Natural Source Zone Depletion and Conceptual Site Models

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P&O - remediation management
production & operations

Natural Source Zone Depletion

Represents a Conceptualization and Quantification of LNAPL source degradation in the subsurface

Primary mechanisms include

- Volatilization or soil gas transport
- Biodegradation
- Solubilization - estimated to representing a lesser component

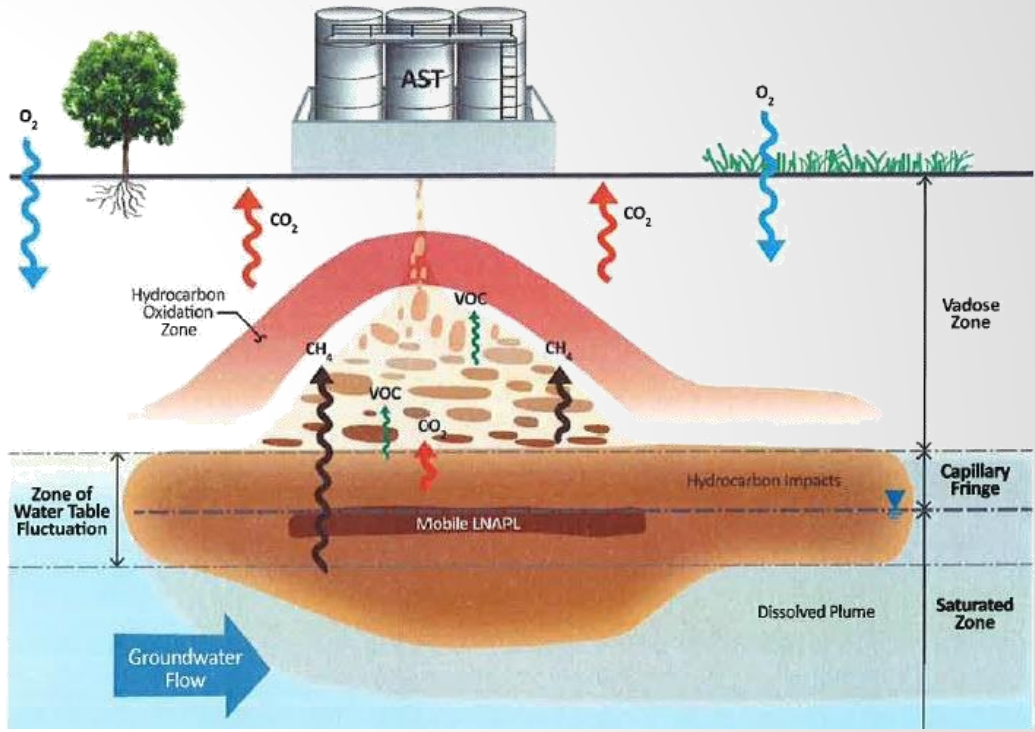
As oxygen becomes depleted or limiting in the source area other pathways that include additional electron acceptors or fermentation and methanogenesis are utilized by microbes

The methane produced rises in the vadose zone where it meets oxygen

Additional microbes then use the methane as substrate with oxygen and release heat and CO2 byproducts

The process results in compositional change of the source LNAPL

- More labile and volatile compounds are removed earlier in the sequence



API, 2017

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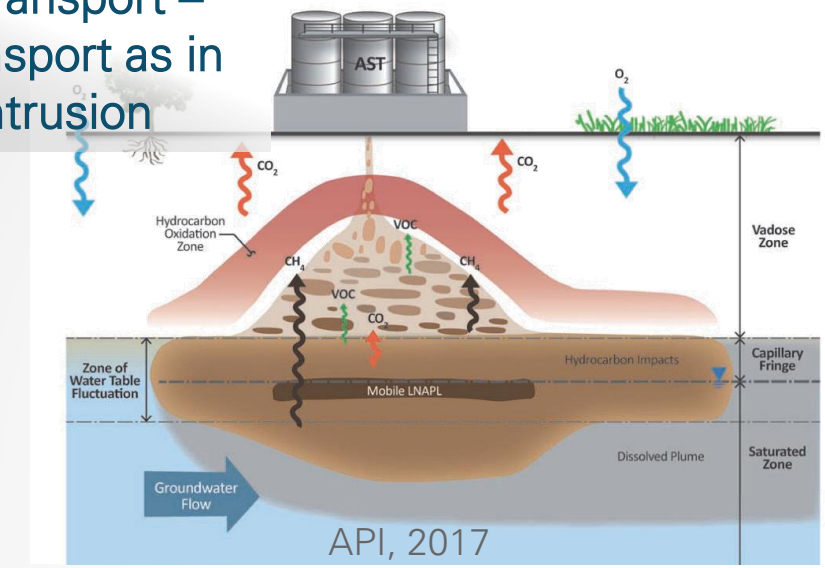
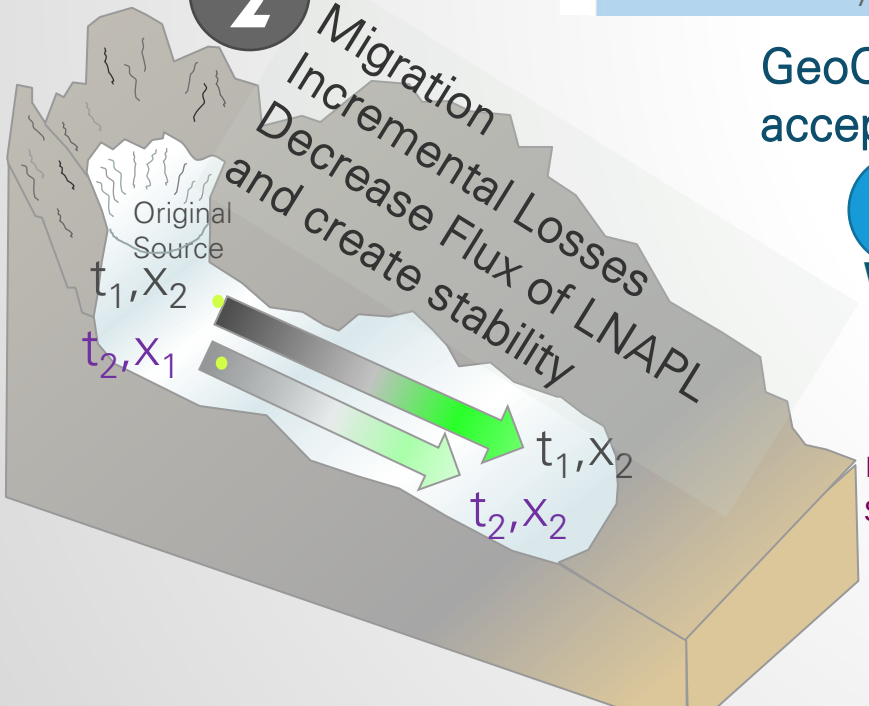
Natural Source Zone Depletion Disciplines

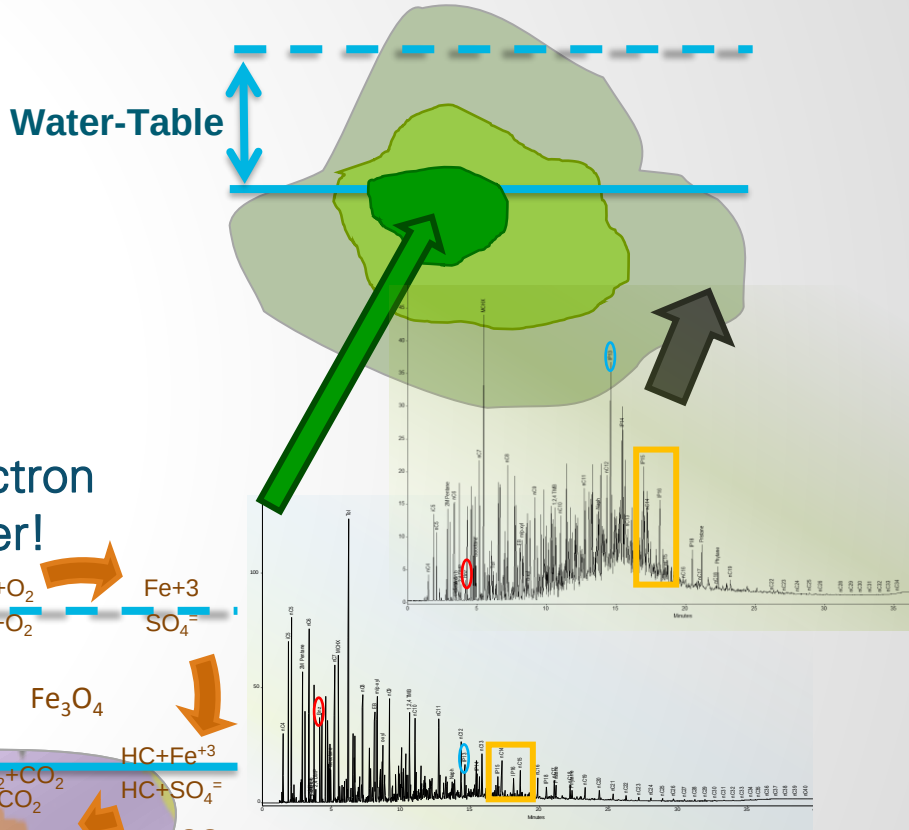
1 Vertical Soil Gas Transport – Same Soil gas transport as in petroleum vapor intrusion



2 Migration Incremental Losses Decrease Flux of LNAPL and create stability



3 Composition – Varies in the source zone over time and space



GeoChemistry – its not just dissolved electron acceptors and lateral flow, Minerals Matter!

