LNAPL CONCEPTUAL SITE MODEL & MINIMIZING REBOUND WHEN APPLYING IN-SITU CHEMICAL TREATMENT

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May 4, 2017

Agenda

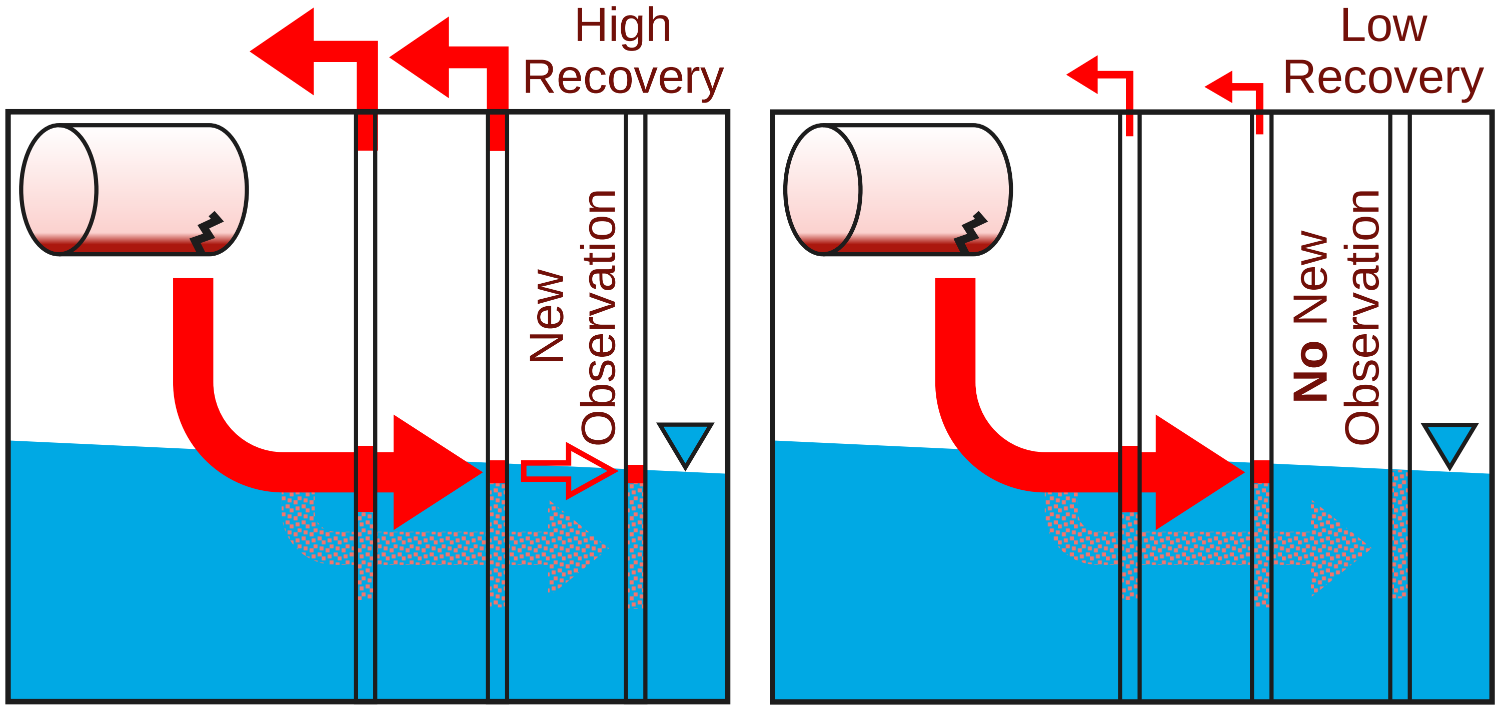
- LNAPL Science – What Happens When LNAPL Is Released?
- The LNAPL Conceptual Site Model – What Should We Know?
- The LNAPL Conceptual Site Model – What Should We Do?
- Alternatives to LNAPL Removal – Phase Change
- ISCO – What Causes Rebound?
- Other Phase Change Alternatives

Introduction

What’s wrong with the old approach to LNAPL?

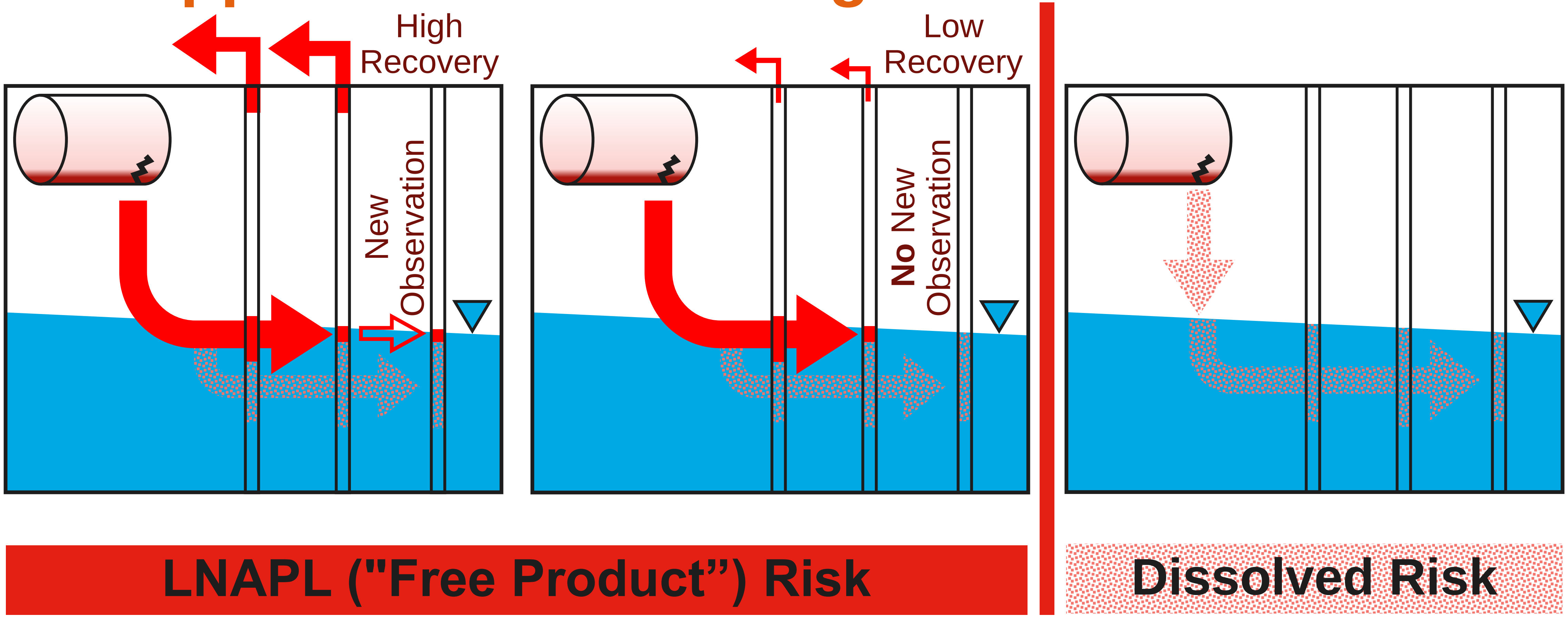
What’s a better approach?

Old Approach to Assessing LNAPL Risk



LNAPL ("Free Product") Risk

Old Approach to Assessing LNAPL Risk



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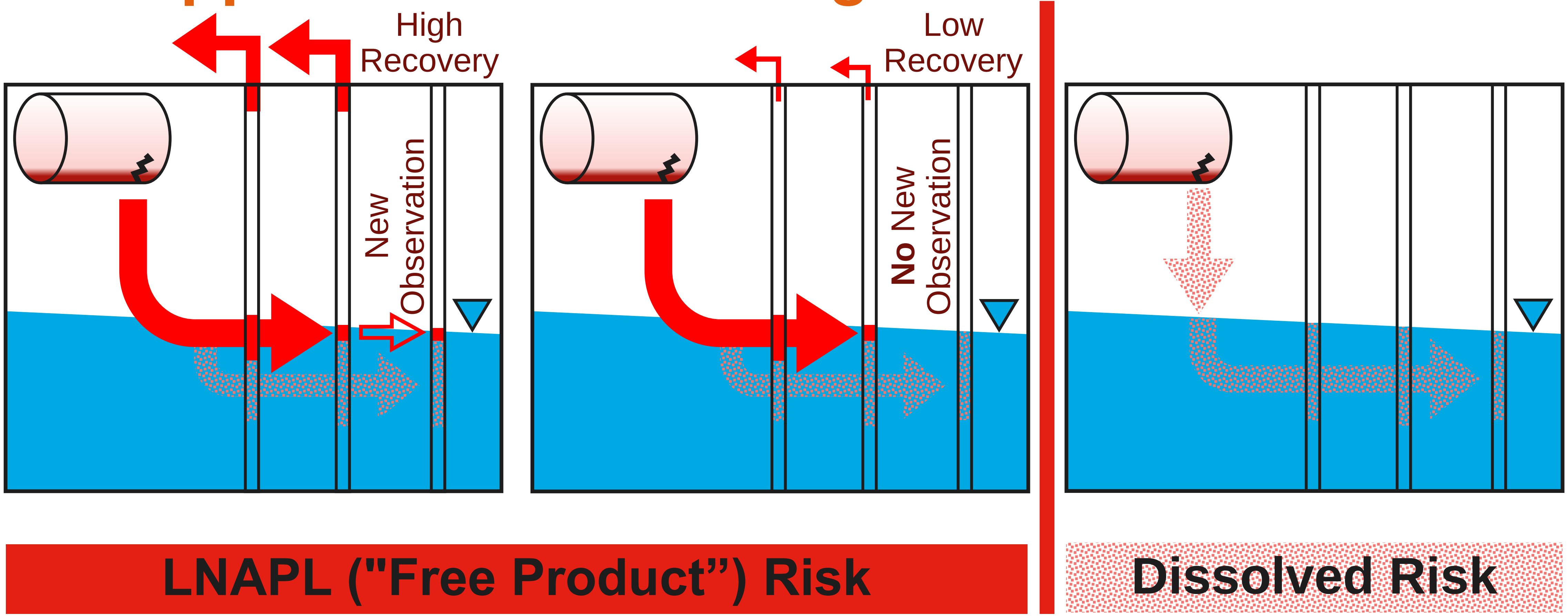
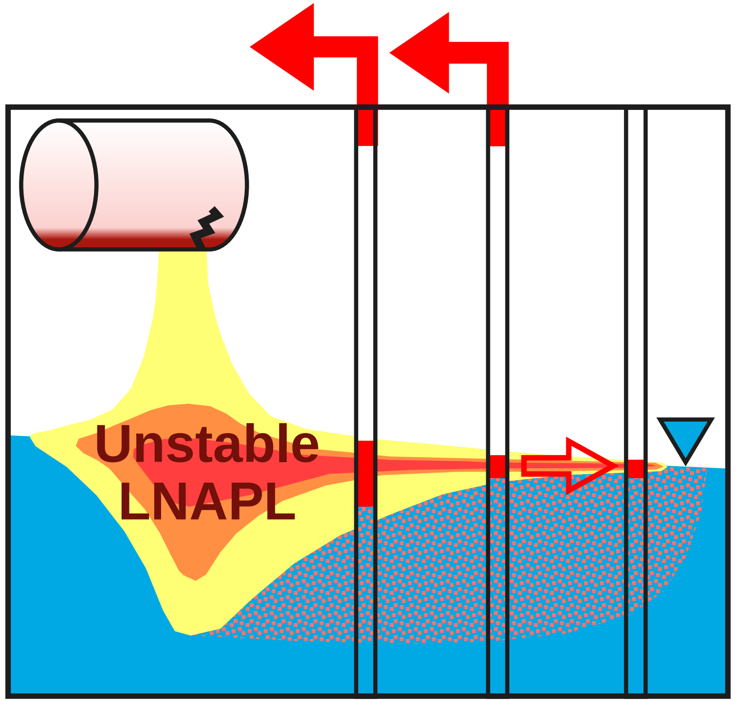


LNAPL ("Free Product") Risk | **Dissolved Risk**

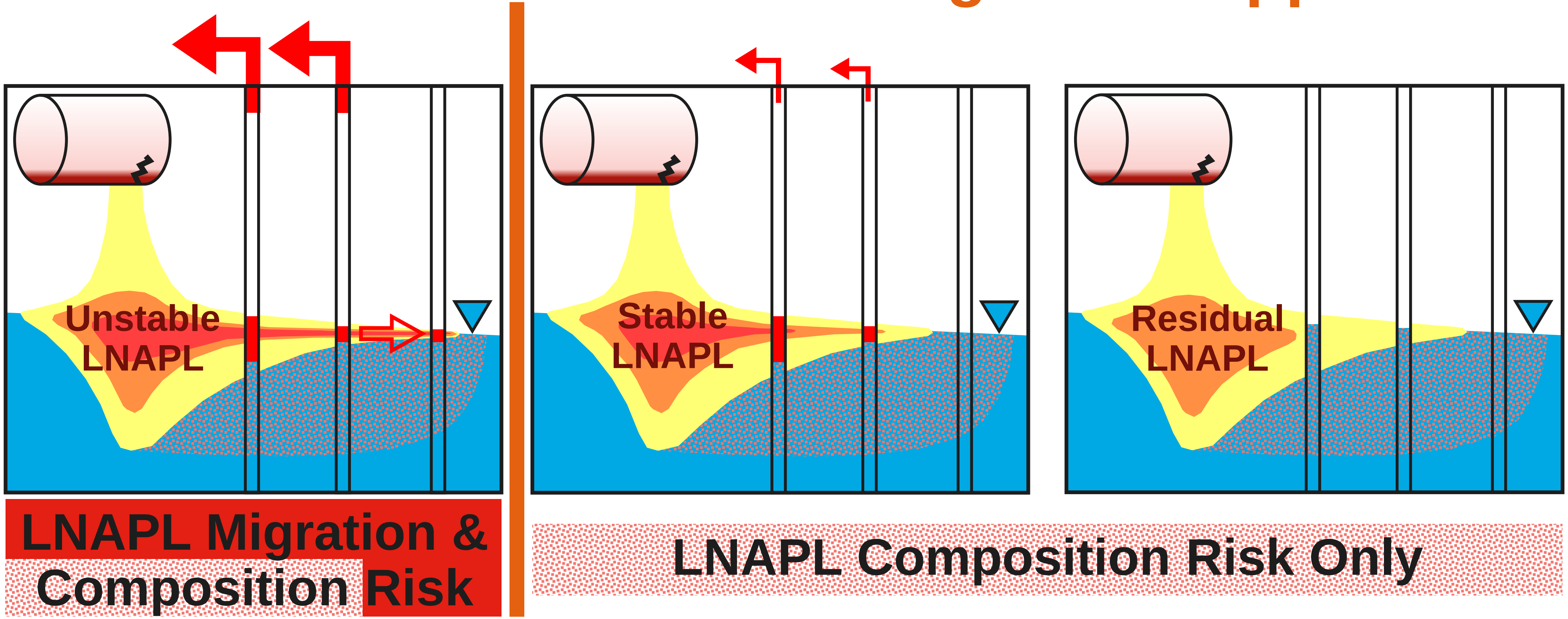
Risk = LNAPL Thickness in Wells, then Dissolved (if still present)

New Risk-Based LNAPL Management Approach



LNAPL Migration & Composition Risk

New Risk-Based LNAPL Management Approach



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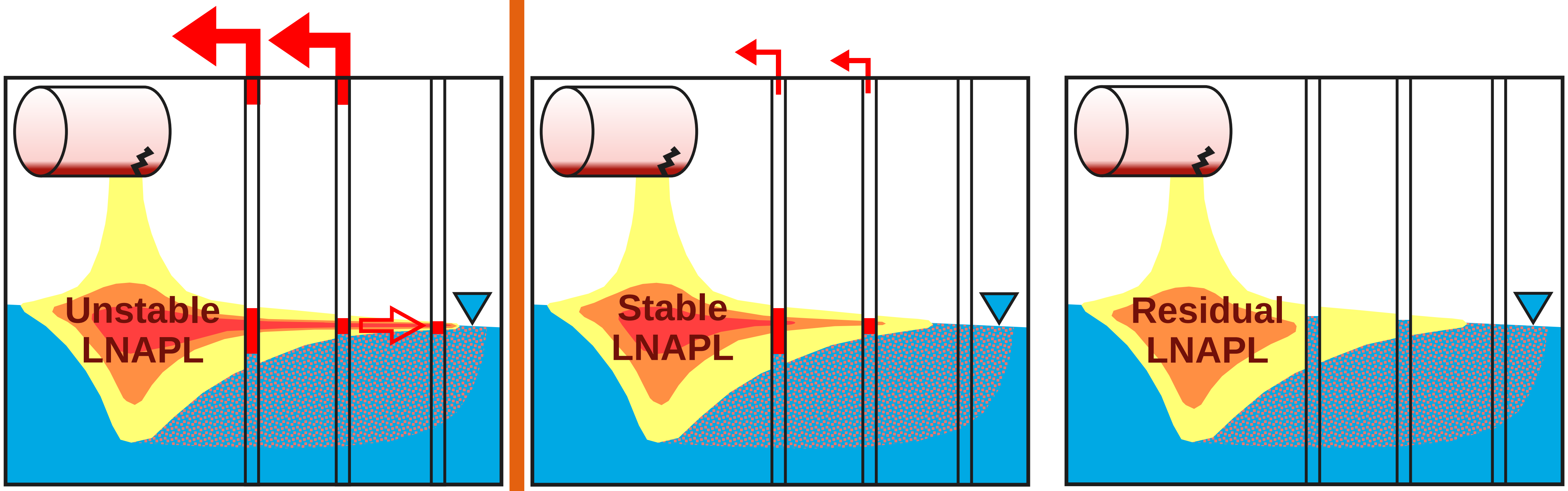
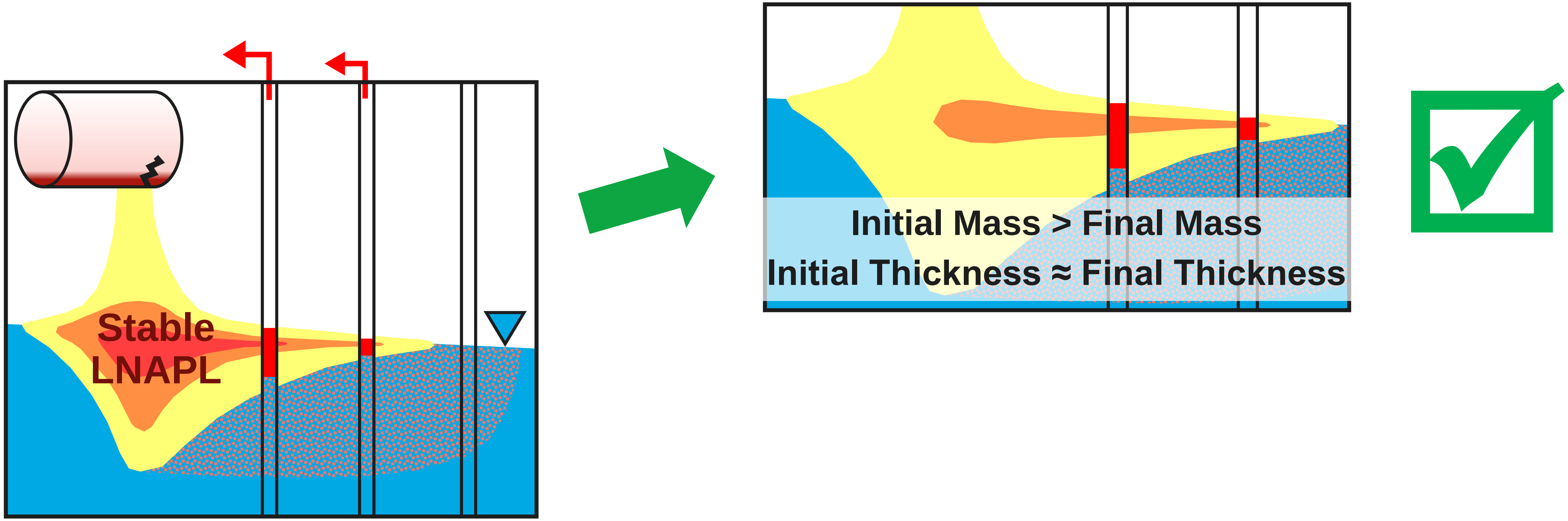


LNAPL Migration & Composition Risk

LNAPL Composition Risk Only

Risk = LNAPL Instability + LNAPL Composition

What About Free Product Removal to MEP*?



* Maximum Extent Practicable

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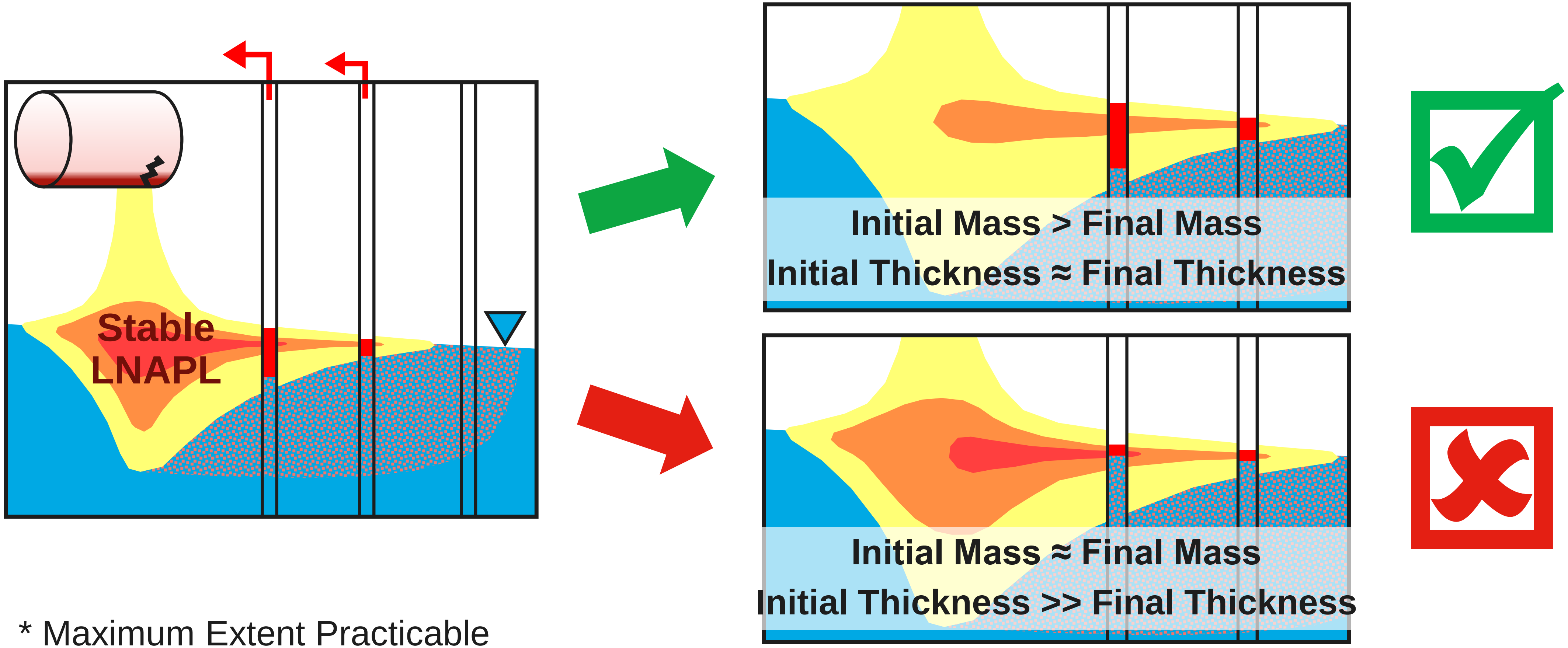

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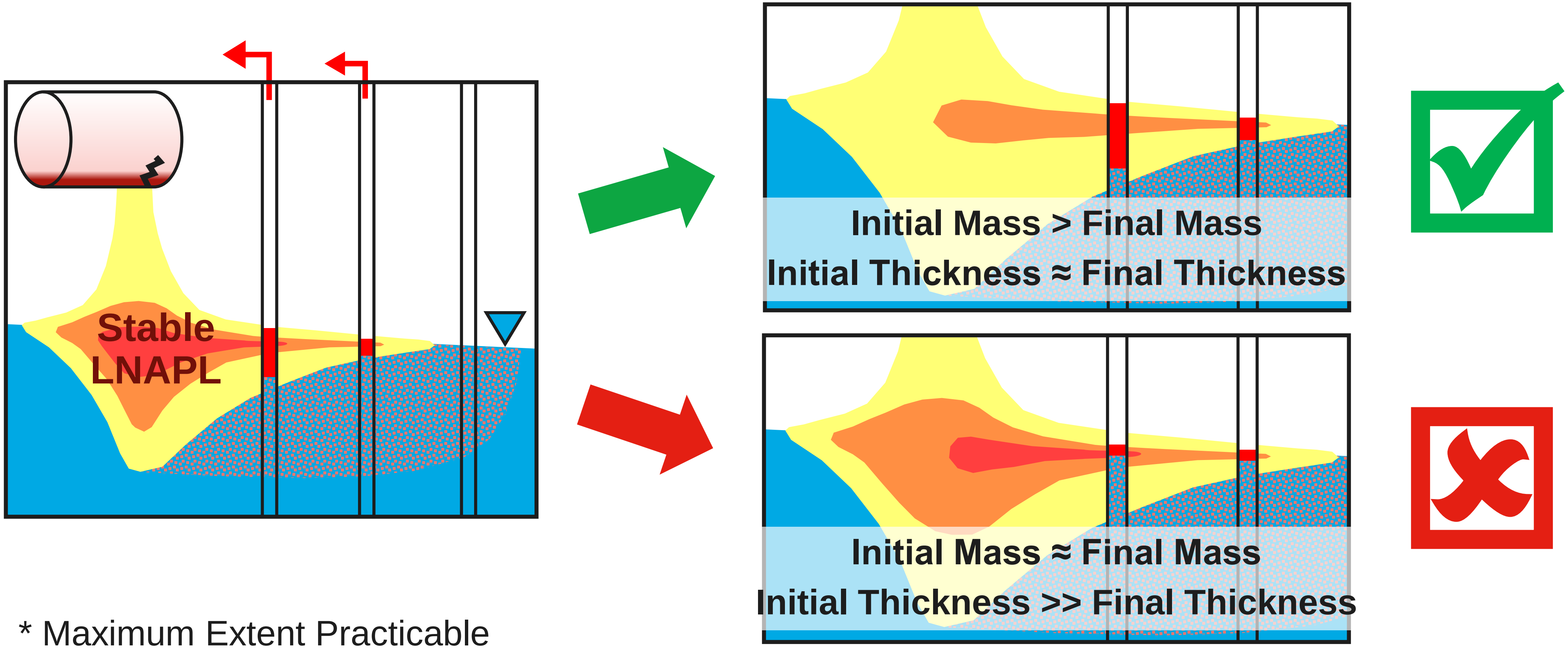
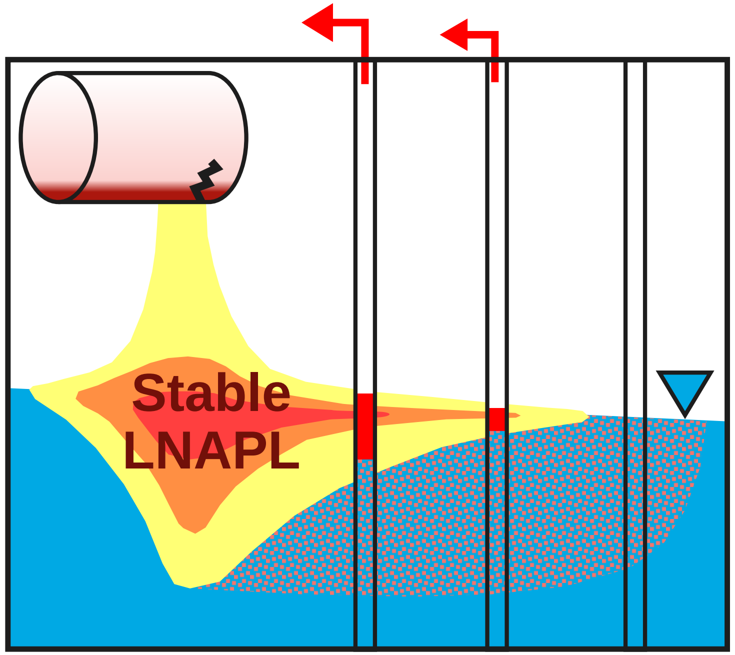


* Maximum Extent Practicable

Key Question: "Will LNAPL Recovery Significantly Change LNAPL Mass?"

How To Avoid Ineffective LNAPL Recovery

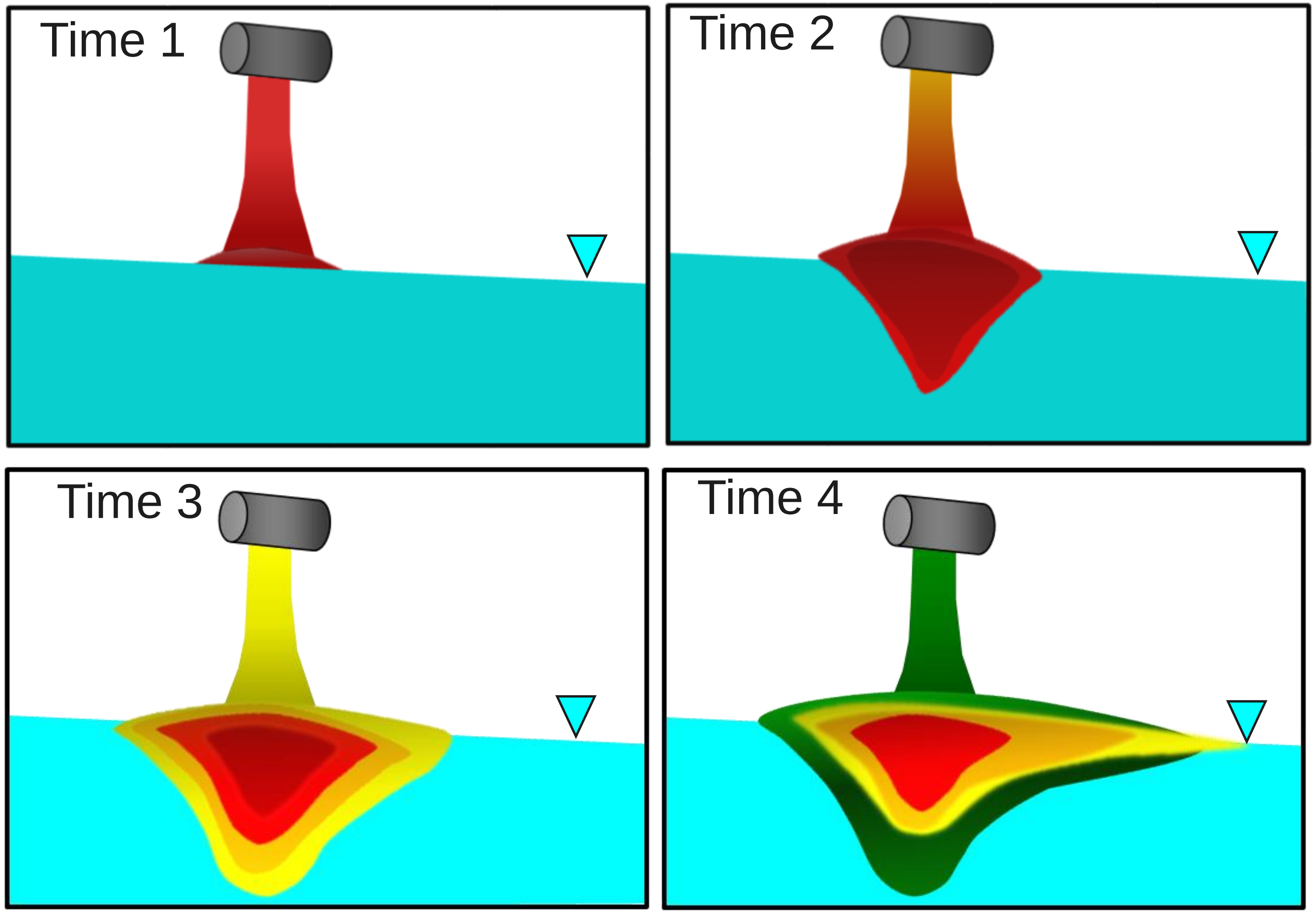


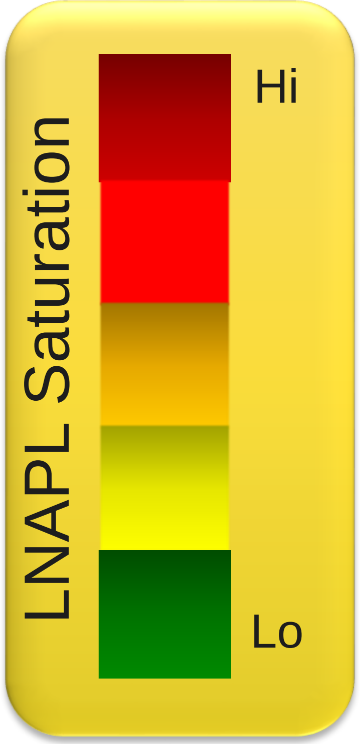
Risk-Based LNAPL Management

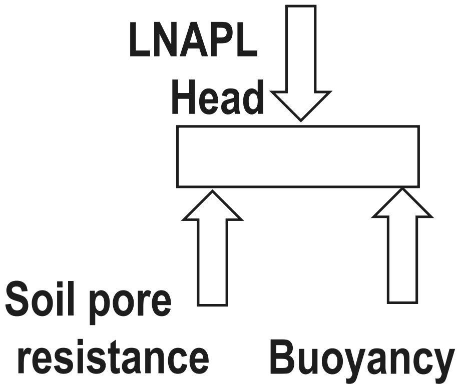
- ☑ LNAPL Stability
- ☑ LNAPL Recoverability
- ☑ Natural Source Zone Depletion
- ➡ LNAPL Composition Risk

Evolution of an LNAPL Site: The Basic Science

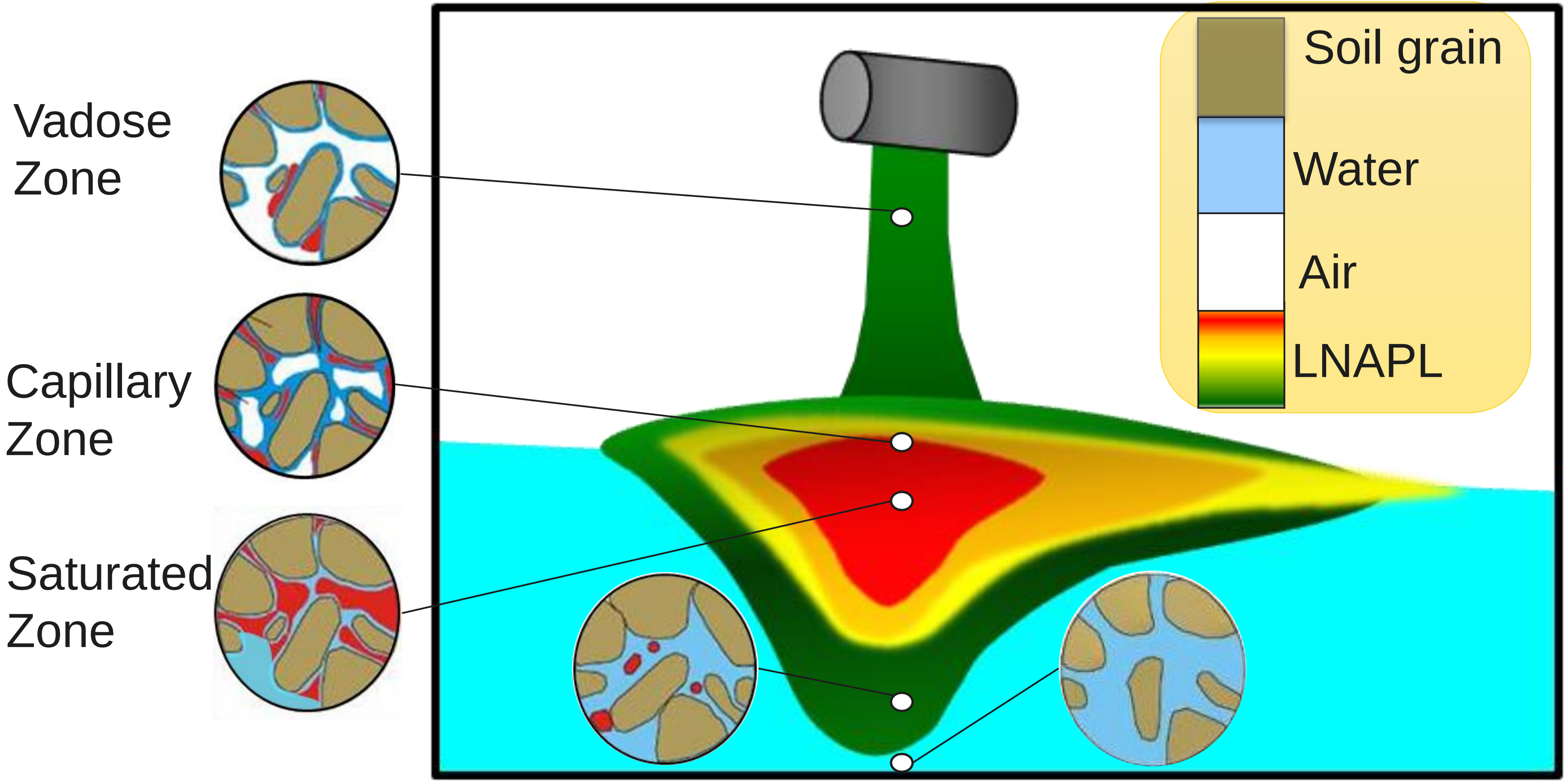
What Happens When LNAPL is Released?





