Understanding the Cumulative Effect of NSZD through Compositional Analysis

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Why Compositional Changes?

- LNAPL composition is important for physical behaviour and environmental consequence, and will evolve over time
- Direct measure of the effect of NSZD on source composition
- Understand how (multiple) NSZD mechanisms (weathering) varies across a site, and in terms of specific components
- Potentially, attribute difference in weathering to LNAPL distribution relative to water-table, soil type, moisture content, or other features.

Consider

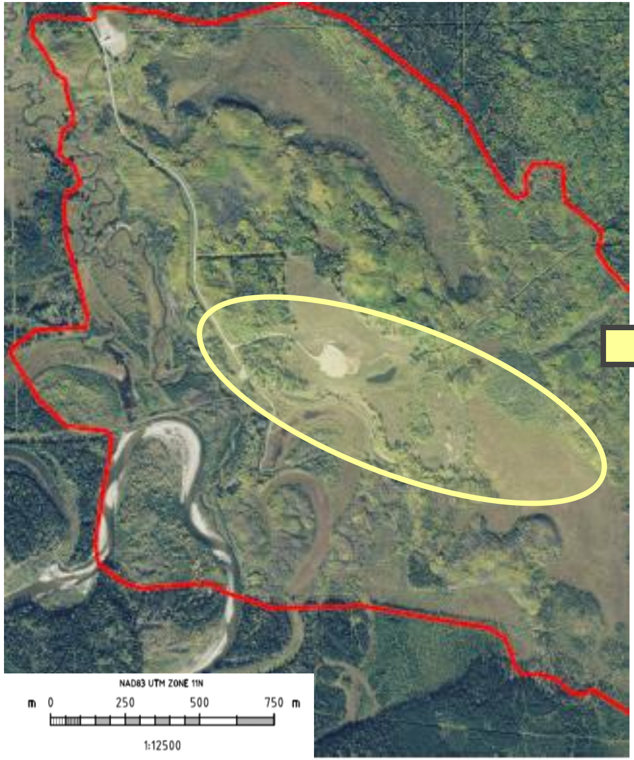
- May be able to measure differences in bulk rates across a site
  → Could we gain more insight on source area risk remaining?

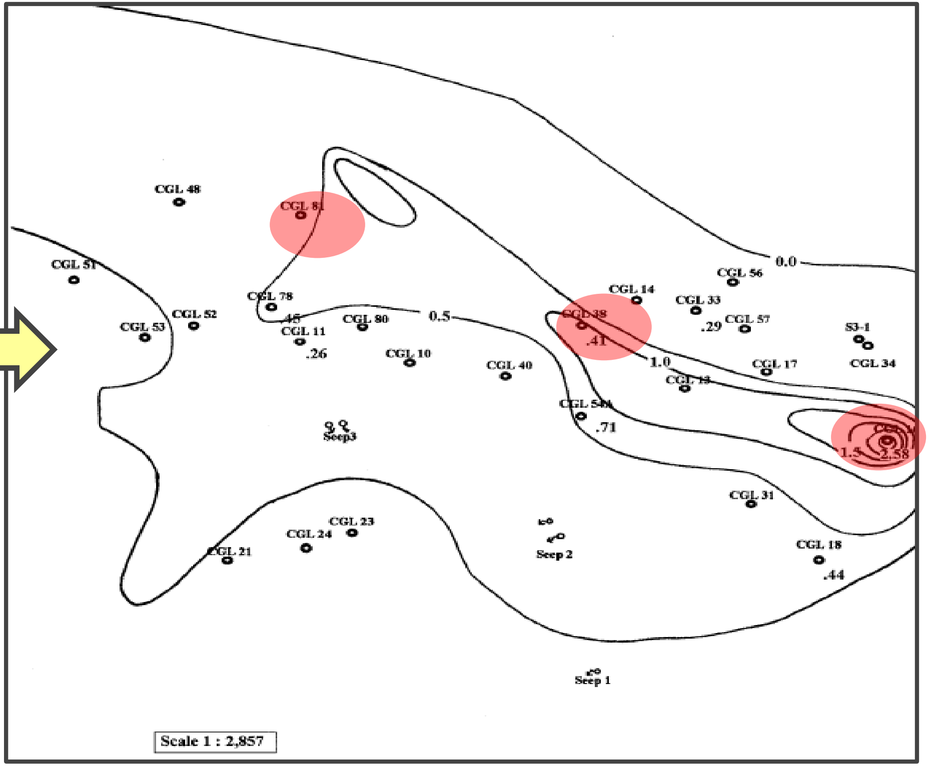
- Enhancement of our CSMs, such that:
  → improved selection of remedial technologies
  → improved targeting for remediation areas
  → improved understanding of processes and effect on NSZD rates?