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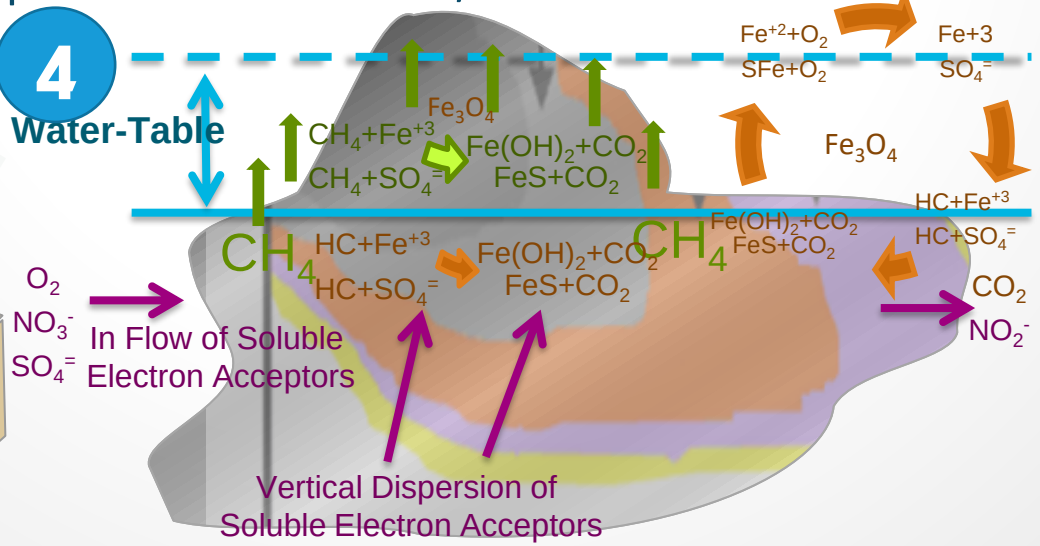

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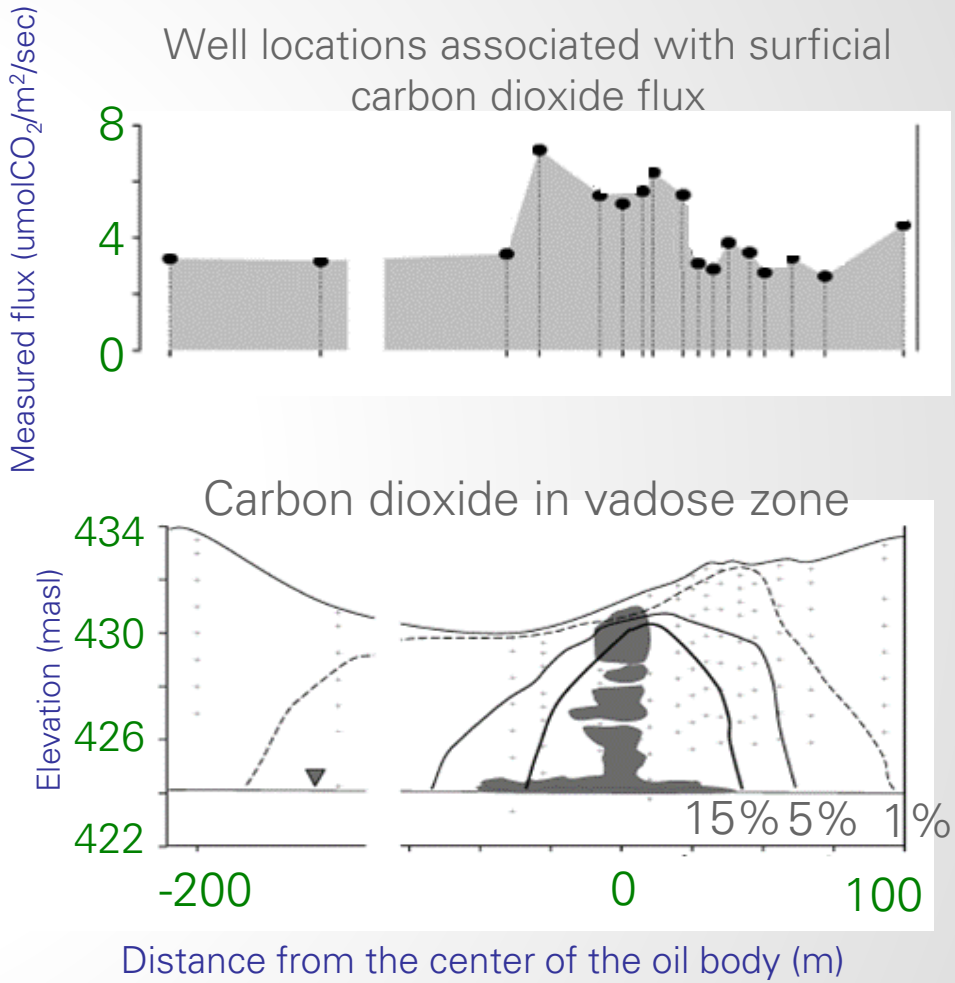
Soil Gas Use
Case Example: Bemidji, MN

- Soil gases measured at ground surface can support identification of LNAPL body
- Leverage monitoring wells screened across the water-table could also be used.
- Measure biogenic gases of CO2, CH4 and Oxygen can support identification of residual LNAPL source areas
- This also provides evidence for on-going biodegradation



Sihota et al. 2011

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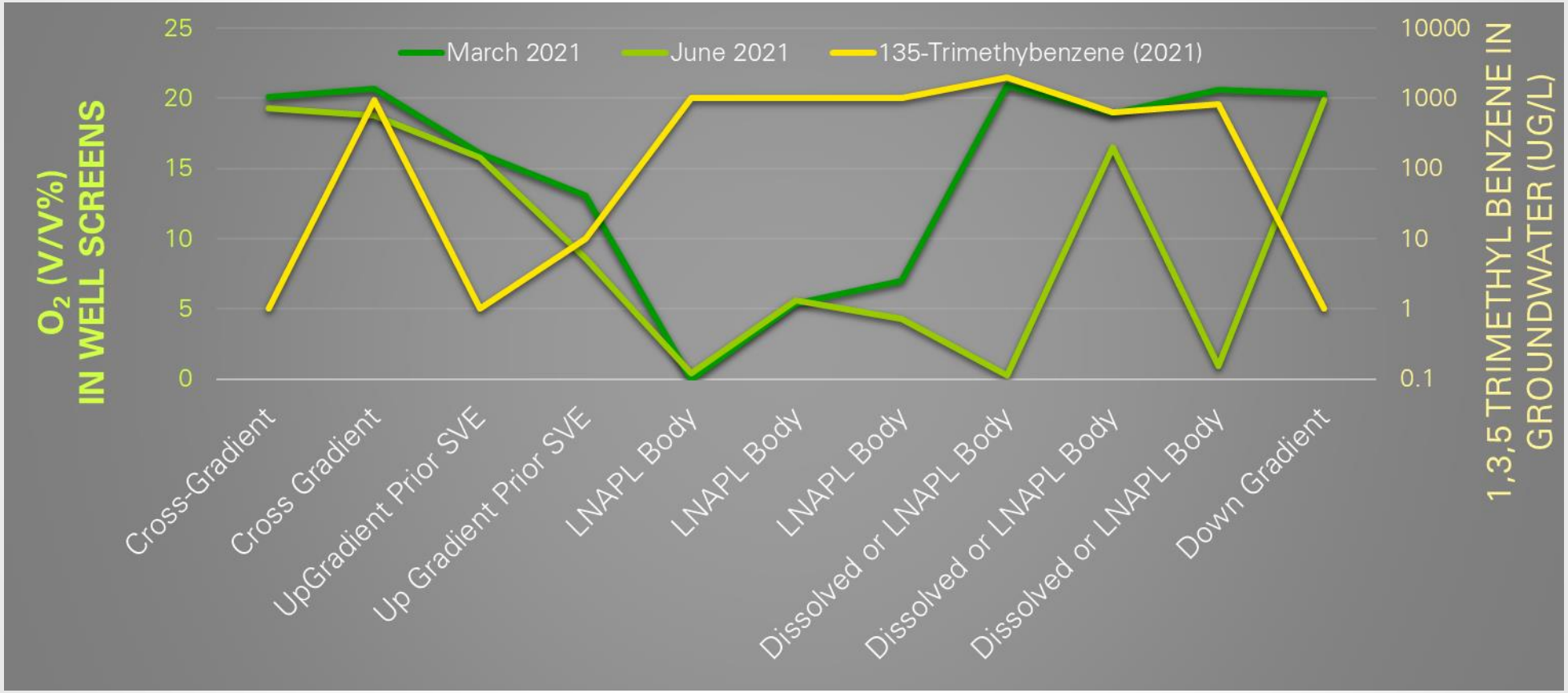
Oxygen Across a Site



Past Soil Vapor Extraction Treatments have resulted in benzene being removed from some source areas

Trimethylbenzene in groundwater was used in-lieu of benzene to represent both treated and untreated LNAPL source types

