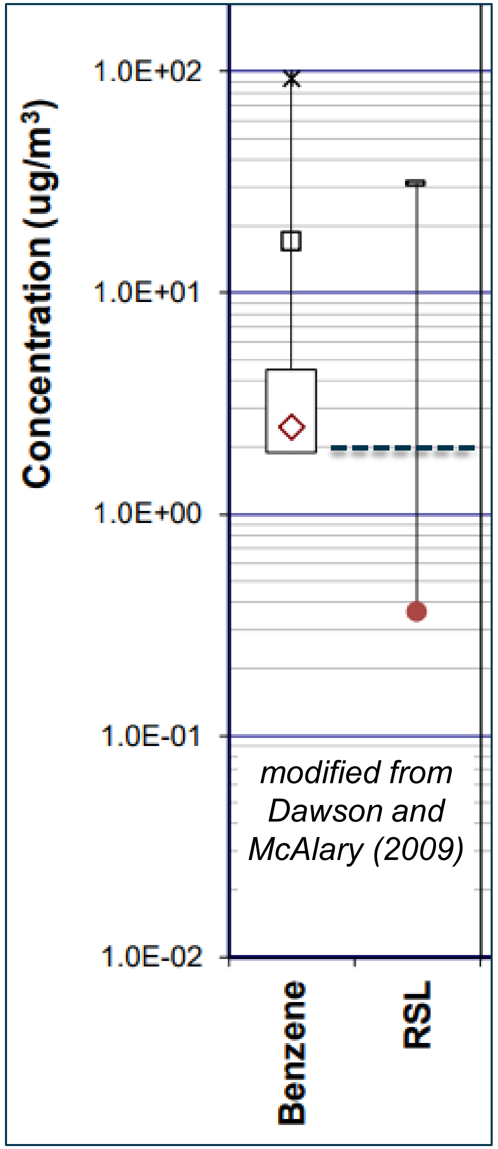

Soil Gas, Subslab Measurements

Indoor Air Measurements

# Challenges of Receptor (Building) Characterization

**Mobile & Residual LNAPL**

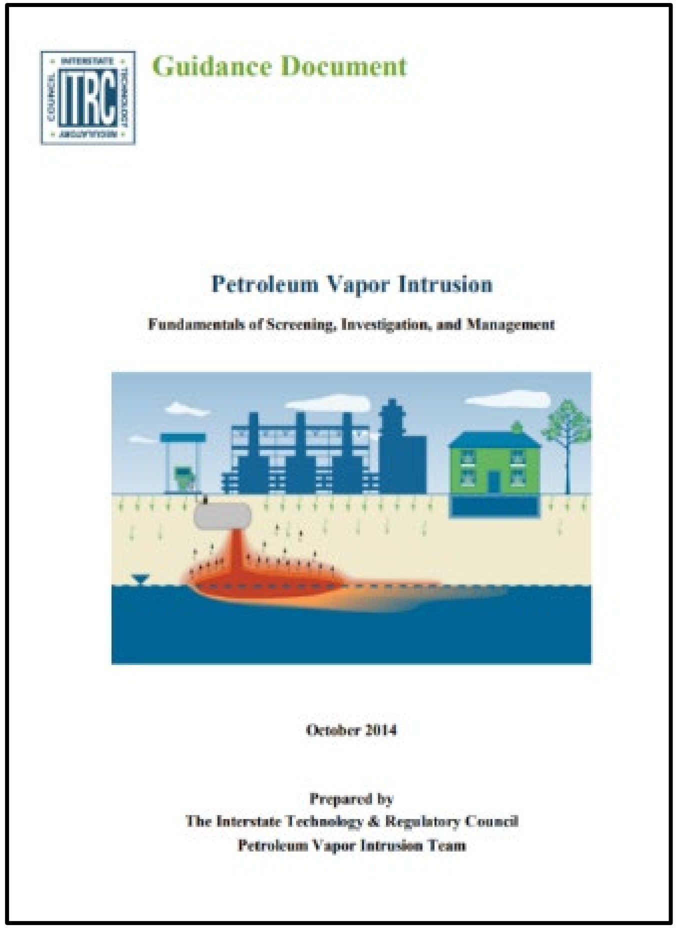



Background concentrations in indoor air (benzene) can exceed Risk (based) Screening Level (RSL) for $10^{-6}$ Target Risk

# Best Practice on Sampling and Analysis for PVI

**Mobile & Residual LNAPL**


Guidance Document

Petroleum Vapor Intrusion

Fundamentals of Screening, Investigation, and Management

October 2014

Prepared by
The Interstate Technology & Regulatory Council
Petroleum Vapor Intrusion Team

Groundwater sampling [4.2.2.1]

Soil sampling [4.2.2.6]

Soil Gas sampling [4.2.2.2]

Crawl space sampling [4.2.2.5]

Indoor air sampling [4.2.2.3]

Ambient air sampling [4.2.2.4]

Difference in sampling between petroleum and chlorinated

Supplemental Tools & Data Useful for VI Investigations [Appendix G]

Analysis Methods [Appendix G]

https://projects.itrcweb.org/PetroleumVI-Guidance/

# Questions

# Key Message 6

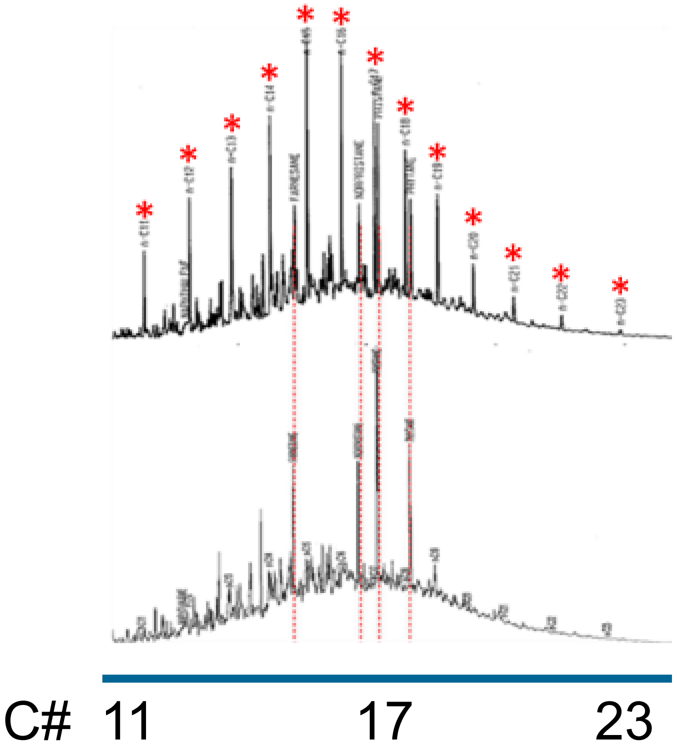
TPH is not necessarily "total",
not necessarily all from petroleum,
& not necessarily all hydrocarbons

# TPH in the Environment

**Mobile & Residual LNAPL**

TPH is a measurement that helps focus the risk assessment:

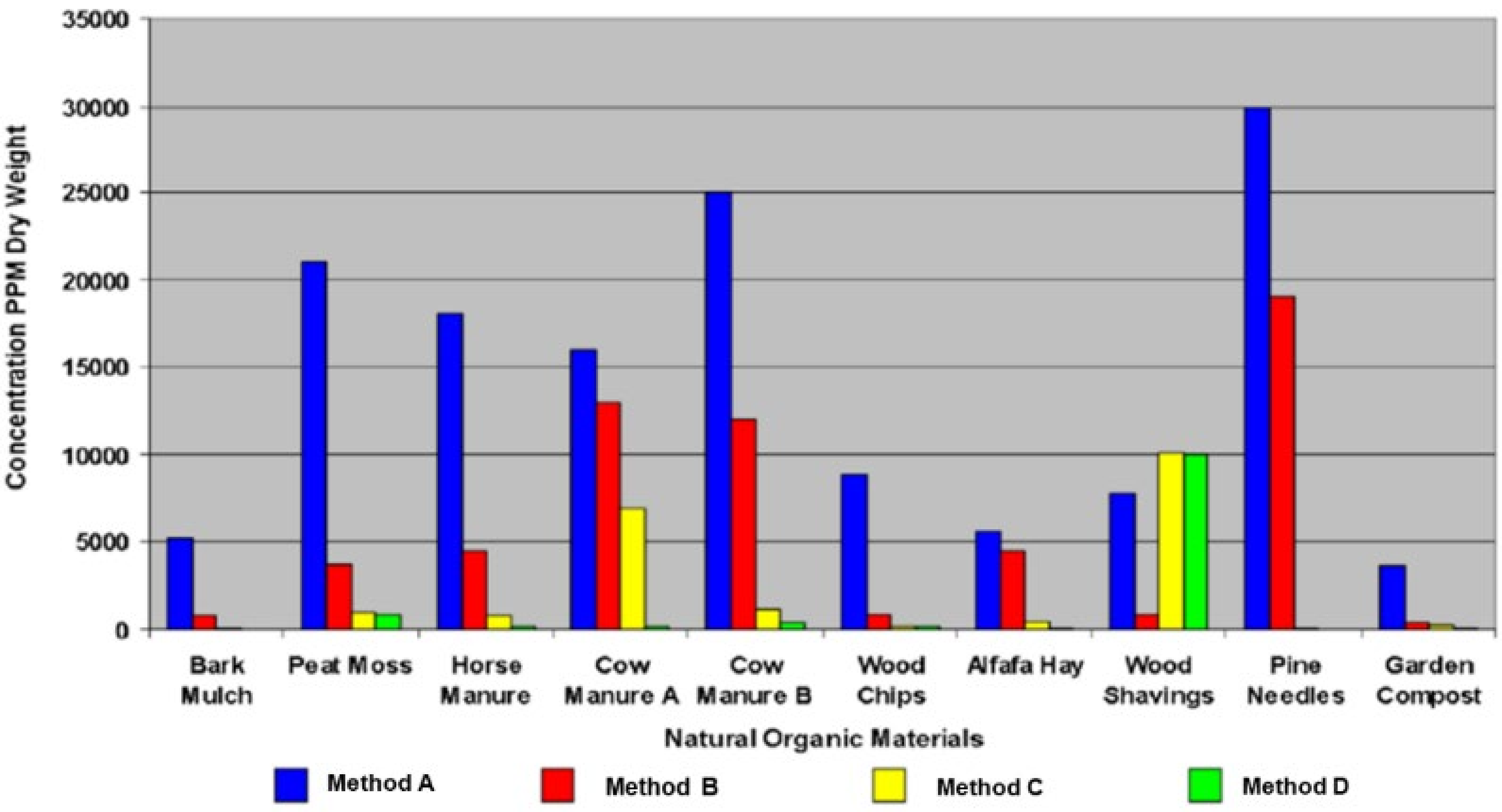
- ✓ Defined by the analytical method used to measure it
- ✓ Provides an approximate concentration of the total hydrocarbons in a complex mixture
- ✓ Provides information about the type, volume, and distribution of hydrocarbons in LNAPL




ITRC TPHRisk-1 Figure A5-4

https://tphrisk-1.itrcweb.org

# Four TPH Methods Will Yield Four Different Results




**Mobile & Residual LNAPL**

And will measure "TPH" for non-petroleum hydrocarbons!

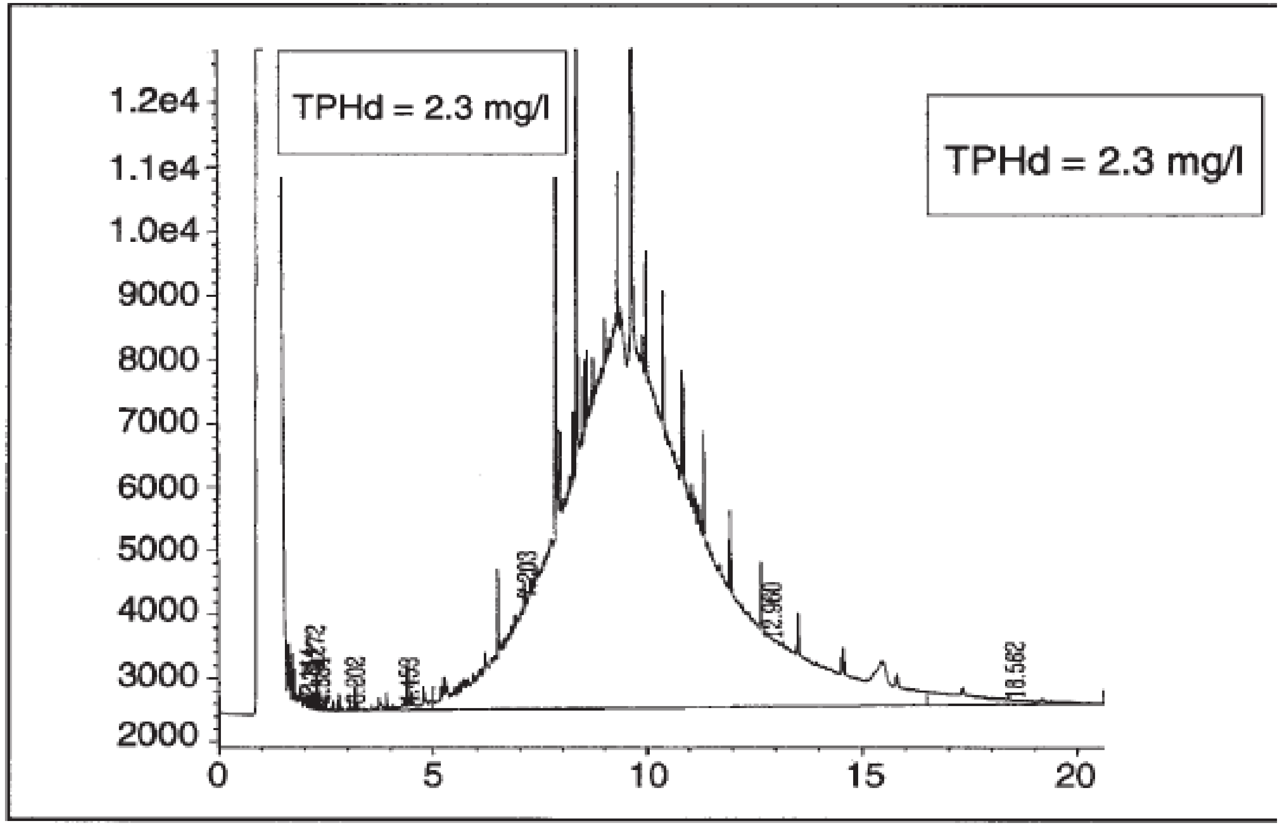
ITRC TPHRisk-1 Figure 5-3 (NewFields. 2002)