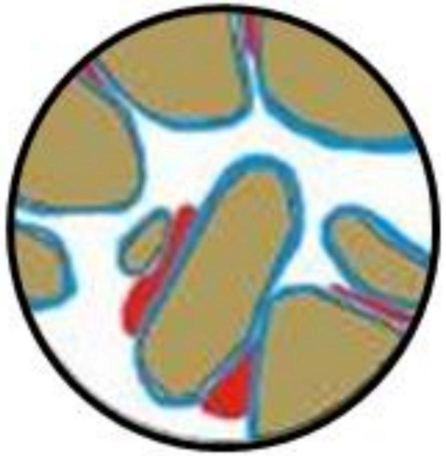


Stable LNAPL Distribution

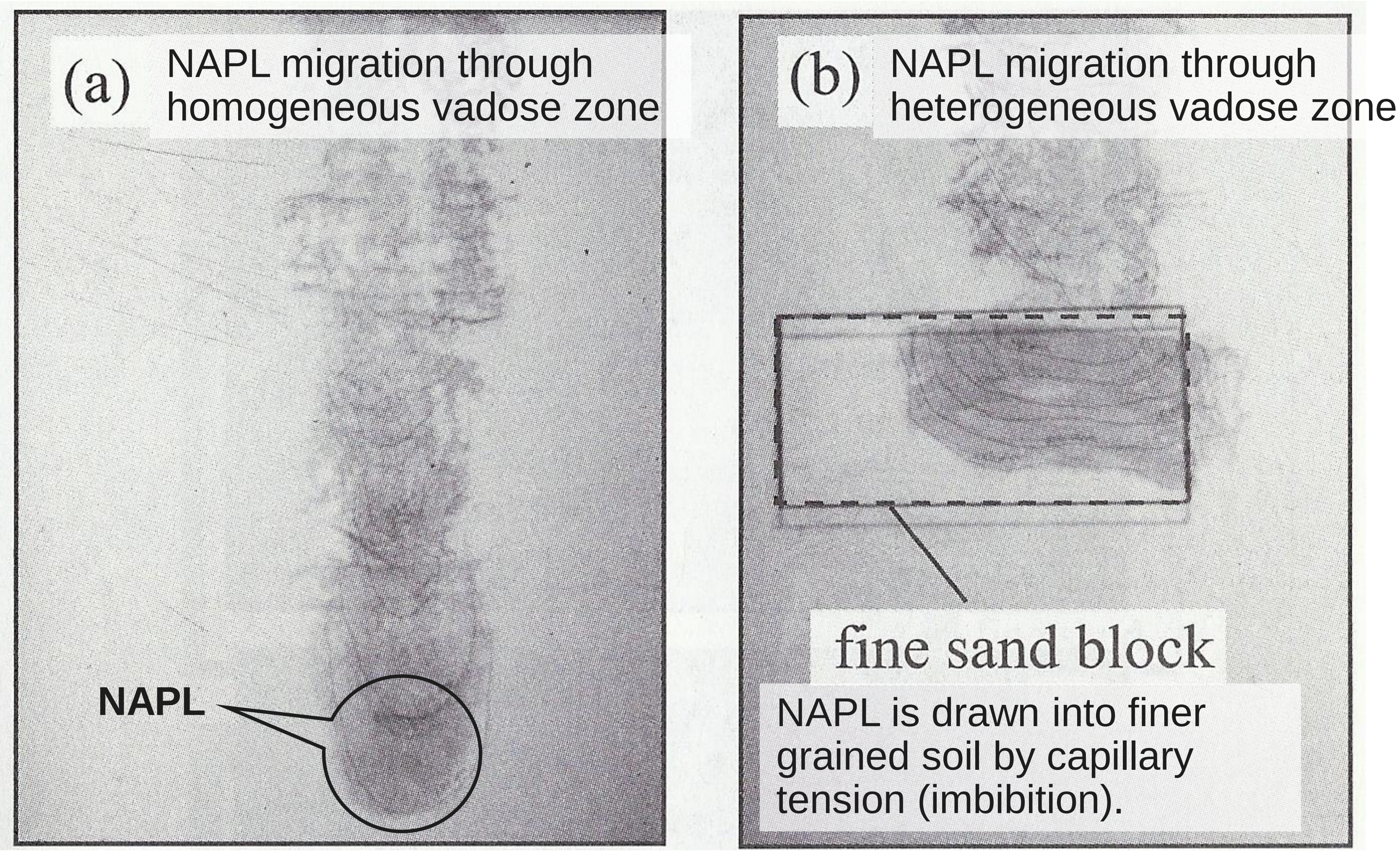


Key Point: LNAPL shares the pores with groundwater and soil vapor

Three-Phase Behavior (Vadose Zone)



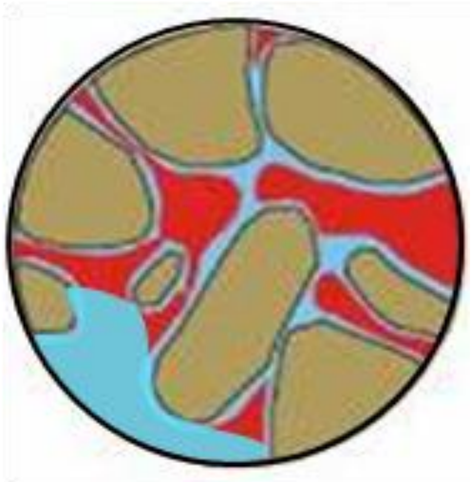
NAPL is “intermediate” wetting phase



Mayer & Hassanizadeh. 2005. Soil and Groundwater Contamination: Nonaqueous Phase Liquids. AGU.

Relative Permeability

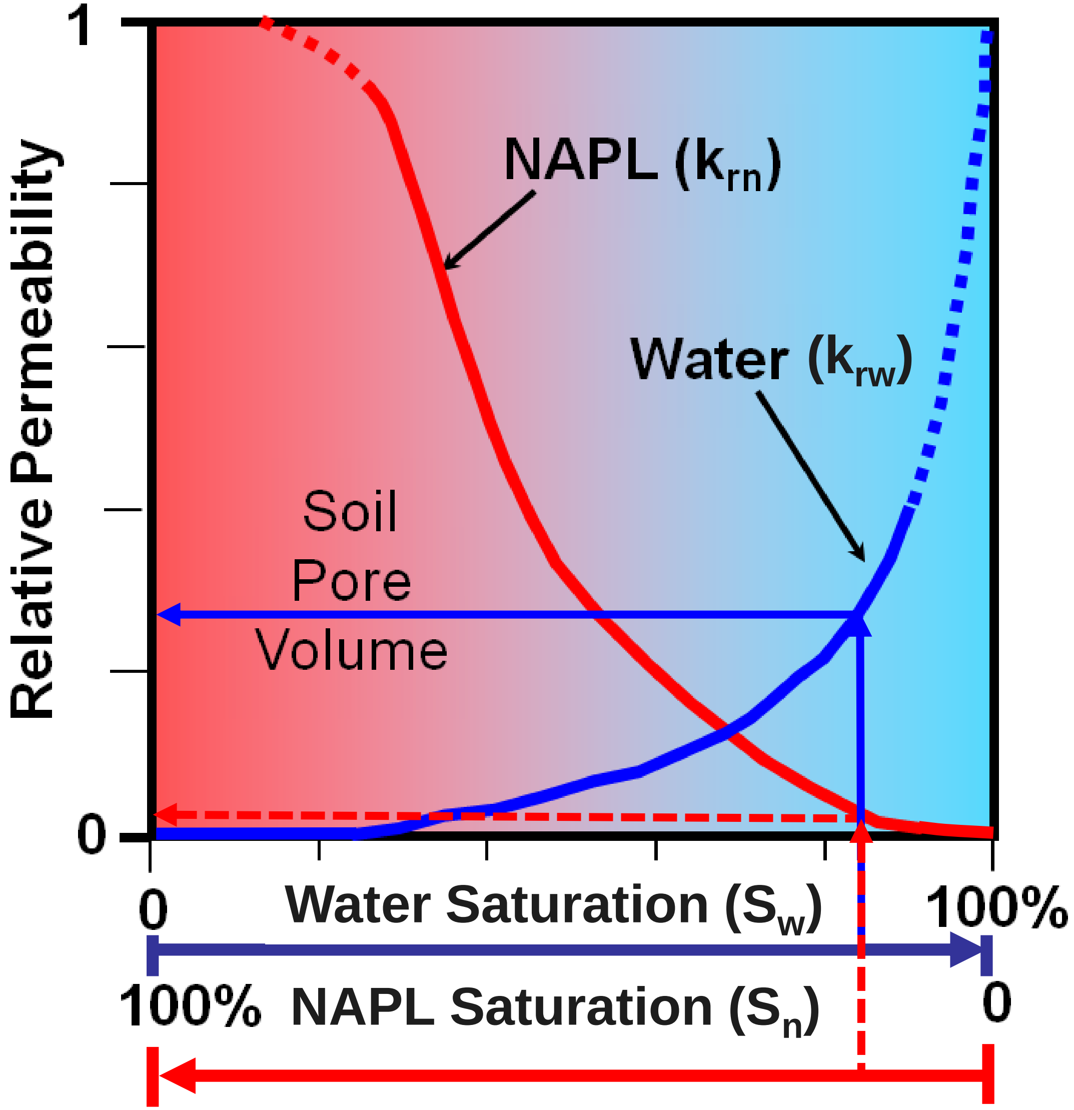
Reduces effective permeability to both water and LNAPL



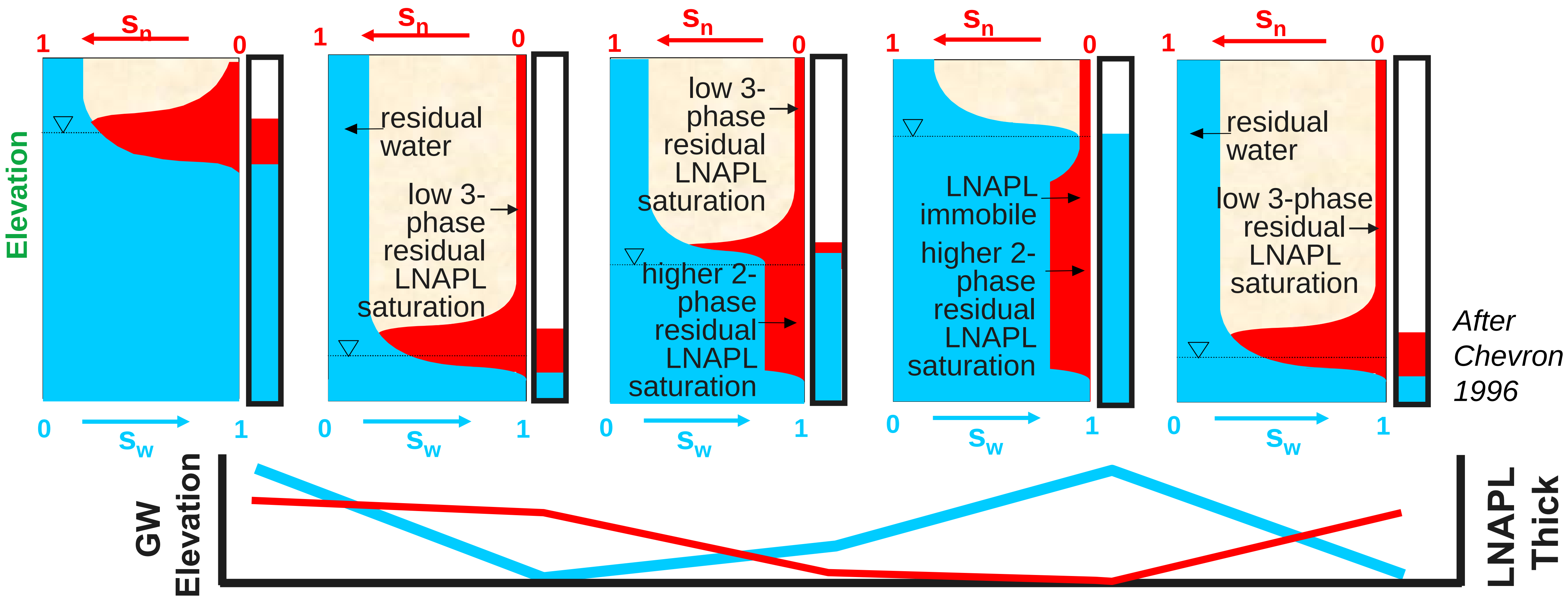
Saturated Zone example

$S_n = 15\% \rightarrow k_{rn} = 0.02$

$S_w = 85\% \rightarrow k_{rw} = 0.26$



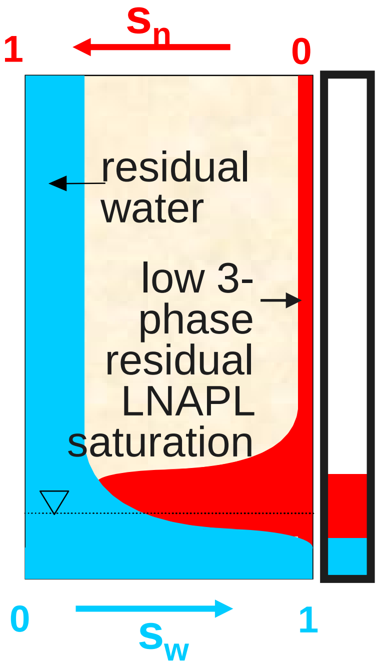
LNAPL "Smearing"

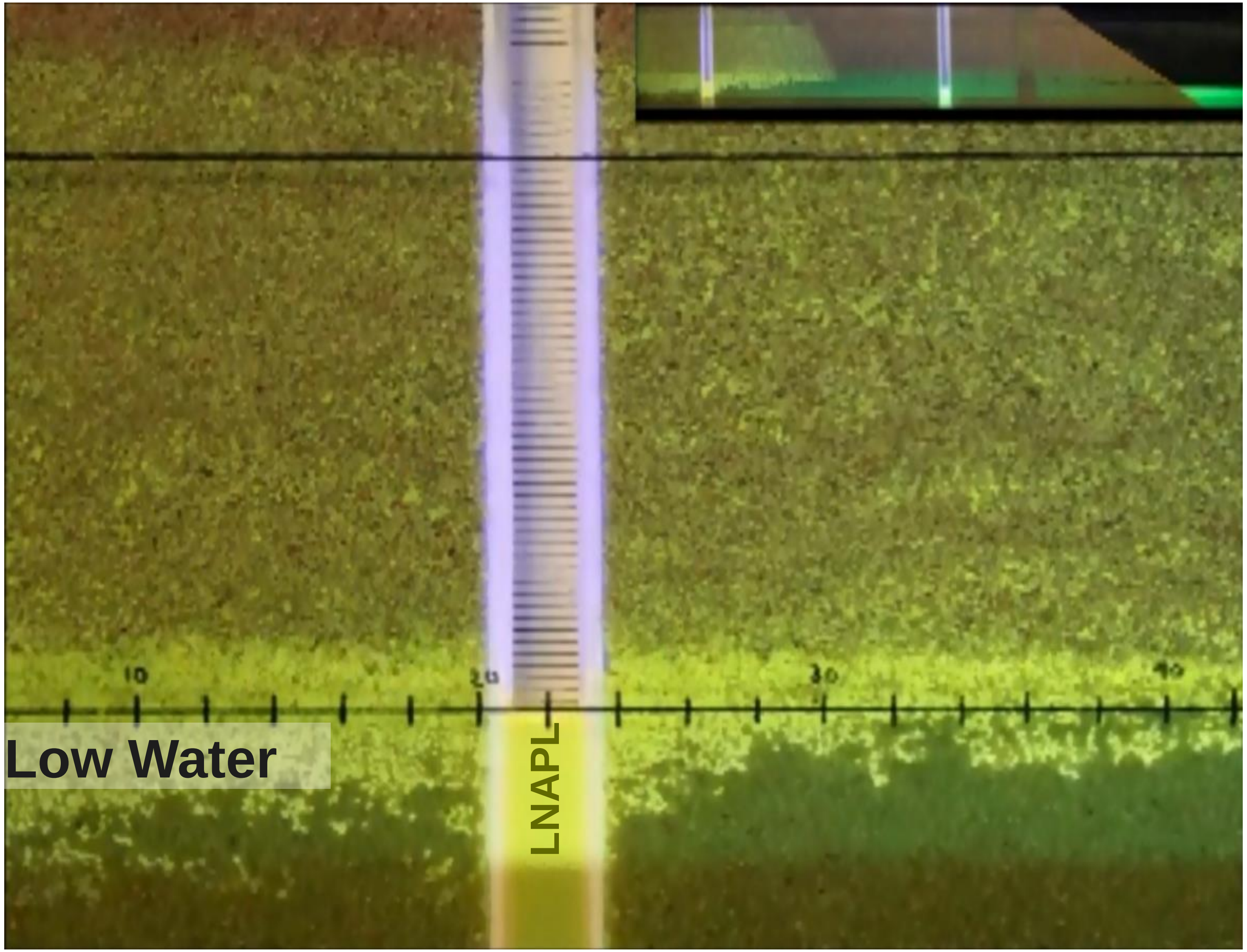


After Chevron 1996

Traps LNAPL above and below the mobile LNAPL interval

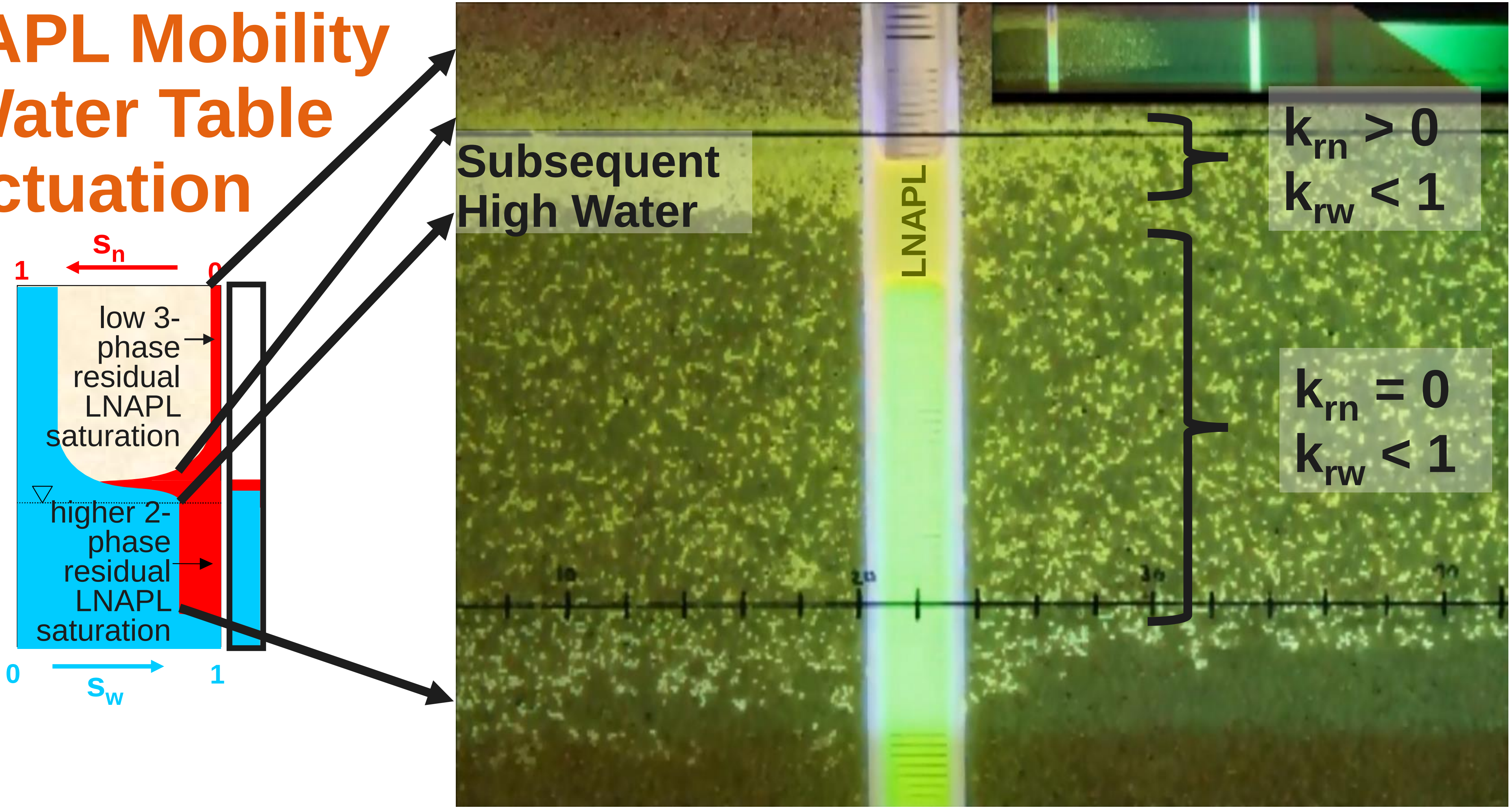
LNAPL Mobility & Water Table Fluctuation





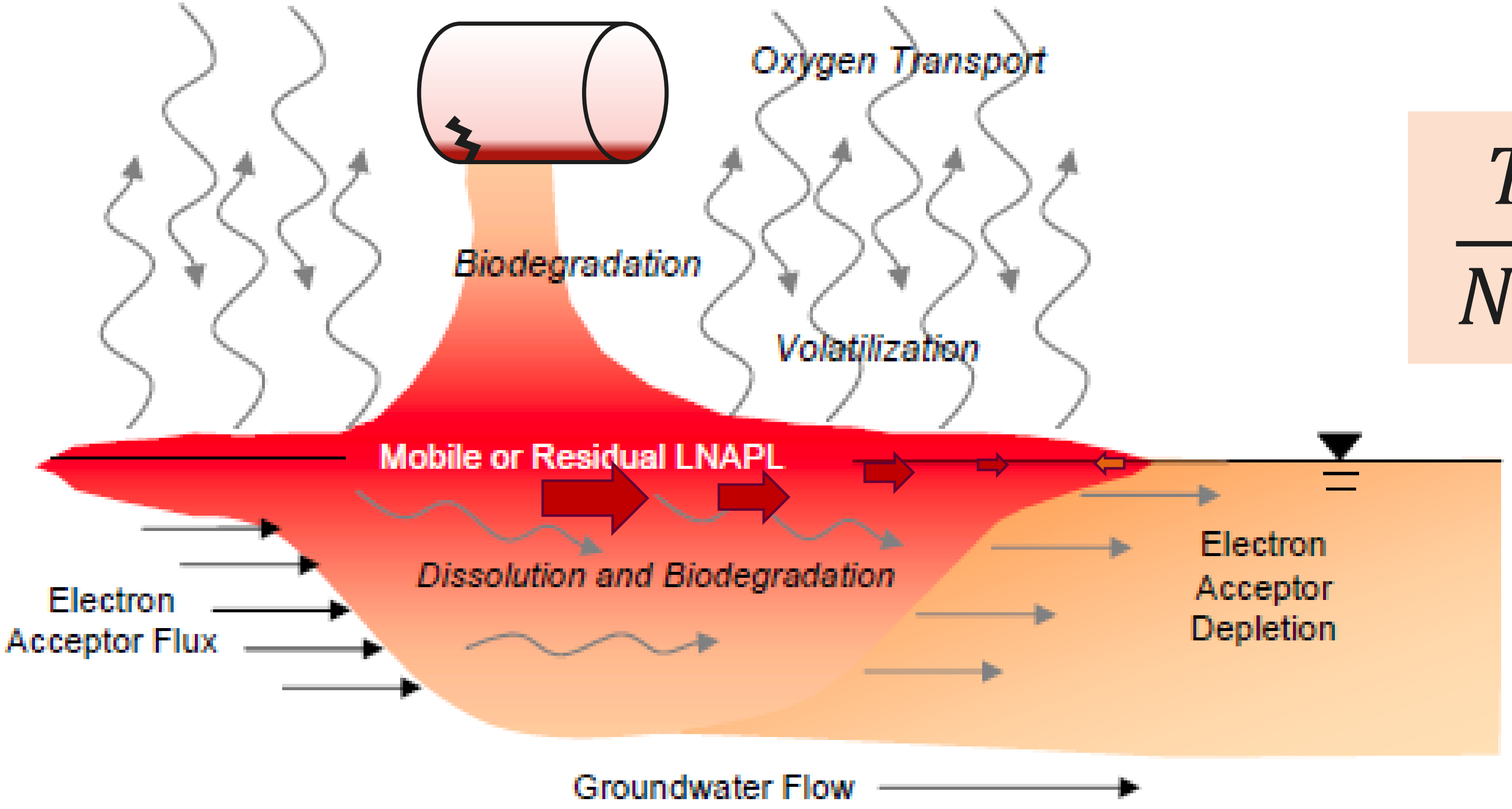
Harmon et al., Colorado State University