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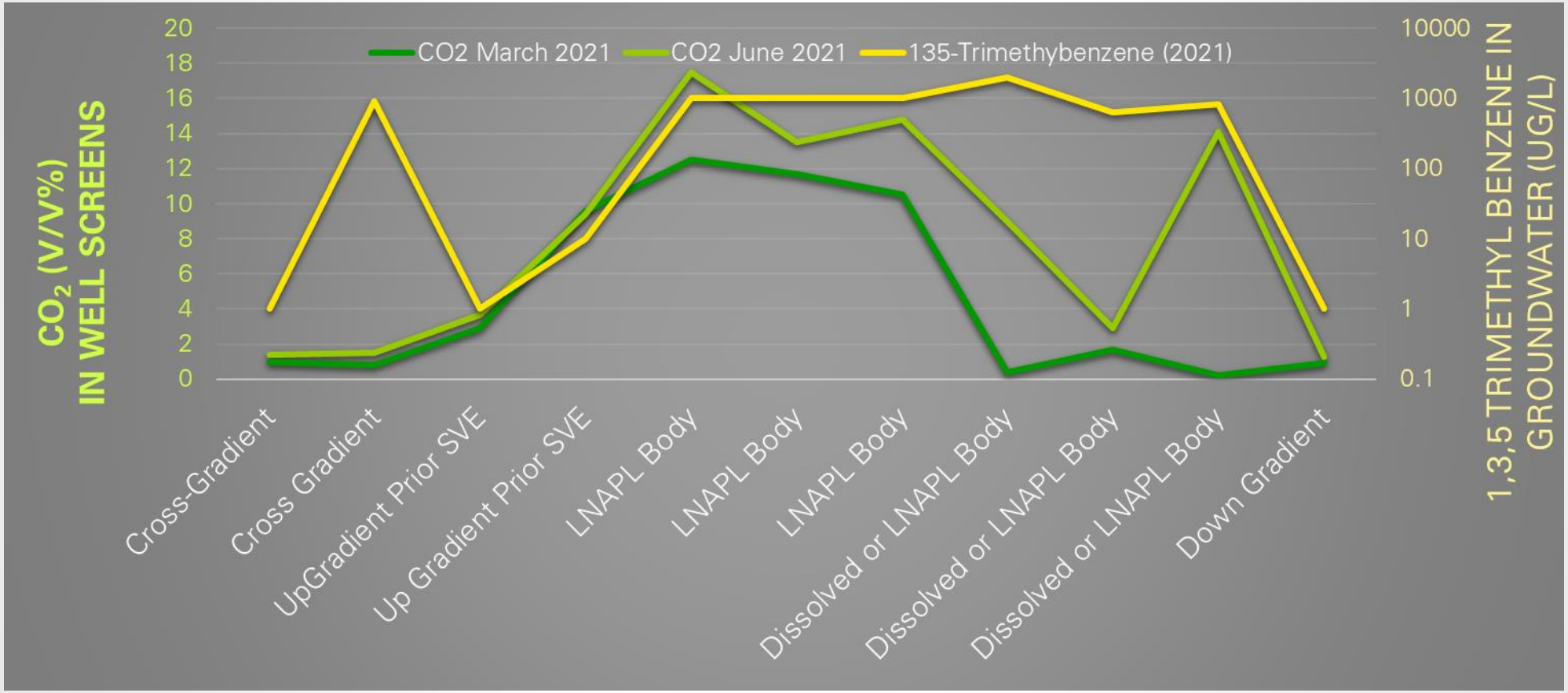
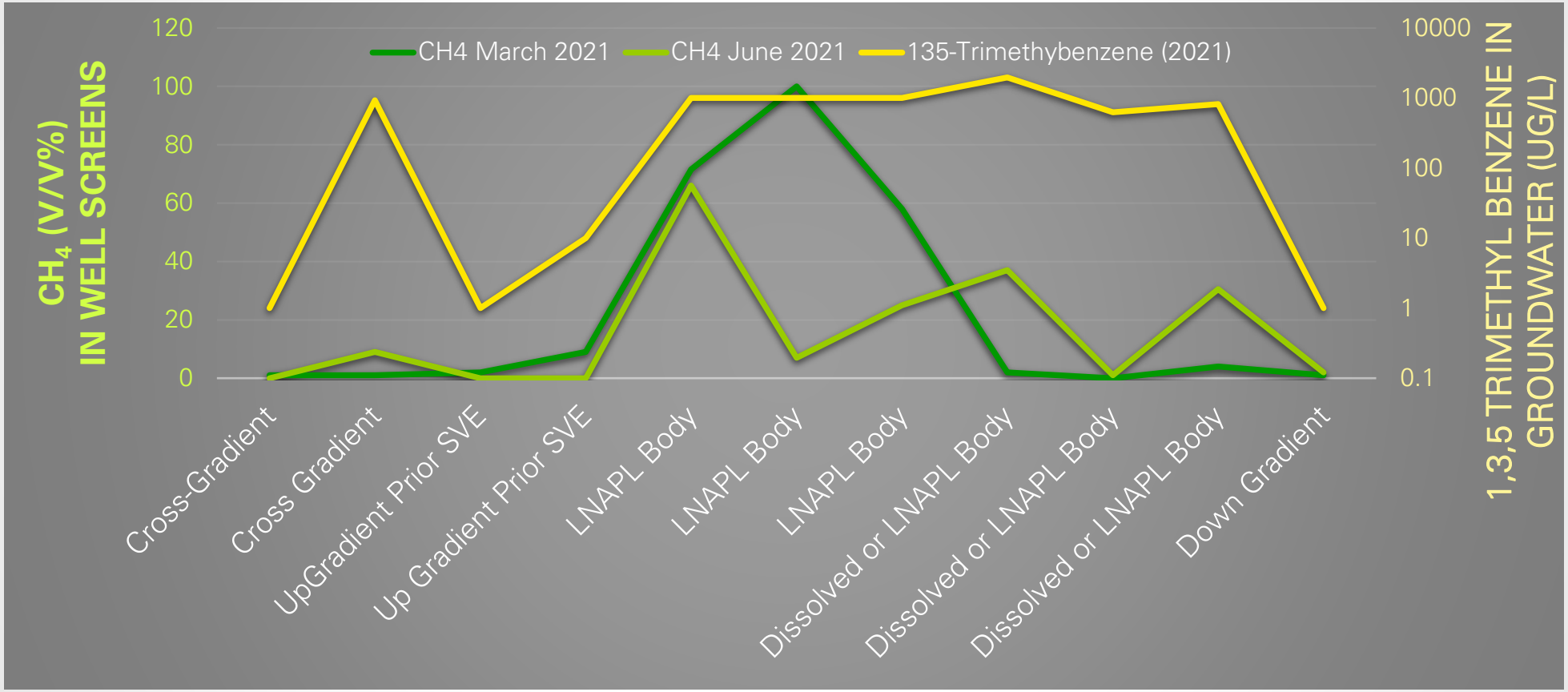
Carbon Dioxide Across a Site



Methane Across a Site – Note Improved Field Procedures needed



Confirming Biodegradation at A Site

Routine MNA Indicators

Declining dissolved concentrations

Qualitative Electron acceptor review (D.O., Methane, Nitrate, sulfate, iron)

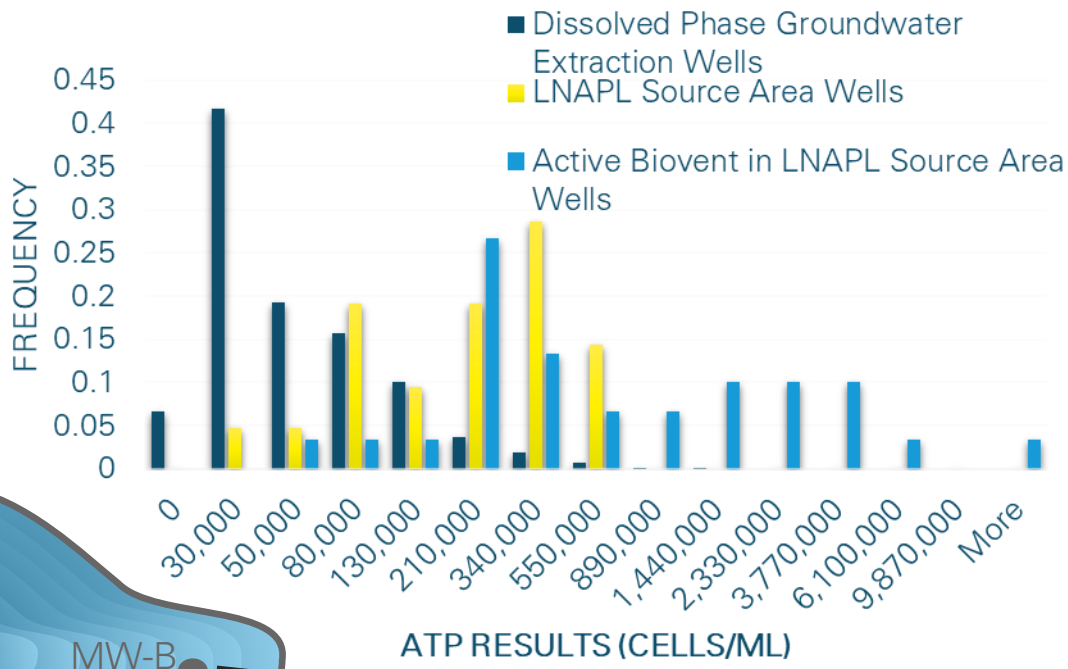
Dissolved phase focused without focus on source