# Not All TPH Is Petroleum Hydrocarbon

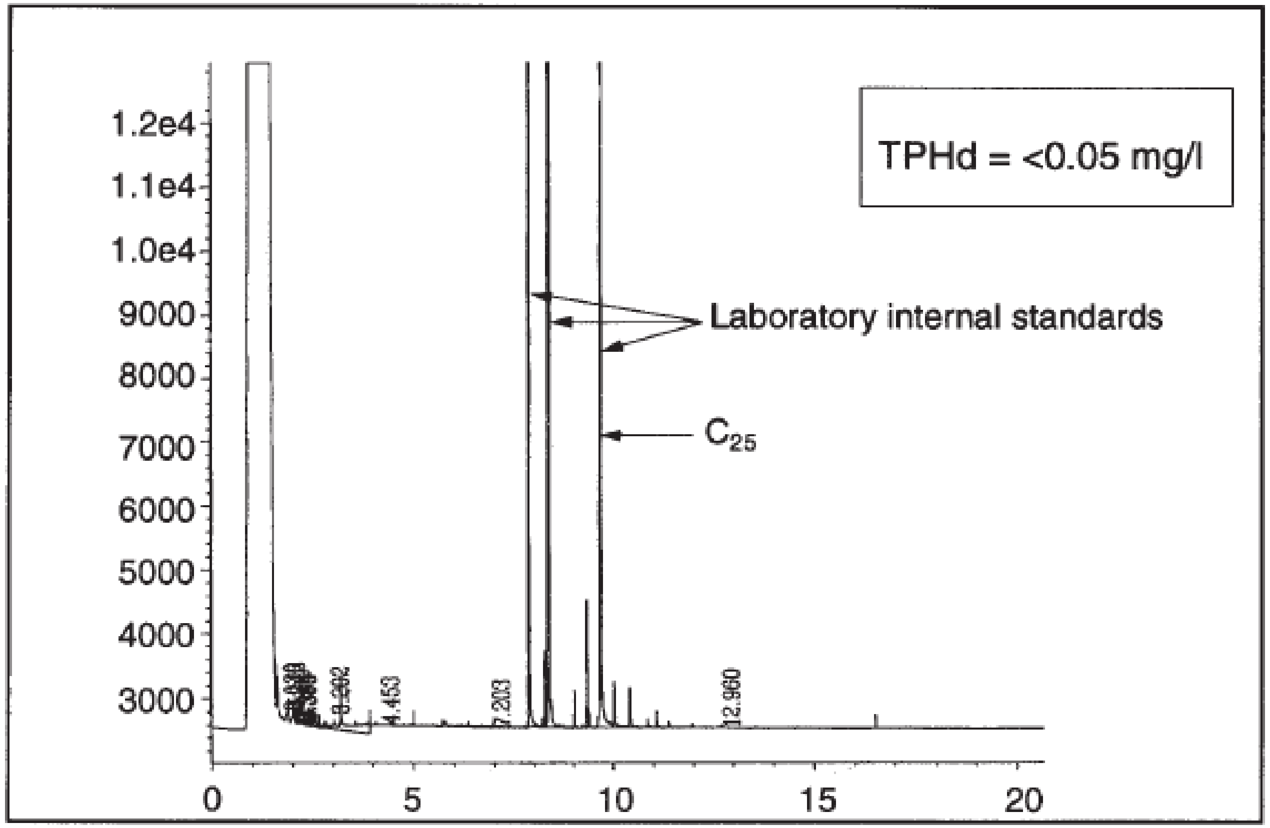
**Mobile & Residual**

**LNAPL**

## Before Silica Gel Cleanup




## After Silica Gel Cleanup




ITRC TPHRisk-1 Figure A5-5 (Zemo 2016)

# Selecting Appropriate TPH Lab Methods

Mobile & Residual LNAPL

| Category | Example Methods | Application | Pros | Cons |
|---|---|---|---|---|
| Bulk TPH | EPA 8015/8260, TX1005, KS LRH/MRH/HRH | Initial site assessment, overall extent | Inexpensive | May overpredict hydrocarbons, limited risk assessment usability |
| Fractionation | TX1006, MADEP VPH/EPH, WA Dep Ecology | Improve site conceptual model | Better define fate/transport and risk characteristics | Expensive |
| Silica Gel Cleanup | EPA Method 3630C with Bulk TPH Methods | Remove non-hydrocarbons, including polar metabolites, from results | Better define extent, fate/transport, and risk of hydrocarbons | Removes polar metabolites from the assessment |

# Measuring TPH

Mobile & Residual LNAPL

TPH provides an approximate concentration of total hydrocarbons in a medium:

- ✓ Provides information on hydrocarbon size and distribution
- ✓ Result will vary by analytical method used to measure it
- ✓ Result may include non-hydrocarbons depending on method used

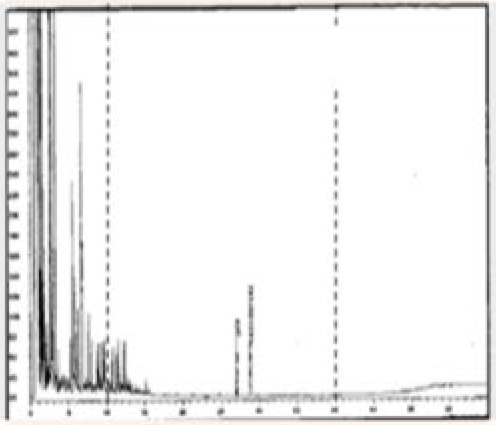
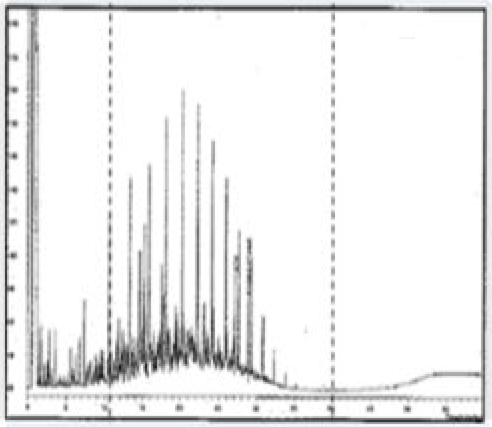
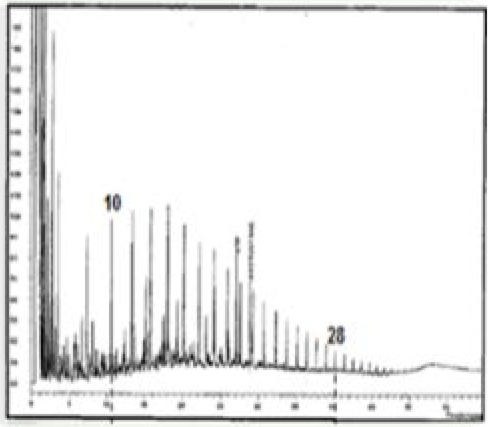
REMEMBER Key Message 5: TPH is not necessarily “total”, not necessarily all from petroleum, and not necessarily all hydrocarbons

# Key Message 7

Composition of the fuel matters for assessing the risk of mobile or residual LNAPL

# Bulk TPH – What's In That Number?

**Mobile & Residual LNAPL**

| | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|
| Example Numeric Result by GC-FID (8015B) Extractable | 15,000 mg/kg | 15,000 mg/kg | 15,000 mg/kg |
| Example chromatogram for same analysis (Chromatograms courtesy of Chevron) |  |  |   |

Note that the first dotted line on the chromatograms is at C10, the second at C28

| Gasoline | Diesel Fuel | South Louisiana Crude |
|---|---|---|

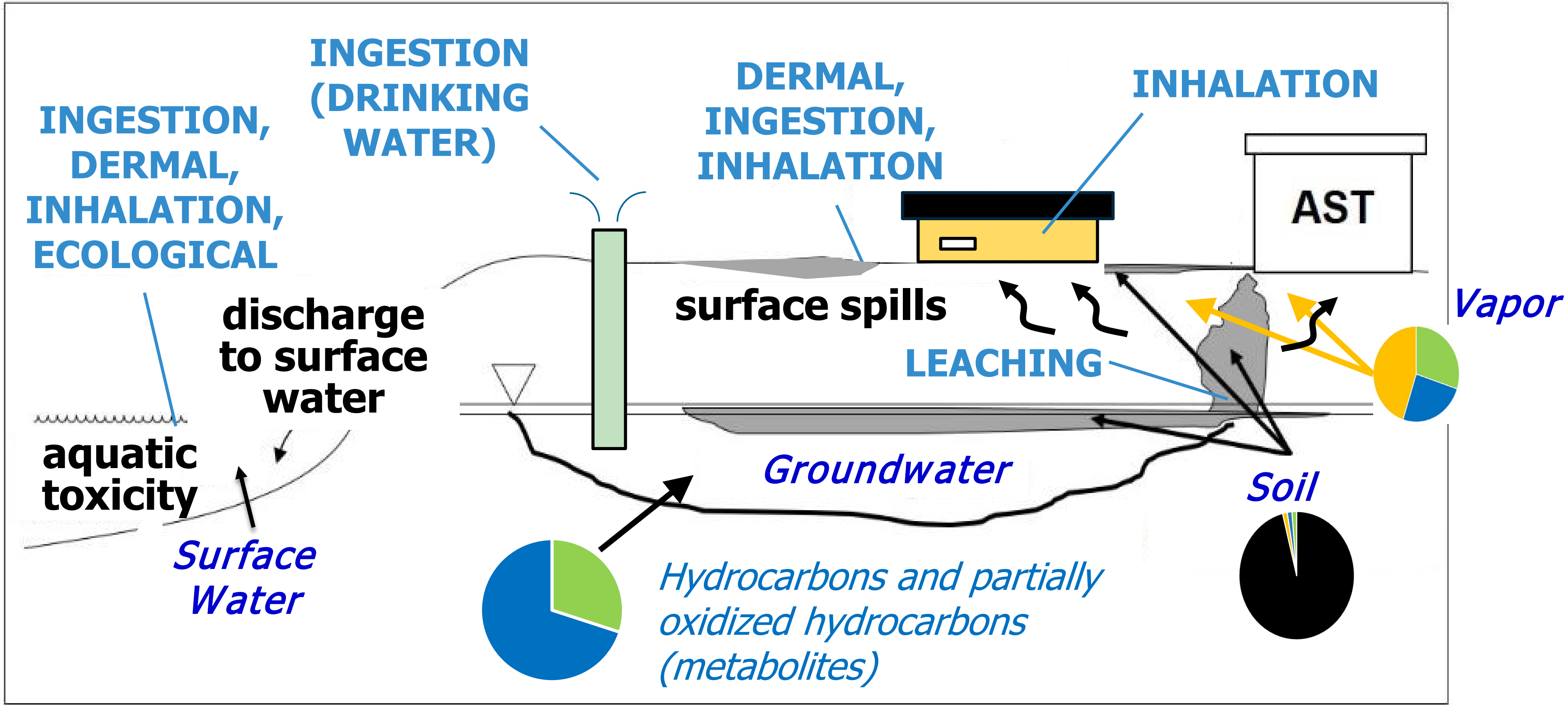
# Unique Characteristics of TPH Effect Exposure