LNAPL Mobility & Water Table Fluctuation



Harmon et al., Colorado State University

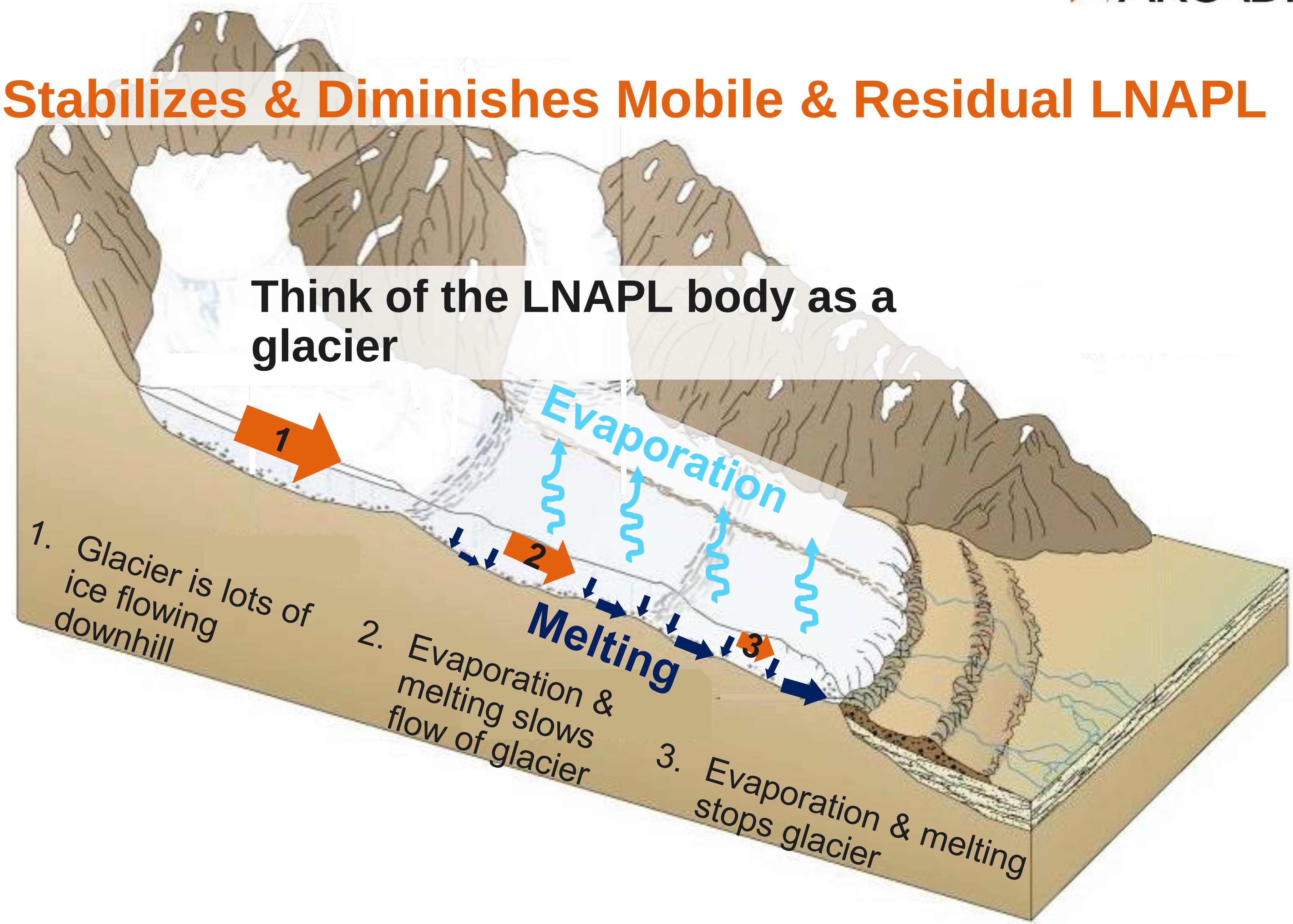
(Mobile) LNAPL Stabilized & Diminished by NSZD



$$\frac{T_n i_n}{NSZD} = \text{Dist.}$$

LNAPL flow toward edges of body is balanced (or overwhelmed) by natural losses

NSZD Stabilizes & Diminishes Mobile & Residual LNAPL



The LNAPL Conceptual Site Model (LCSM): The Backbone of a Robust Response

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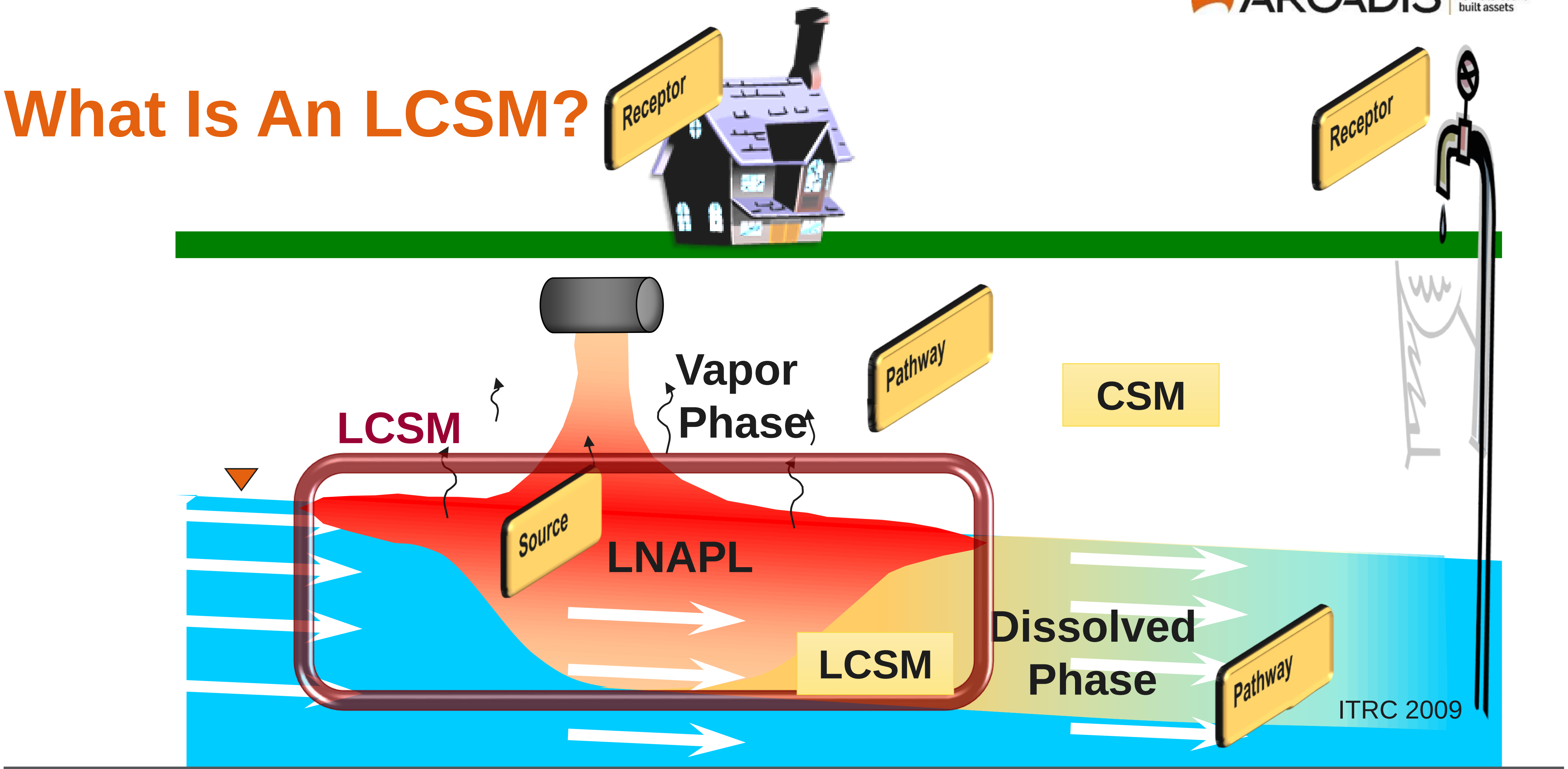
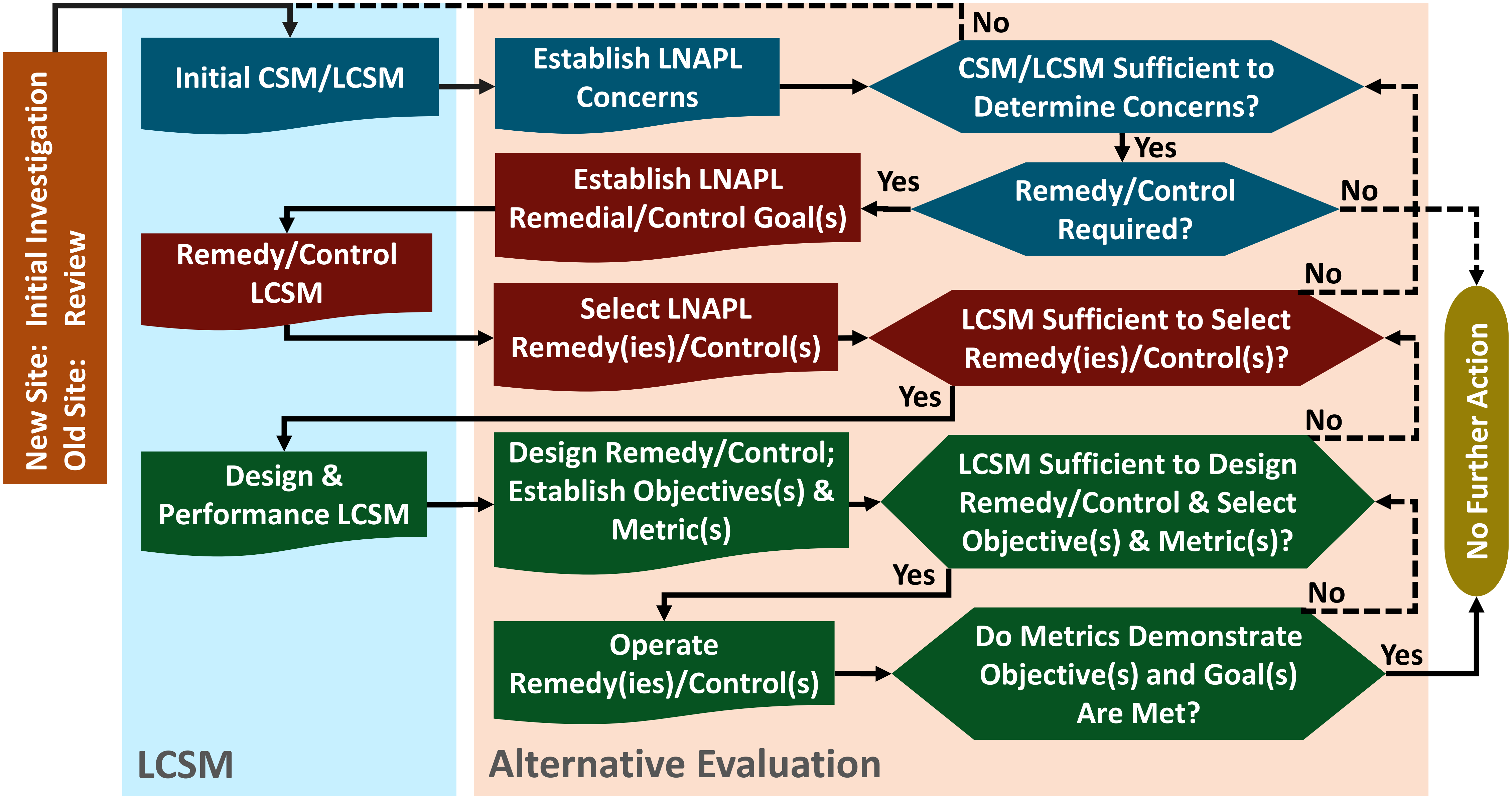
What Is An LCSM?

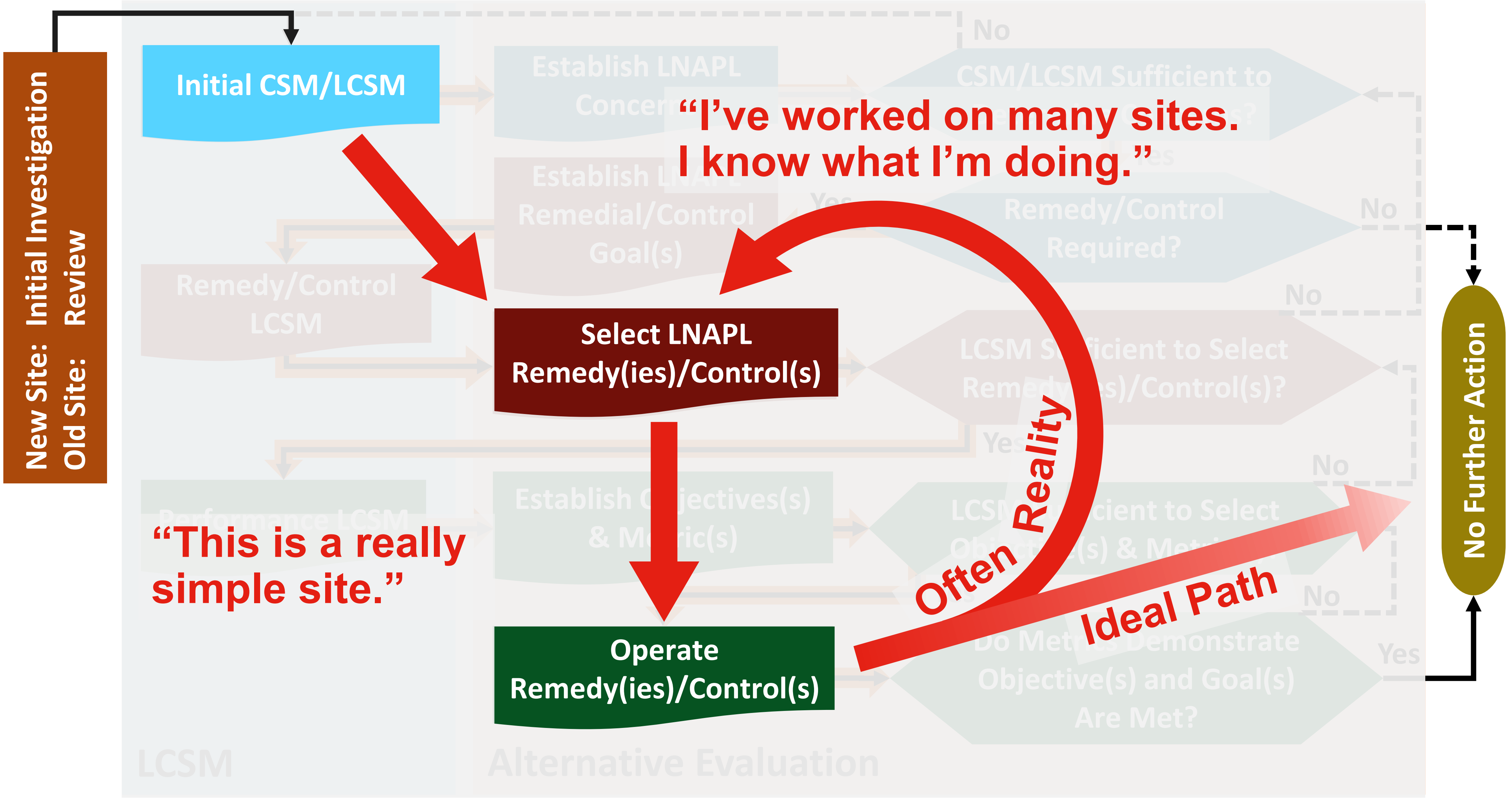


LNAPL Conceptual Site Model

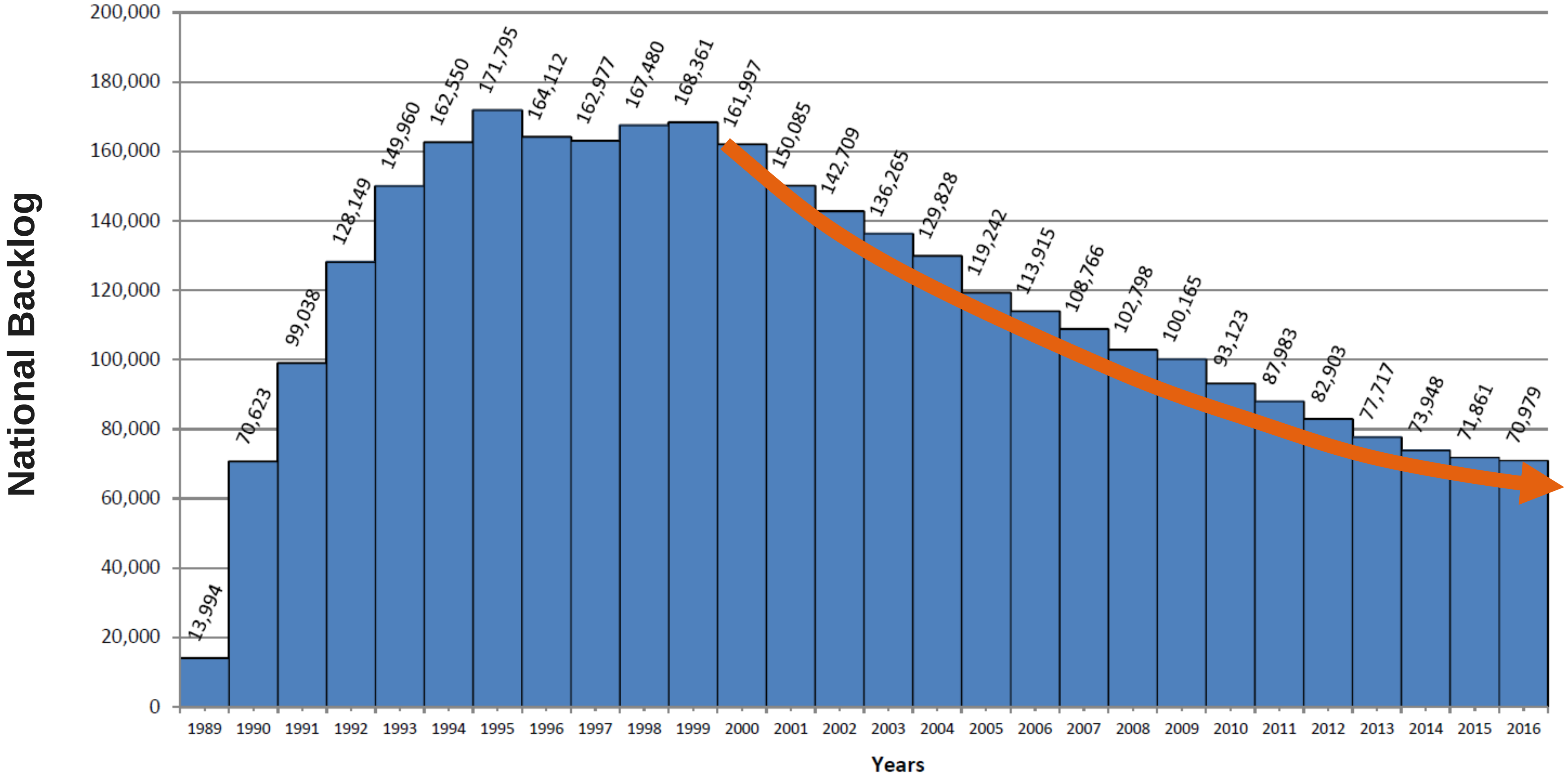
LCSM & Alternative Evaluation



The Wrong Way

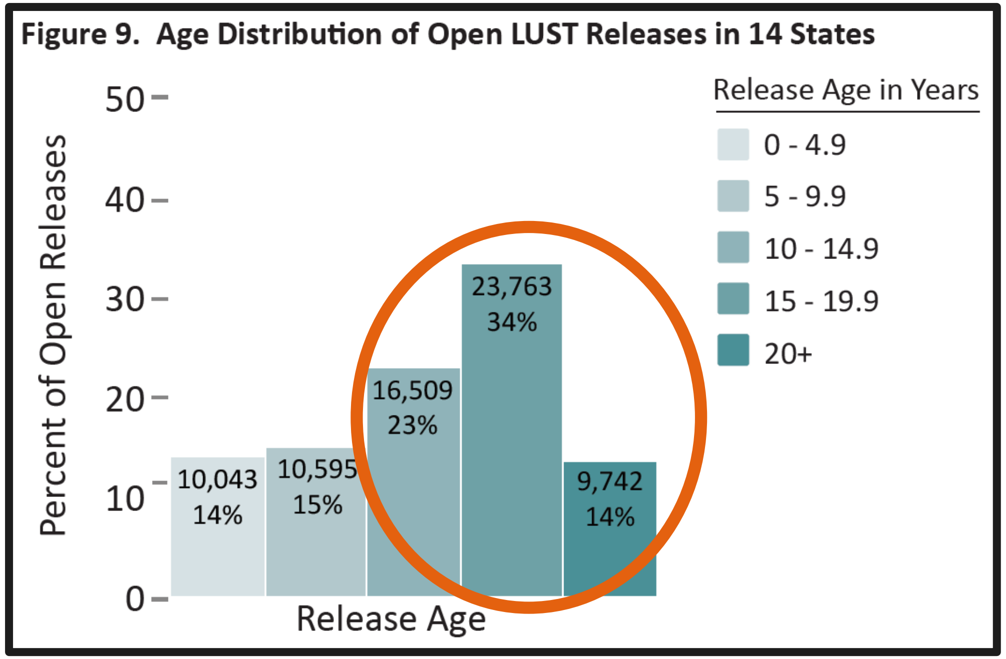


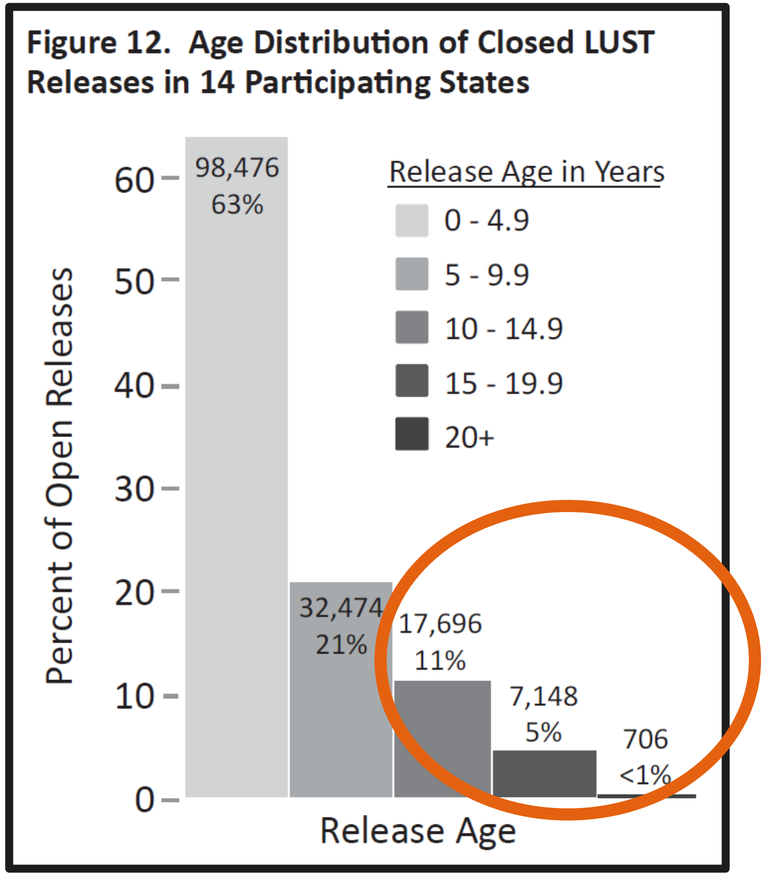
Slowing Trend of Backlog Reduction



EPA. 2016. Semiannual Report Of UST Performance Measures, End Of Fiscal Year 2016 (October 1, 2015 – September 30, 2016). Office of Underground Storage Tanks. November.

Balance Tipping to Older Open Cases





EPA. 2011. The National LUST Cleanup Backlog: A Study of Opportunities. September.

Closure of Complex (Groundwater) Sites Lags Proportion of Complex Sites

Figure 23. Distribution of Closed Releases per Year in 11 States, by Known Media Type (FY 1990 – 2008)

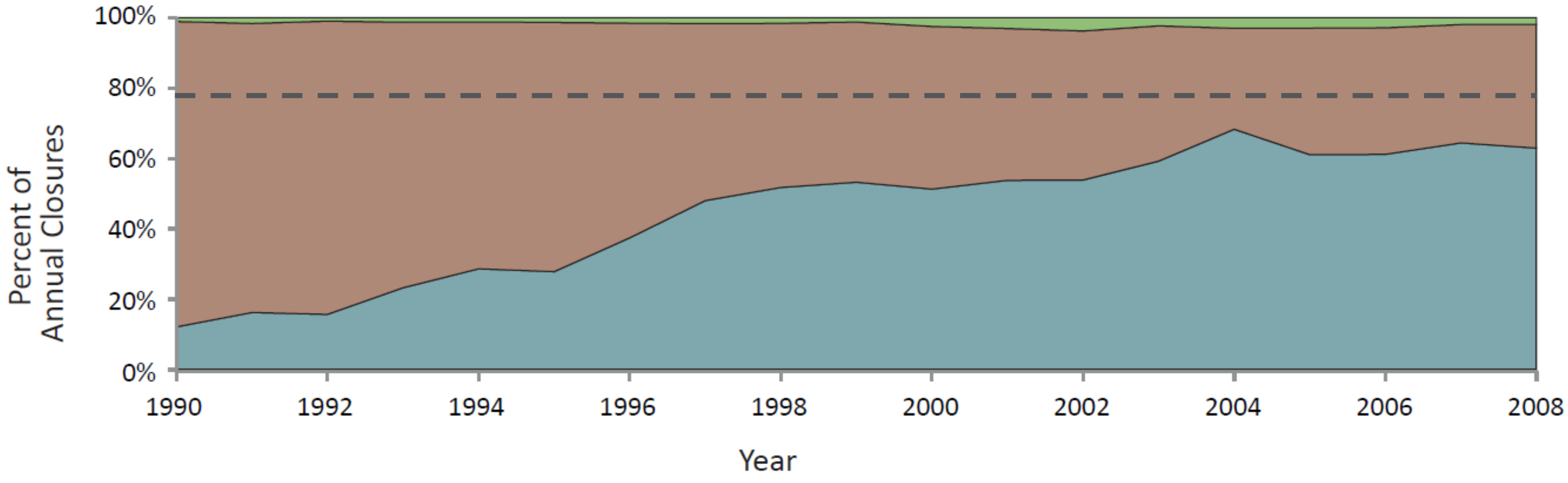
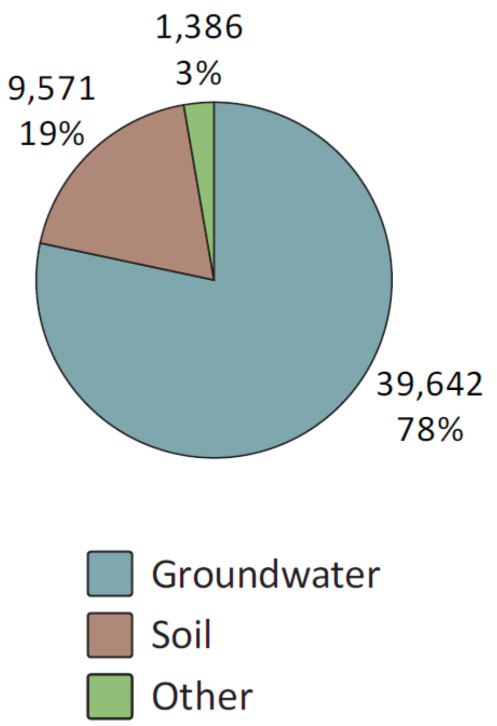
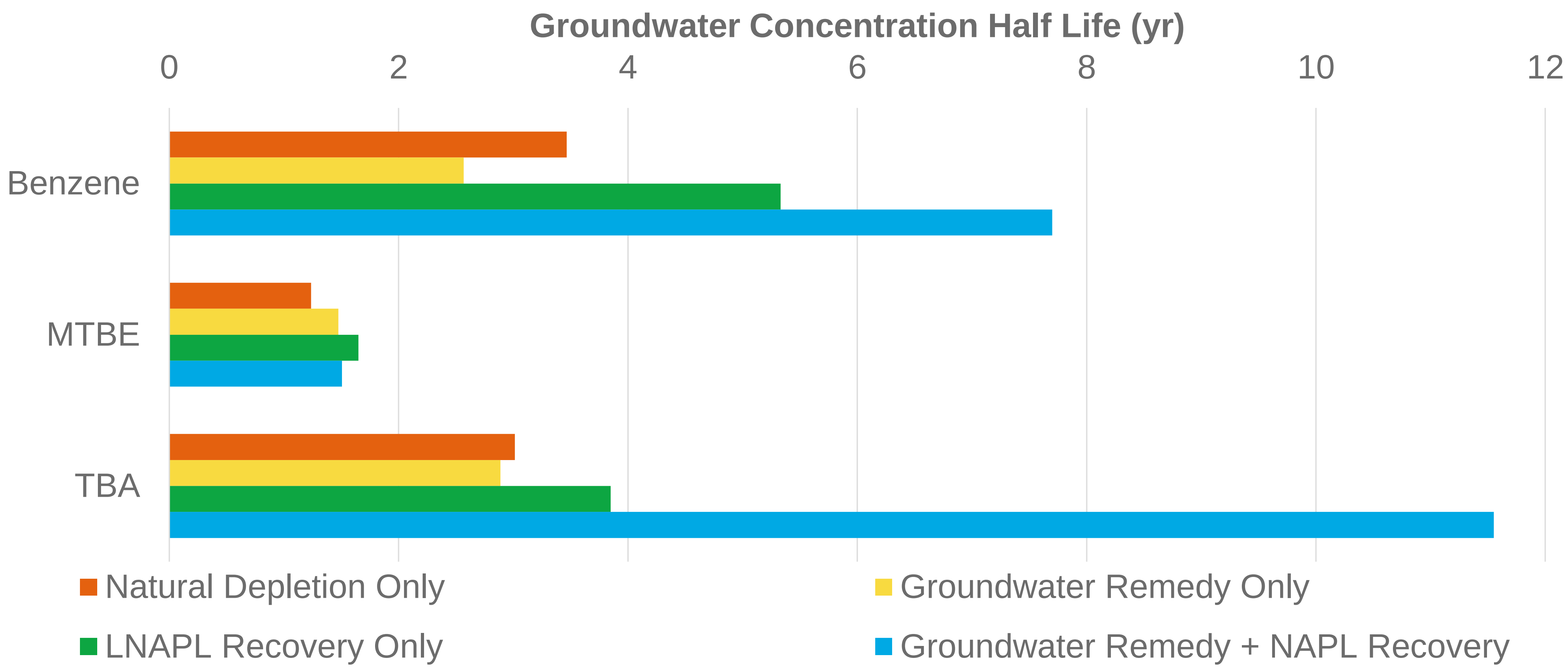


Figure 19. Distribution of Open LUST Releases in 11 States by Media Contaminated



EPA. 2011. The National LUST Cleanup Backlog: A Study of Opportunities. September.

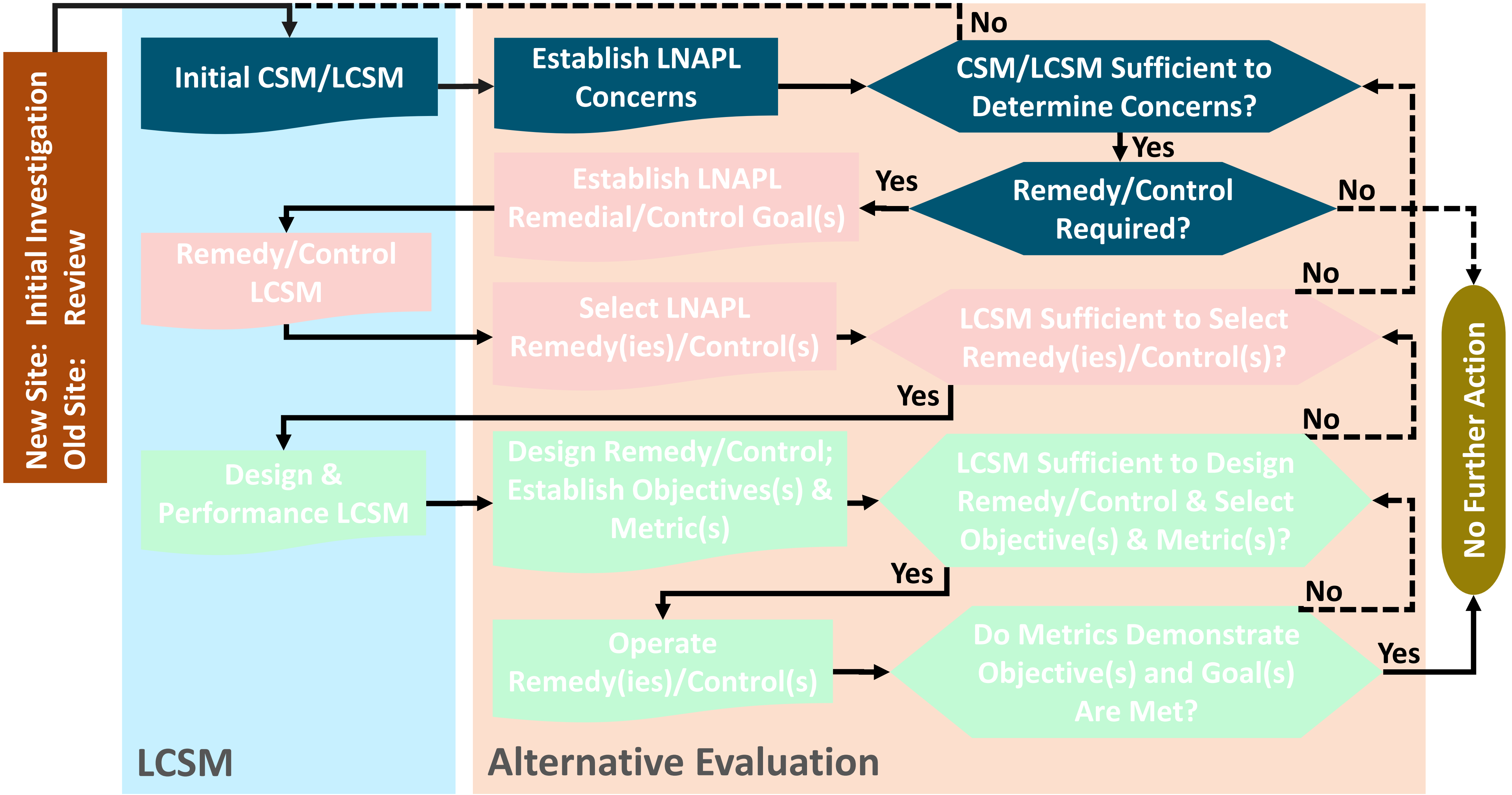
Remediation of LNAPL in Groundwater is Complicated



R. Kamath, J. A. Connor, T. E. McHugh, A. Nemir, M. P. Le, and A. J. Ryan. Use of Long-Term Monitoring Data to Evaluate Benzene, MTBE, and TBA Plume Behavior in Groundwater at Retail Gasoline Sites. J. Environ. Eng., 2012, 138(4): 458-469

Building an LNAPL Conceptual Site Model: An Iterative Approach

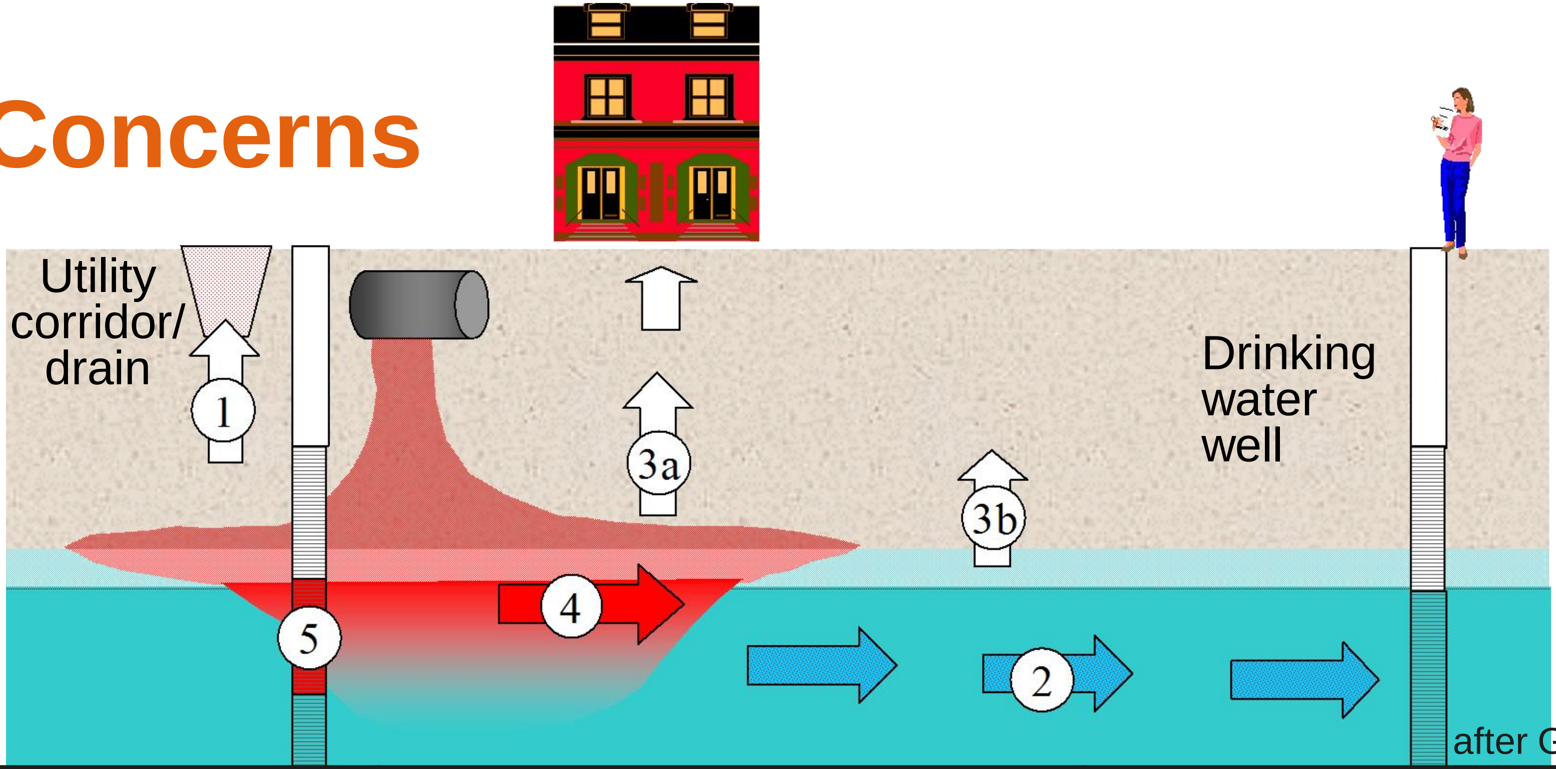
1. Initial LCSM & Concerns



Initial LCSM Questions

- Is the LNAPL body (source zone) delineated horizontally and vertically?
  - Is the LNAPL body stable, i.e., is the total LNAPL footprint not expanding?
- How does stratigraphy relate to LNAPL distribution and potential migration?
  - Does the potential for preferential pathways exist?
- Is there LNAPL in wells?
  - Is the LNAPL recoverable?
- Are dissolved or vapor issues expected based on LNAPL composition?
  - Are dissolved and/or vapor plumes characterized?
- Do soil, soil vapor, or groundwater exceed criteria?
  - Are receptors pathways complete or incomplete?