Objectives

- Approach
- Key learnings
- *Application to an Alberta Site

Former Blowout Site





Product Thickness (m), 1983

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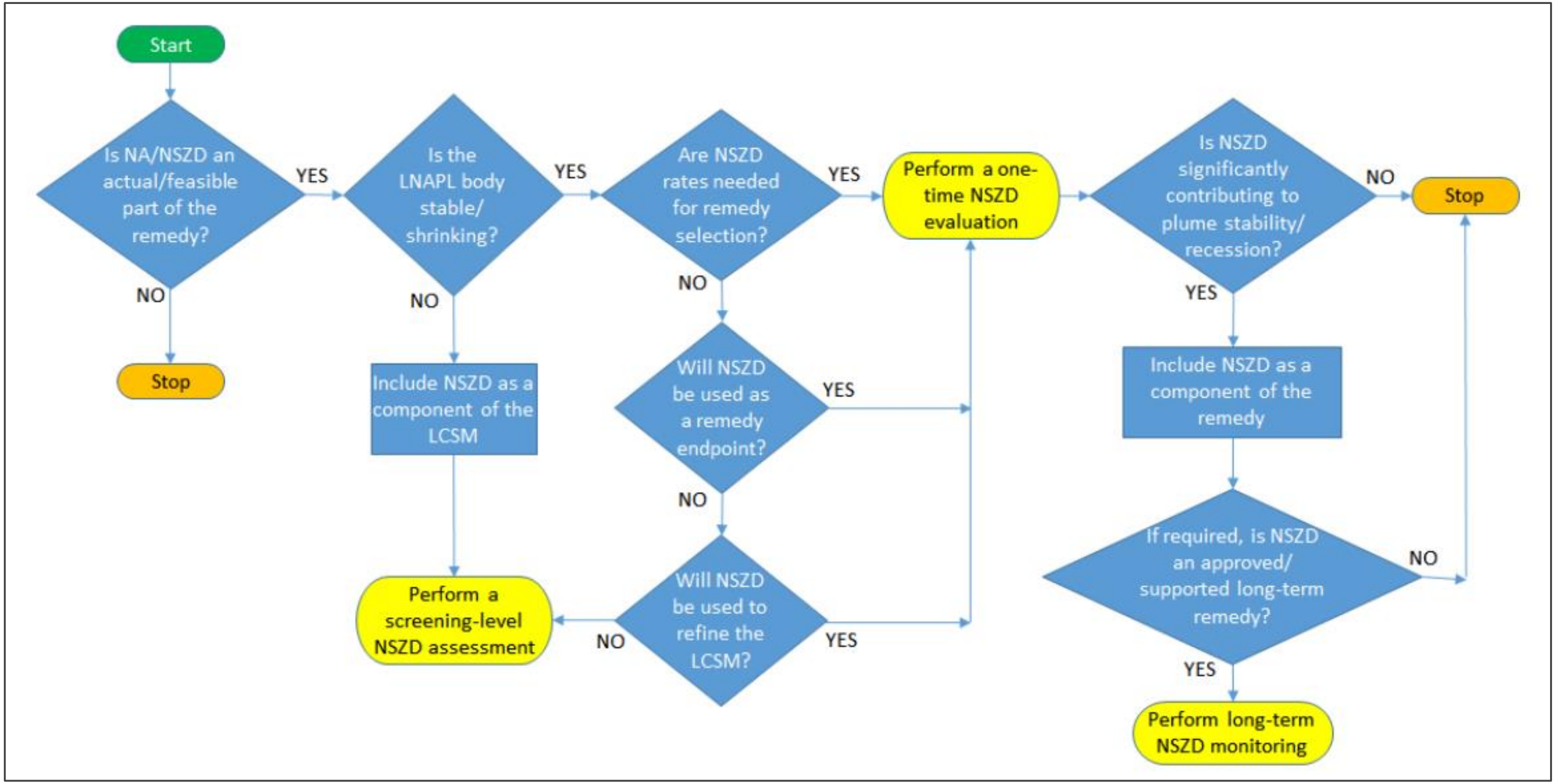
Goal: Sustainability Assessment, NSDZ as "base case"



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Decision logic flowchart for selection of NSZD measurement data quality levels; Technical measurement guidance for LNAPL natural source zone depletion; CRC Care, 2018

Approach

A mixture of two compounds

Initial Time
1 mole
1 L
1 M

Evaporation

Affects only 1 constituent

Future Time
1 mole
X (Final Volume)
1.6 M

Volume Lost = 1 L - X

$$Volume\ Lost = V_{T,i}\left(1 - \frac{C_{\alpha,i}}{C_{\alpha,t}}\right)$$

=1 *(1-1/1.6)