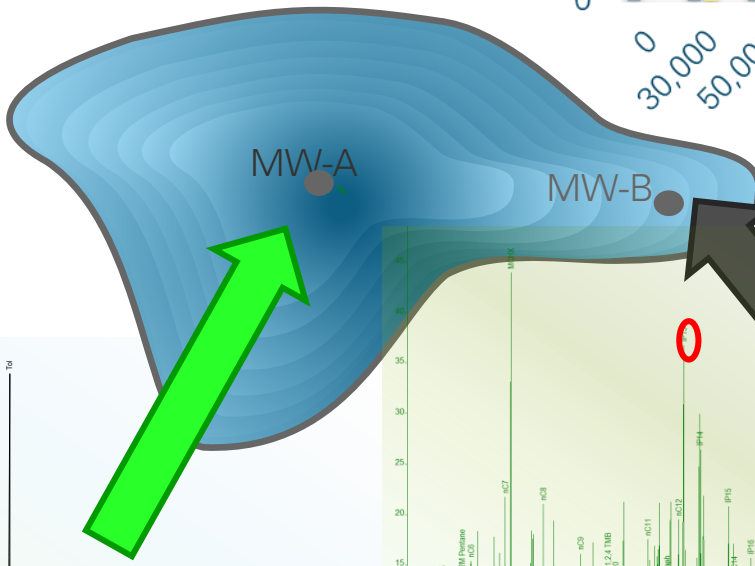
Additional Indicators Based on NSZD

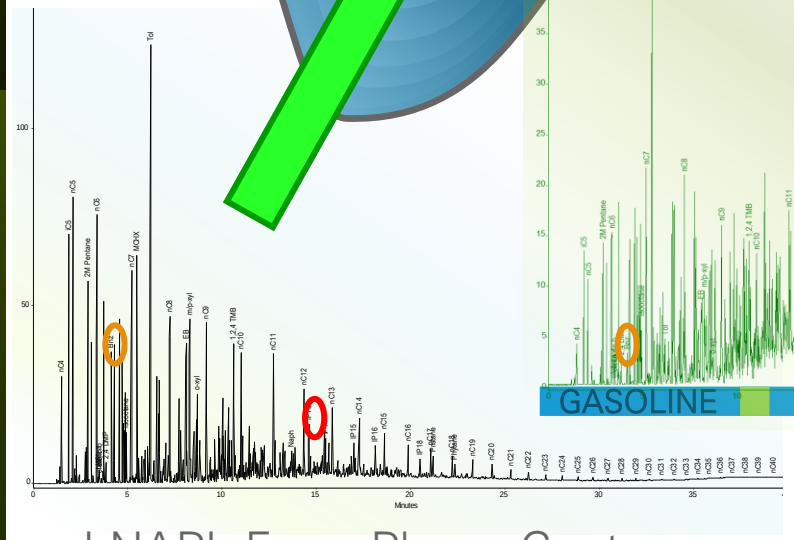
Soil gas using monitoring wells

Adenosine Triphosphate

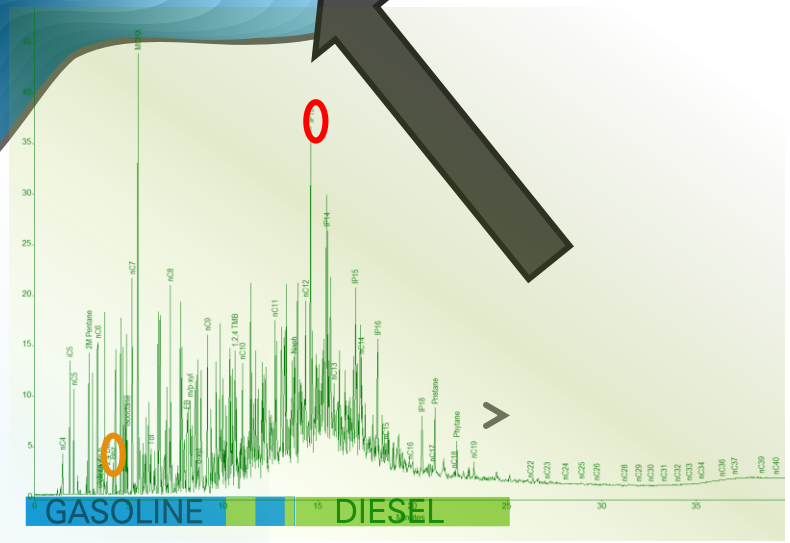
Compositional LNAPL change







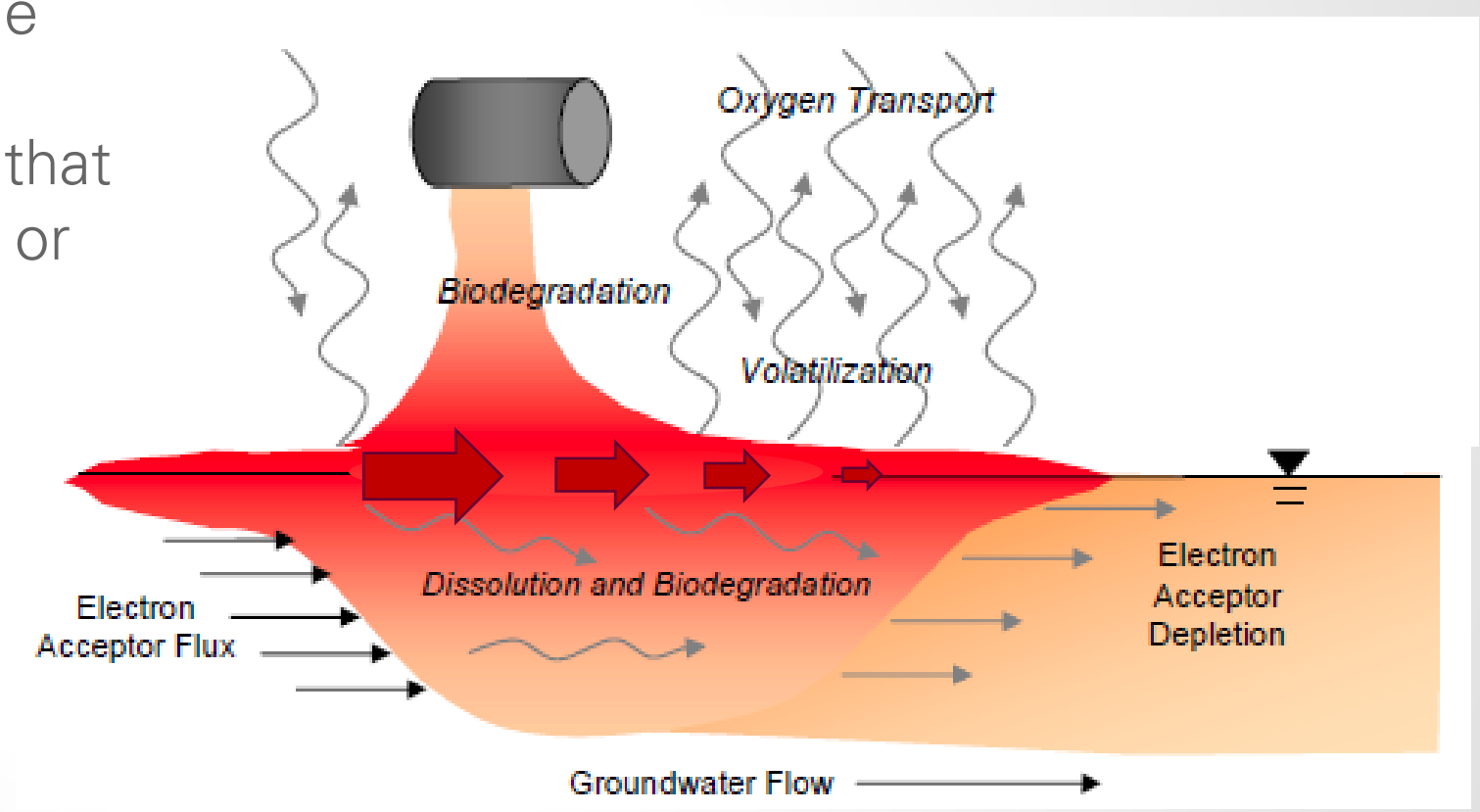
LNAPL From Plume Center



LNAPL near Plume Edge

LNAPL Body Stability vs Losses

Plume stability occurs when the perimeter of the plume attains sufficient size or location such that attenuative mechanisms equal or exceed the mass flux at that boundary. (DOE, 1999)



After ITRC

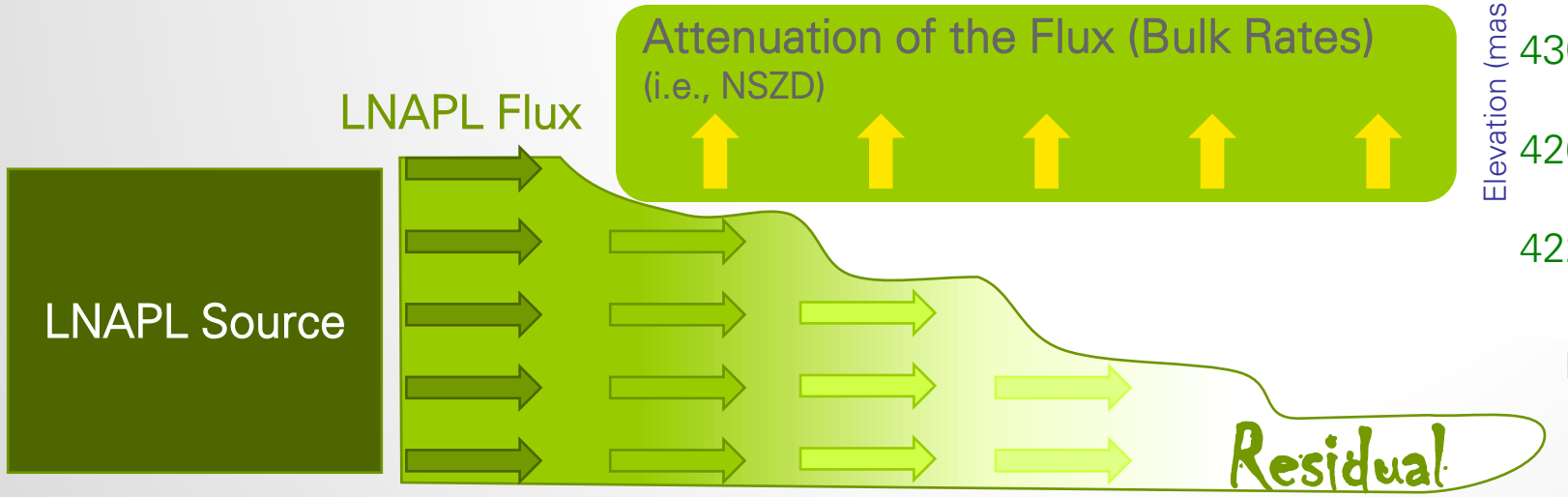
Plume Stability
Case Example: Bemidji, MN

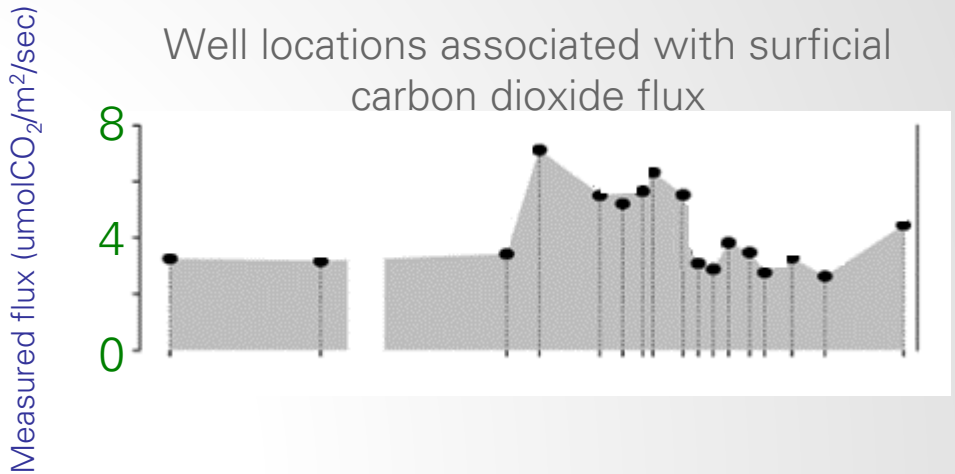
- Measured LNAPL discharge compared to Measure Losses
- $Q_{oil} = k_{oil}\ i_{oil}$ Area
- 2.2 kg/d leaving infiltration area