LNAPL Concerns



after Garg and ITRC 2009

LNAPL emergency issues when LNAPL in the ground	LNAPL considerations when LNAPL in the ground	Additional LNAPL considerations when LNAPL in wells
1 Vapor accumulation in confined spaces causing explosive conditions	2 Groundwater (dissolved phase)	4 LNAPL potential mobility (offsite migration, e.g. to surface water, under houses)
Not shown - Direct LNAPL migration to surface water	3a LNAPL to vapor	5 LNAPL in well (aesthetic, reputation, regulatory, recoverable)
Not shown - Direct LNAPL migration to underground spaces	3b Groundwater to vapor	
	Not shown - Direct contact/ingestion	

LNAPL Migration LNAPL Saturation LNAPL Composition

2. Remedy/Control Selection

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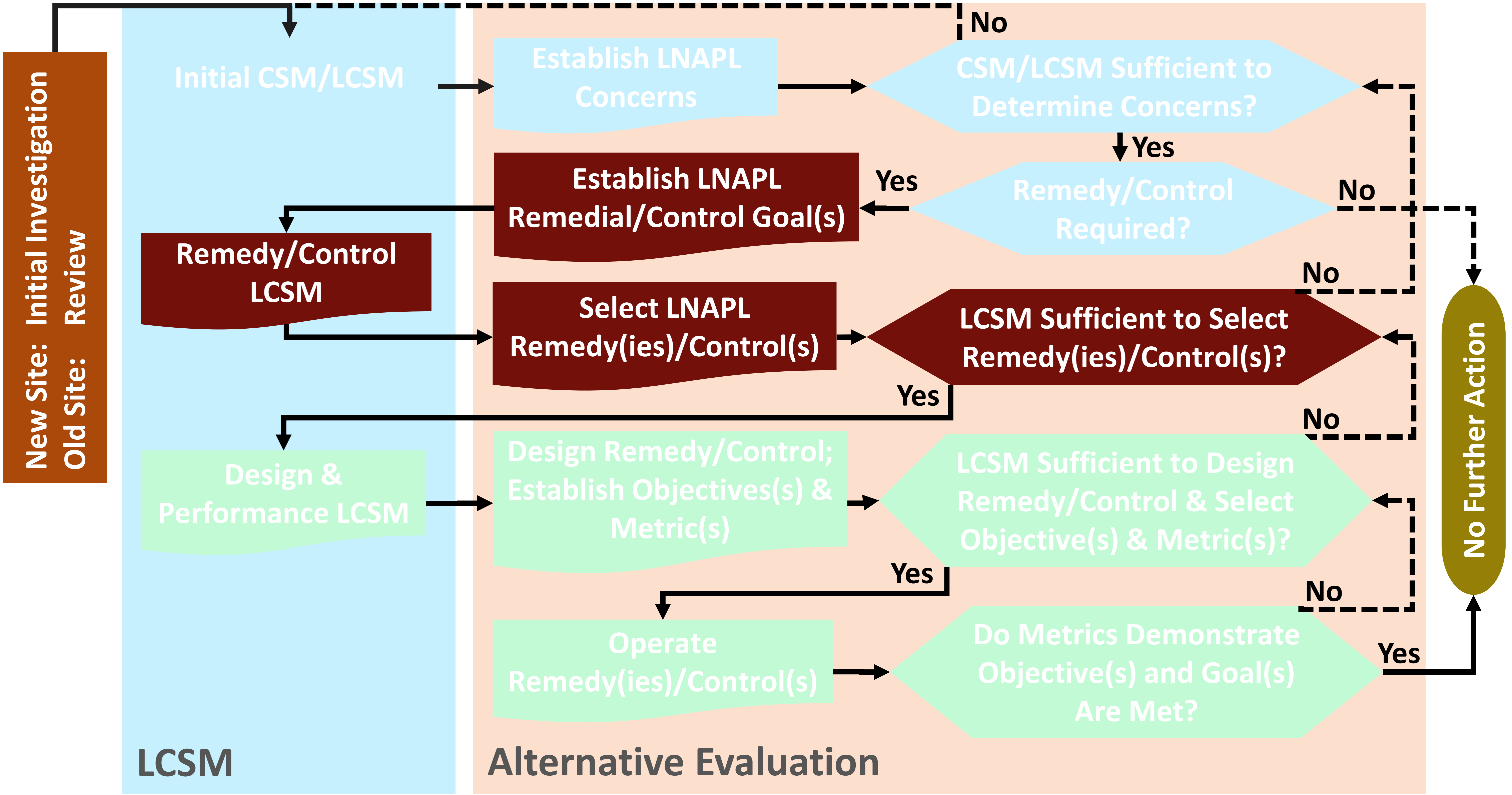
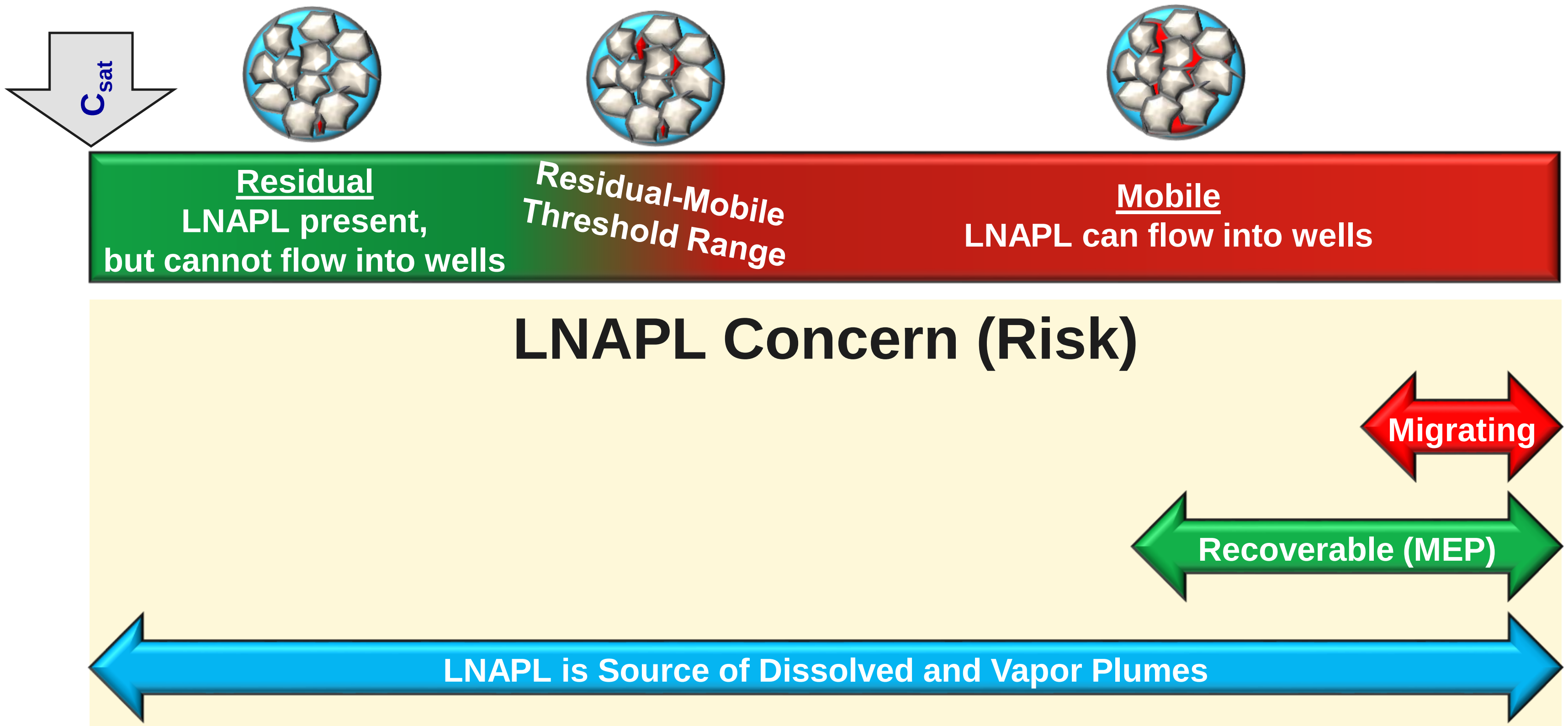


Link Concern to LNAPL Management Approach



Remedial Technology Groups

- Mass Control
- Mass Recovery
- Phase Change

Respond to Actual LNAPL Risk

Remedy LCSM Questions

- What Concern Drives The Objective For Most LNAPL Depletion?
- How Is The LNAPL Distributed Above And Below The Water Table?
- How Permeable Is The Soil?
  - How Heterogeneous and/or Layered Is The Permeability?
- How Volatile Is The LNAPL?
  - What Fraction Is Volatile?
- Can Biodegradation Be Enhanced?

LNAPL Remedial Technologies

Mass Control

- Physical containment
- In-situ soil mixing

Mass Recovery

- LNAPL skimming
- Bioslurping/EFR
- Dual pump liquid extraction
- Multi-phase extraction
- Excavation
- Water/hot water flooding
- Cosolvent flushing
- Surfactant-enhanced subsurface remediation

Phase Change

- Natural source zone depletion (NSZD)
- Air sparging/soil vapor extraction (AS/SVE)
- In situ chemical oxidation
- Heating
  - Steam injection
  - Electrical Resistance
  - Conduction
- Dewatering & SVE (DPE)
- Biovent/Biosparge
- Anaerobic Bio-Oxidation

LNAPL Remedial Technologies

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- Physical containment
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Mass Recovery

- LNAPL skimming
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- Dual pump liquid extraction
- Multi-phase extraction, dual pump
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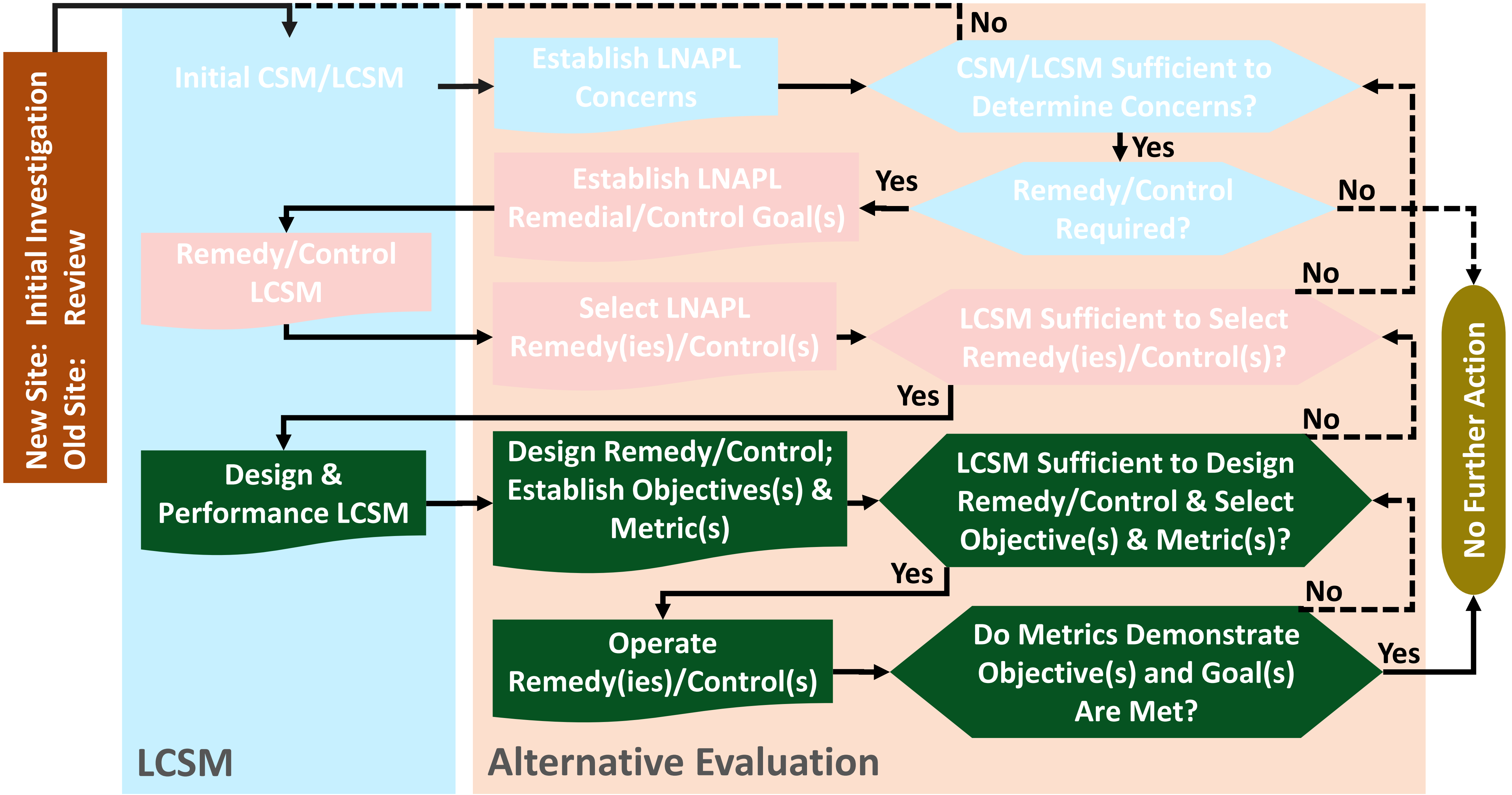
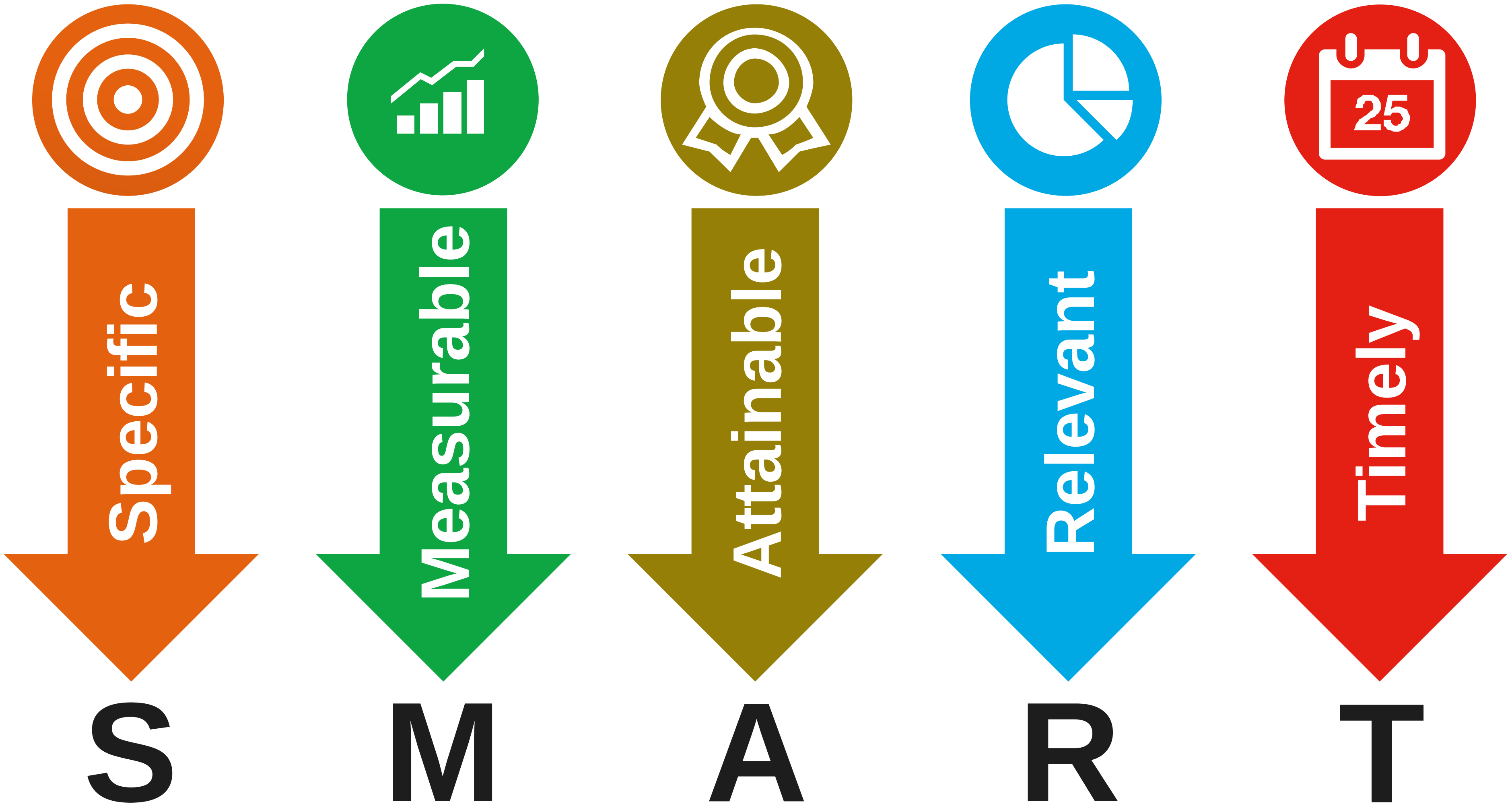
3. Remediation/Control & Closure



Design & Performance LCSM Questions

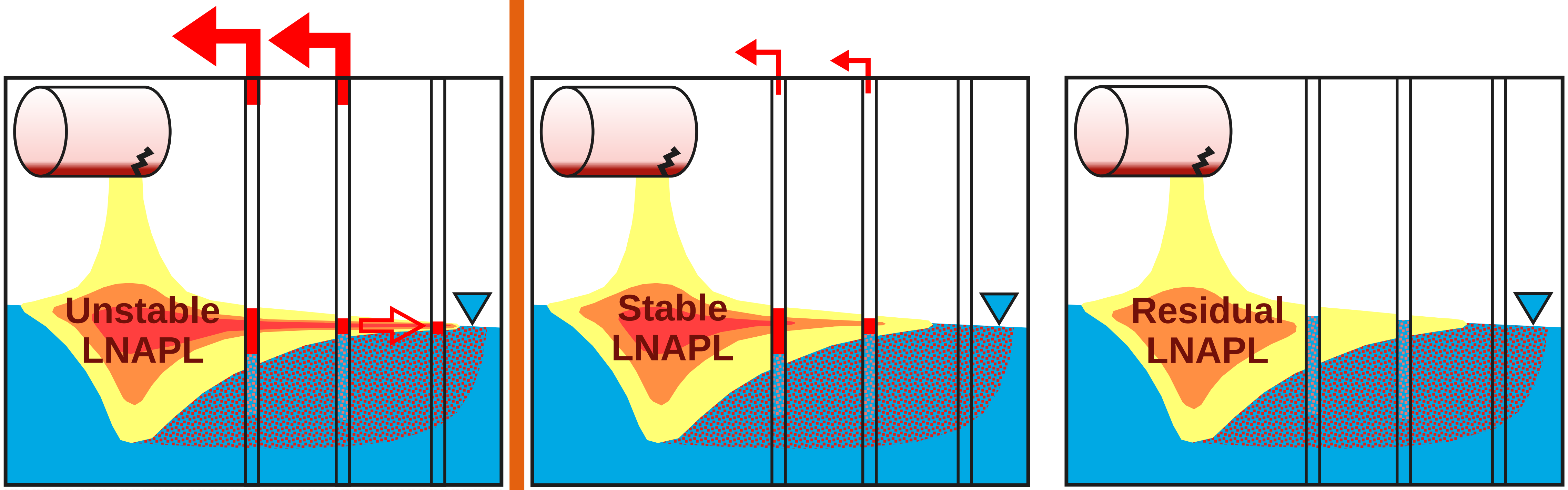
- What Conditions Should A Technology Change?
  - What Conditions Will Demonstrate Desired LNAPL Changes?
  - What Post-Remedial Conditions Will Demonstrate Success?
- When, For The Technology Selected, Will The Cost Of Incremental Change Become Too High?
  - What Are The Lifecycle Costs Of Subsequent Technologies?

S.M.A.R.T. Remedial Objectives & Metrics



If LNAPL Recovery isn't Effective, Then What?

LNAPL Composition Risk

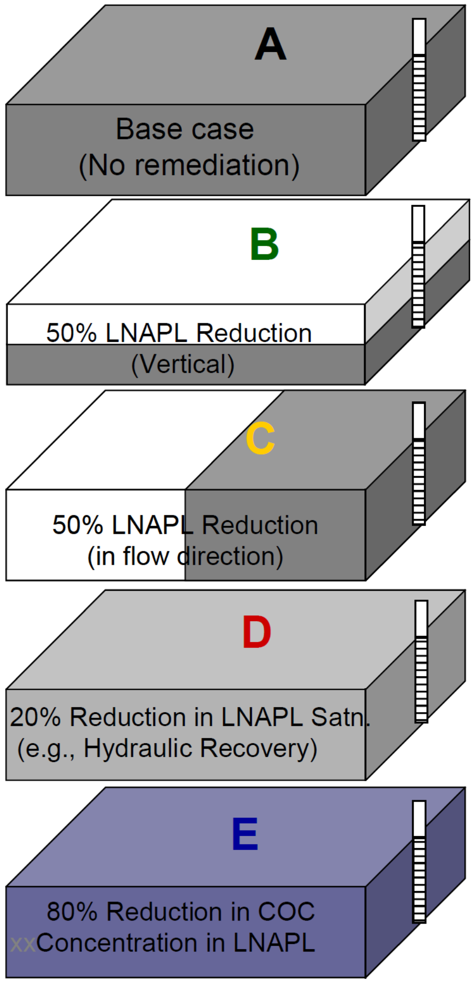


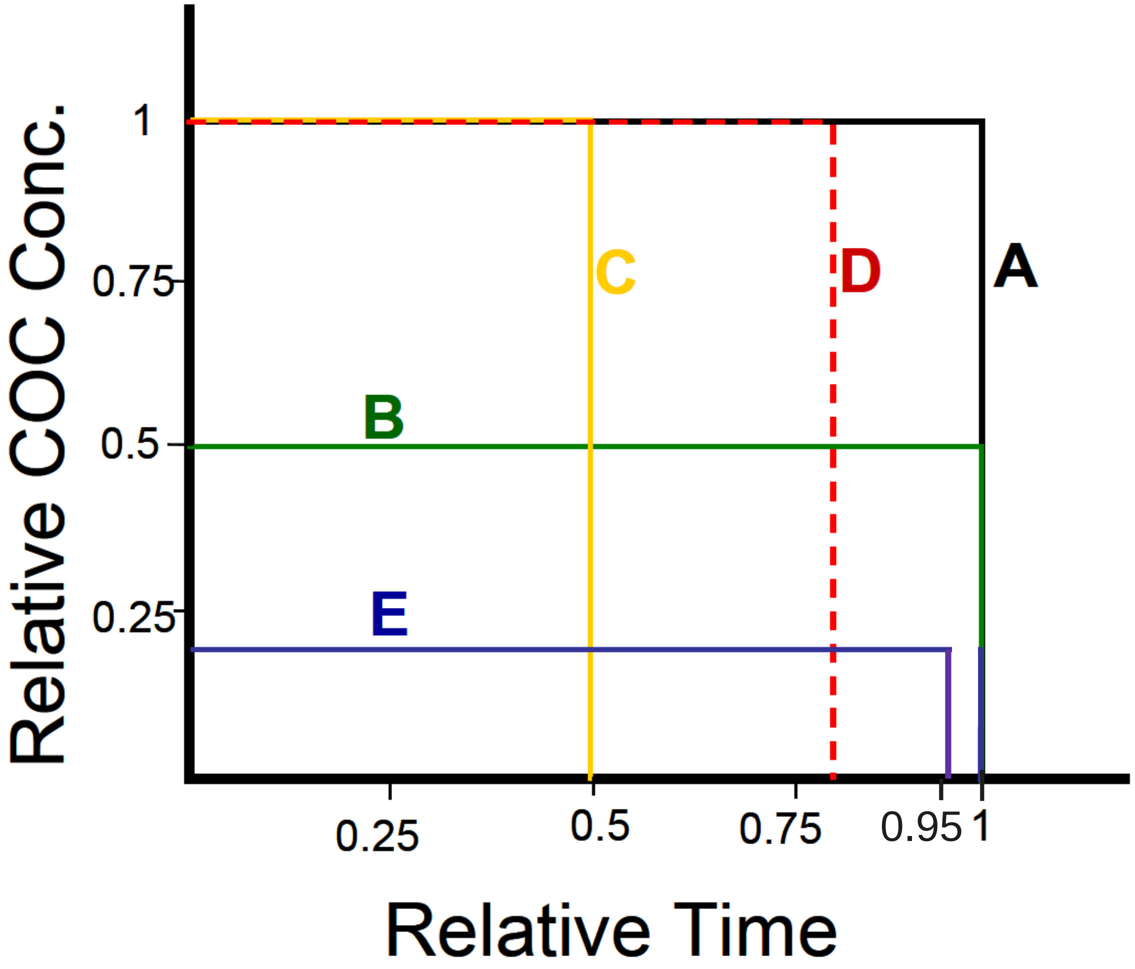
LNAPL Migration & Composition Risk

LNAPL Composition Risk Only

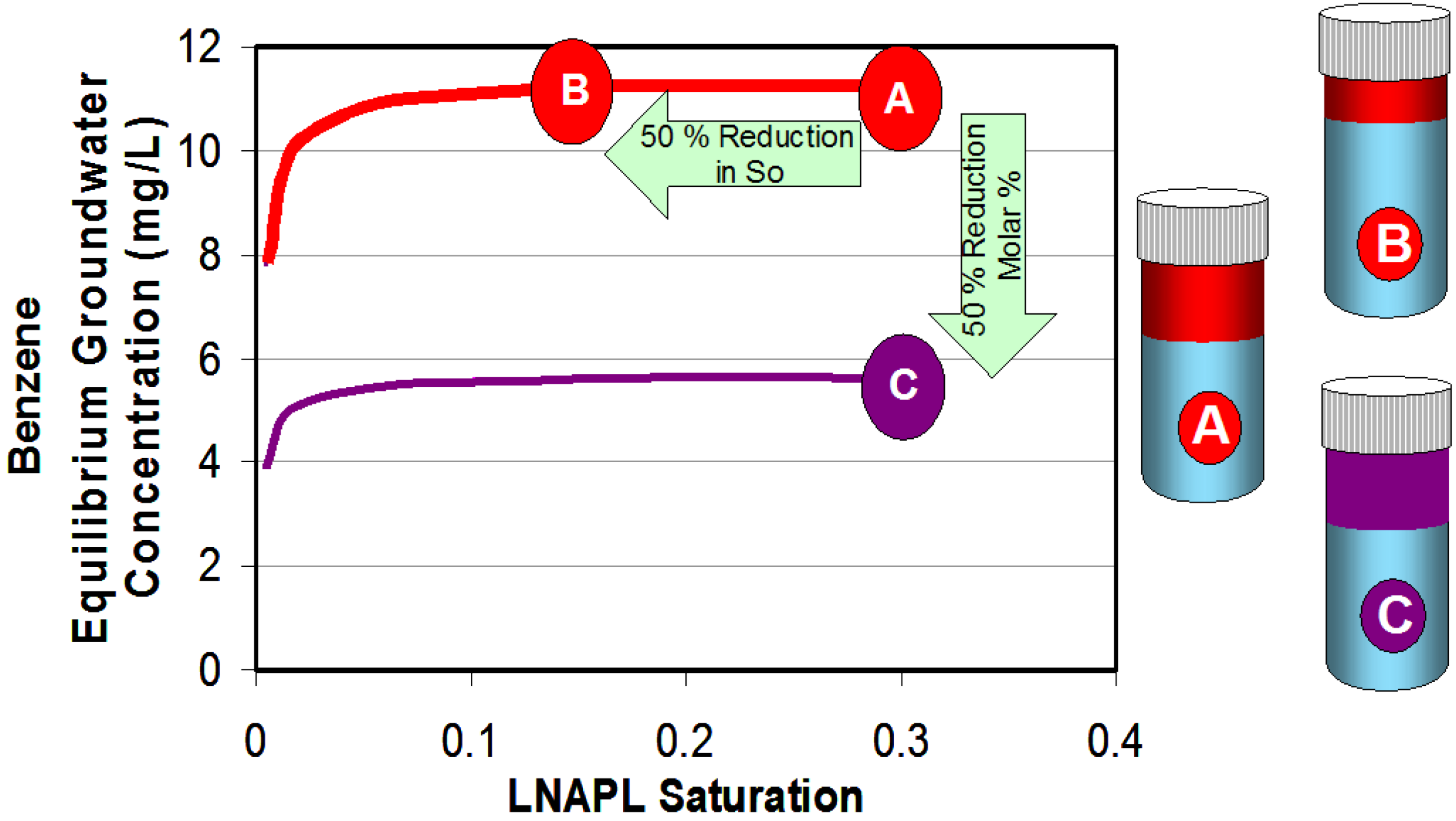
Risk = LNAPL Instability + LNAPL Composition

Mass Reduction & Composition Change

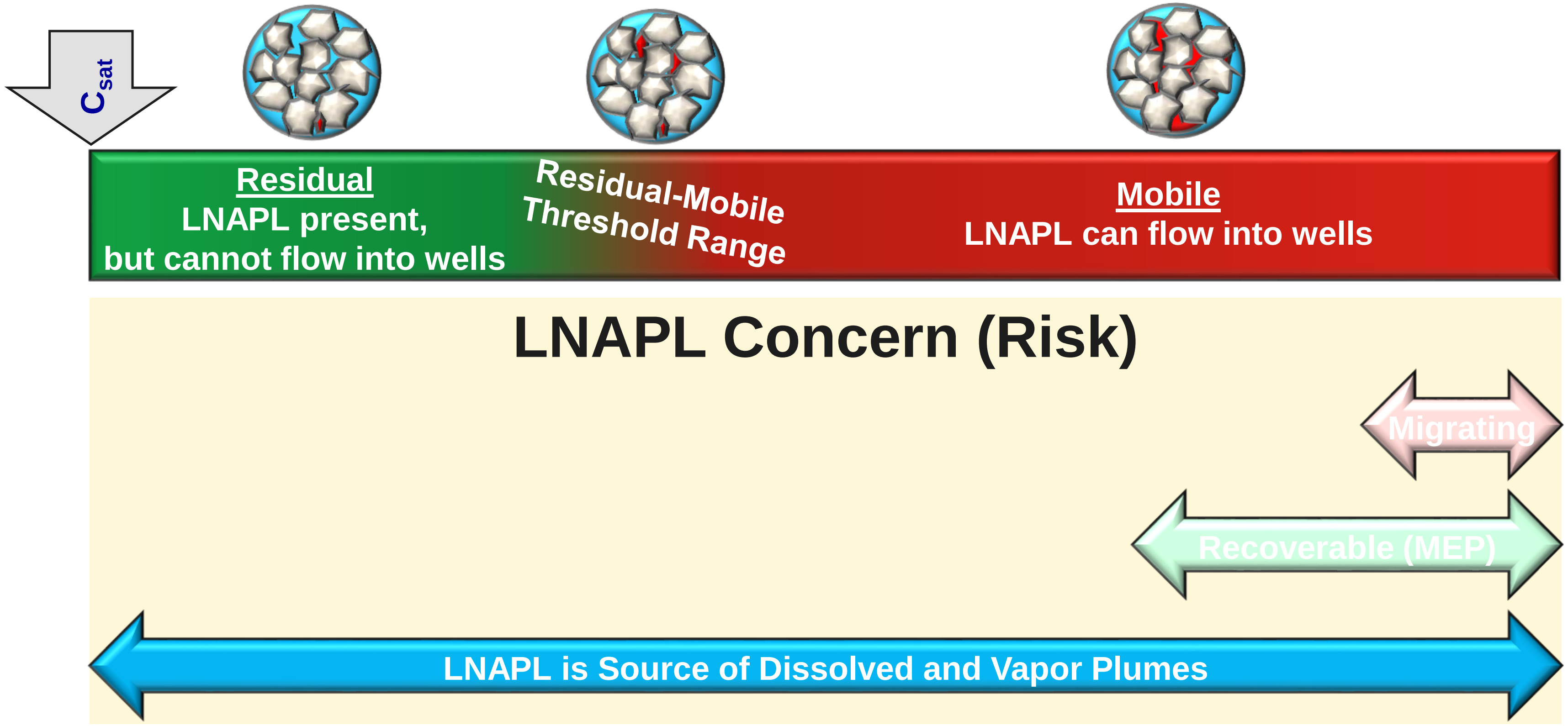




Mass Reduction vs. Composition Change



Phase Change Technologies for All LNAPL



Remedial Technology Groups

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Active Phase Change Depletes Mass Just Like NSZD

LNAPL Phase Change Technologies

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How about ISCO?