= 375 mL

… and over time

Cumulative Loss in Mixture as a whole

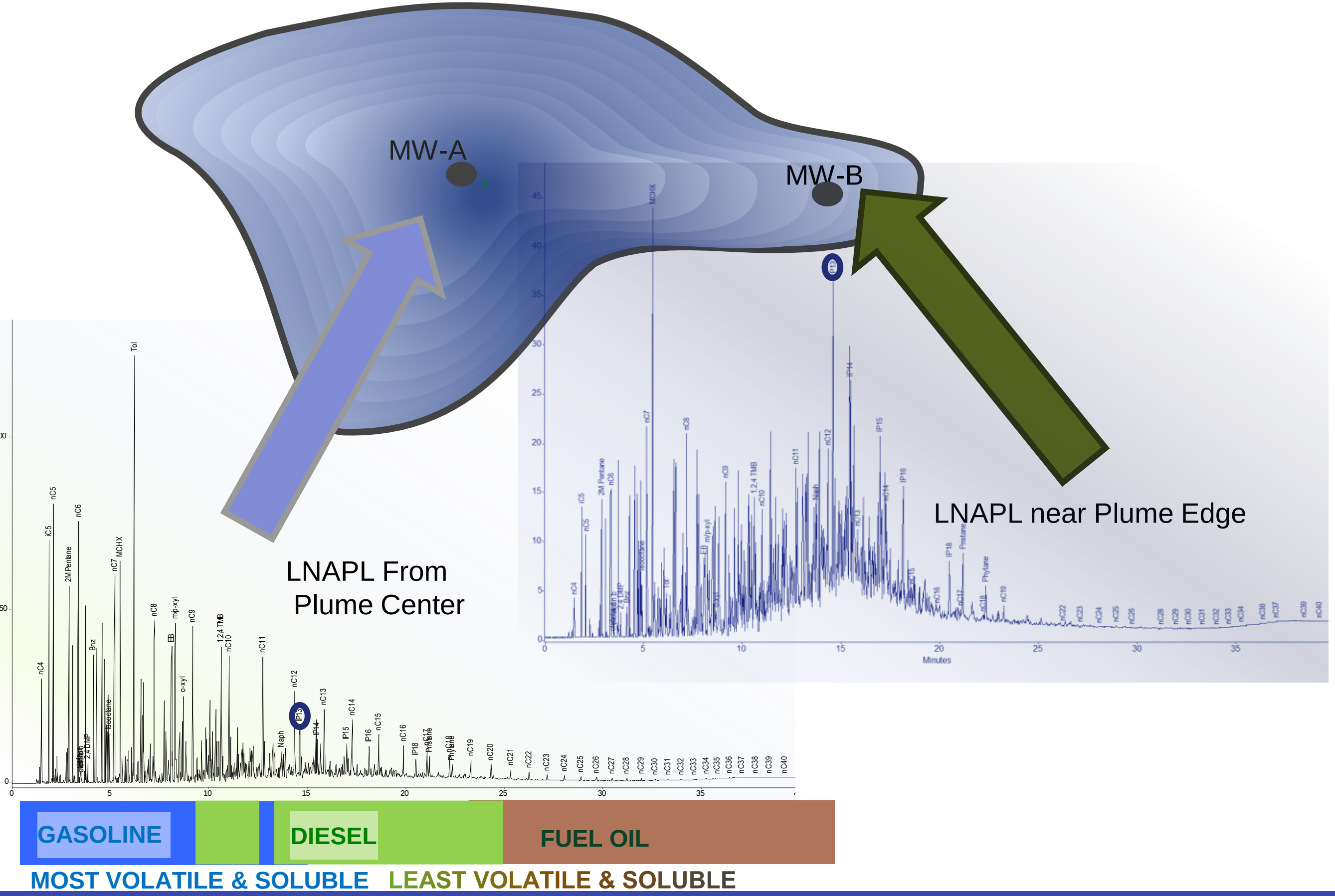
Same Theory Applied to Hydrocarbon & Chromatograms – Gas Chromatography, Flame Ionization Detector (GC-FID)

Total moles of the mixture decreases over time

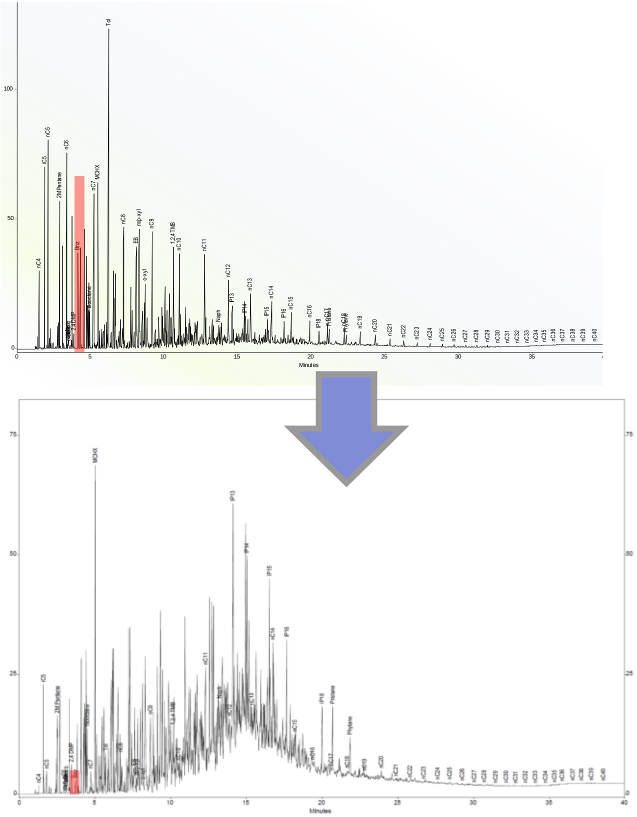
Bio markers (α) are compounds with moles staying constant (not degraded) - mole fraction continuously increases

Modified equation represents **Cumulative LNAPL Fraction Lost:**

$$\frac{\sum L_t}{M_{T,i}} = \left(1 - \frac{X_{\alpha,i}}{X_{\alpha,t}}\right)$$



Loss of Specific Constituents



We may want to consider individual constituents within the mixture, and their rate of loss… say benzene.