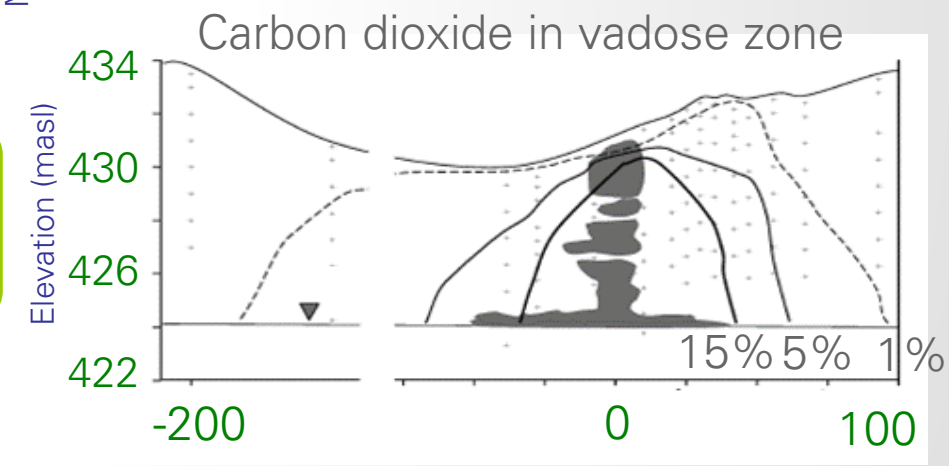
CO2 flux, proxy for LNAPL mass depletion

- 4.3 kg/d over downgradient area

Lundy, 2012 and Sihota et al. 2011







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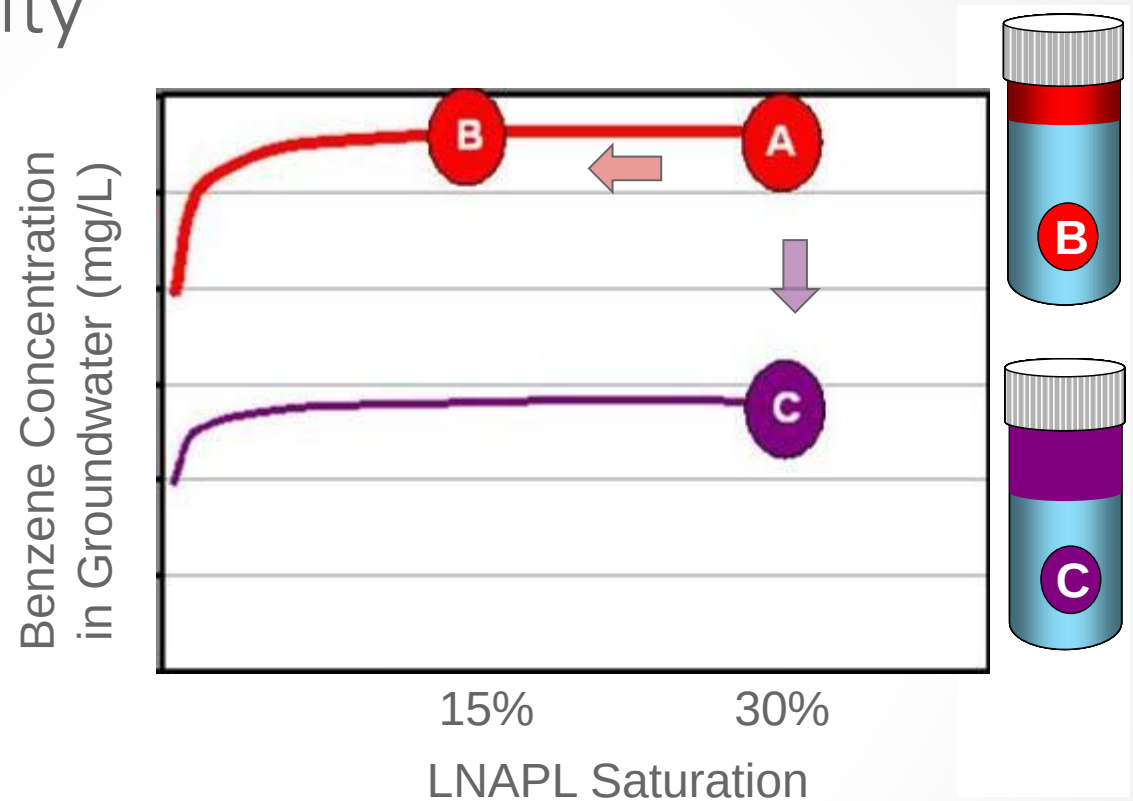
Composition of the LNAPL generally drives Groundwater Solubility

- ITRC discusses the concepts of <u>composition vs saturation</u>
- Compositional or Phase change technologies remove more toxic compounds such as benzene which reduces benzene in groundwater and soil vapor
  - e.g., Sparging, soil Vapor extraction, biodegradation
  - NSZD can result in compositional change



Source: Dr. Sanjay Garg and ITRC LNAPL training

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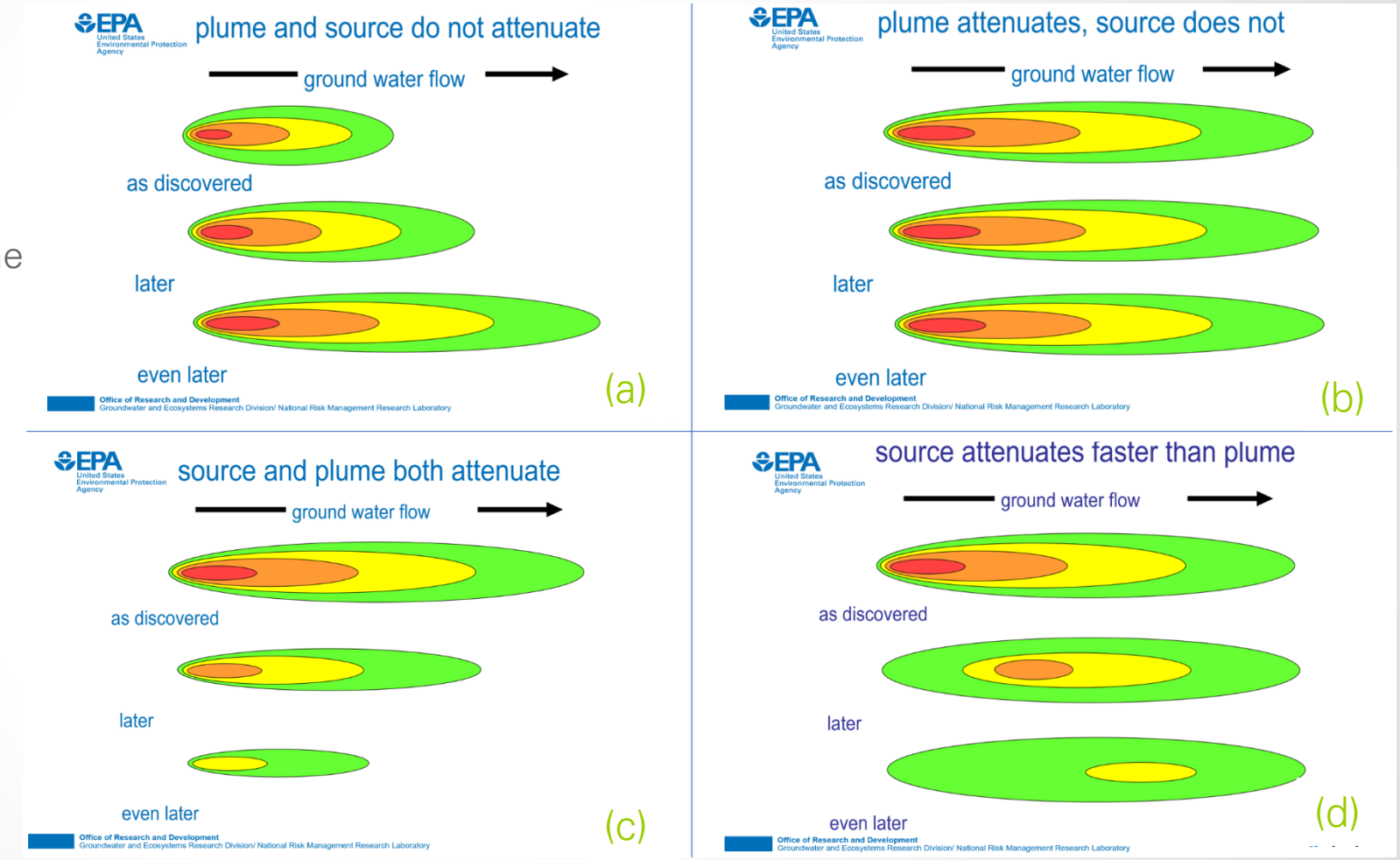
Stability and evolutions of the Source is reflected in Dissolved Phase Trends

The extent of dissolved is controlled by attenuation in the dissolved phase

The evolution of dissolved phase over time controlled by source attenuation



Source: Wilson et al., 2005 and Wilson, 2010

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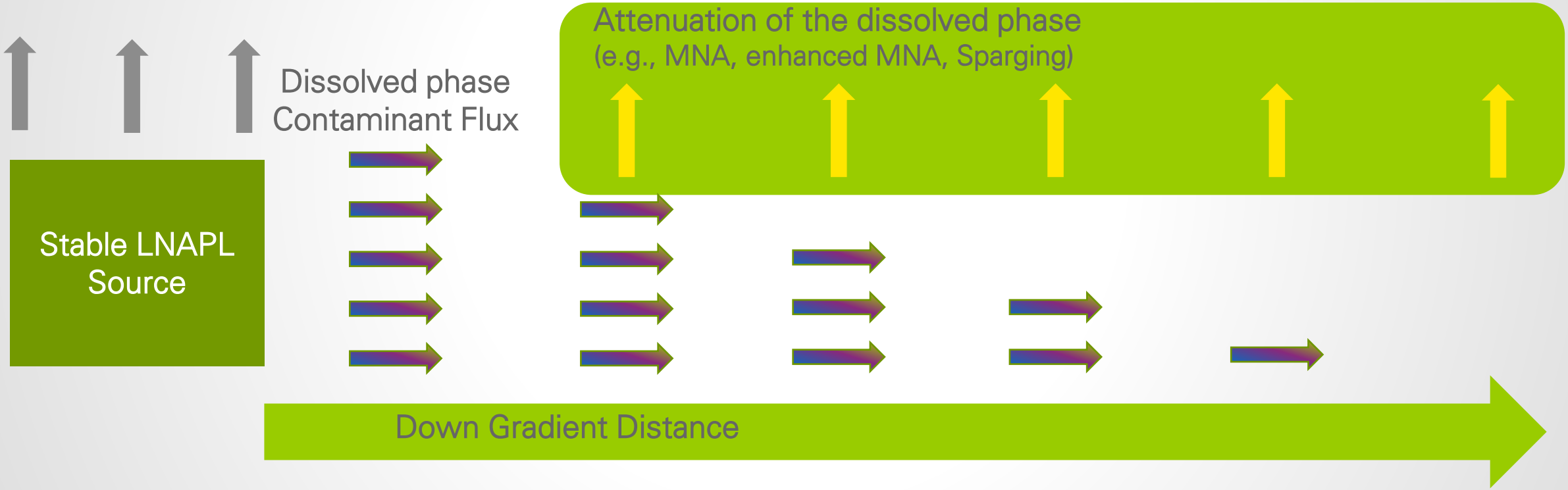
LNAPL and Dissolved Attenuation Pattern