**PHASE**

- NAPL (non-aqueous phase liquid)
- Air/Vapor
- Water
- Sorbed

*MEDIA*

**EXPOSURE PATHWAY**




Source: modified from HIDOH Case Study #1, Figure 1-3 (HIDOH 2018)

# Human Health Toxicity Assessment

Mobile & Residual LNAPL

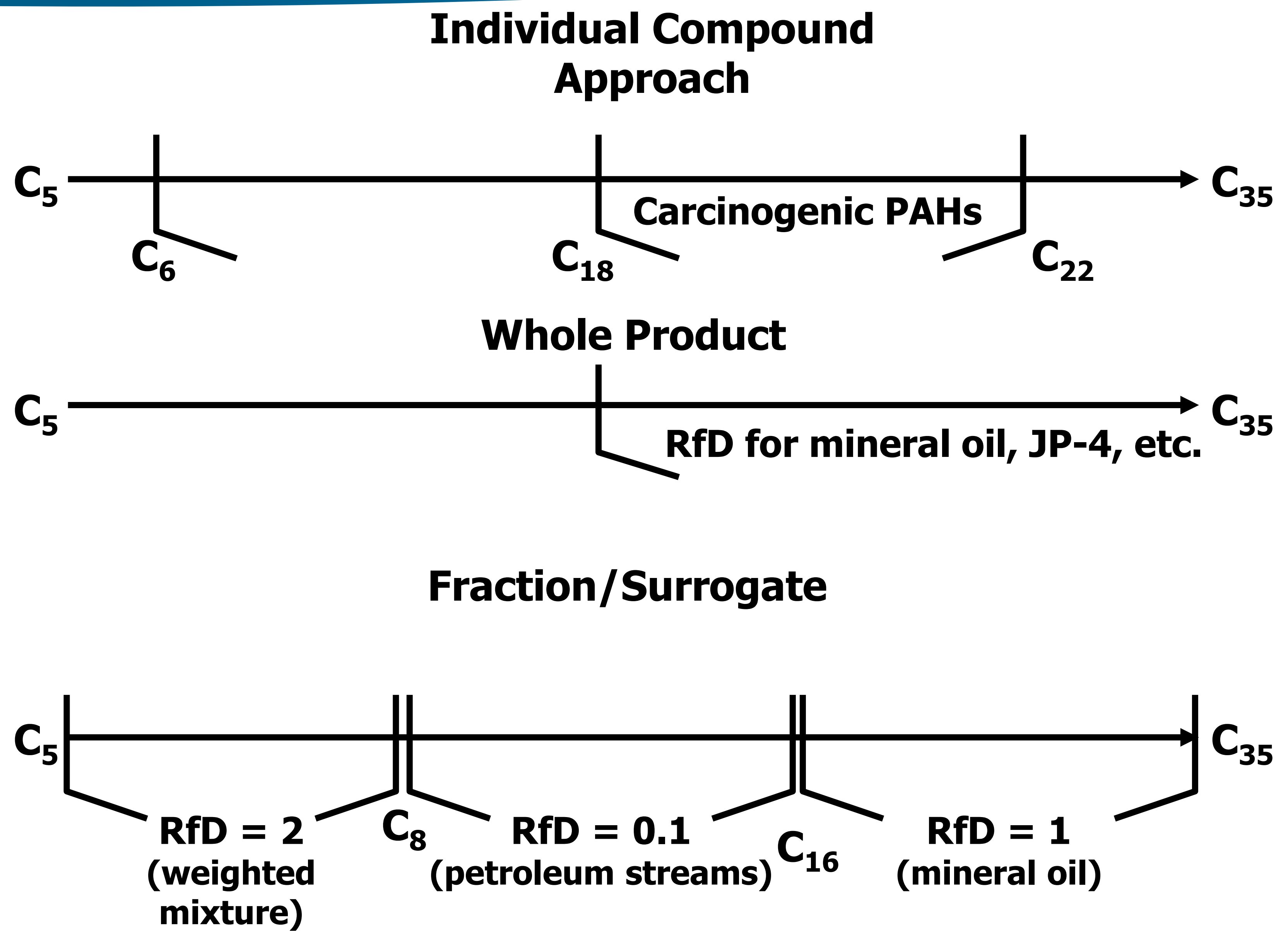
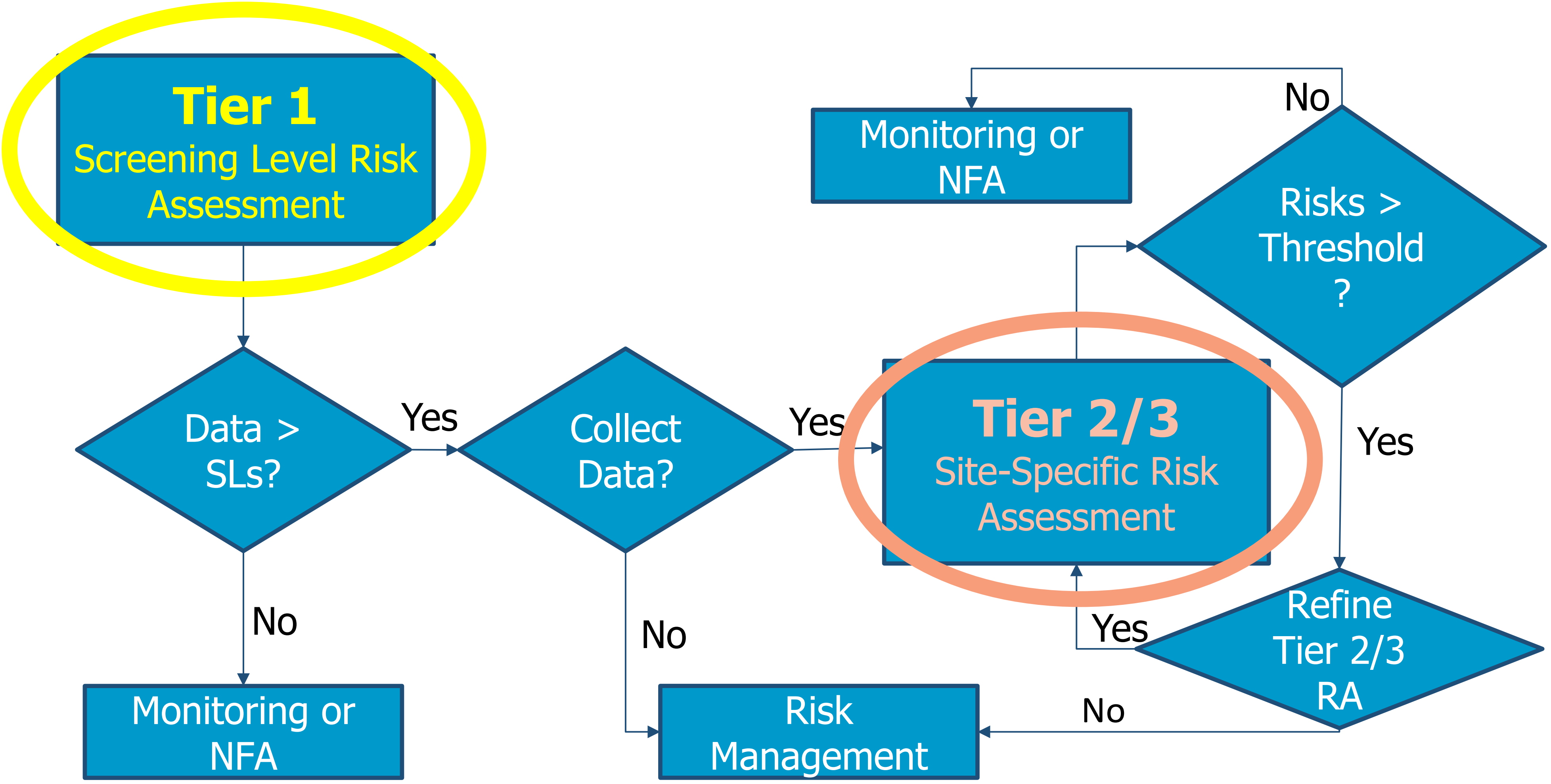