The moles of benzene remaining (M_B) at any given time t,

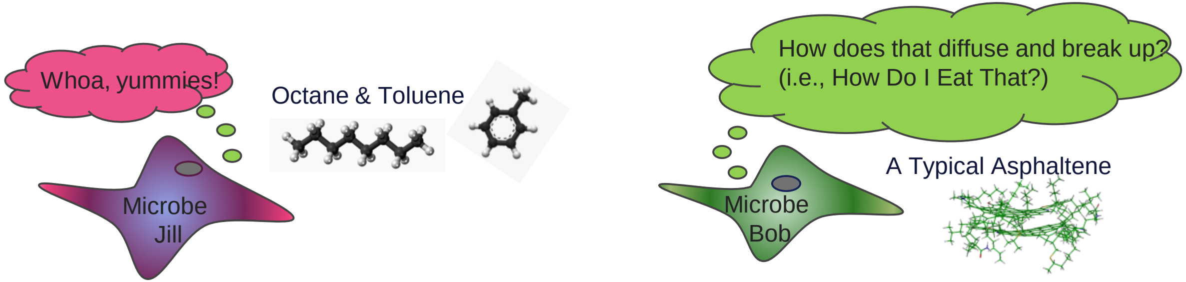
Has to be related back to the initial number of moles.

This is done by correcting the mole fraction (X_{B}) for the cumulative LNAPL fraction loss, based on the biomarker (X_α).

$$\frac{M_{B,t}}{M_{T,i}} = X_{B,t} * X_{\alpha,i} \,/\, X_{\alpha,t}$$

Biodegradation and Molecular Structure (After ITRC)

- Simpler the structure or one aspect of the structure, easier for microbe to break down
- More branching, more difficult to biodegrade
- Geometry of branches matters; branches next to each other are more difficult than branches further way
- Leverage this behavior in estimating the fraction of LNAPL degraded/weathered/lost.



Key Learnings

a) Selecting Optimal/Multiple Marker Constituents
b) Spatiotemporal Understanding

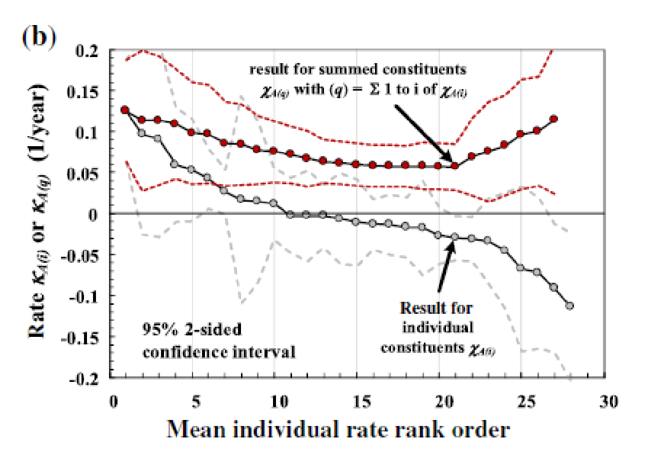
Selecting Biomarkers – DeVaull et al., 2020

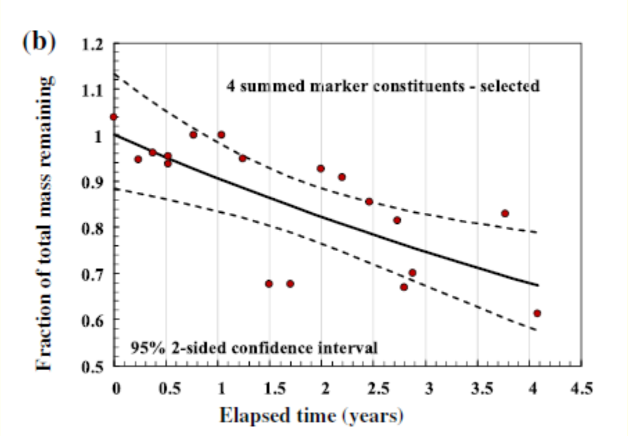
Appropriate for finite LNAPL mass with no additional sources or releases over the investigation time.

Method: Select the most appropriate conserved marker constituents: measured composition data; parameter transformations; regression analyses.

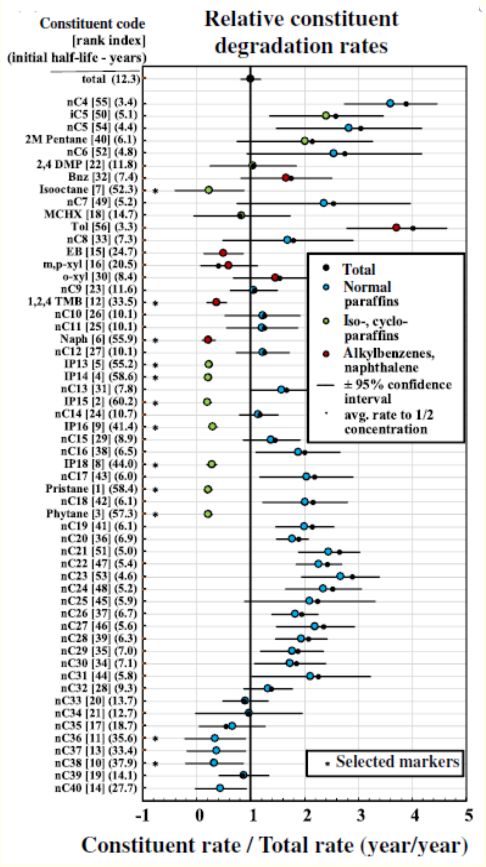
Where there are N constituents, the most conserved constituent has the highest positive (kappa) $\kappa_{A(i)}$ value (rank ordered: rate of change of concentration)