Losses Balance out the Flux

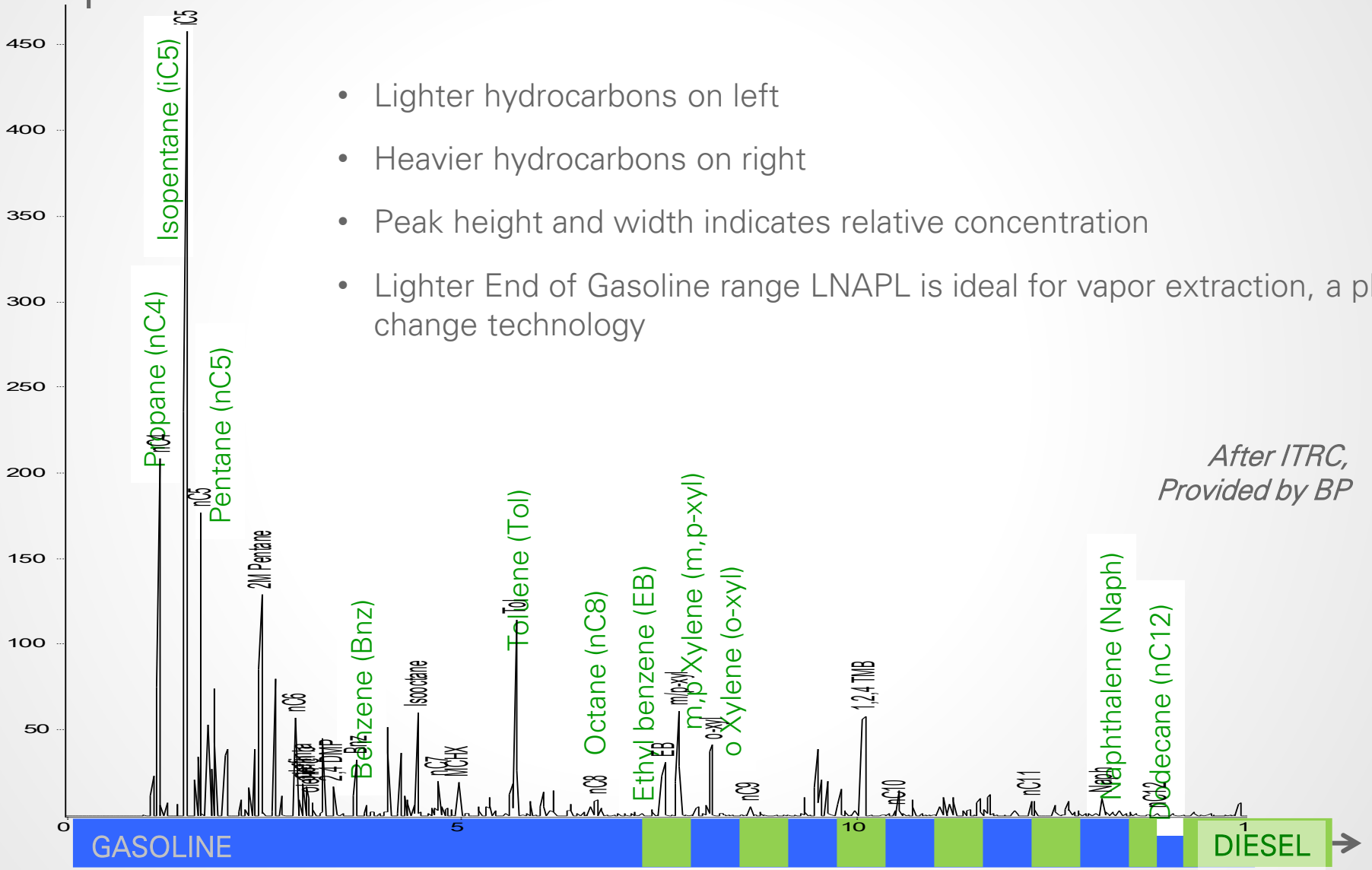
Scenario 2
Source Compositional Change Ongoing
Attenuation or Mass Control of Flux



See ITRC LNAPL-3 documents for more information on compositional change

LNAPL composition data

- Lighter hydrocarbons on left
- Heavier hydrocarbons on right
- Peak height and width indicates relative concentration
- Lighter End of Gasoline range LNAPL is ideal for vapor extraction, a phase-change technology



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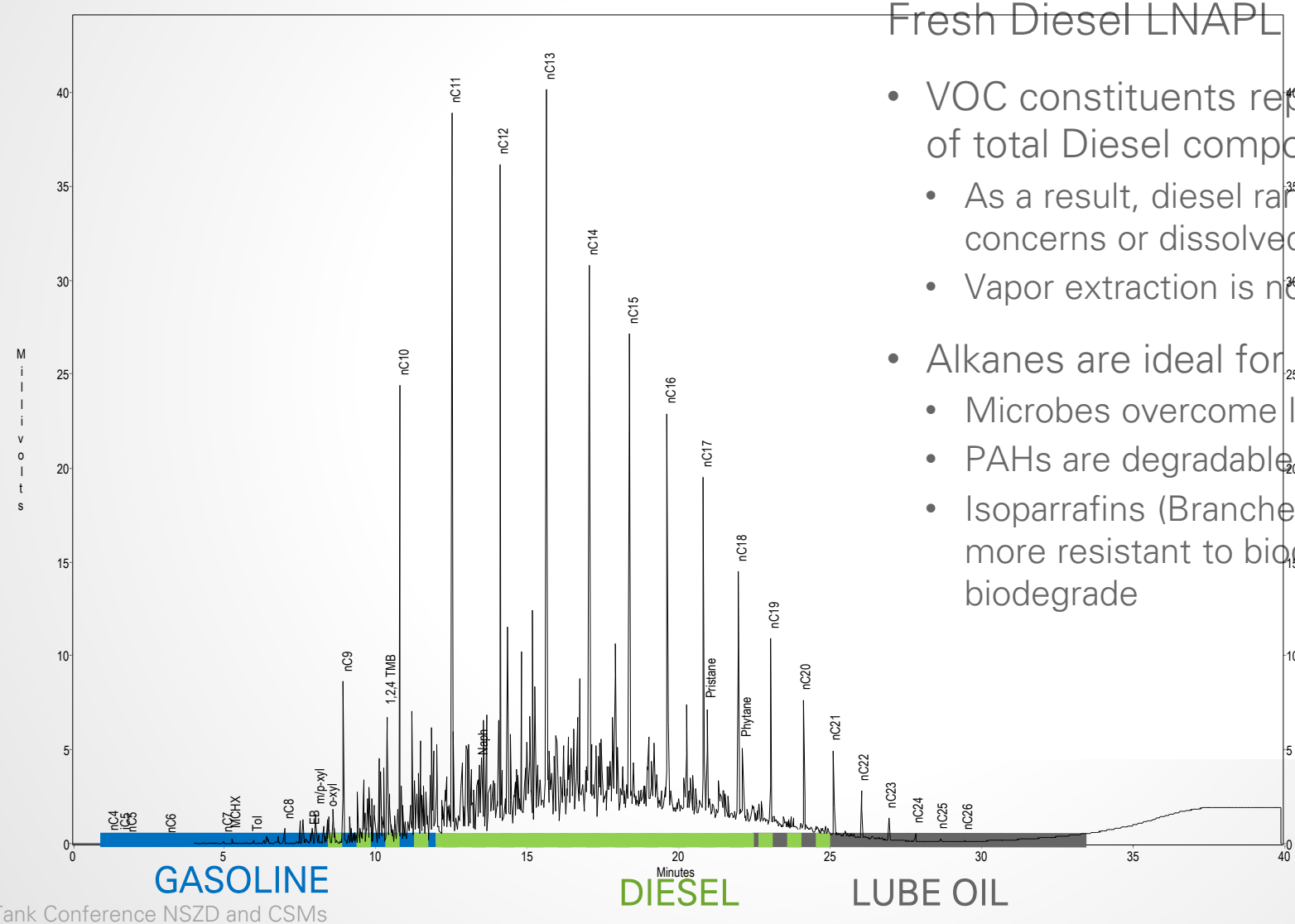
Low Volatility LNAPL- Diesel



Fresh Diesel LNAPL Example

- VOC constituents represent a tiny fraction of total Diesel composition
  - As a result, diesel rarely generates vapor concerns or dissolved phase BTEX concerns
  - Vapor extraction is not effective
- Alkanes are ideal for biodegradation
  - Microbes overcome low solubility of alkanes
  - PAHs are degradable but at lower rates
  - Isoparrafins (Branched Hydrocarbons) are also more resistant to biodegradation but still biodegrade