Image: Figure 6-2. TPH toxicity assessment methods TPHCWG 1999

# Tiered TPH Risk Assessment Framework

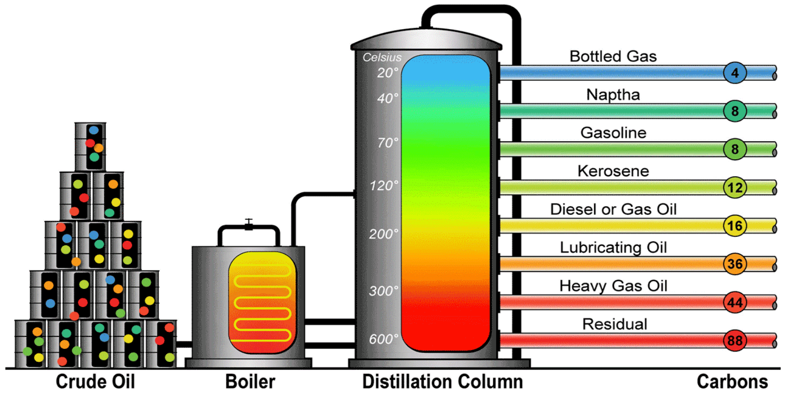
Mobile & Residual LNAPL



# Assessing Risk from TPH

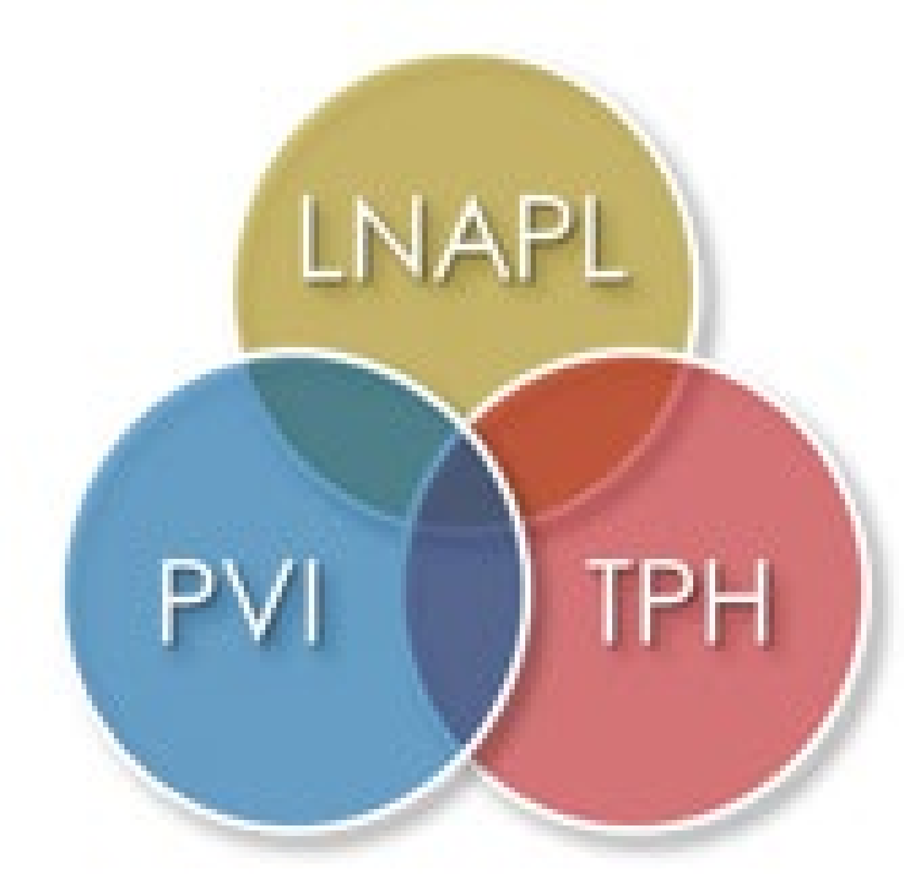
**Mobile & Residual LNAPL**

- TPH is a complex mixture
- Unique fate and transport properties of TPH affect how risk should be assessed
- Varying types of TPH data lend themselves to a tiered assessment approach
  - **Tier 1 Screening Level Risk Assessment:** bulk TPH data and indicator compounds
  - **Tier 2/3 Site-specific Risk Assessment:** TPH fraction data
- Understanding analytical data, CSM, and regulatory framework is critical in appropriately assessing risk