More than one marker: Improved quantification certainty





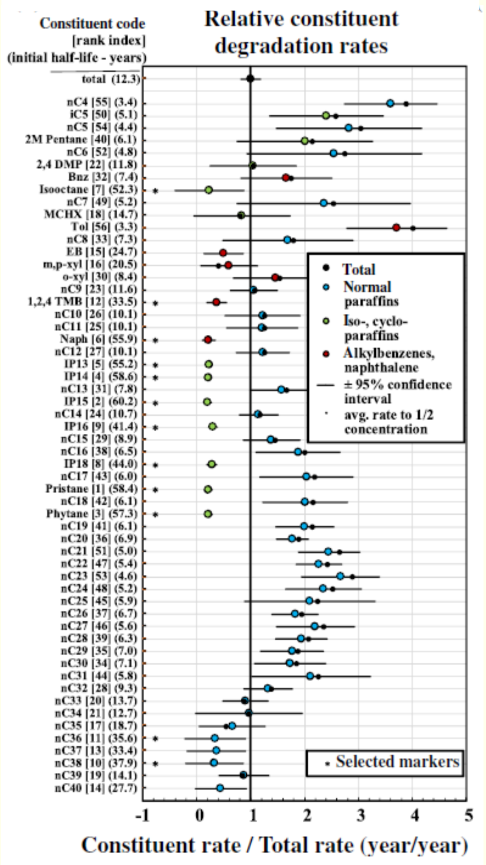
Crude Oil Weathering in Shallow Subsurface (Bemidji, Minnesota; C4 to C40)



Toluene: Fastest Initial rate; approx. 3.7 x total mean depletion rate

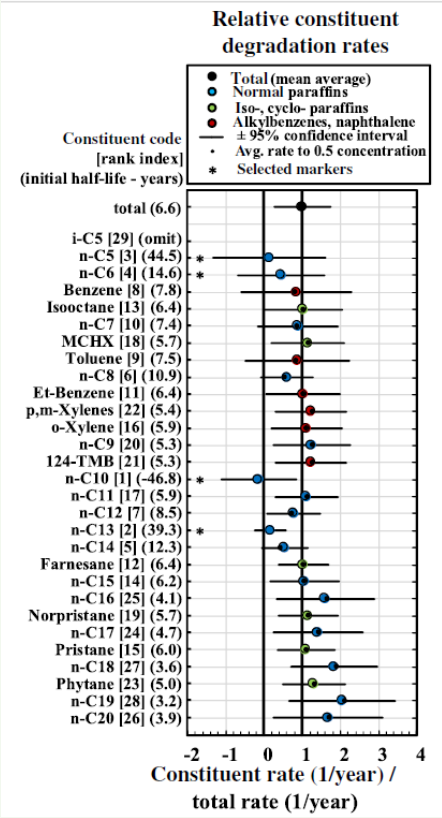
Marker:
Iso-paraffins: pristane, IP15, phytane, IP14, IP13, IP18, IP16
Naphthalene
Isooctane (2,2,4-trimethylpentane), nC38, nC36,
1,2,4 TMB (1,2,4-trimethylbenzene).

Crude Oil Weathering in Shallow Subsurface (Bemidji, Minnesota; Multiple wells C4 to C40)



Toluene: Fastest Initial rate; approx. 3.7 x total mean depletion rate

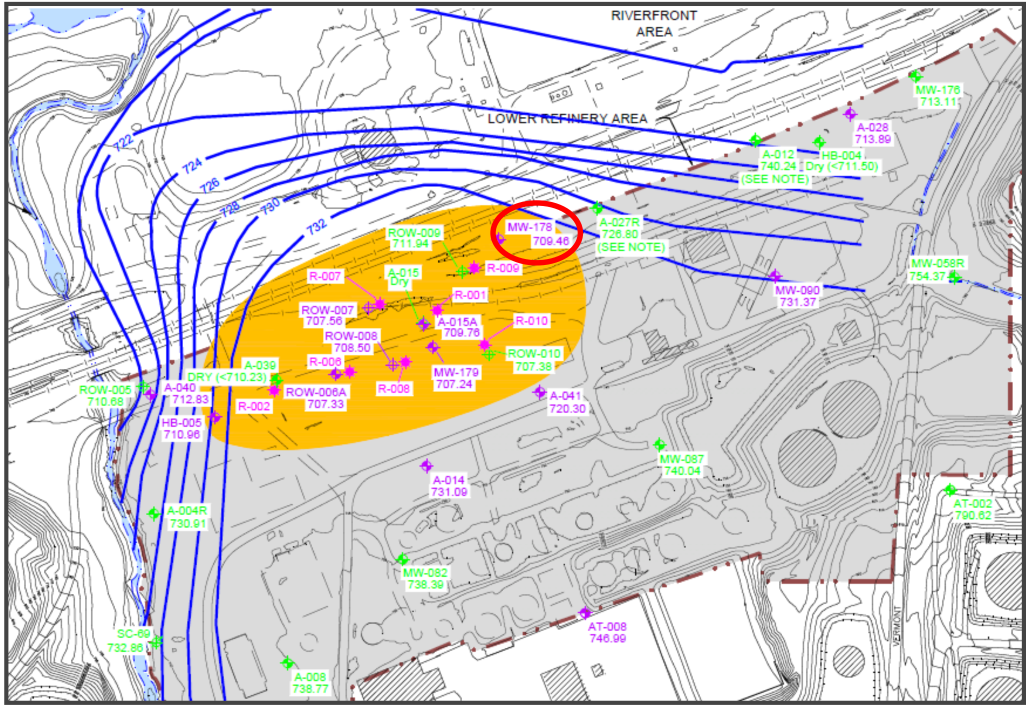
Gasoline and Diesel Mixture Weathering (Petroleum Terminal Site; Single Well C5 to C20)