After ITRC , Provided by BP

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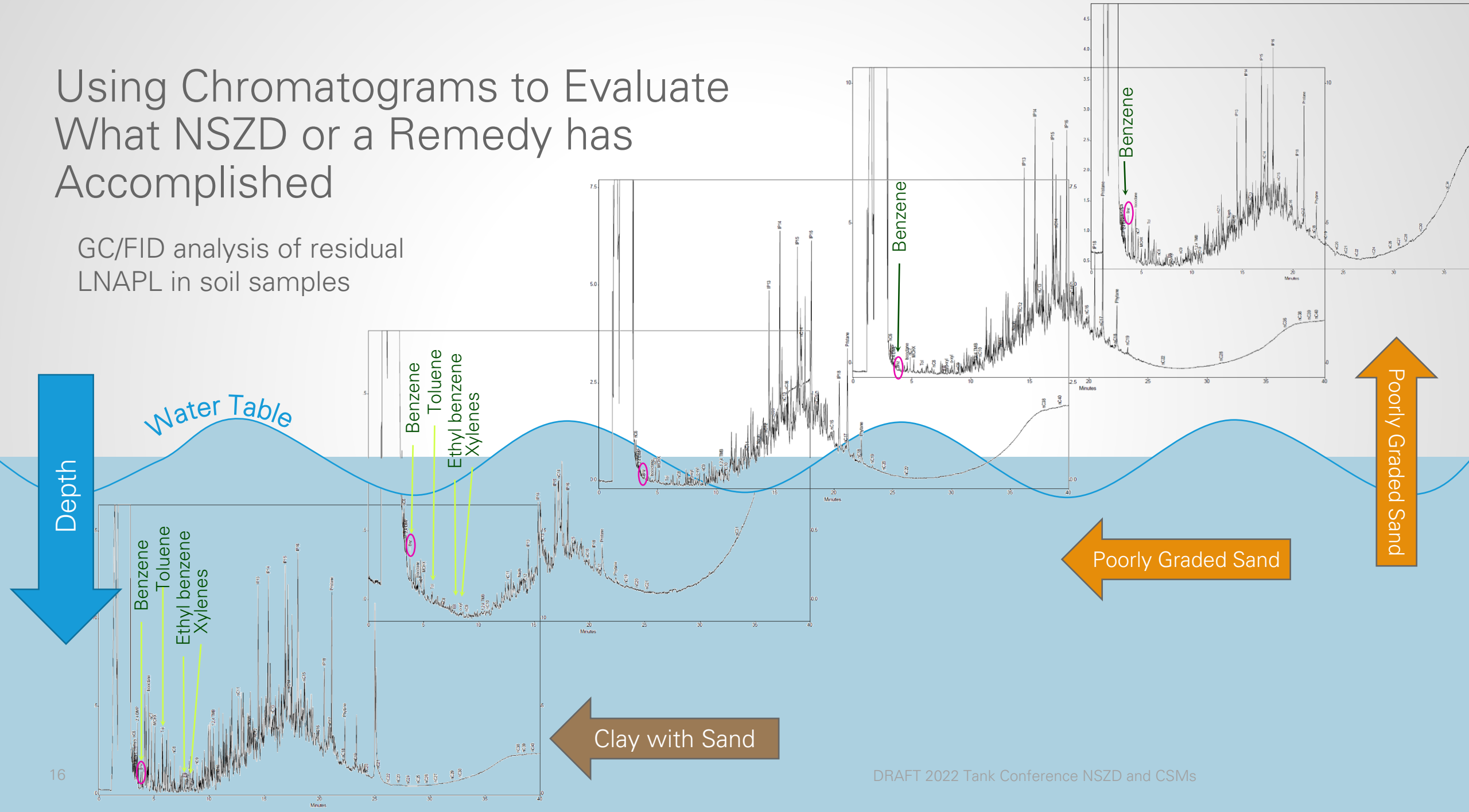
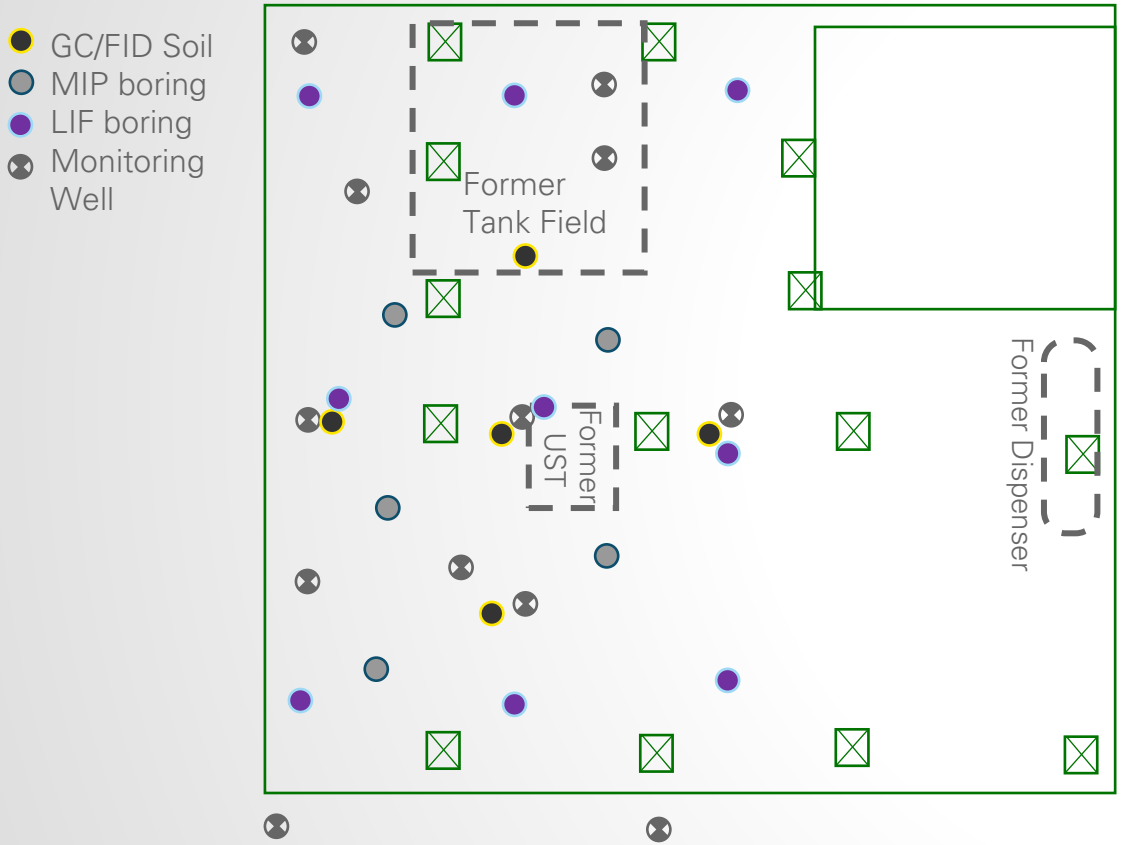
Using Chromatograms to Evaluate What NSZD or a Remedy has Accomplished

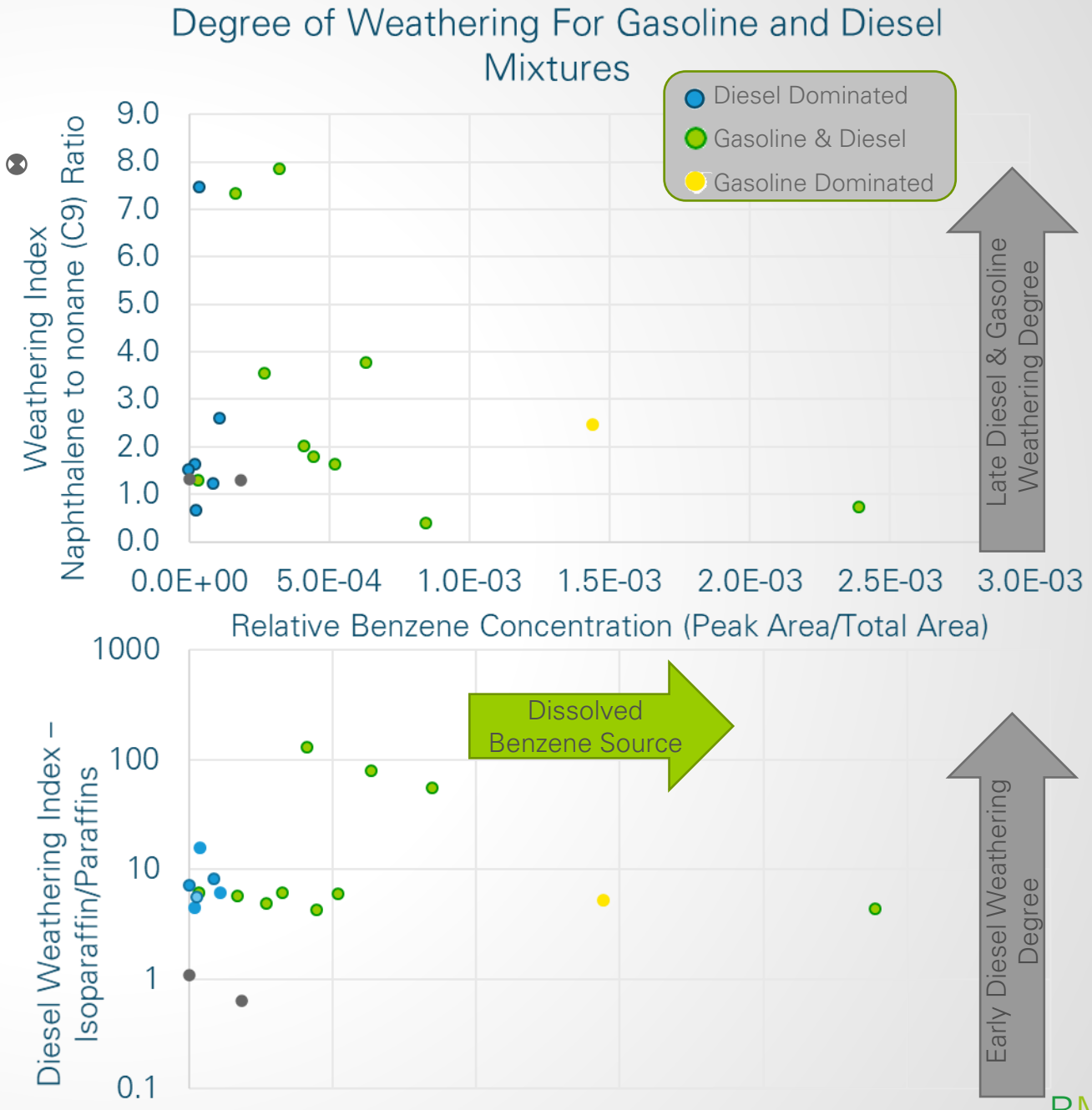
GC/FID analysis of residual LNAPL in soil samples