*Source: Haley & Aldrich*

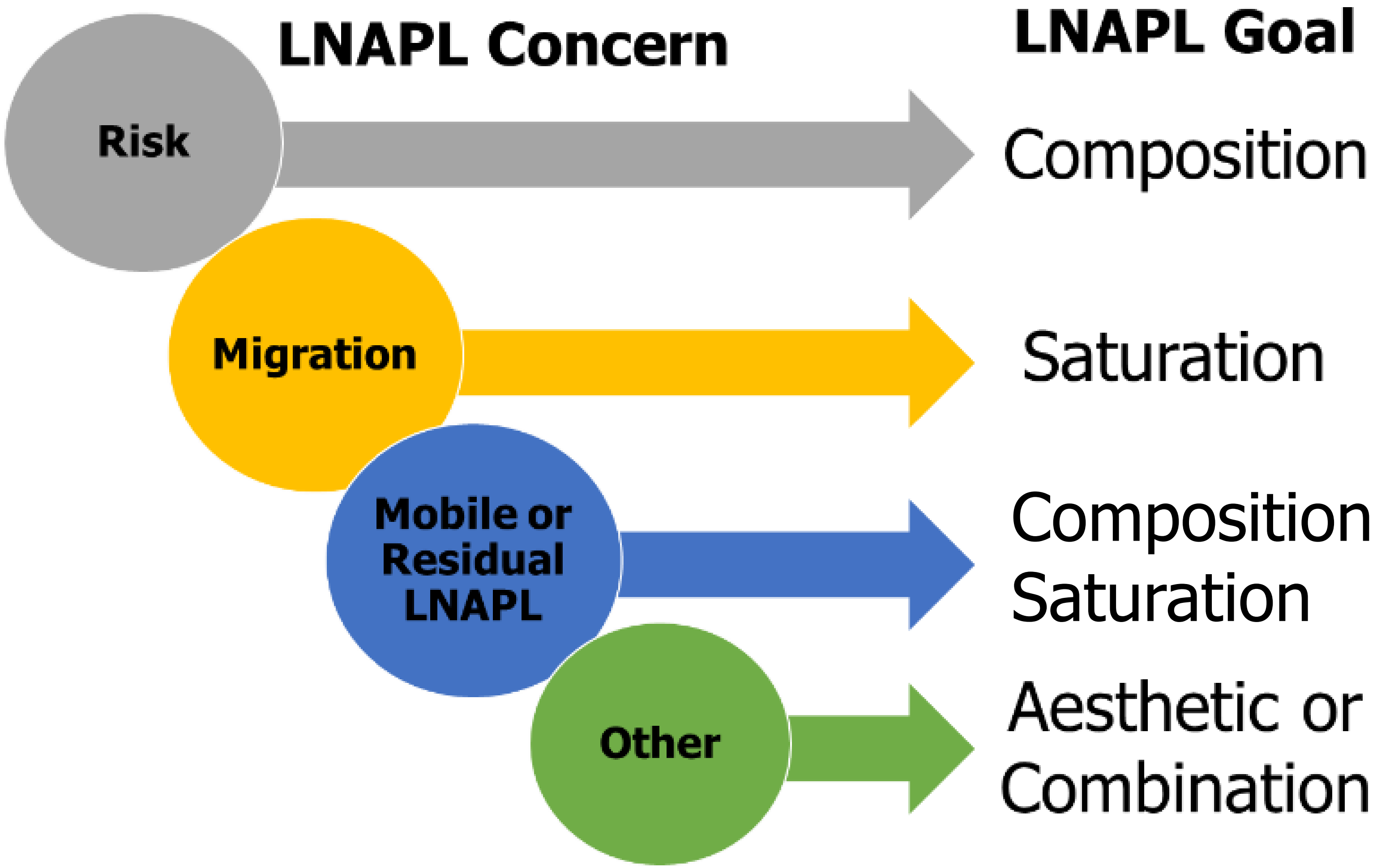
# Risk Management



# Petroleum Risk Management Options

| Risk Management Option |
| --- |
| **Additional Data Collection** |
| **Remedial Action**<br>(e.g., cleanup based on LNAPL or dissolved-phase concerns) |
| **Mitigation**<br>(e.g., PVI active or passive systems) |
| **Engineering Controls**<br>(e.g., barrier wall) |
| **Institutional Controls**<br>(e.g., deed restrictions) |