Conventional markers (>C20) not present

nC19: Fastest Initial rate; approx. 2 x mean depletion rate - Methanogenic conditions

Building a Spatiotemporal, Site-Wide Model



LEGEND

- MW-048 MONITORING WELL, OBSERVATION WELL, OR PIEZOMETER WITH NO MEASURABLE LNAPL
- MW-179 MONITORING WELL, OBSERVATION WELL, OR PIEZOMETER WITH MEASURABLE LNAPL
- R-008 RECOVERY WELL
- 740.04 GROUNDWATER ELEVATION (ft. AMSL) (CORRECTED FOR LNAPL WHERE PRESENT)
- GROUNDWATER ELEVATION CONTOUR (ft. AMSL)(CONTOUR INTERVAL = 10 ft)
- AREA THAT IS PERENNIALLY OR EPHEMERALLY DRY (BOUNDARY ESTIMATED)
- ESTIMATED CAPTURE AREA

- Legacy Releases (1904-1960s)
- LNAPL recovery started in the 1980s, recovery well system
- Prior to recovery, LNAPL body and dissolved phase stabilized (not migrating or expanding)

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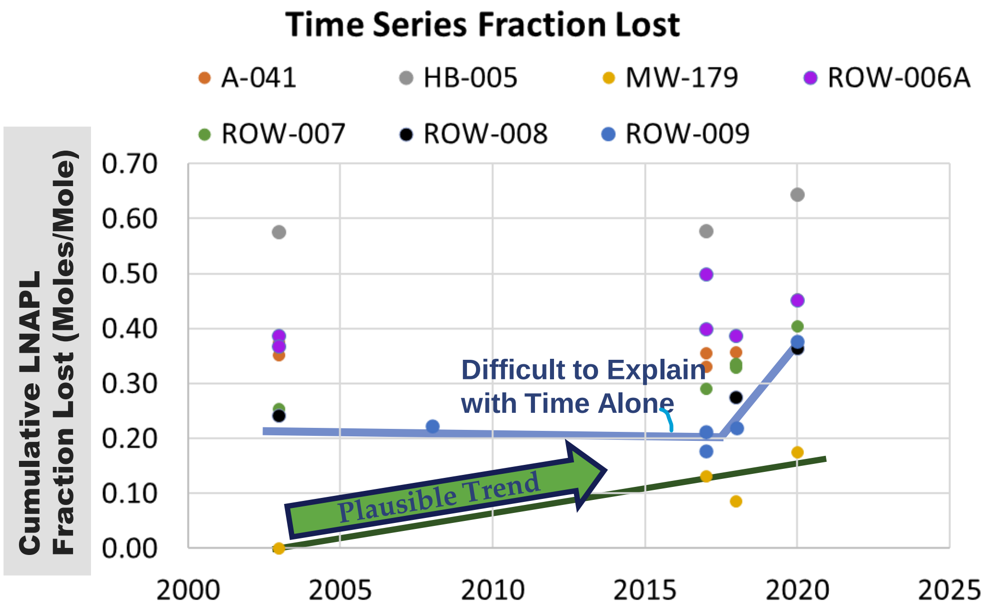
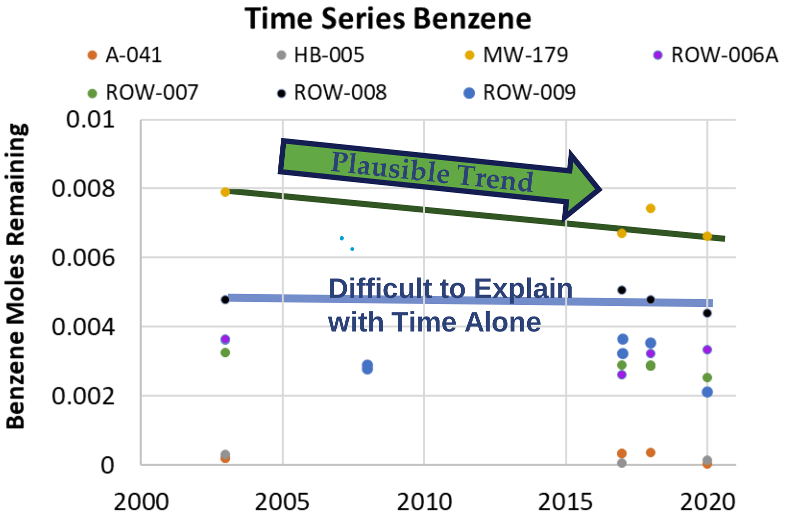
Well by Well (36 Samples, 9 Wells, 2003-2020); IP13 as marker

- The difference in degree of weathering for a given time point between locations identifies that the samples should not be lumped into a singular Losses over time model.