Pros:
- Inject in existing wells
- Short duration
- no ongoing O&M

Cons:
- … Let's examine

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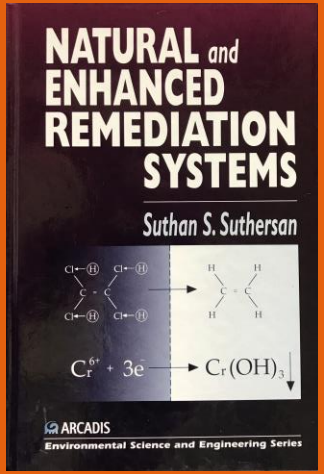
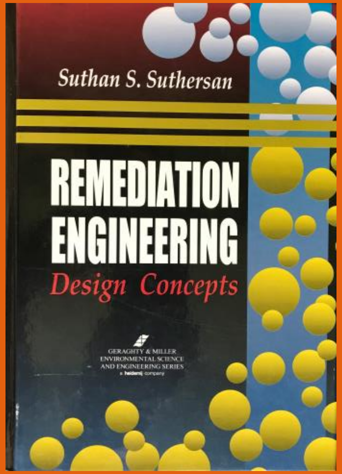
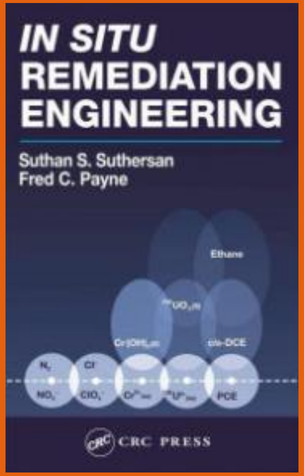
Groundwater Monitoring&Remediation — Advances in Remediation Solutions

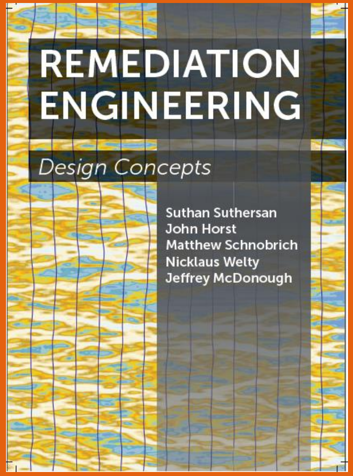
In Situ Chemical Treatment: A Love–Hate Relationship

by Suthan Suthersan, Jeff McDonough, Matt Schnobrich, Craig Divine









Objectives

Define site characteristics that present challenges to in situ chemical treatment

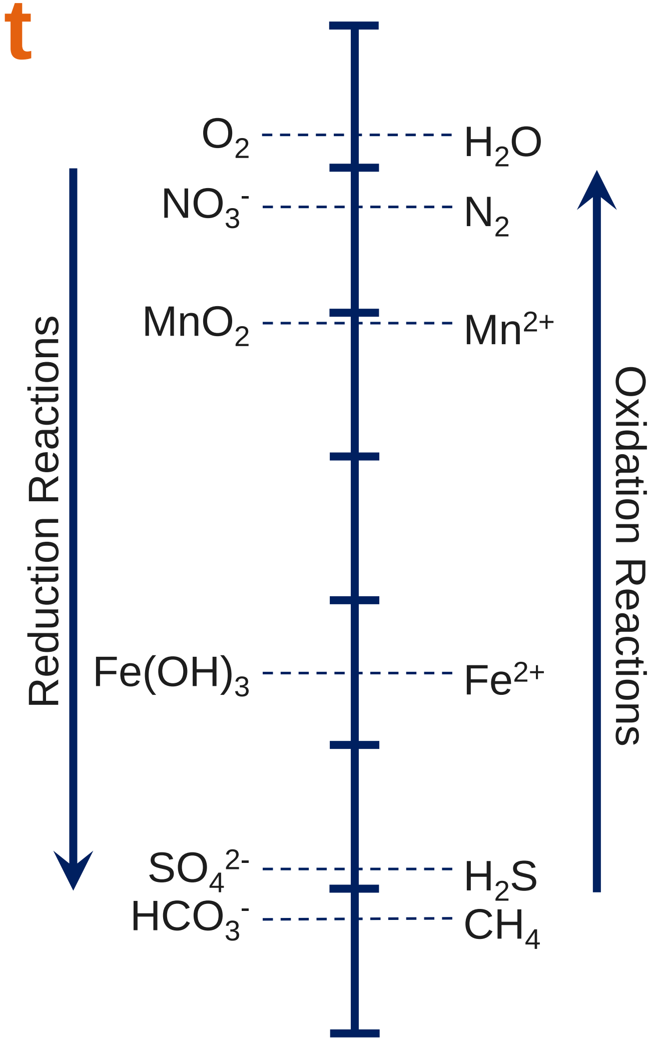
Discuss design considerations for in situ chemical treatment focused on management of contaminant “rebound”

Agenda

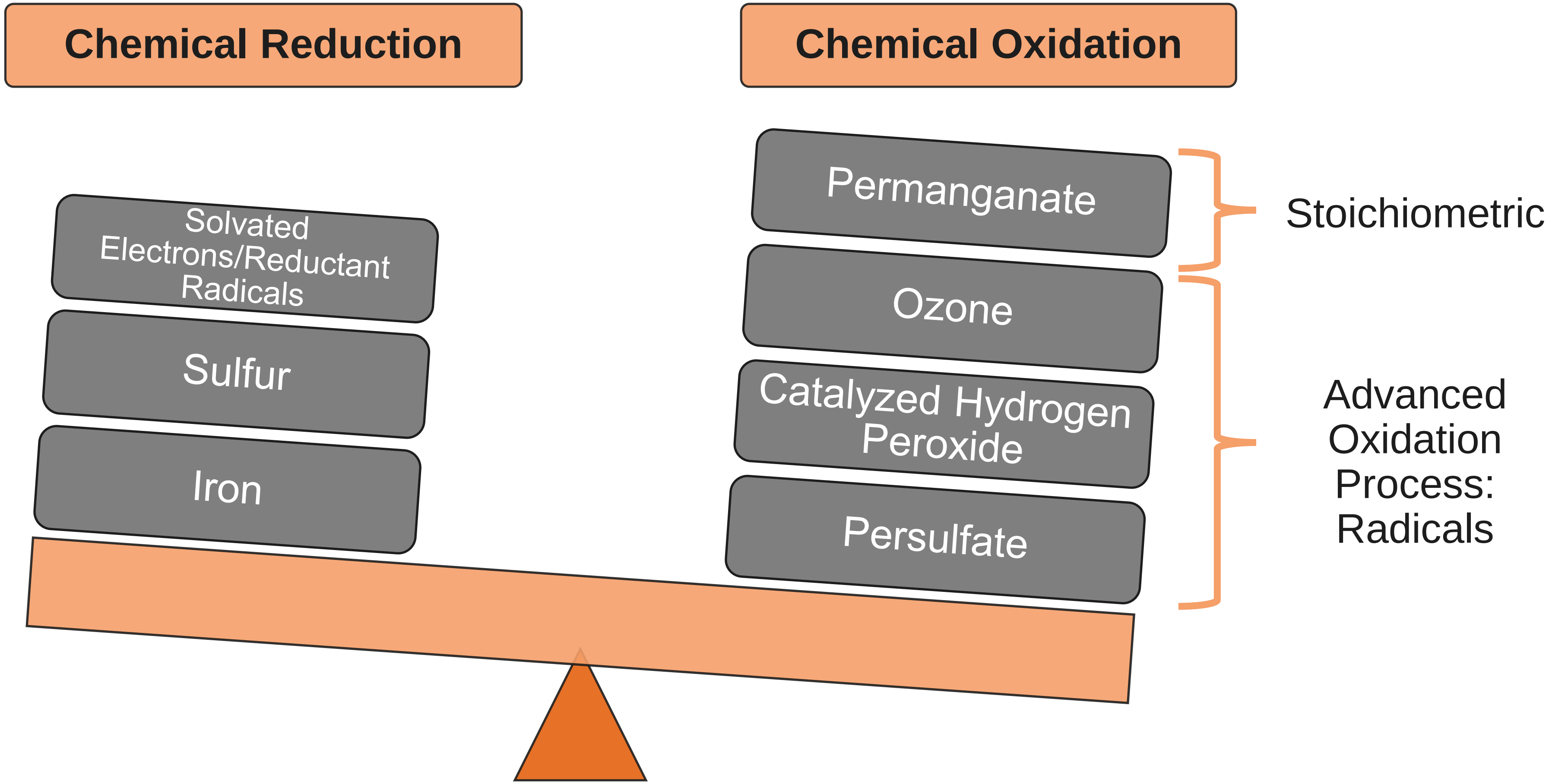
- What is in situ chemical treatment?
- The cause of the bounce…
- Defining the in situ chemical treatment sweet spot
- Chemical treatment design considerations
- Summary

Defining In Situ Chemical Treatment

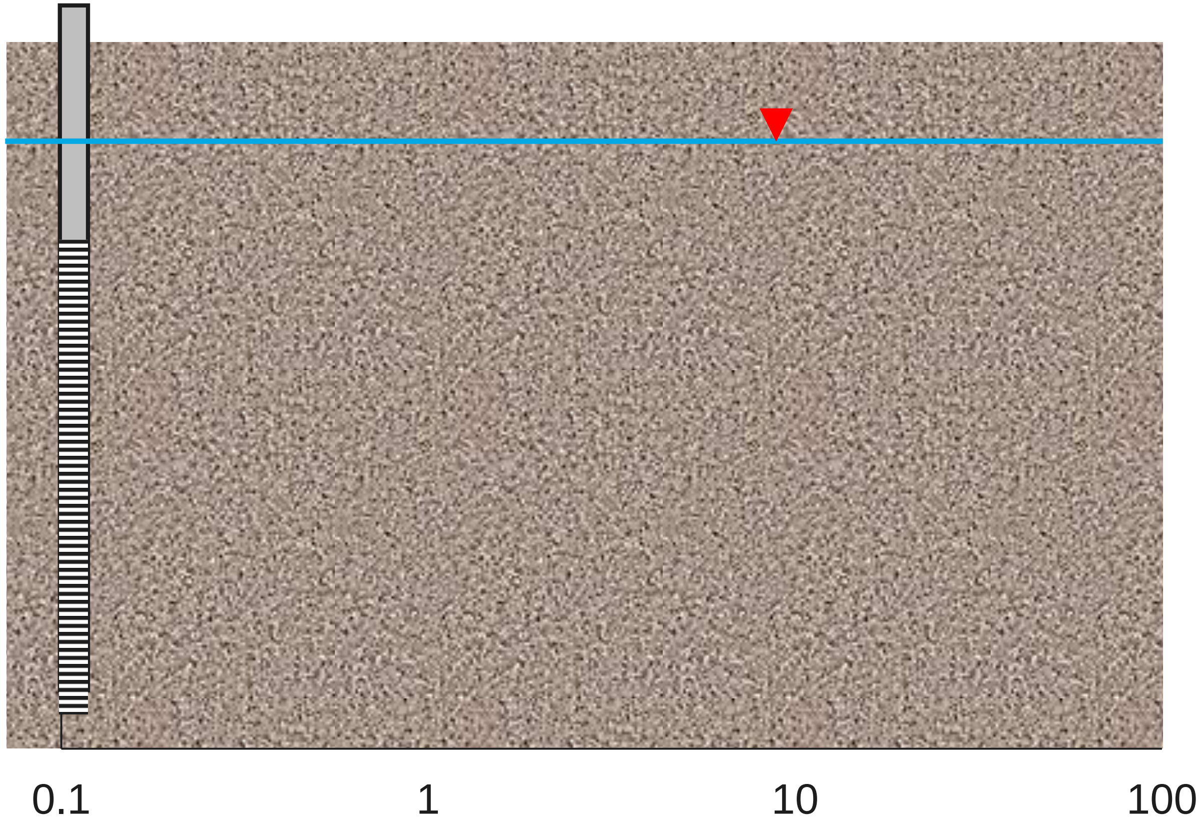
- Manipulating oxidation-reduction potential of constituents of concern (COC) to reduce mobility/toxicity
- Conventional oxidation and reduction reactions applied to soil and groundwater
- Complicated by site-specific hydrogeology, geochemistry, and nature and extent of COCs
- Success predicated on achieving meaningful contact times between reagents and COCs
- Fast kinetics, short residence times



Available Treatment Chemistries



Oxidant Persistence Comparison



Distance in Meters from Injection Point Where Oxidant Concentration = 10% of the Injected Concentration

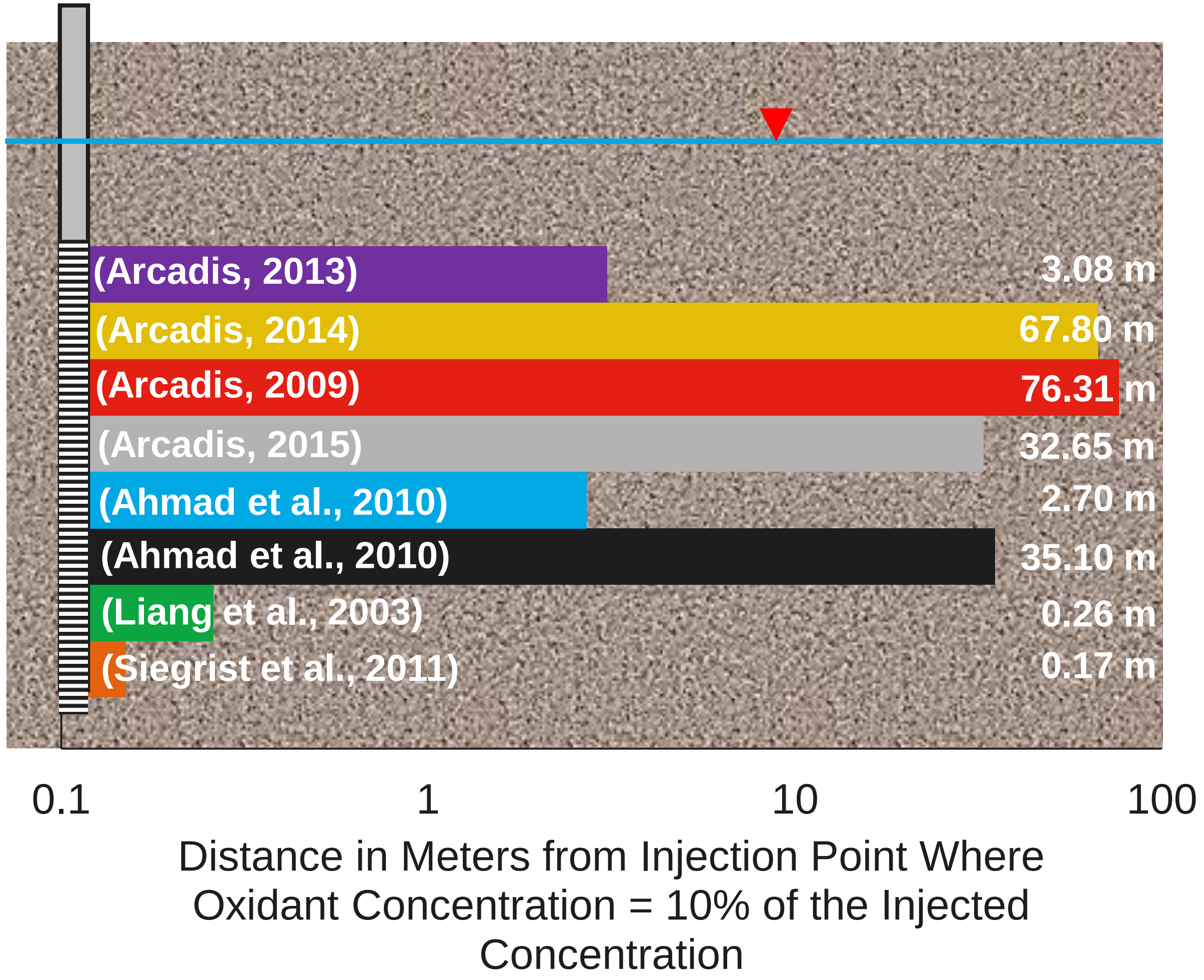
- Assumes constant groundwater velocity of 0.3 m/d
- Pseudo-first order kinetics

NaP Therm	CHP
NaP Alk 1	NaP Acid
NaP Ambient	NaP Alk 2
Permanganate	Ozone

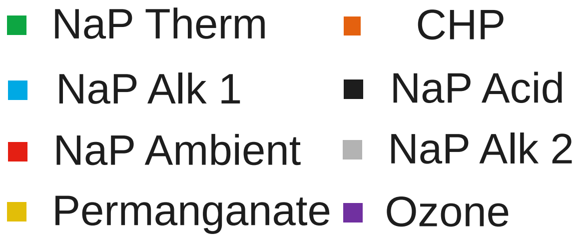
Applicable oxidants for petroleum hydrocarbons are CHP, ozone, and persulfate

ISCO for petroleum hydrocarbons is challenging, but persulfate can provide a longer in situ residence time than CHP and ozone

Oxidant Persistence Comparison

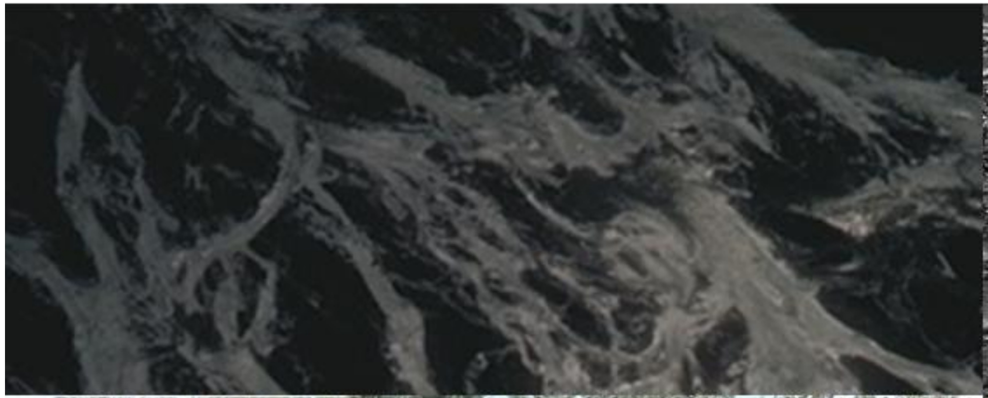
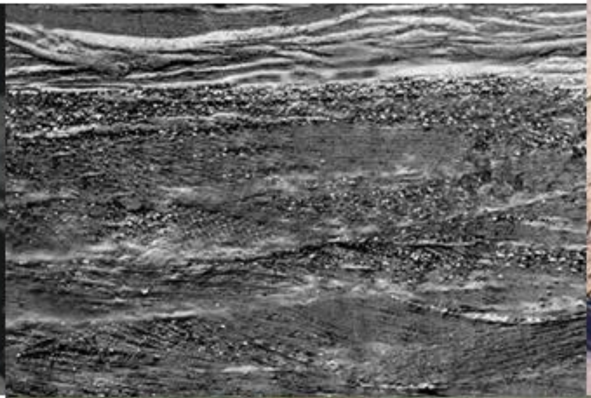


- Assumes constant groundwater velocity of 0.3 m/d
- Pseudo-first order kinetics

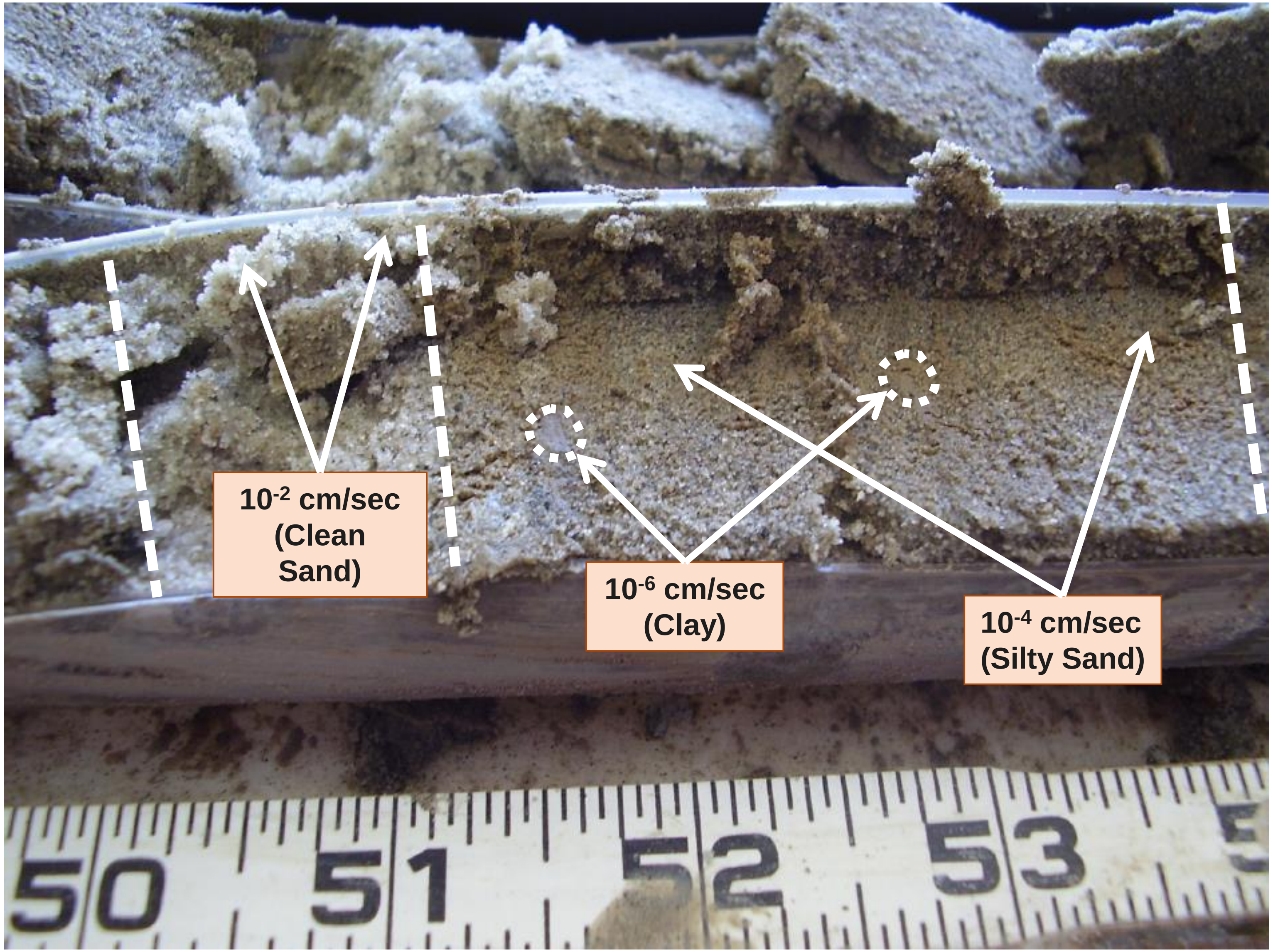


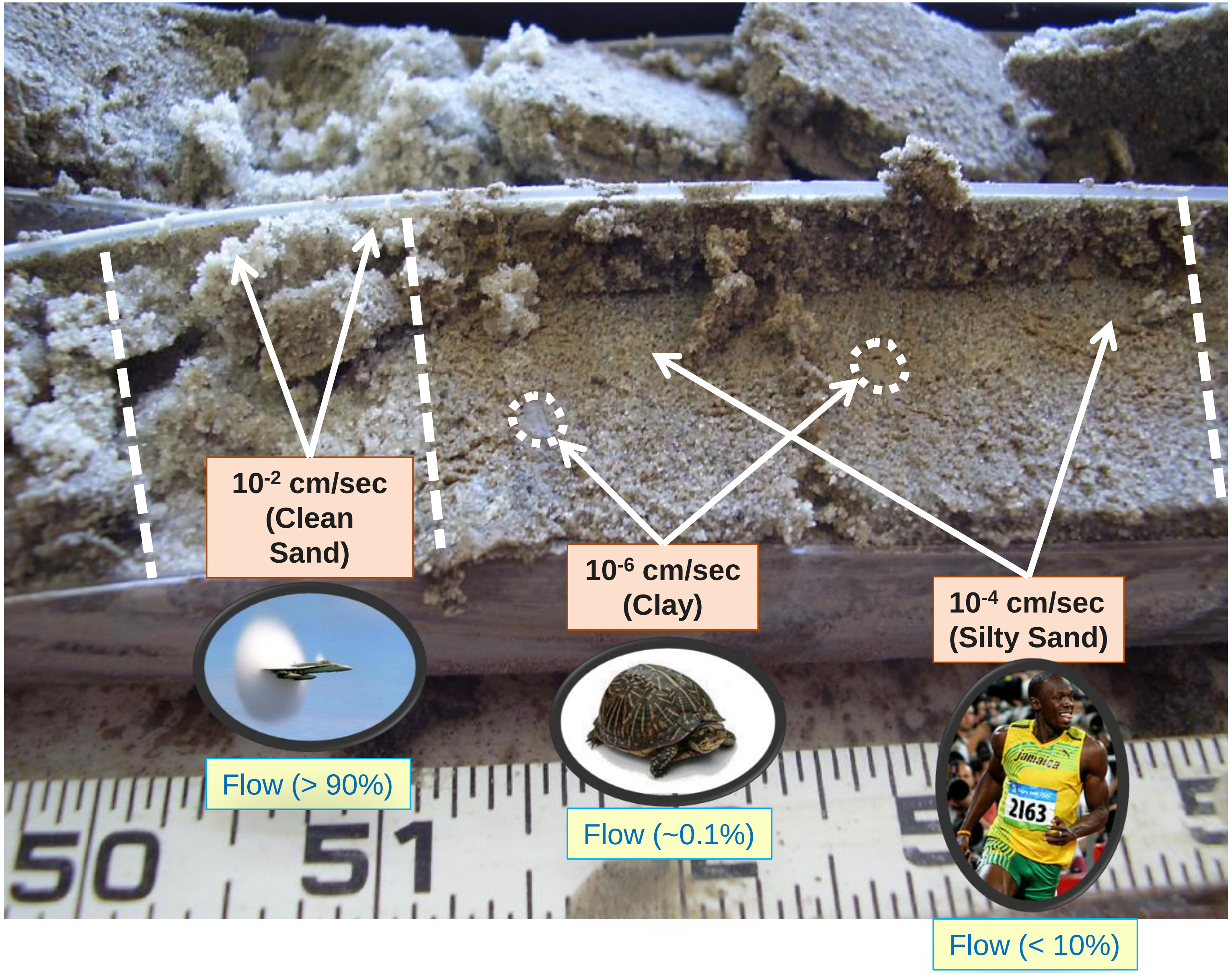
Applicable oxidants for petroleum hydrocarbons are CHP, ozone, and persulfate

ISCO for petroleum hydrocarbons is <u>challenging</u>, but persulfate can provide a longer in situ residence time than CHP and ozone


All hydrogeological systems are heterogeneous and anisotropic


10^{-2} cm/sec (Clean Sand)
10^{-6} cm/sec (Clay)
10^{-4} cm/sec (Silty Sand)
50
51
52
53


10^{-2} cm/sec
(Clean Sand)
Flow (> 90%)
10^{-6} cm/sec
(Clay)
Flow (~0.1%)
10^{-4} cm/sec
(Silty Sand)
Flow (< 10%)

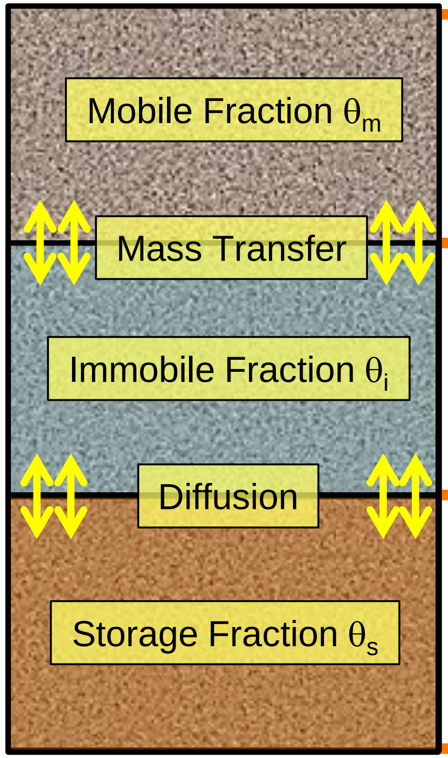
Three Compartment Model
New Standard of Practice

Flow

90% Fast GW

9% Slow GW

1% Static GW



Advective Zones – Pure Advection *(Mobile Fraction)*

Sand & Gravel

Hydraulic Conductivity > 10^{-2} cm/sec

Advective & Storage Zones – Slow Advection *(Immobile Fraction)*

Silty and Clayey Sand

10^{-4} < Hydraulic Conductivity < 10^{-2} cm/sec

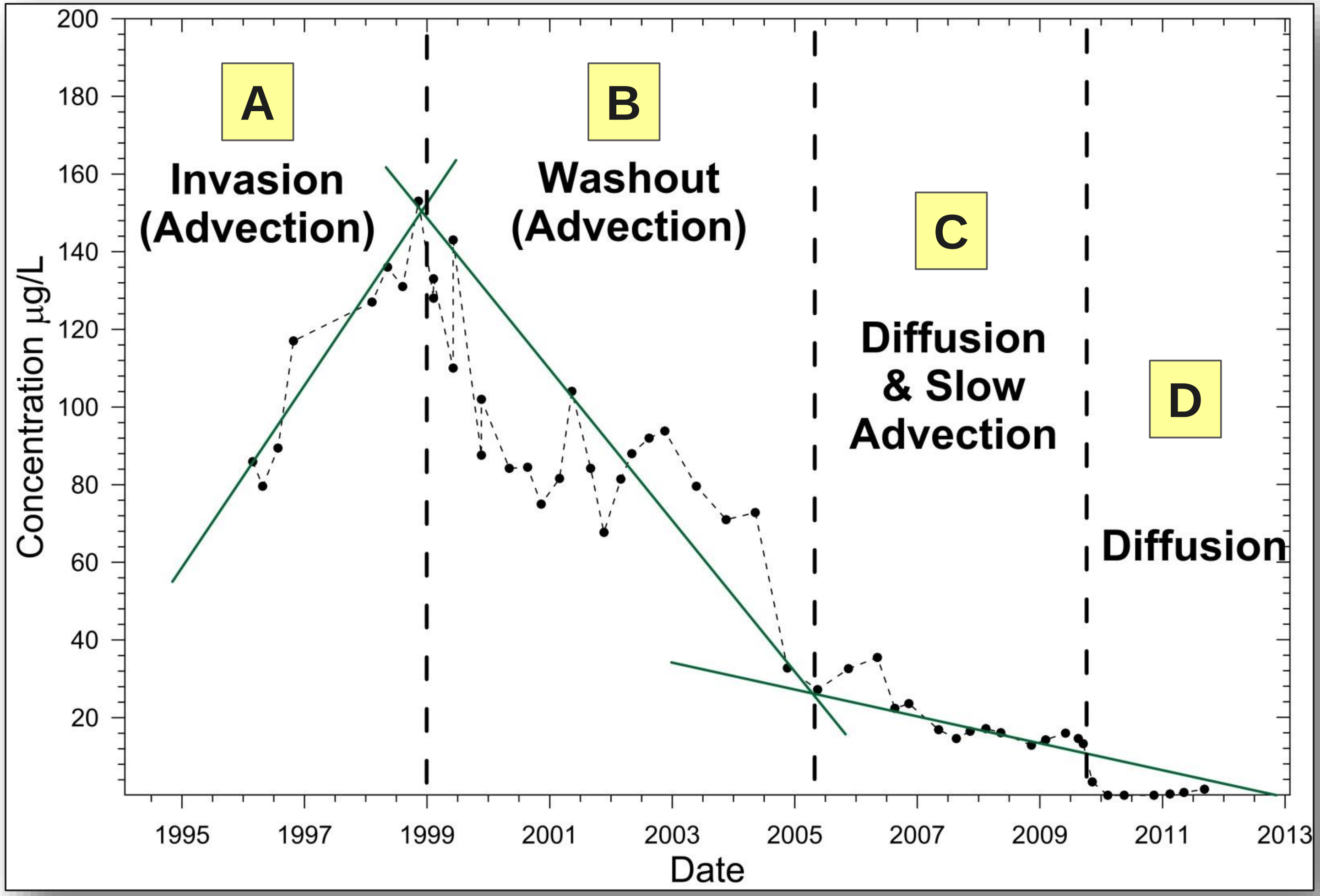
Storage Zones – Static Water *(Storage Fraction)*

Sandy Silt, Silt, and Clay

Hydraulic Conductivity < 10^{-4} cm/sec

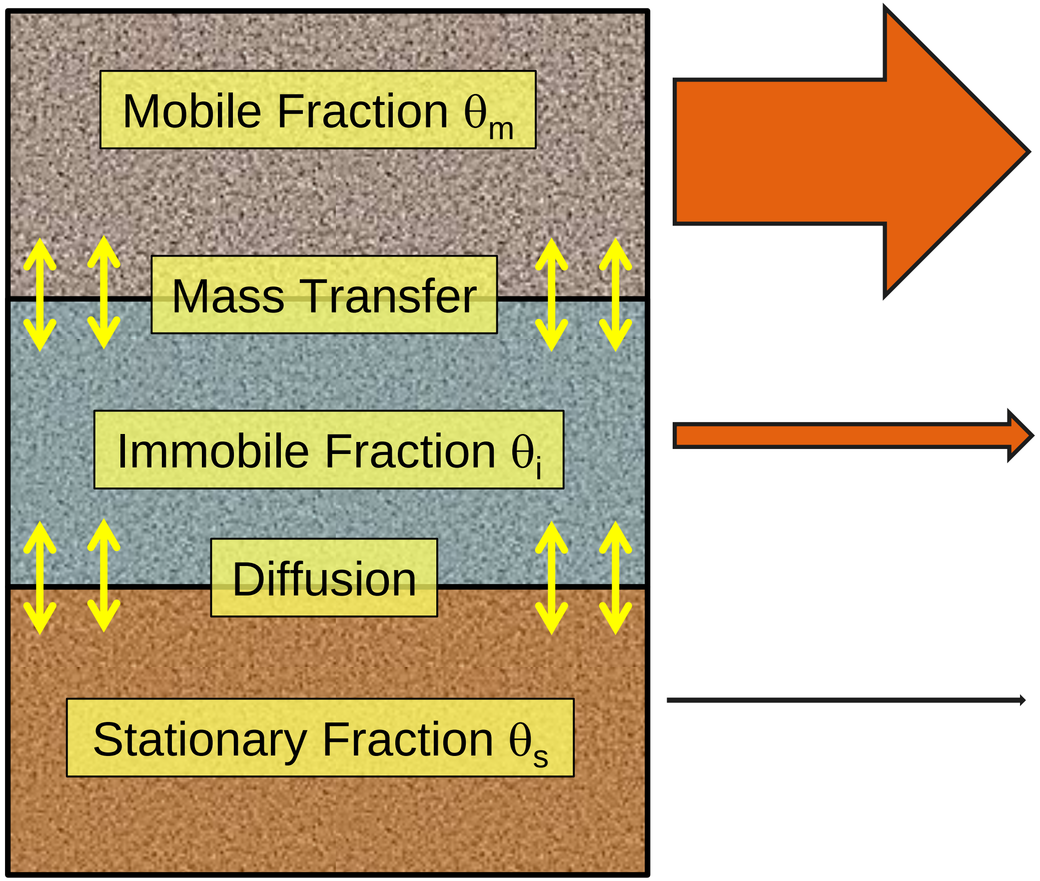
Advection / Advection & Diffusion / Diffusion

Plume Development | Washout profile during aquifer flushing



Conceptual Site Model (CSM)

Reference CSM   Mass Flux



Readily addressed by In Situ Treatment

Potentially addressed by In Situ Treatment

Difficult to address with In Situ Treatment

Discusses where COCs are; <u>equally</u> important is how much remains

Chemical Treatment Sweet Spot

"Delivery" means reagent distribution at a working strength.