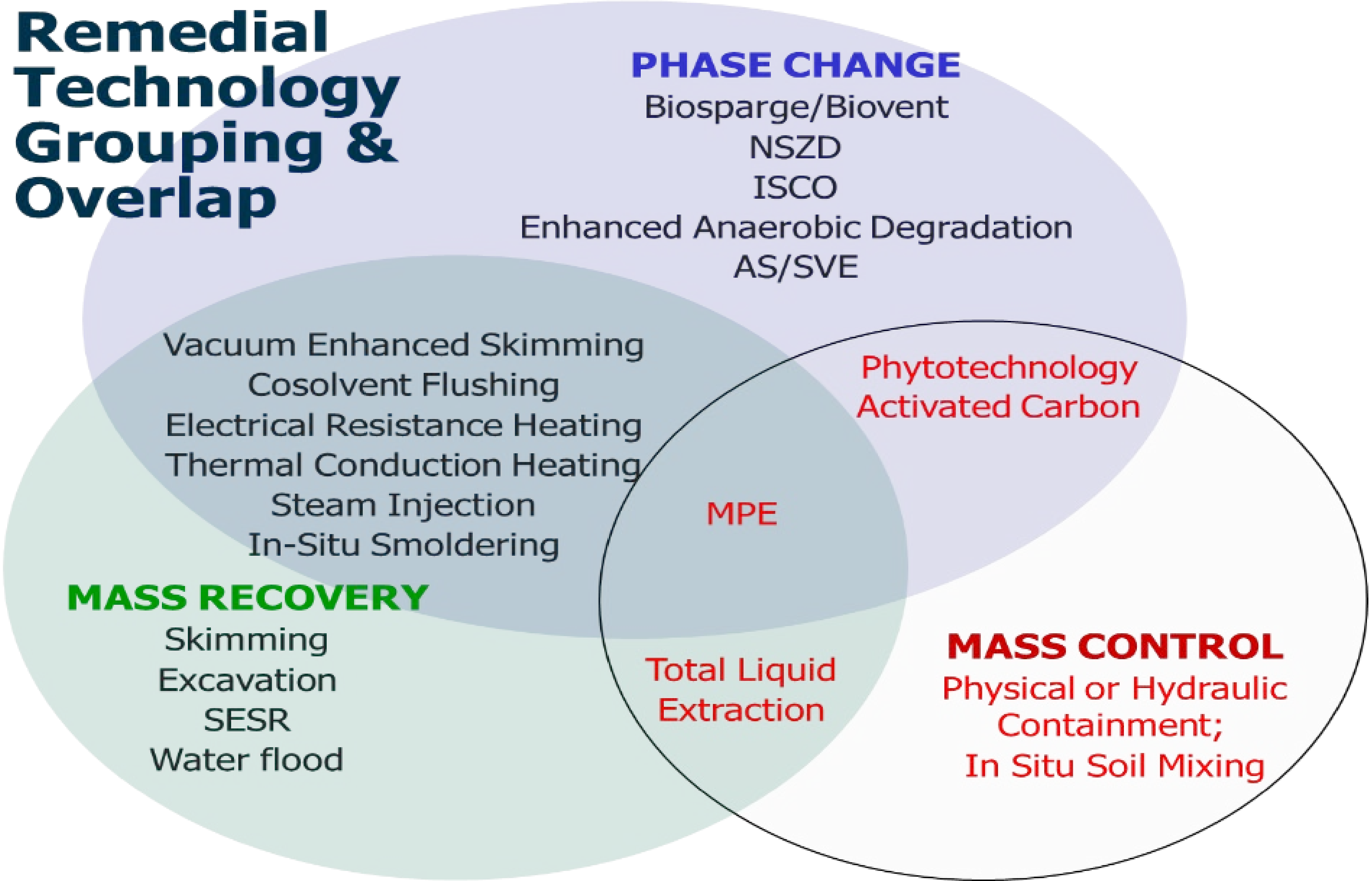
# Select Remedial Goals



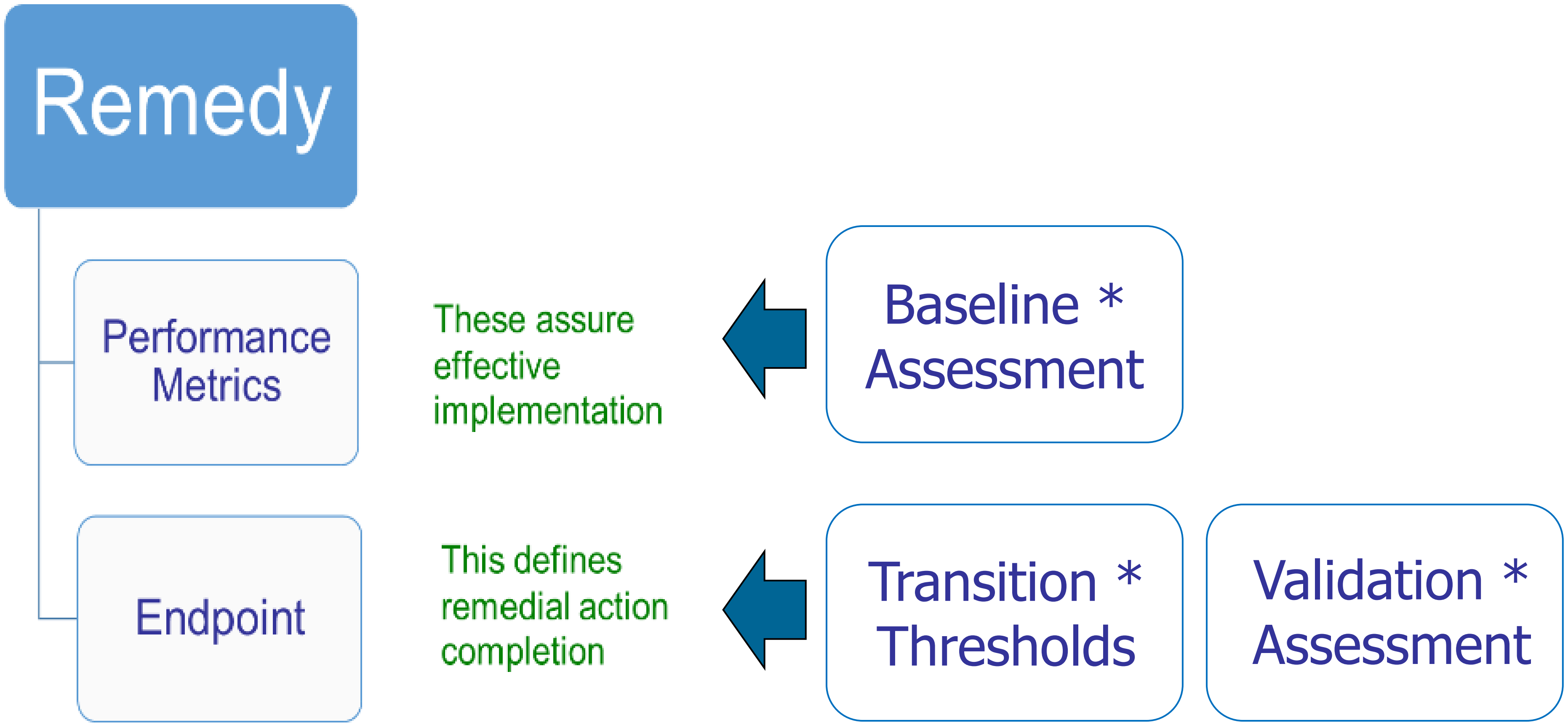
# Select Remedial Goals

- **Saturation Goal**
  - Objective:  LNAPL mass control/recovery
  - Examples: stop LNAPL migration by containing LNAPL or Reduce LNAPL saturation by recovering LNAPL
- **Composition Goal**
  - Objective: LNAPL phase change
  - Example: Change LNAPL characteristics by phase change
- **Aesthetic Goal**
  - Objective: eliminate cause (LNAPL Saturation or Composition)
  - Example: stop LNAPL from seeping to river

# Select Remedy That Aligns With Remedial Goals



# Identify Performance Metrics & Endpoints



# Performance Metrics: Example – ASTM WK78867

| Example Performance Metrics | |
|---|---|
| **System Related** | **Subsurface Related** |
| • TPH/COC concentration in influent/effluent (C)<br>• Fluid recovery rates (LNAPL, water, gas)<br>• LNAPL to vapor or water ratios (S)<br>• Flow rate, pressure/vacuum, temperature (S or C)<br>• Drawdown, water-level mounding (S or C)<br>• Radius of influence (C or S) | • Groundwater, soil, or soil-gas concentrations over time, space (C)<br>• COC mass flux or discharge in groundwater or soil vapor (C)<br>• LNAPL presence or thickness in wells (S)<br>• LNAPL transmissivity (S)<br>• Electron acceptor distribution (oxygen) (C) |

(S) = Saturation Concern
(C) = Composition Concern

* From WK78667 Draft ASTM Guide for Advancing Stalled Corrective Action Sites Toward Site Closure

# Endpoints (Transition Thresholds): Example – ASTM WK 78667

| Example Transition Thresholds |
|---|
| • LNAPL transmissivity below an ITRC (2018) threshold of 0.1 to 0.8 $ft^2$/day (S) |
| • Recovery of 95% of LNAPL based on a decline curve analysis (ITRC, 2018) (S) |
| • Concentrations or mass discharge at (or approaching) established regulatory target levels within accepted statistical certainty (C) |
| • Active mass recovery rates similar to (or less than) natural source-zone depletion rates (ASTM, 2022) (S) |
| • Active attenuation rates similar to (or less than) natural attenuation rates (ASTM, 2022) (C) |
| • No (or limited) rebound in concentrations or mass following temporary termination of corrective action (partial or complete) (S and/or C) |
| • Mass removal or concentration attenuation rates by active recovery approaching asymptotic levels while ratio of GHG emissions per unit reduction in mass or concentration is rapidly increasing (S and/or C) |
| • Mass removal or concentration attenuation rates by active recovery approaching asymptotic levels while ratio of costs per unit reduction in mass or concentration is rapidly increasing (S & C). |

(S) = Saturation Concern
(C) = Composition Concern

* From WK78667 Draft ASTM Guide for Advancing Stalled Corrective Action Sites Toward Site Closure

# Training Summary

The characterization of TPH, LNAPL, and PVI requires an integrated approach that is communicated through a CSM

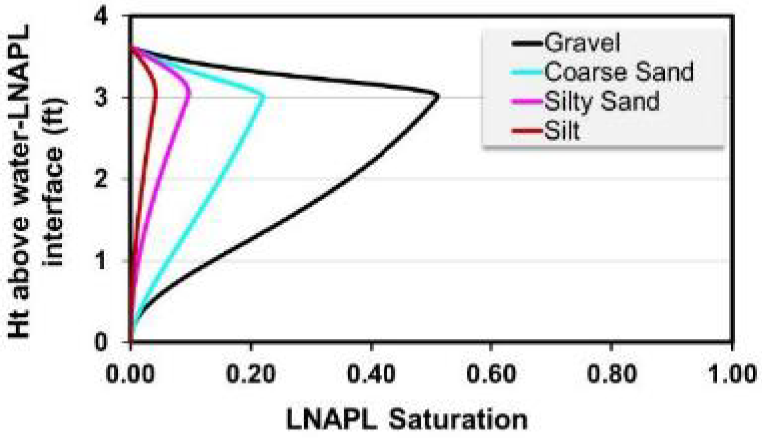
## TPH key messages

- TPH is defined by analysis
- TPH analysis characterizes nature/extent and whether biodegradation is occurring (i.e., presence of petroleum metabolites)
- Type of TPH analysis depends on site investigation goals (i.e., fractionated TPH analysis provides results that have associated toxicity values; therefore, can quantify human health risks)

# Training Summary

## LNAPL key messages

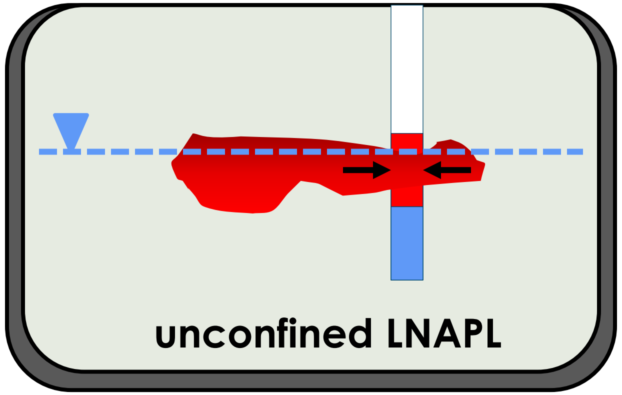
- LNAPL is the source of long-term vapor, sorbed and dissolved phases
- LNAPL can be present in the soil pores even if not visible in wells
- LNAPL bodies typically stabilize quickly



# Training Summary

## LNAPL key messages

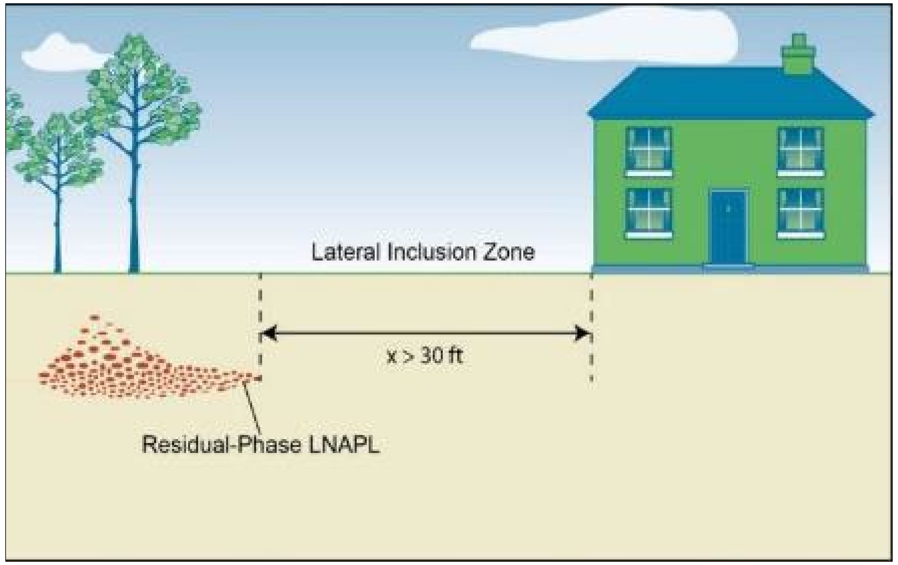
- Mobile LNAPL in wells does not mean that the LNAPL body is migrating (or recoverable)
- LNAPL thickness in wells is affected by soil type, water table fluctuations, and the LNAPL hydrogeologic condition
- Biodegradation processes deplete LNAPL source mass and helps stabilize LNAPL bodies
- Remedial technology selection based on the LNAPL concern(s): saturation, composition, and/or aesthetic