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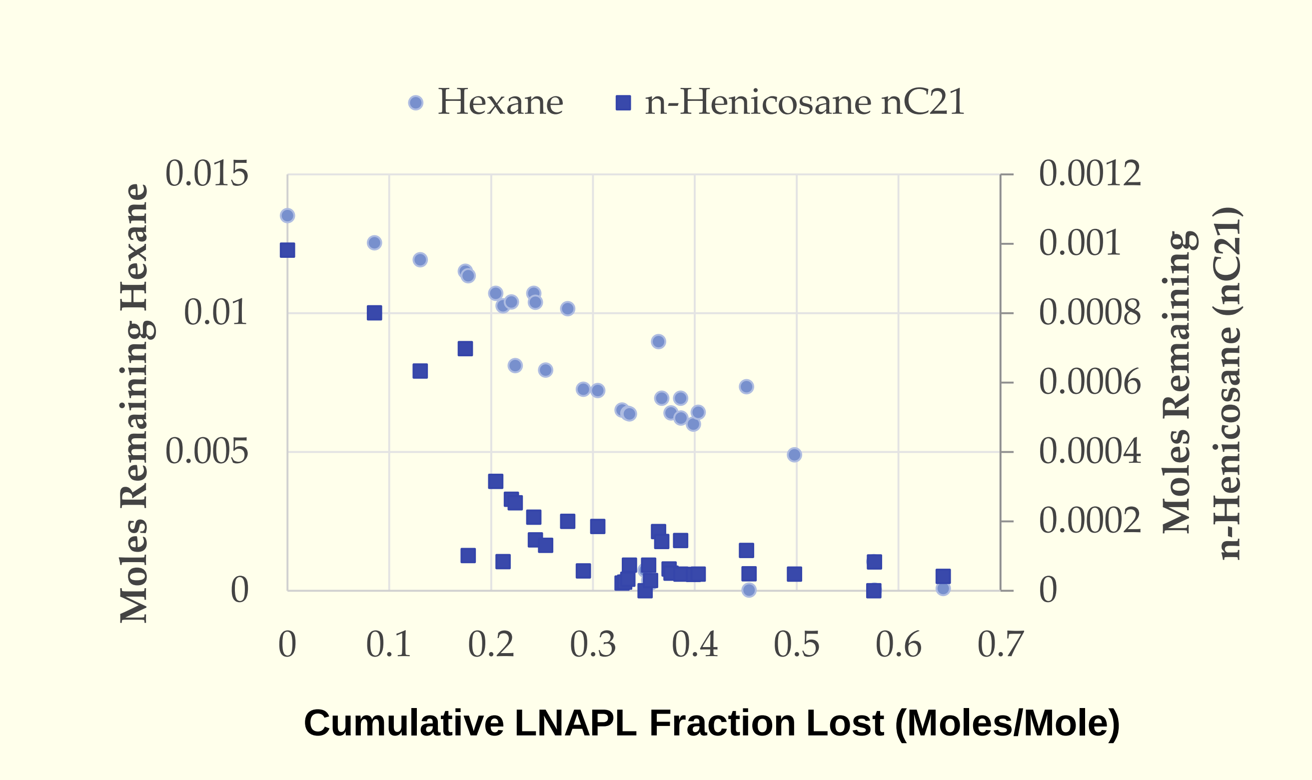
Entire LNAPL Body: Constituent Decline Curve Vs LNAPL Weathering

Includes All data points from 2003 to 2020



Preferential degradation of heavier and lower concentration alkane C21

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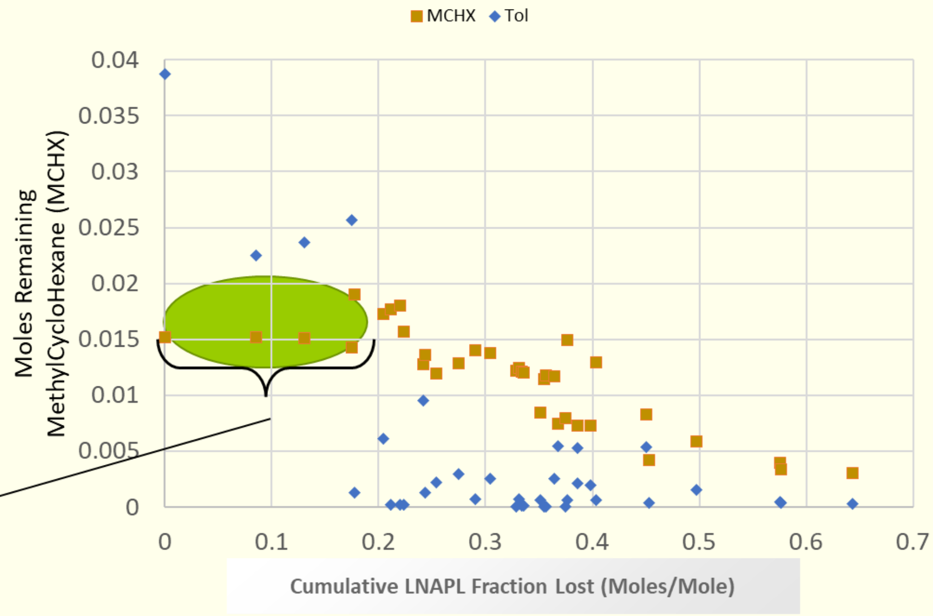
Data Potentially Supports Sequential Hydrocarbon Degradation