ARCADIS Design & Consultancy for natural and built assets

Chemical Treatment Sweet Spot

“Delivery” means reagent distribution at a working strength.

“Contact” time of reagent and contaminant is critical.

Chemical Treatment Sweet Spot

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"Access" to source mass refers to where its located and how much remains.

Chemical Treatment Sweet Spot

Delivery — “Delivery” means reagent distribution at a working strength.

Contact — “Contact” time of reagent and contaminant is critical.

Access — “Access” to source mass refers to where its located and how much remains.

Regulatory — Flexible regulatory framework.

Designing Chemical Treatment

<u>Optimizing of Reagent Distribution</u>

- ✓ Sufficient permeability to support injections
- ✓ Volume to distribution relationship
- ✓ Reagent residence time (i.e., washout versus consumption)

Continuous “down-hole” specific conductivity measurements

Designing Chemical Treatment

Optimizing of Reagent Distribution

- ✓ Sufficient permeability to support injections
- ✓ Volume to distribution relationship
- ✓ Reagent residence time (i.e., washout versus consumption)

Role of Treatability Testing

- ✓ Oxidant/reductant demand?
- ✓ Buffering capacity?
- ✓ Leverage experience to reduce cost

Continuous “down-hole” specific conductivity measurements

ISCO treatability testing

Designing Chemical Treatment

Optimizing of Reagent Distribution

- ✓ Sufficient permeability to support injections
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Role of Treatability Testing

- ✓ Oxidant/reductant demand?
- ✓ Buffering capacity?
- ✓ Leverage experience to reduce cost

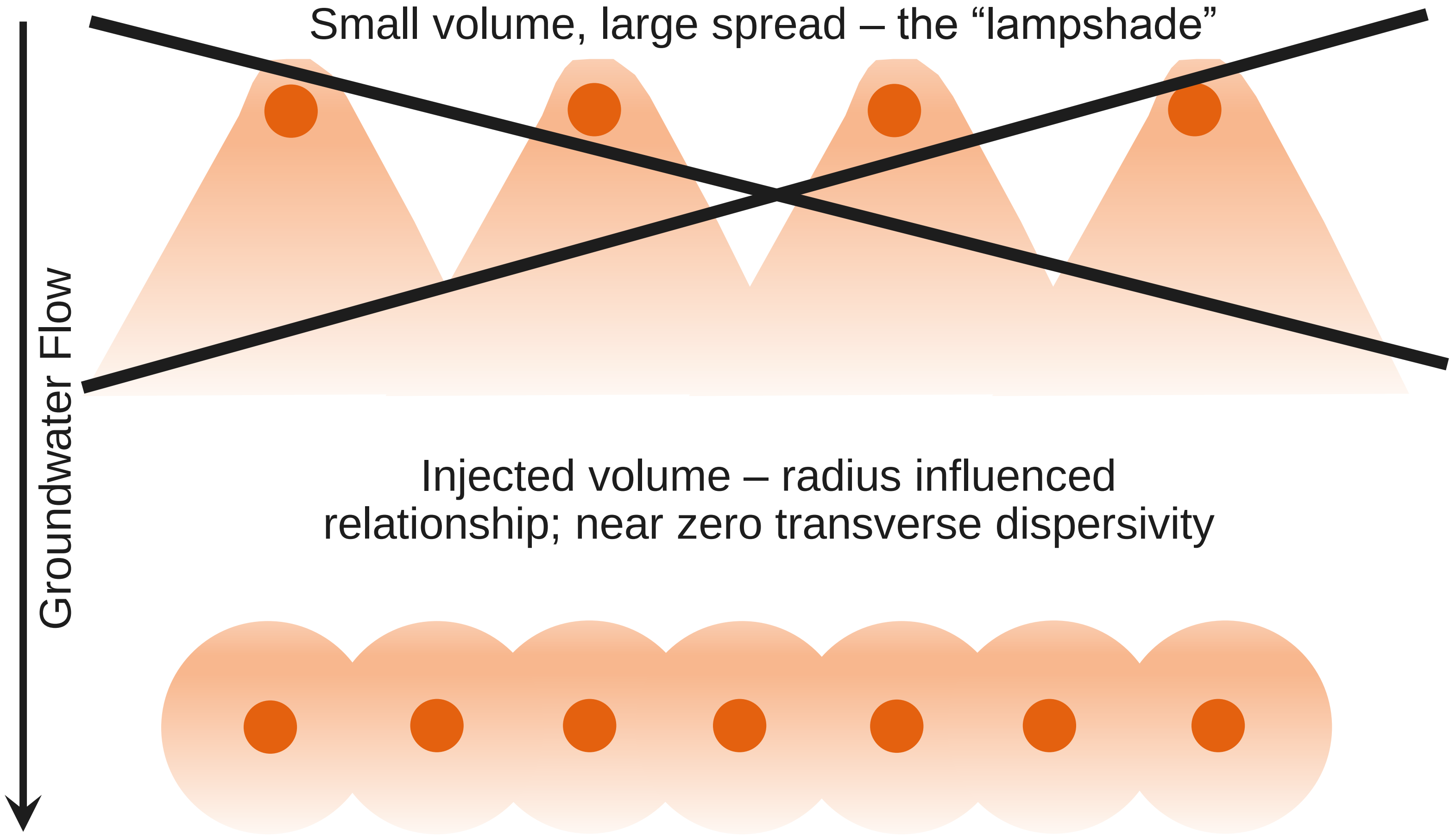
Nature and Extent of Contamination

- ✓ NAPL?
- ✓ Adsorbed mass (soil concentrations)?
- ✓ Historical contaminant concentrations and groundwater elevations ("smear zone")?

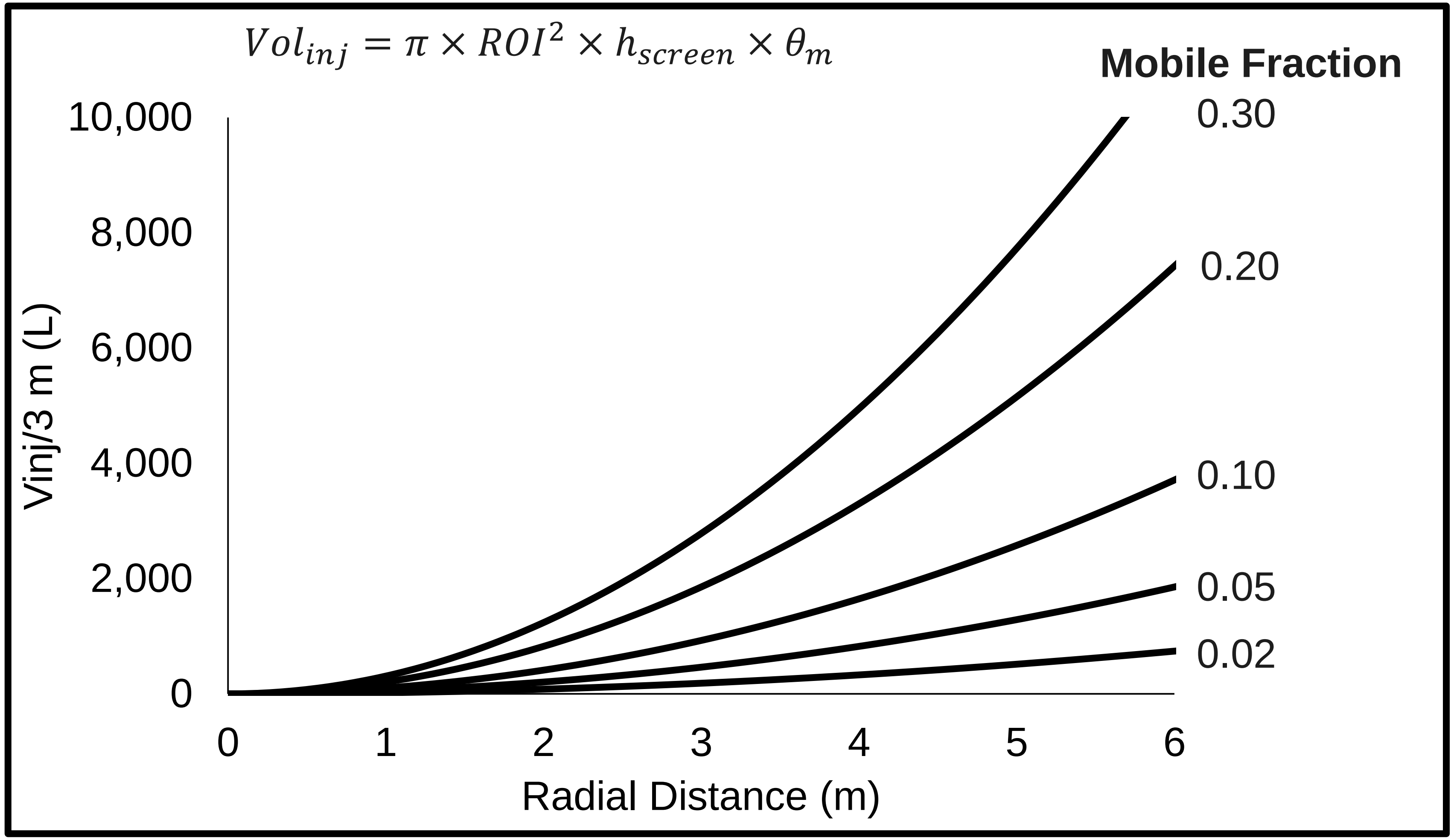
Continuous "down-hole" specific conductivity measurements

ISCO treatability testing

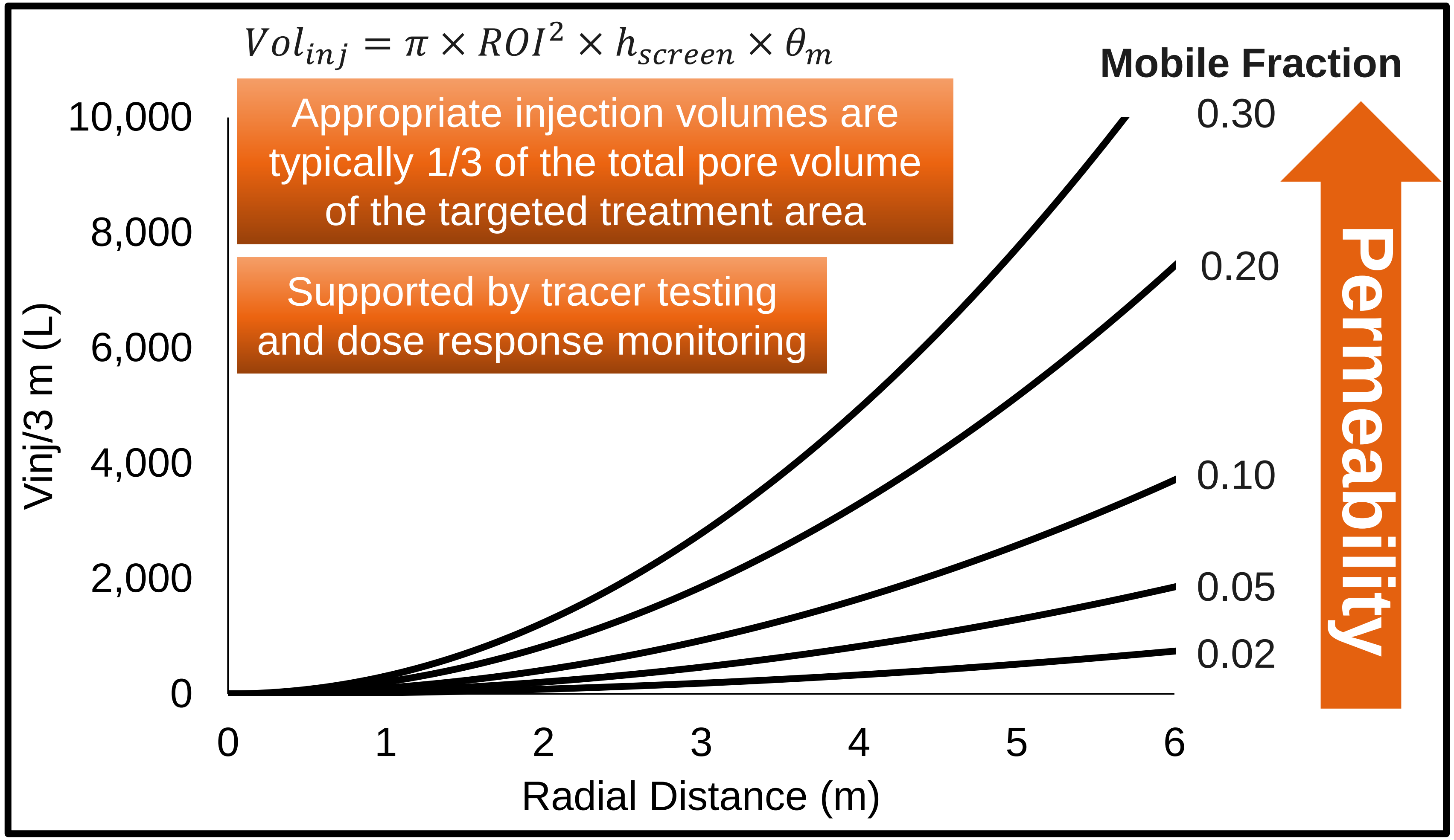
Dispersion and Remediation



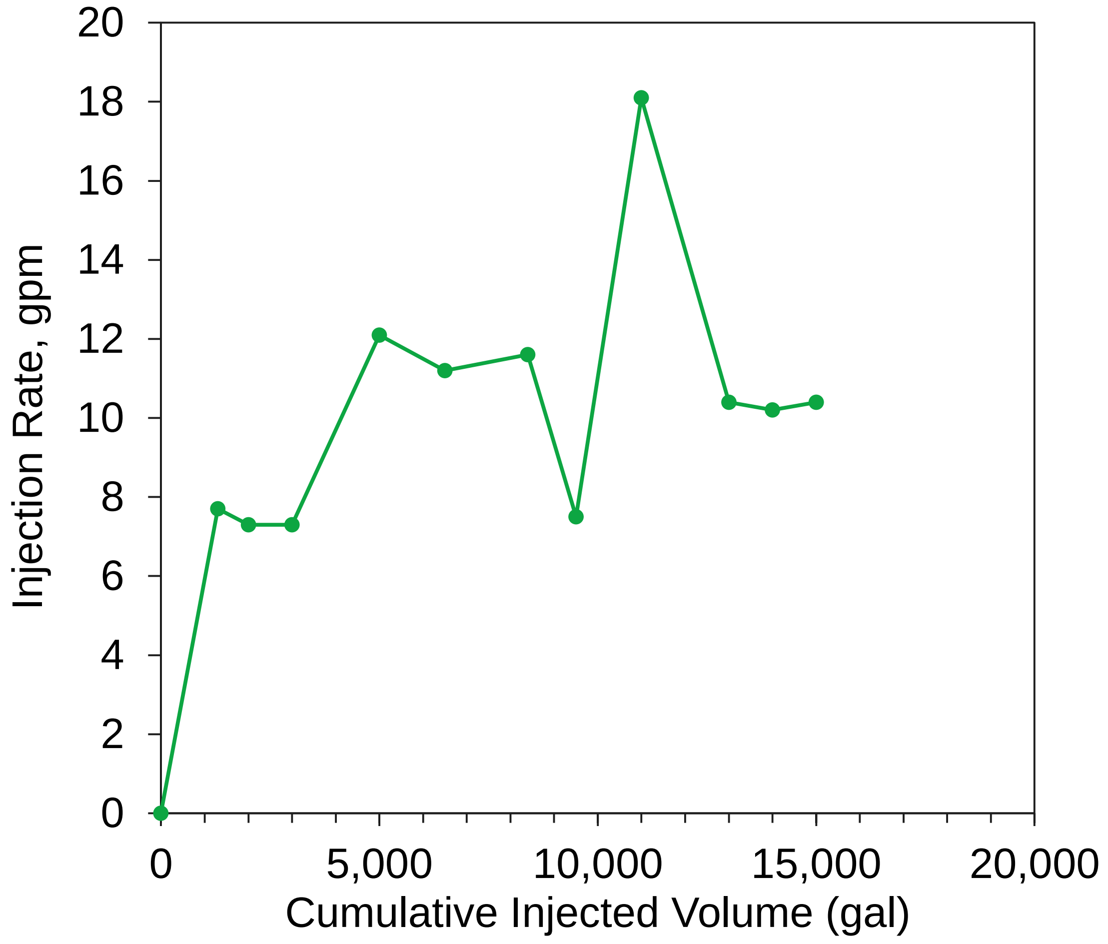
Optimizing Reagent Distribution

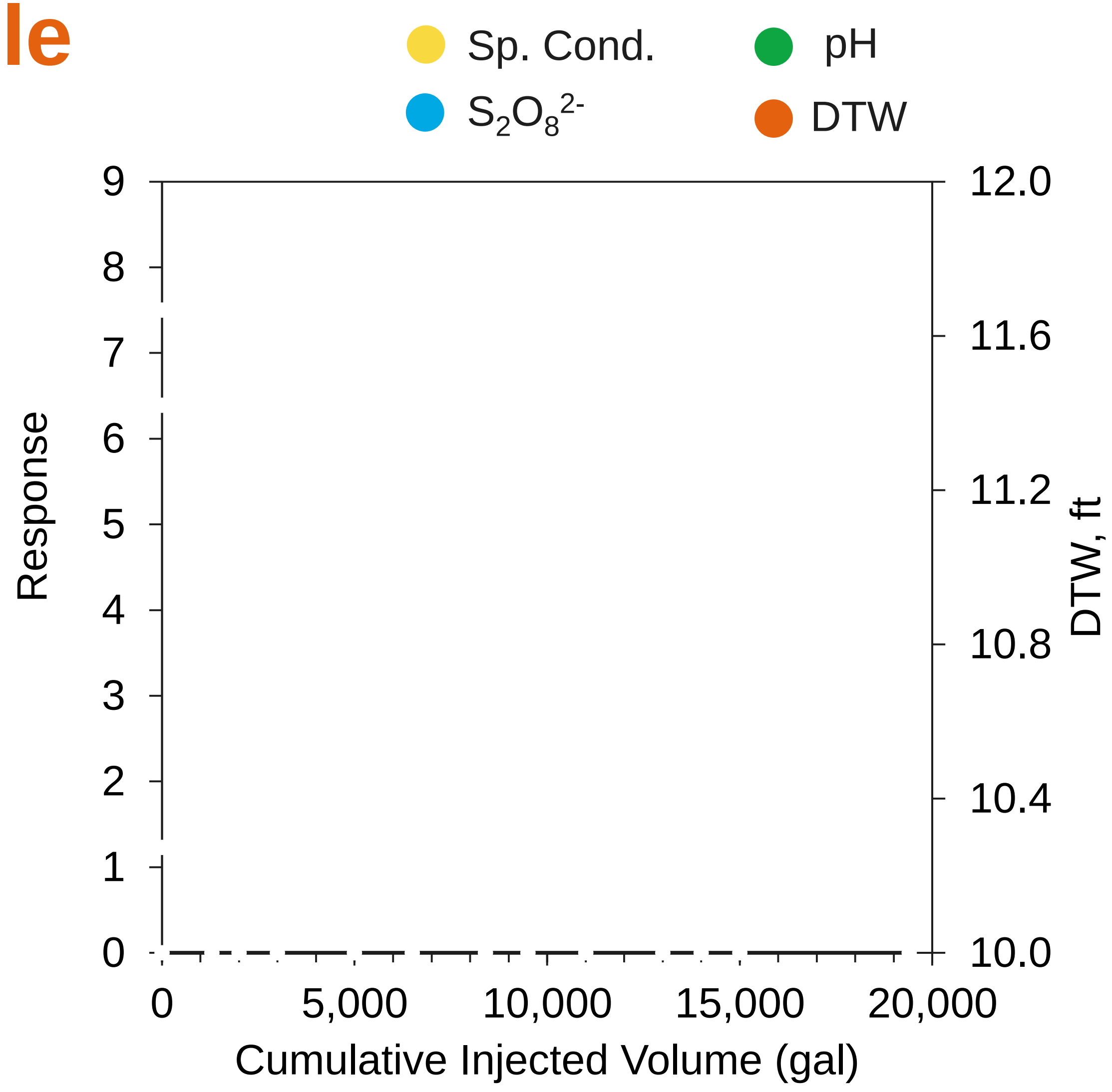


Optimizing Reagent Distribution

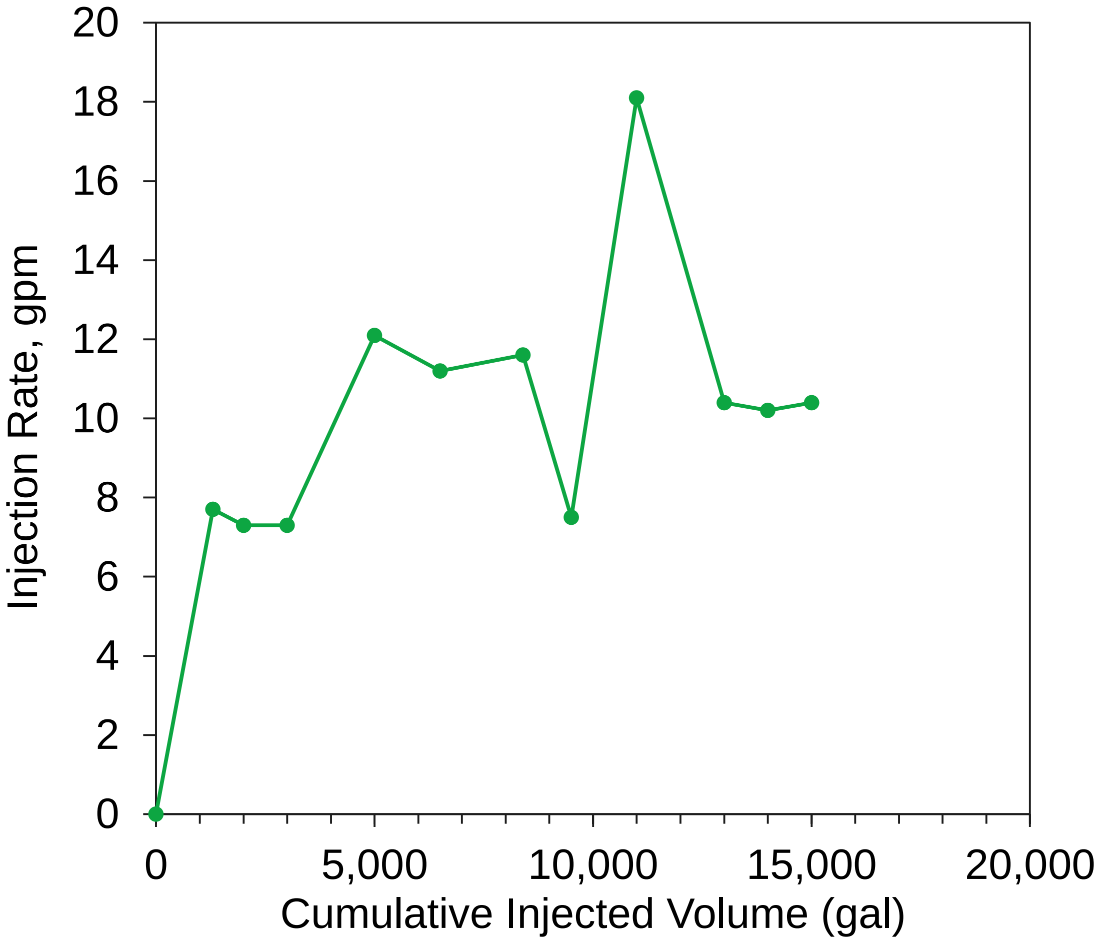


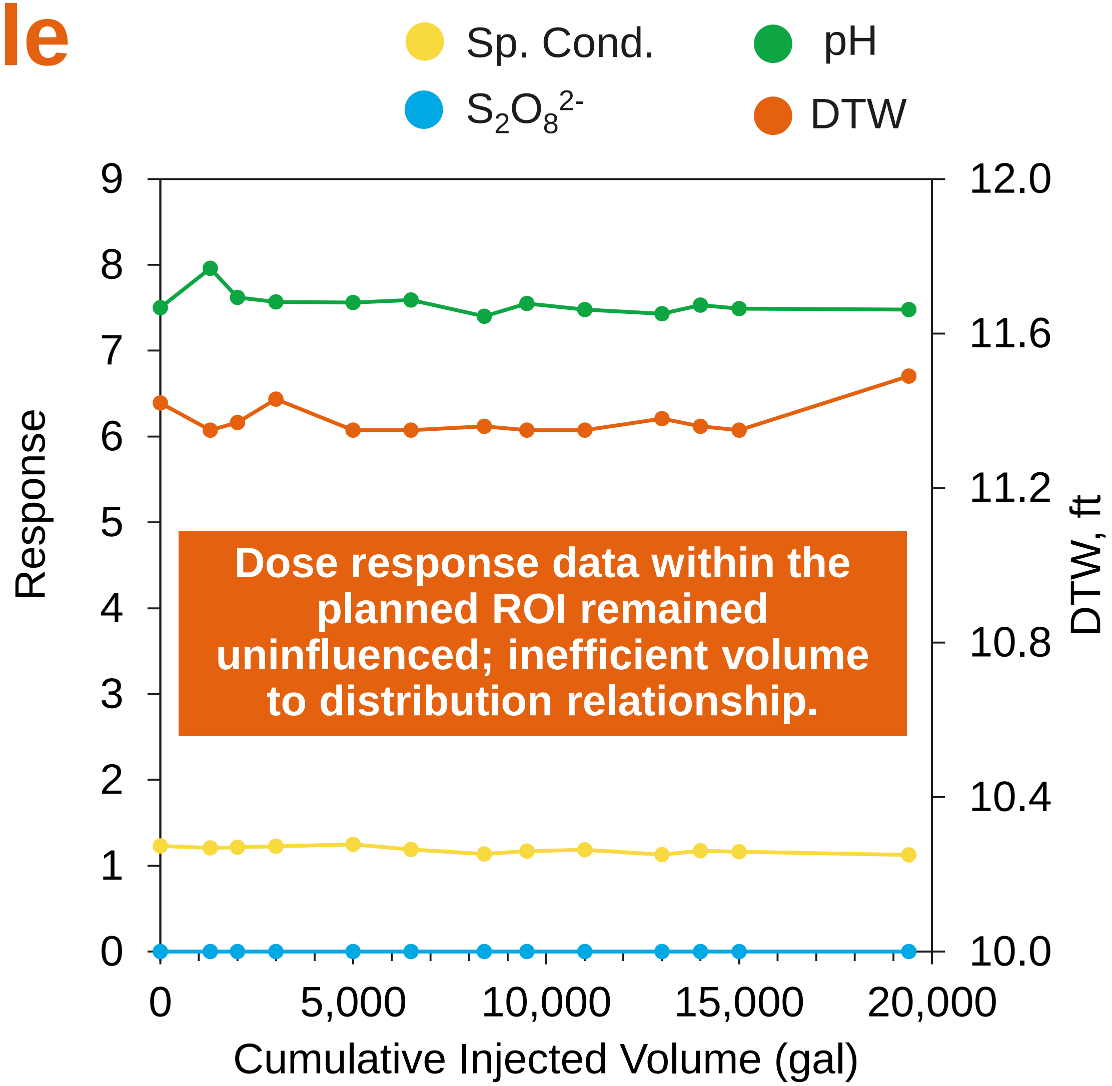
Reagent Distribution Example





Reagent Distribution Example





Role of Treatability Testing

Laboratory Treatability Test
Verify chemistry if novel contaminant or questionable site geochemistry
Proof of concept
Establish oxidant and activator dosing
Focus on required reagent, not the natural oxidant demand (NOD) or total oxidant demand (TOD)
Screen secondary effects – VOCs and metals