# Training Summary

## PVI key messages

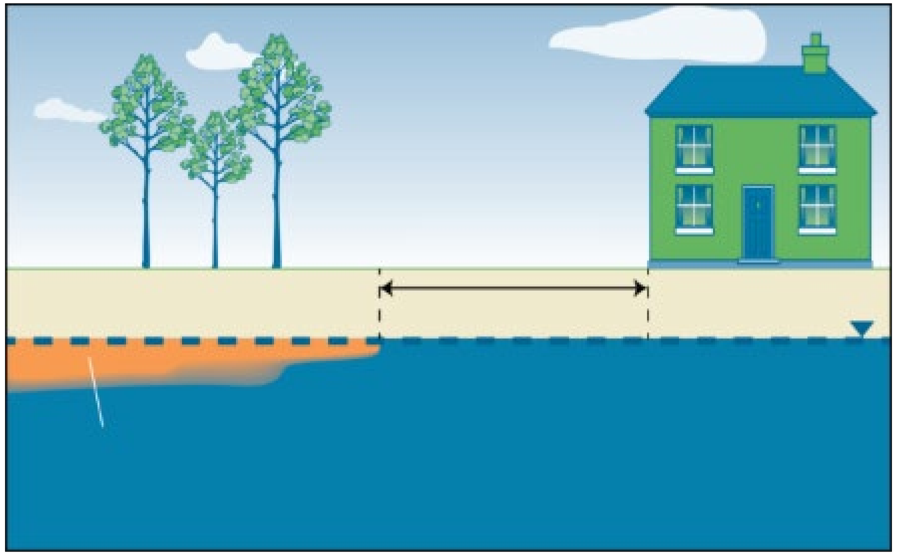
- Biodegradation in the vadose zone limits the potential for PVI and serves as the basis for lateral and vertical screening distances
- PVI risks are mainly associated with LNAPL (gasoline)



# Training Summary

## PVI key messages

- Proper identification of residual LNAPL sources is critical
- Site characterization should focus on the vadose zone given the high likelihood of encountering gasoline-related COCs in indoor air above risk-based screening levels



# Questions

## PVI

https://projects.itrcweb.org/PetroleumVI-Guidance/

## LNAPL

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

## TPH

https://tphrisk-1.itrcweb.org/

## Hydrocarbons Sites

https://hyd-1.itrcweb.org/

Certificate of Completion https://www.clu-in.org/conf/itrc/Hydrocarbons/
*emailed after you complete the Feedback Form*

# References and Citations


API (American Petroleum Institute), 2004.  API Interactive LNAPL Guide Version 2.0.4. API Publishing Services, 1220 L. Street, NW, Washington, DC. February 2006. https://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/interactive-guide.

API (American Petroleum Institute), 2017. Quantification of vapor phase-related natural source zone depletion processes. American Petroleum Institute Publication #4784.  API Publishing Services, 1220 L. Street, NW, Washington, DC. May 2017. https://store.accuristech.com/standards/api-publ-4784?product_id=1984357.

ASTM International, 2006. Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface. Standard Guide E2531-06. ASTM International, West Conshohocken, PA.

Dawson, H.E., and T. McAlary, 2009.  A compilation of statistics for VOCS from post-1990 indoor air concentration studies in North American residences unaffected by subsurface vapor intrusion. Groundwater Monit. Remed., 29, 60-69. https://doi.org/10.1111/j.1745-6592.2008.01215.x.

Hua Y., He, X, Xie, W., Xiong, J., Sheng, H., Guo, S., Huang, C., Zhang, D., and K. Zhang.  2014. Elastase LasB of Pseudomonas aeruginosa promotes biofilm formation partly through rhamnolipid-mediated regulation. Can J. Microbiol. 60, 227-235.  https://doi.org/10.1139/cjm-2013-066.

ITRC (Interstate Technology & Regulatory Council). 2023. Effective Application of ITRC Guidance to Hydrocarbons Sites HYD-1. Washington, D.C., www.itrcweb.org.

ITRC (Interstate Technology & Regulatory Council). 2023. Effective Application of ITRC Petroleum Risk Evaluation Checklist. Washington, D.C., https://hyd-1.itrcweb.org/petroleum-risk-evaluation-checklist/.

ITRC, 2018. LNAPL-3: LNAPL Site Management – LCSM Evolution, Decision Process, and Remedial Technologies. Interstate Technology and Regulatory Council. March 2018. https://lnapl-3.itrcweb.org/

# References and Citations

ITRC (Interstate Technology & Regulatory Council). 2018. TPH Risk Evaluation at Petroleum-Contaminated Sites. TPHRisk-1. Washington, D.C.: Interstate Technology & Regulatory Council, TPH Risk Evaluation Team. https://tphrisk-1.itrcweb.org

ITRC (Interstate Technology and Regulatory Council) 2009. Evaluating Natural Source Zone Depletion at Sites with LNAPL. Interstate Technology and Regulatory Council, Washington, D.C., https://itrcweb.org/wp-content/uploads/2024/09/LNAPL-1.pdf.

Kulkarni, P.R., Walker, K.L., Newell, C.J., Askarani, K.K., Yue, L., and T.E. McHugh. 2022. Natural source zone depletion (NSZD) insights from over 15 years of research and measurements: A multi-site study. Water Research. 225, 119170. https://doi.org/10.1016/j.watres.2022.1191.

Kulkarni, P.R., McHugh, T.E., Newell, C.J., and S. Garg, 2015. Evaluation of source-zone attenuation Palaia, T., and S. Park. 2023. Incorporating Natural Source Zone Depletion (NSZD) into the Site Management Strategy. In Environmental Contamination Remediation and Management, Advances in the Characterisation and Remediation of Sites Contaminated with Petroleum Hydrocarbons, Chapter 13. Editors J. Garcia-Rincon, E. Gatsisos, R.J.Lenhard, E.A. Atekwana, and R. Naidu. Springer. https://link.springer.com/chapter/10.1007/978-3-031-34447-3_13.

Palaia, T. 2017. A Comparison of Natural Source Zone Depletion and Active Remediation Rates. Presented at the 7th International Contaminated Site Remediation Conference - CleanUp 2017, Melbourne Australia, September 13, 2017. https://inis.iaea.org/search/search.aspx?orig_q=RN:52085940.

SOBRA (Society of Brownfield Risk Assessment), 2023. Light Non-Aqueous Phase Liquid – Guidance Notes for their Assessment in Contaminated Land Scenarios in the UK . 3. LNAPL MOBILITY SCREENING TOOL. Version 1.0, April 2023. https://sobra.org.uk/?pmpro_getfile=1&file=2023/06/SOBRA-NAPL-Mobility-Tool-080523-Final-combined-page-12-edited&ext=pdf.

USEPA (U.S. Environmental Protection Agency). 2011. Background Indoor Air Concentrations of Volatile Organic Compounds in North American Residences (1990–2005): A Compilation of Statistics for Assessing Vapor Intrusion. US Environmental Protection Agency Office of Solid Waste and Emergency Response Report EPA 530-R-10-001, June, 2011. https://www.epa.gov/sites/default/files/2015-09/documents/oswer-vapor-intrusion-background-report-062411.pdf.

Zemo, D. A. 2016. White Paper: Analytical Methods for Total Petroleum Hydrocarbons (TPH). Washington, D.C.: Prepared for American Petroleum Institute (API).