Former Retail Site

Elevated building above Parking





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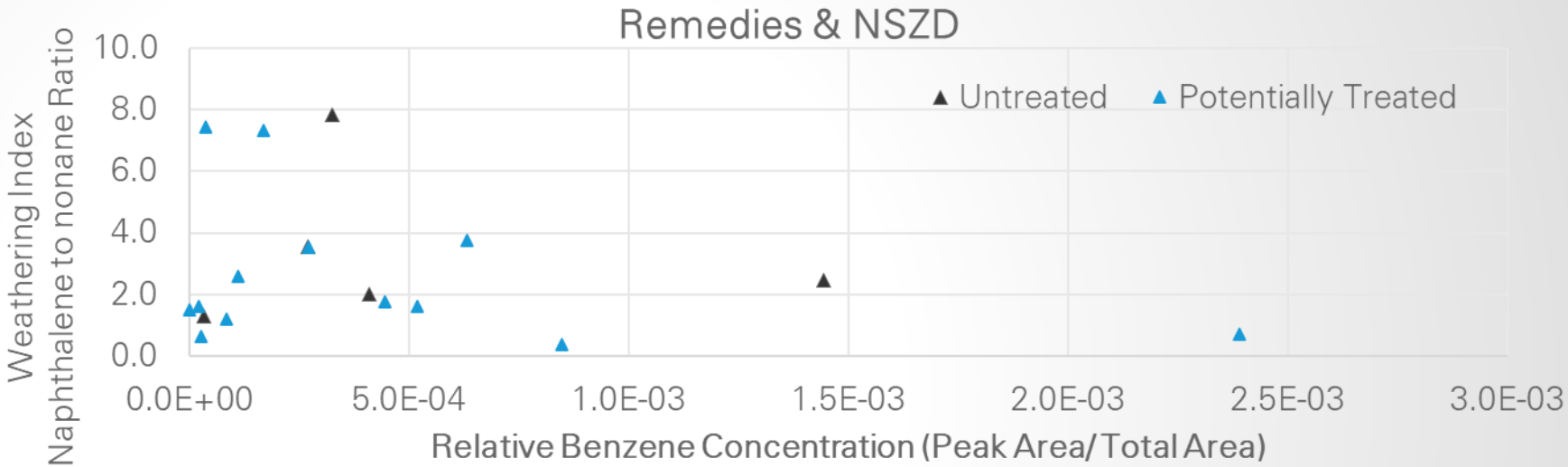
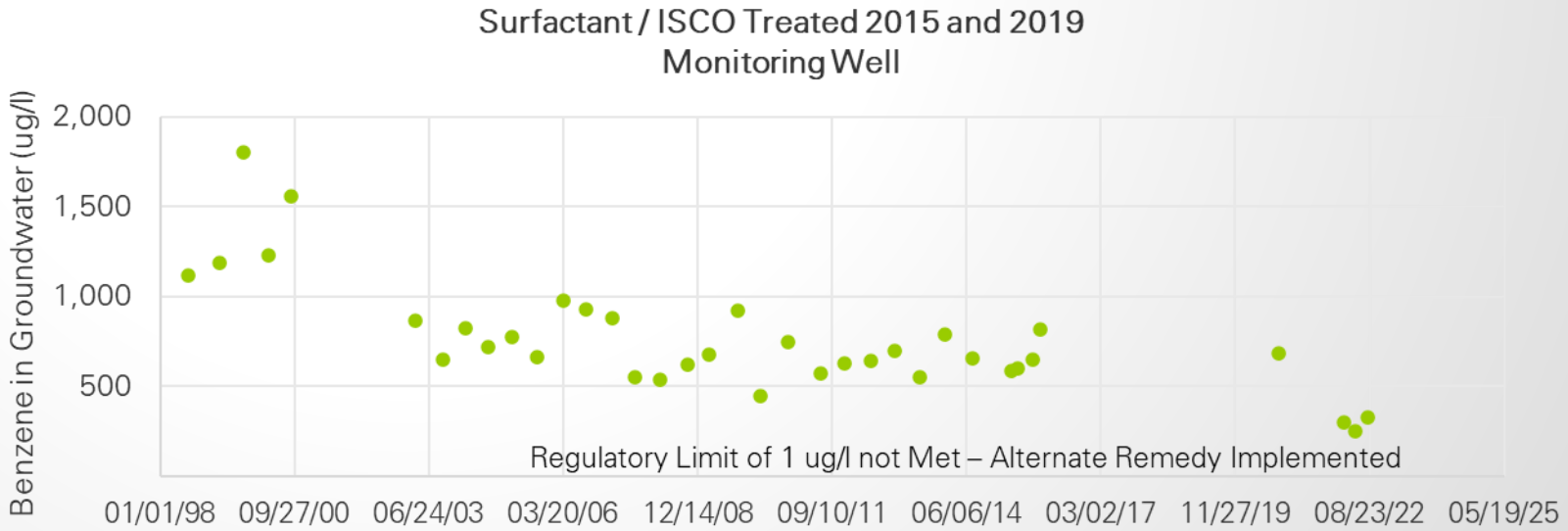
How did remedies fair Relative to Natural Source Zone Depletion

Two groups of data

- Black dots no Remedies applied in this area
- Blue dots had 2 rounds of surfactant and 1 round of ISCO injected with some difficulties in extraction and injection
- Maximum of 300 gallons in total liquid removed /injected per well, per event
- Similar too ~ 3-foot treatment radius across a 5-foot thickness of 30% porosity soil each event.
- Current Remedy is a Permeable Reactive Barrier – activated carbon





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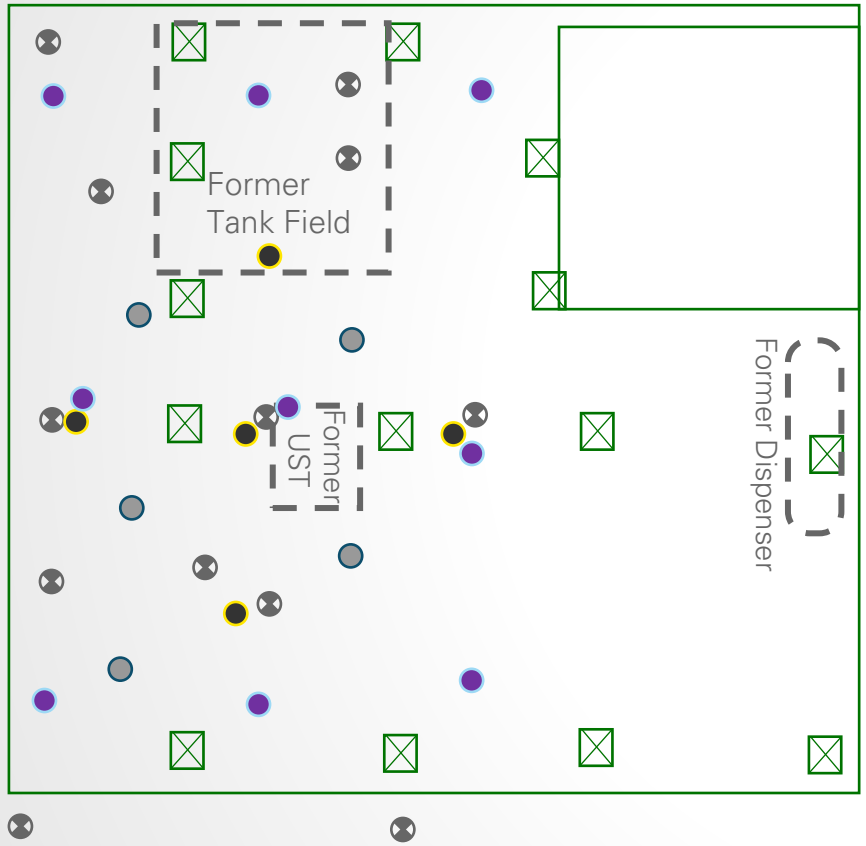
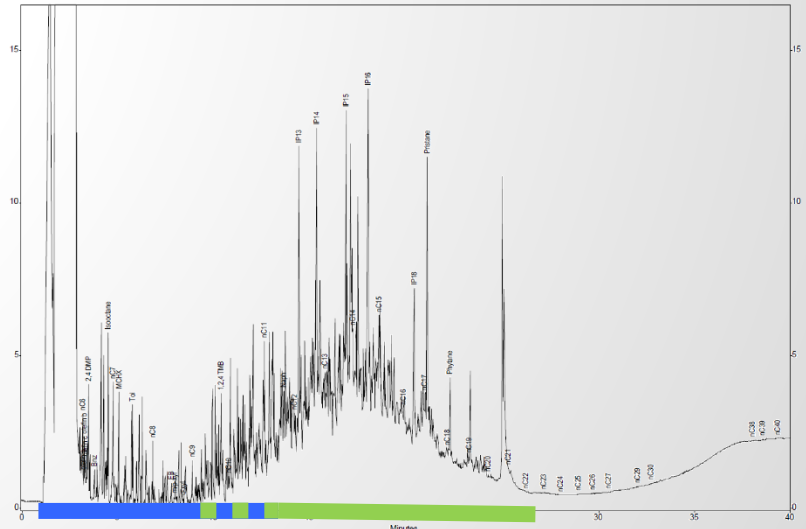
Former Retail Site

Elevated building above Parking

GC/FID Soil
MIP boring
LIF boring
Monitoring Well



- Treated location exhibited on average 10% lower benzene concentration in NAPL than un-treated locations
  - Need an Alternate Approach
- Biodegradation was suggested across the soil profile above and below the water-table
- Remediation should account for the larger oxidation demand supported by residual LNAPL characterization than indicated by groundwater BTEX mass alone



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There is More than Rates to NSZD
It is Part of the current Practice

NSZD characterization typically is focused on measuring a bulk rate of hydrocarbon degradation and aligns with remedial technology selection

Even before remediation phase for legacy sites, NSZD supports

- Plume Stability
- Toxicity reduction of sources
- Additional characterization approaches for sites

The Expression of NSZD can be used in CSM development to support

- Residual LNAPL source delineation
- Demonstration of microbial activity in source area
- Understanding which LNAPL source zones have highest remaining benzene
- Supports understanding dissolved phase contaminant trends in groundwater
- May indicate how to best enhance these processes to support active remedial technology selection

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GUIDANCE ON NATURAL ATTENUATION FOR PETROLEUM RELEASES (epa.gov)

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