Oxidant Reagent Chemistry

Secondary effect example

Chlorinated ethanes formed from chloromethanes

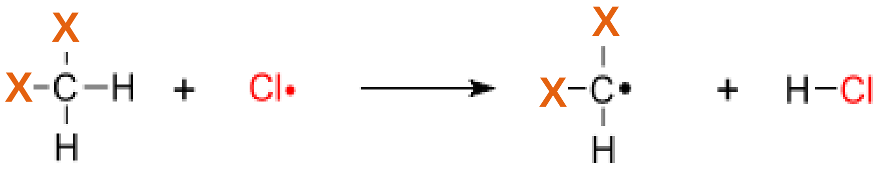
Oxidant Reagent Chemistry

Secondary effect example

Chlorinated ethanes formed from chloromethanes

- Chloroethenes, hydrocarbons, DOC, or NOD react with radical chlorine

X = H or Cl

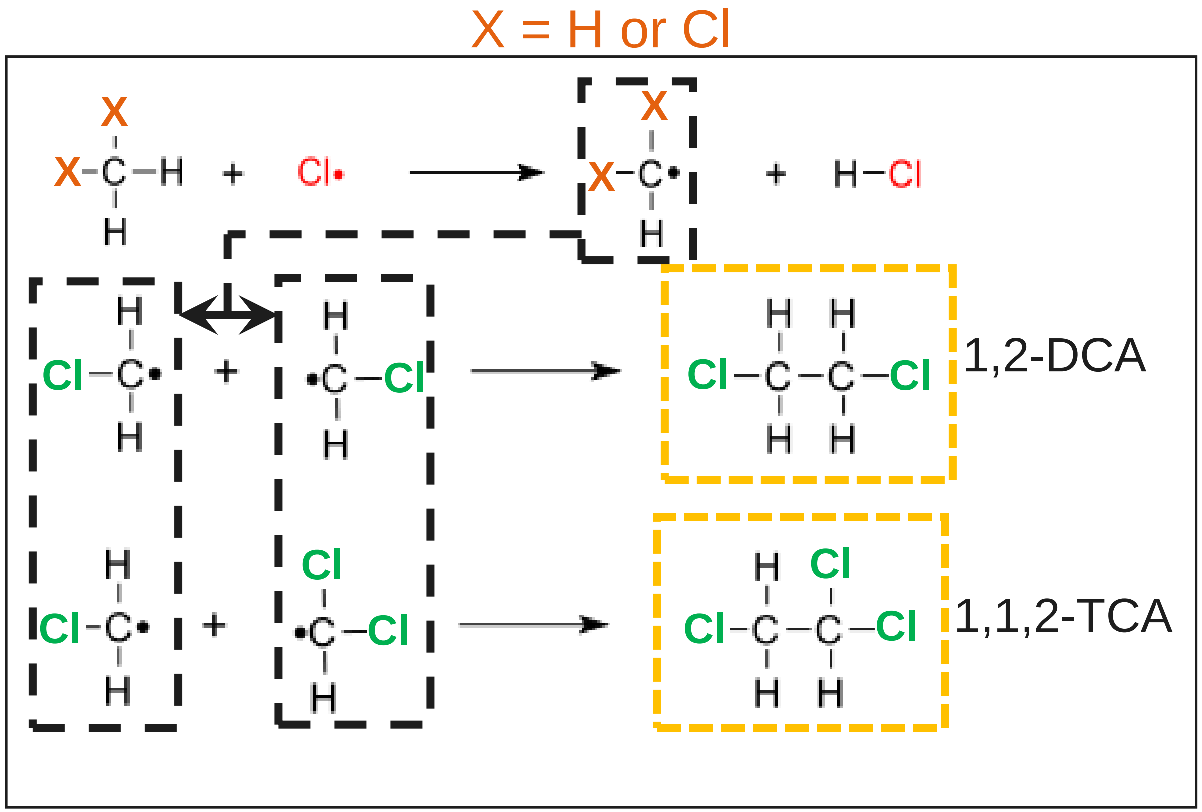


Oxidant Reagent Chemistry

Secondary effect example

Chlorinated ethanes formed from chloromethanes

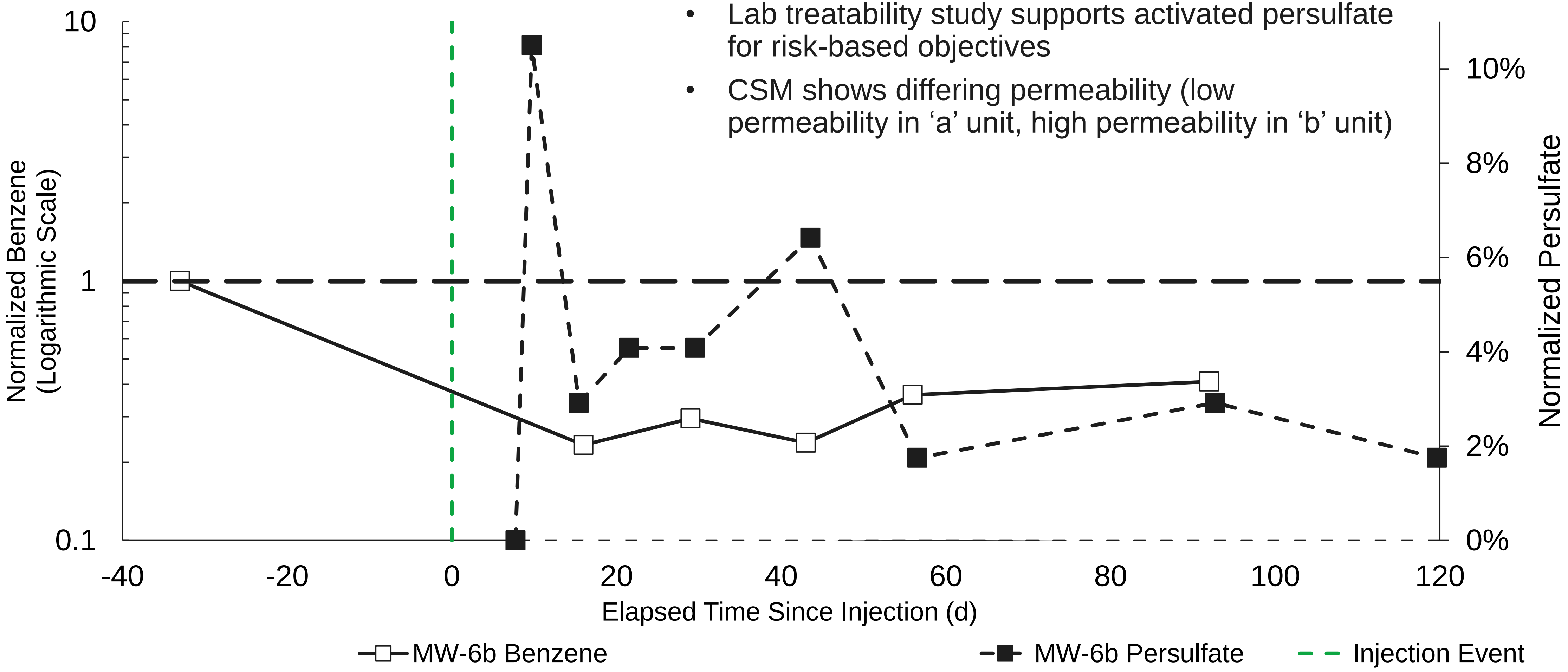
- Chloroethenes, hydrocarbons, DOC, or NOD react with radical chlorine
- Resultant carbon-based radical precusor may form chloroethanes



Organic molecules enhance this process

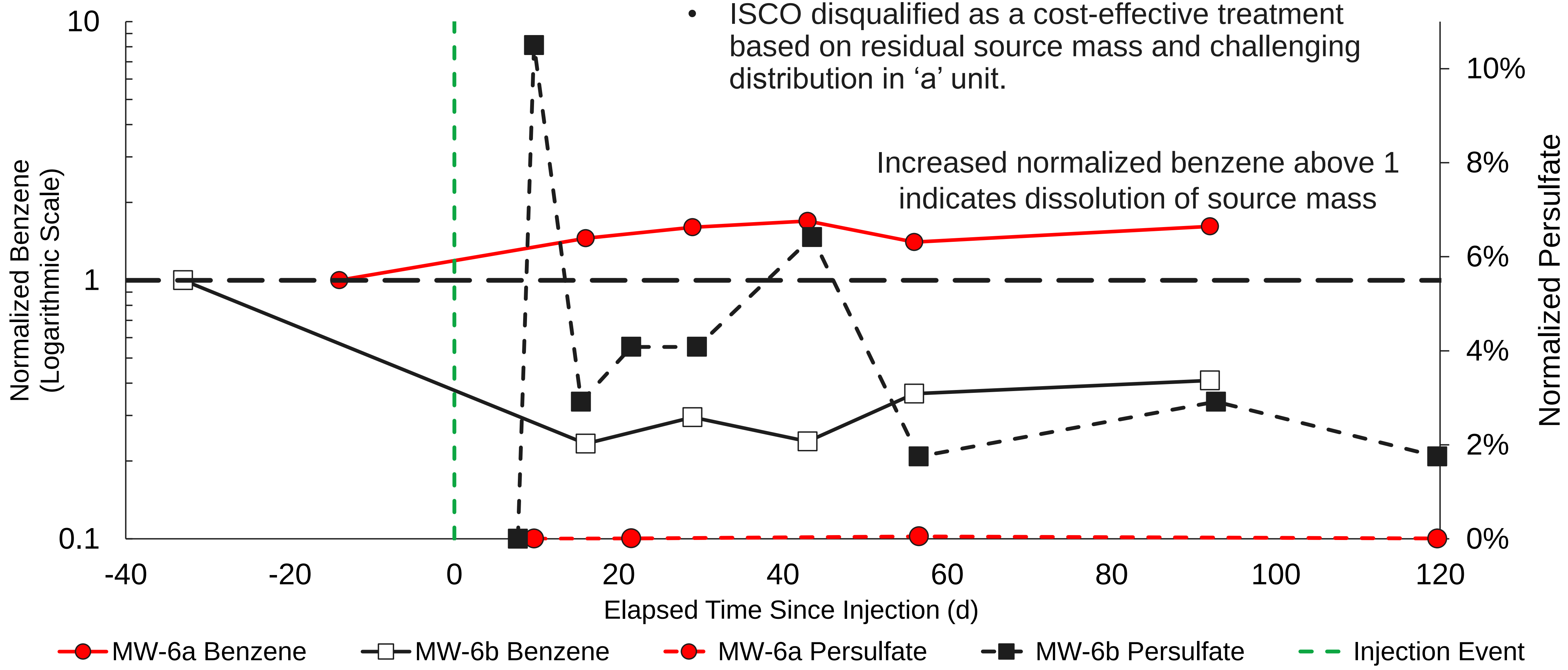
Lab-Scale to Field-Scale

- Lab treatability study supports activated persulfate for risk-based objectives
- CSM shows differing permeability (low permeability in ‘a’ unit, high permeability in ‘b’ unit)

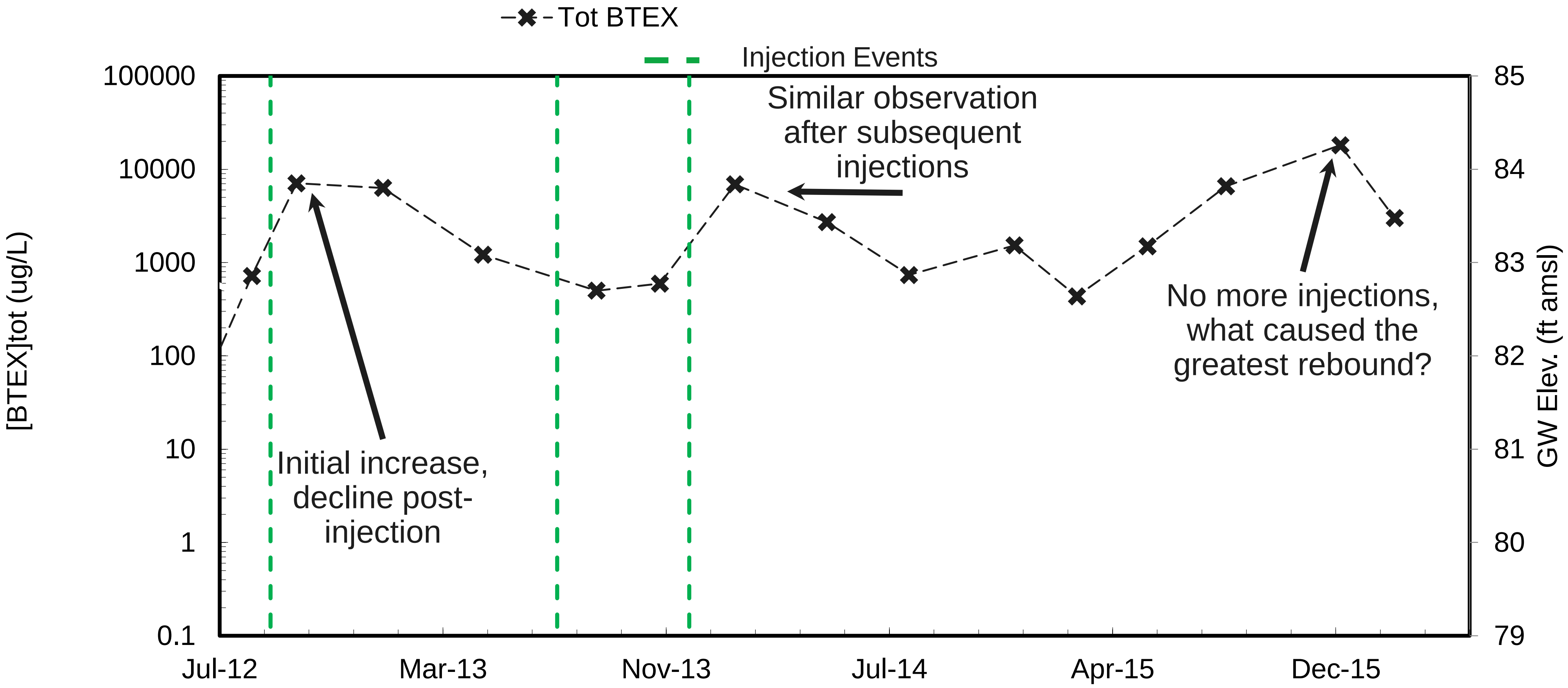


Lab-Scale to Field-Scale

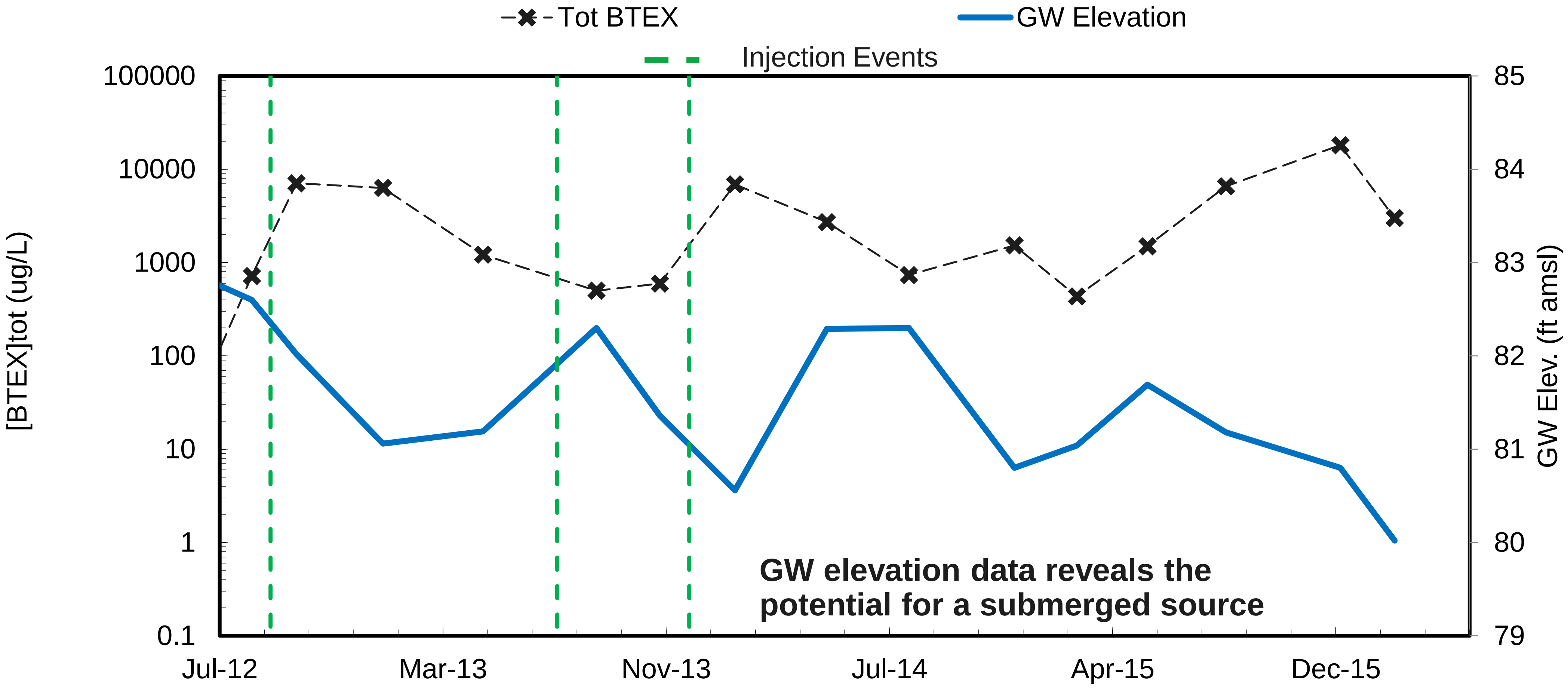
- ISCO disqualified as a cost-effective treatment based on residual source mass and challenging distribution in ‘a’ unit.



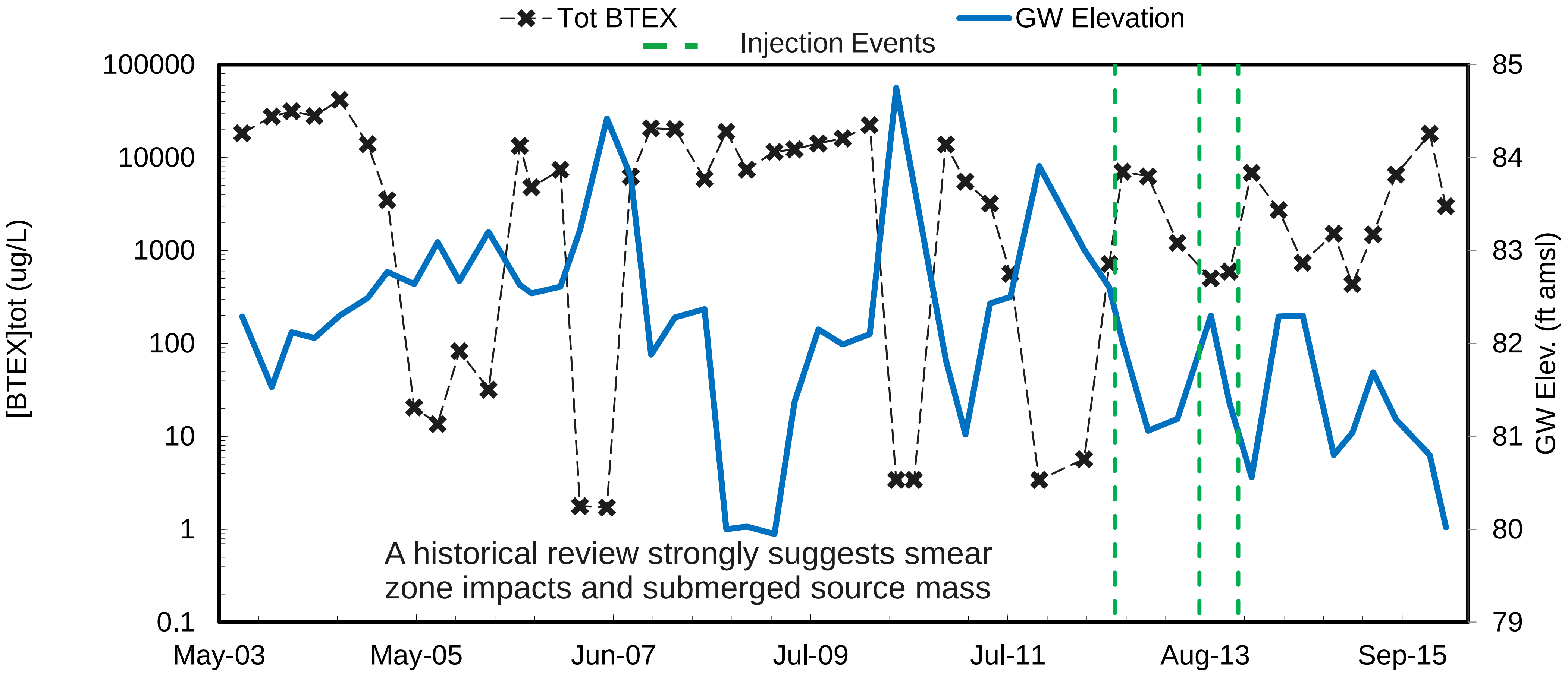
ISCO and the “Smear Zone”



ISCO and the "Smear Zone"

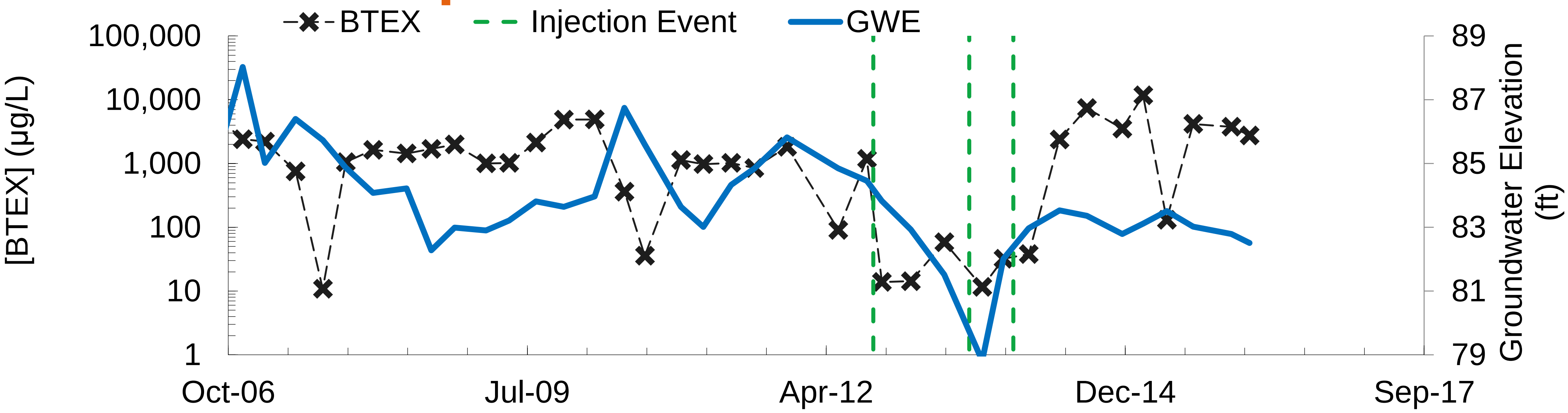


ISCO and the “Smear Zone” (cont.)

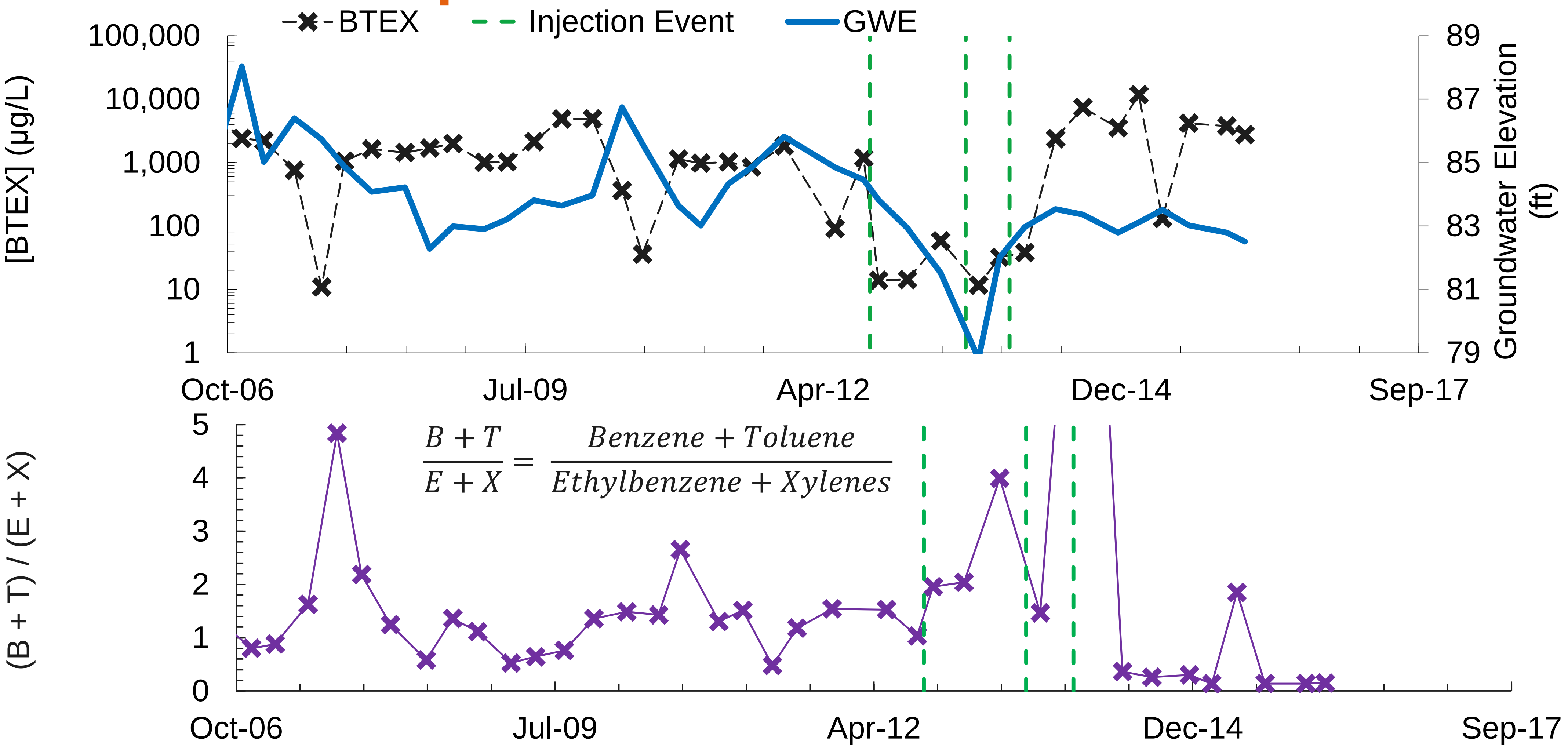


Smear zones can control rebound post ISCO

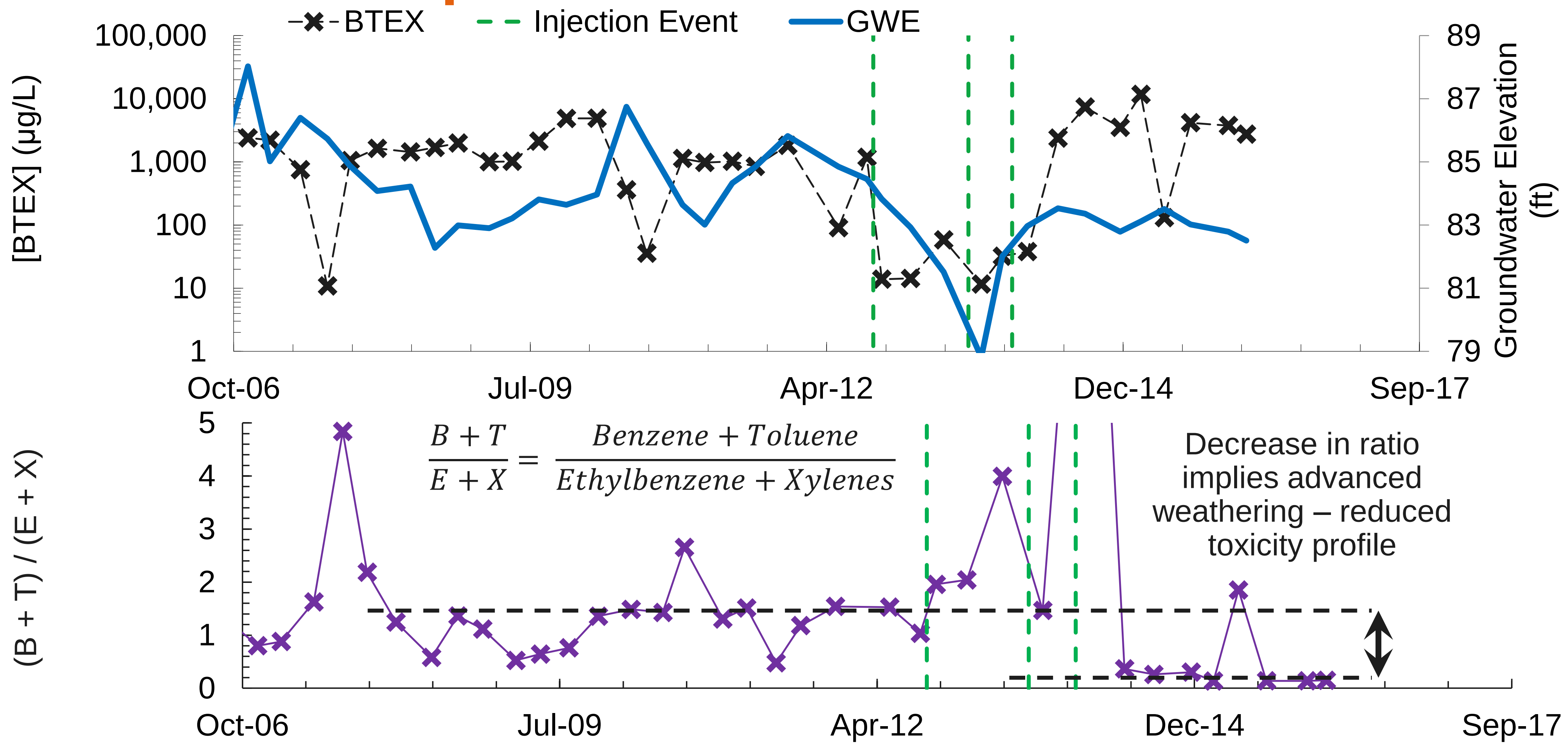
Evidence of Improvement via ISCO



Evidence of Improvement via ISCO



Evidence of Improvement via ISCO



Sweet Spot ISCO

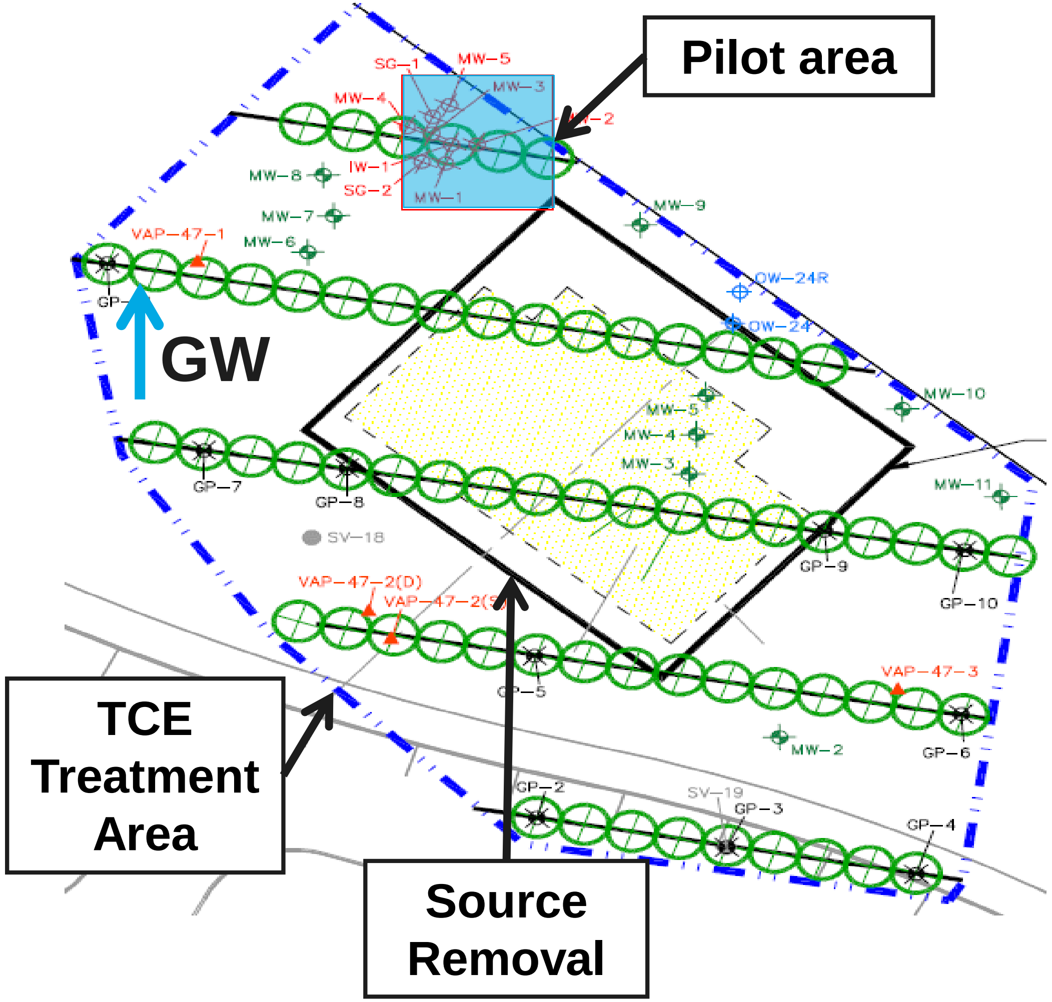
ISCO as a polishing technology following a large source removal

TCE in groundwater (<50 µg/L) above NYSDEC goal (5 µg/L)

ISCO design supported with laboratory treatability testing and field-scale pilot testing

Rely on advective transport for distribution of oxidant (30 day oxidant persistence as confirmed during pilot testing)

Two years post treatment: two locations 5 to 10 µg/L



Summary

Chemical Treatment Applicability

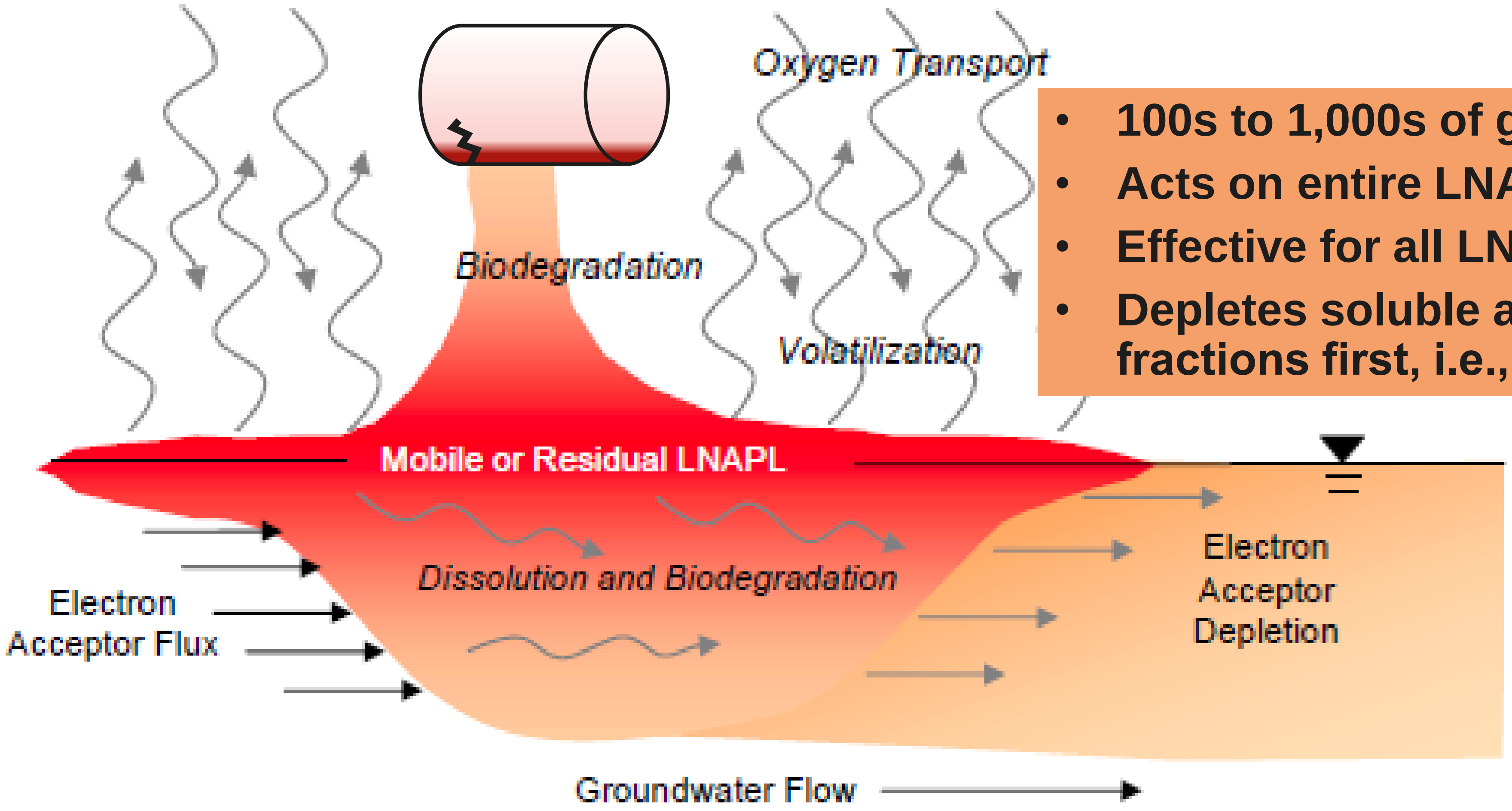
Safe and complete execution: achieving dose response, responding to data, reagent residence time, secondary effects

Robust design: adequate injection volumes, reagent-contaminant contact, reagent chemistries, geochemical considerations, proof of concept

Site characterization: nature and extent of contamination can preclude chemical treatment as an option or dictate its implementation

If ISCO Isn’t Effective, Then What?

Natural Source Zone Depletion



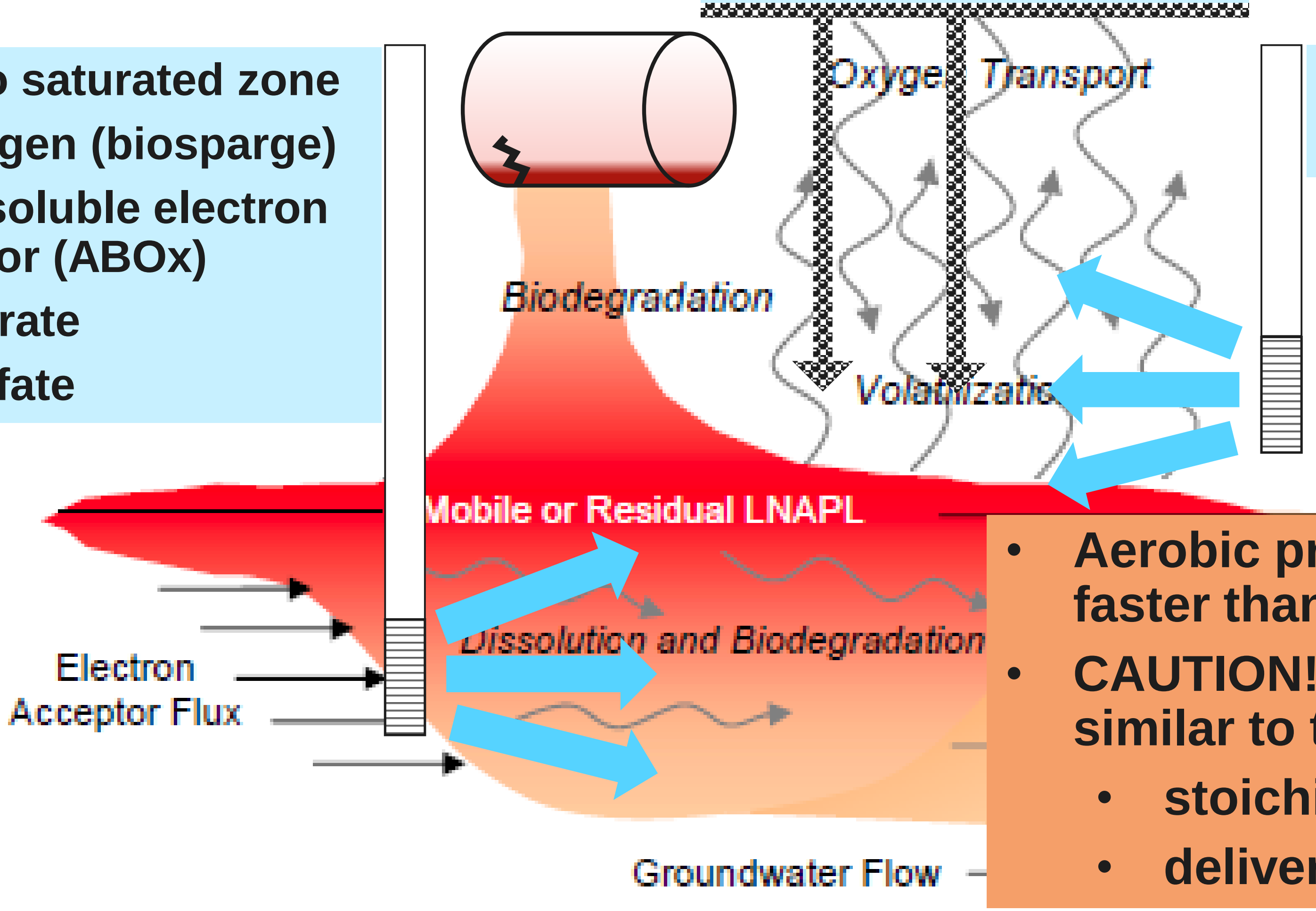
- 100s to 1,000s of gallons/(acre•year)
- Acts on entire LNAPL body
- Effective for all LNAPLs
- Depletes soluble and volatile fractions first, i.e., "weathering"

Enhance NSZD

Surface Application
- **ABOx**

Inject into saturated zone
- **air/oxygen (biosparge)**
- **Inject soluble electron acceptor (ABOx)**
  - **nitrate**
  - **sufate**

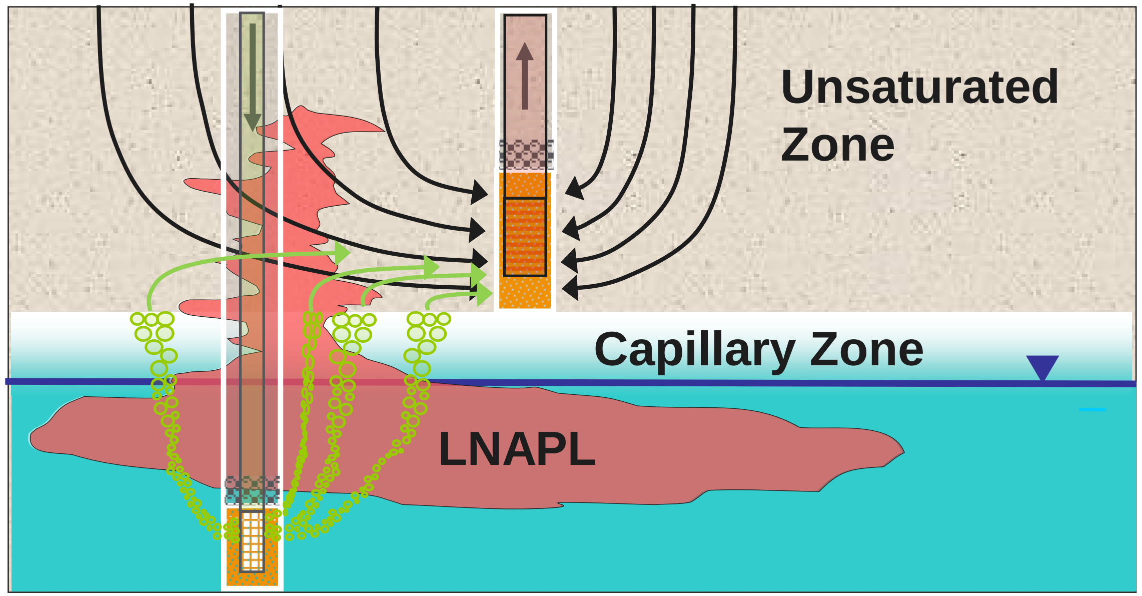
Inject into vadose zone
- **air/oxygen (biovent)**



- **Aerobic processes demonstrated faster than NSZD**
- **CAUTION! Some ABOx challenges similar to those of ISCO**
  - **stoichiometry**
  - **delivery**

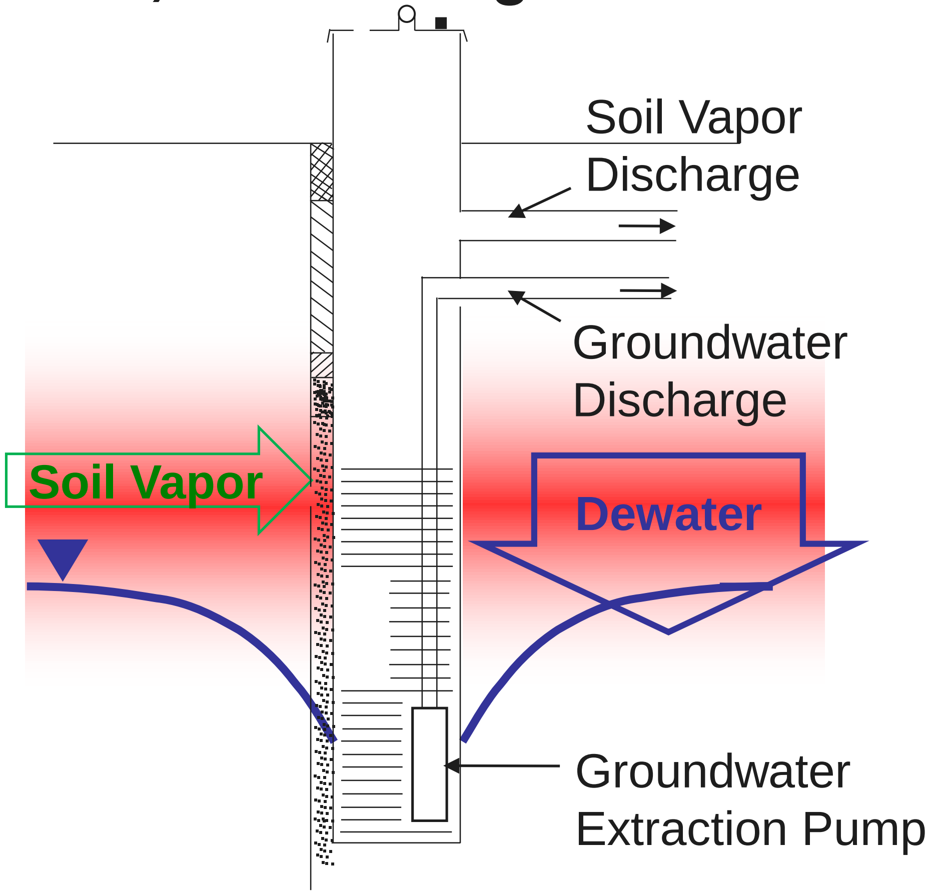
Volatilize LNAPL & Enhance Aerobic Degradation

Air Sparging / Soil Vapor Extraction

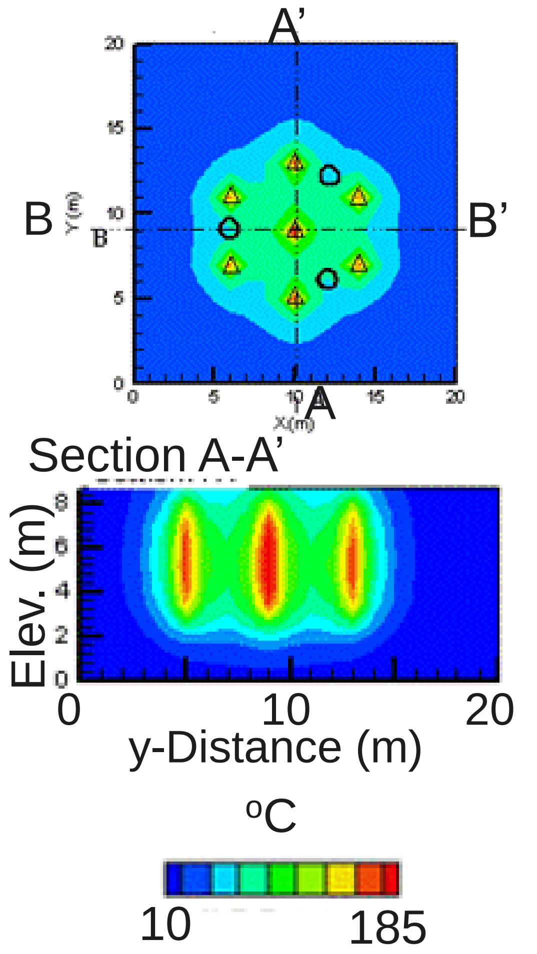


- Effective for volatile LNAPL
- High initial mass reduction

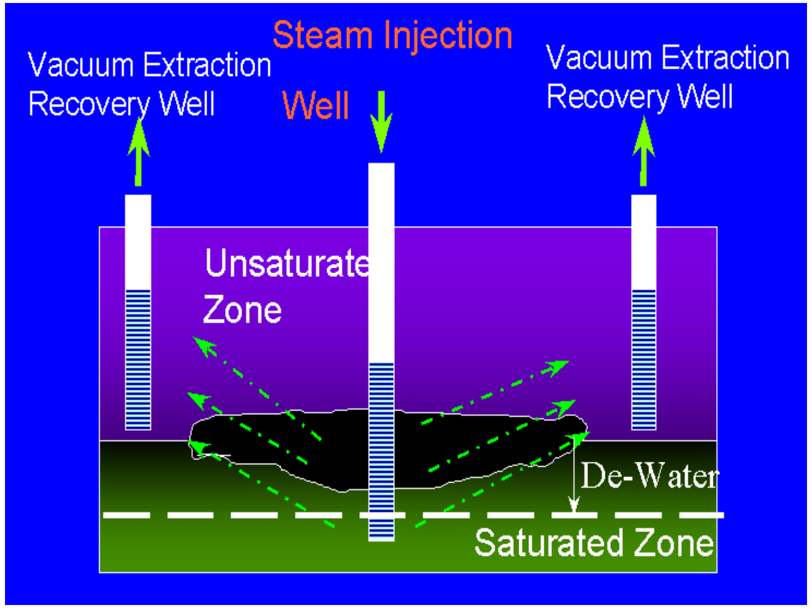
Dual-Phase Extraction aka, Dewatering & SVE

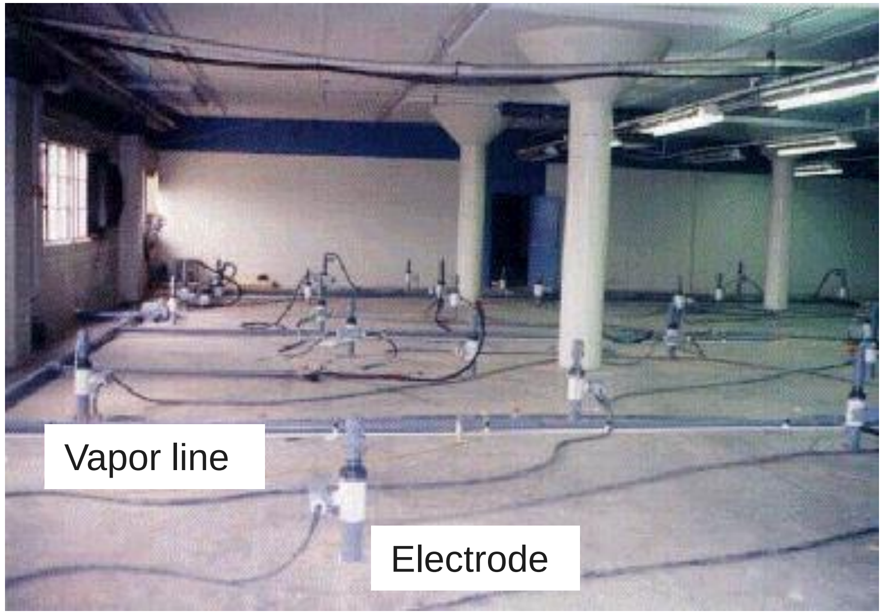


Heating Technologies



ITRC 2010; I. Hers, Golder

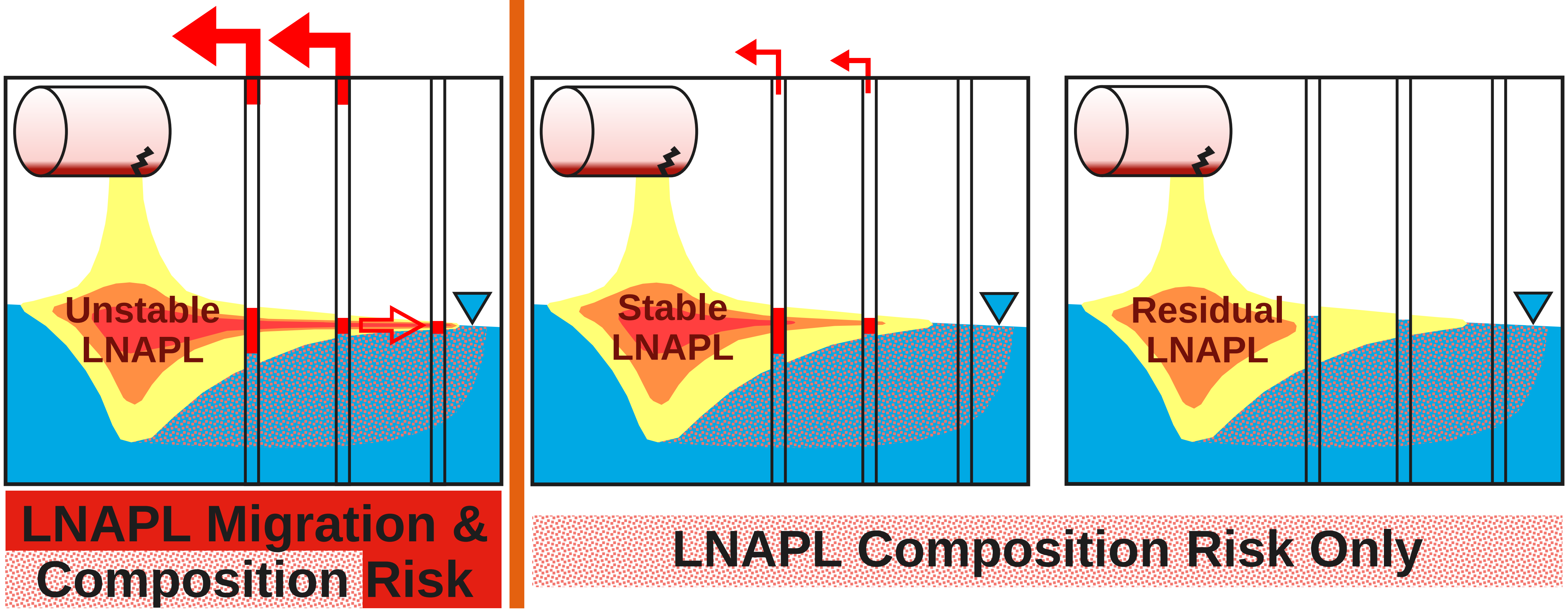




- **Effective for low volatility LNAPLs**
- **Fast depletion of high volatility LNAPL constituents**
- **High mass reduction**

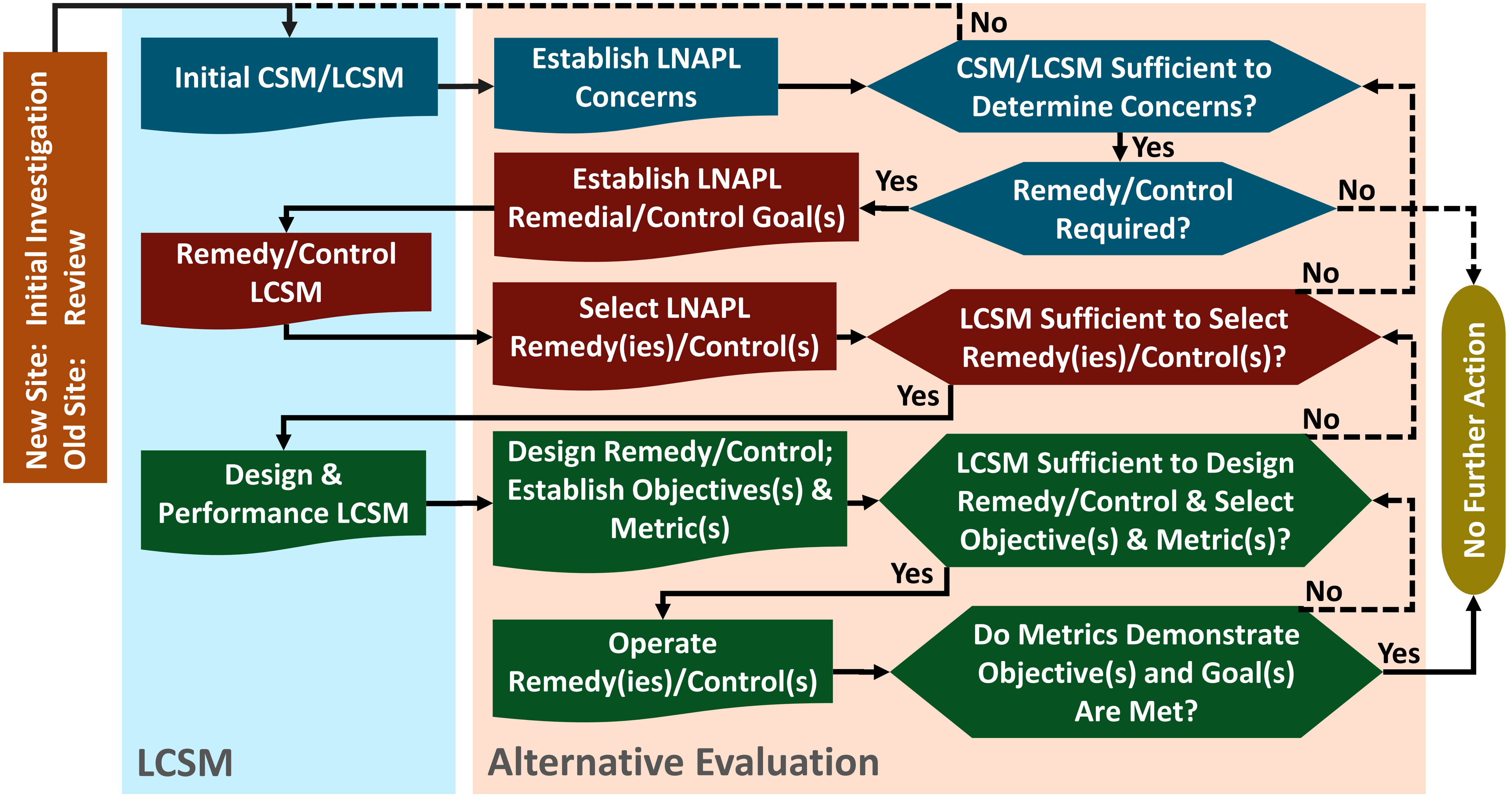
Summary

Risk-Based LNAPL Management Approach

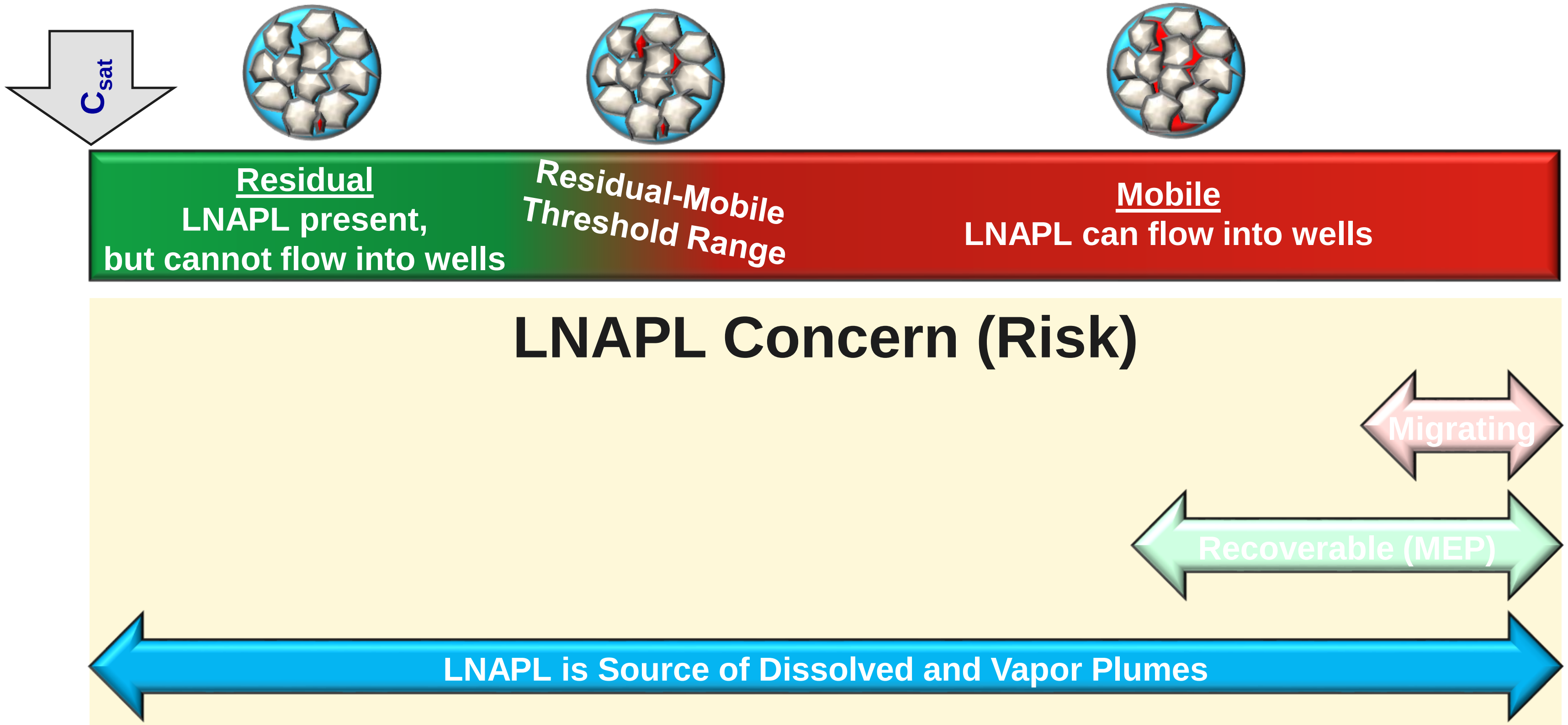


Risk = LNAPL Instability + LNAPL Composition

LCSM Supports Alternative Evaluation



Phase Change Technologies for All LNAPL



Remedial Technology Groups

- Mass Control
- Mass Recovery
- Phase Change

Active Phase Change Depletes Migrating, Mobile & Residual LNAPL

"Ole Reliable" Phase Change Technologies

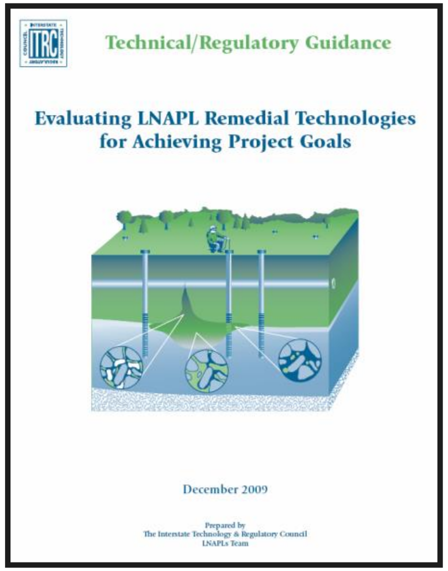
Mass Control
- Physical containment
- In-situ soil mixing

Mass Recovery
- LNAPL skimming
- Bioslurping/EFR
- Dual pump liquid extraction
- **Multi-phase extraction**
- Excavation
- Water/hot water flooding
- Cosolvent flushing
- Surfactant-enhanced subsurface remediation

Phase Change
- **Natural source zone depletion (NSZD)**
- **Air sparging/soil vapor extraction (AS/SVE)**
- In situ chemical oxidation
- Heating
  - Steam injection
  - Electrical Resistance
  - Conduction
- **Dewatering & SVE (DPE)**
- **Biovent/Biosparge**
- Anaerobic Bio-Oxidation

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

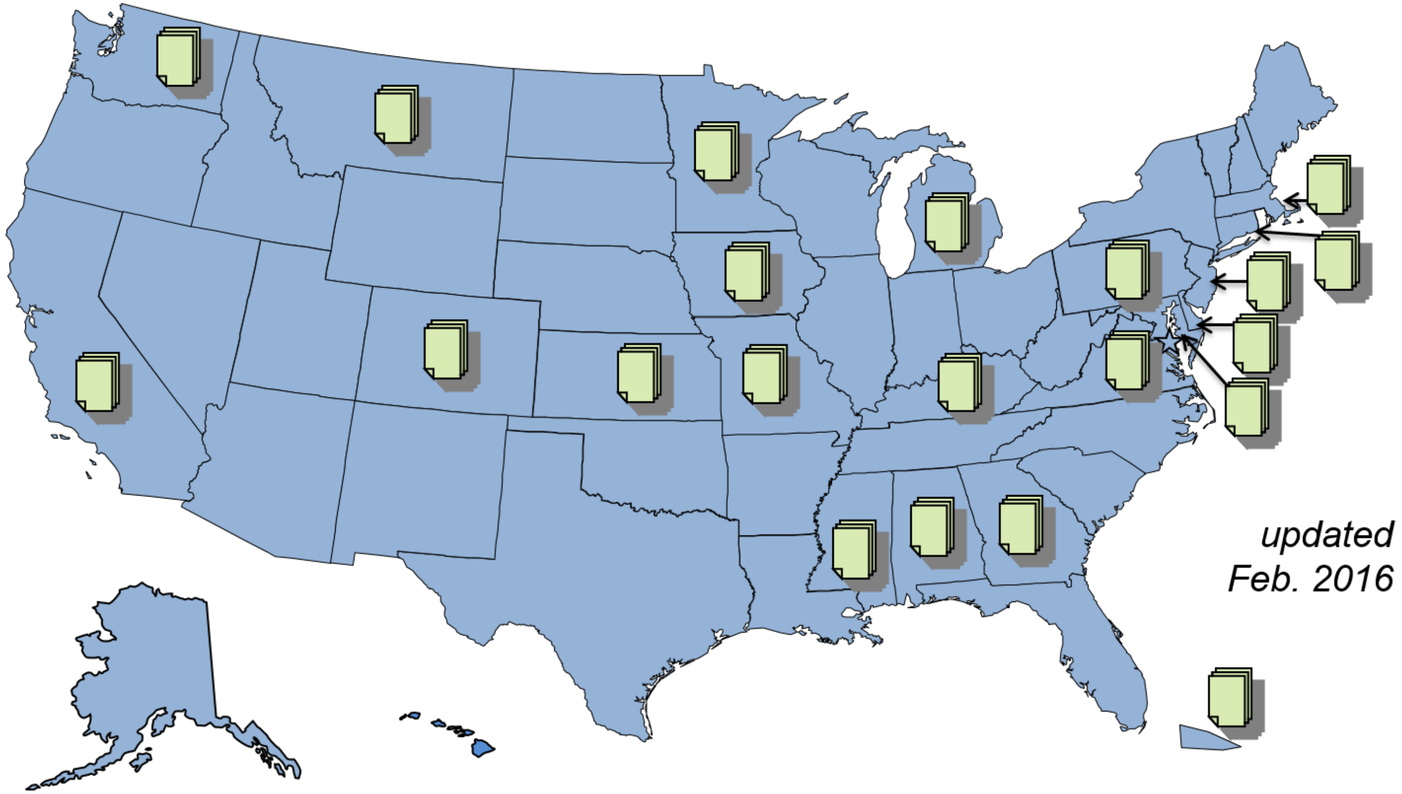
ITRC LNAPL document used or planned use at sites (reports by all environmental sectors)


Technical/Regulatory Guidance

Evaluating LNAPL Remedial Technologies for Achieving Project Goals

December 2009

Prepared by
The Interstate Technology & Regulatory Council
LNAPLs Team



- Link to State Guidance that References ITRC LNAPL Documents at www.itrcweb.org/LNAPLs under “Resources & Links”

Thank you!

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