Consider MW-179 alone: could conclude Methylcyclohexane is not degraded/lost.

Combining Data into a single CSM identifies a likely lag period at MW-179; MCHX will decline once other substrates depleted

Whether Running Time Series on multiple wells or combining multiple wells on a plot like this, multiple wells will give a better understanding of overall degradation as compared to a single well analysis



MW-179 points indicate a potential Substrate Lag rather than lack of methylcyclohexane degradation

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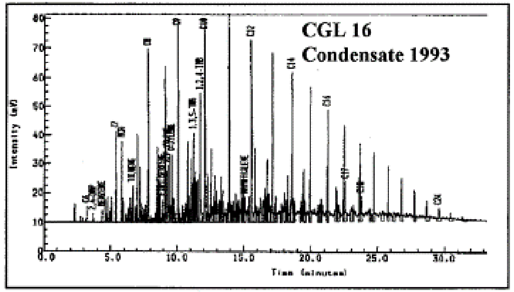
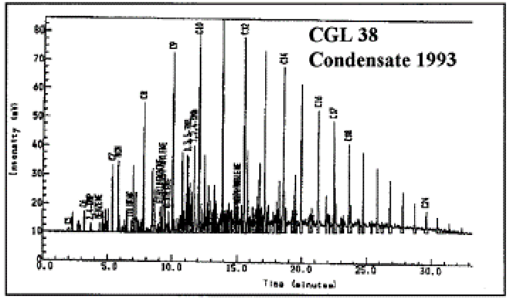
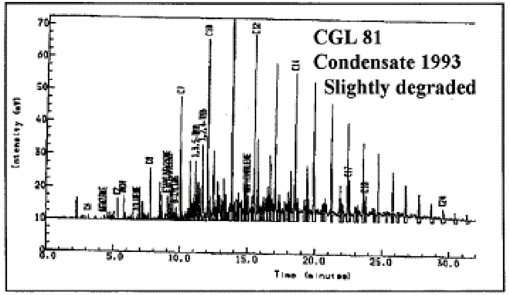
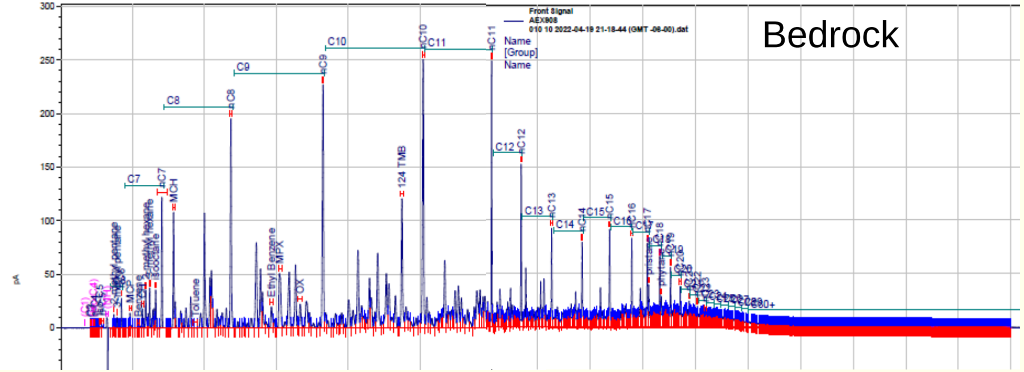
Back to AB.....

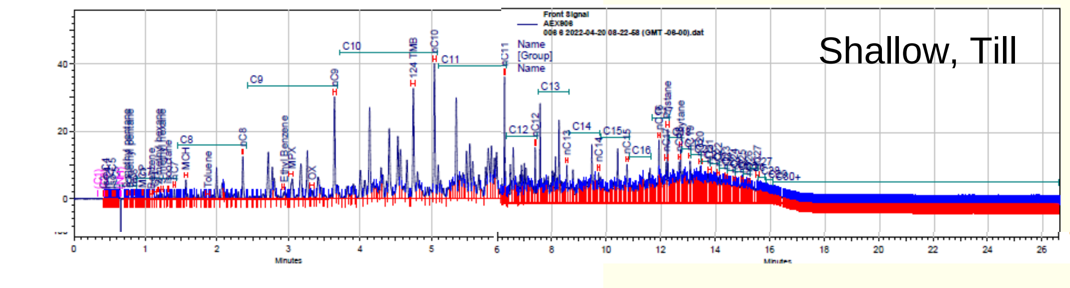
Then (1993) and Now (2021)…..





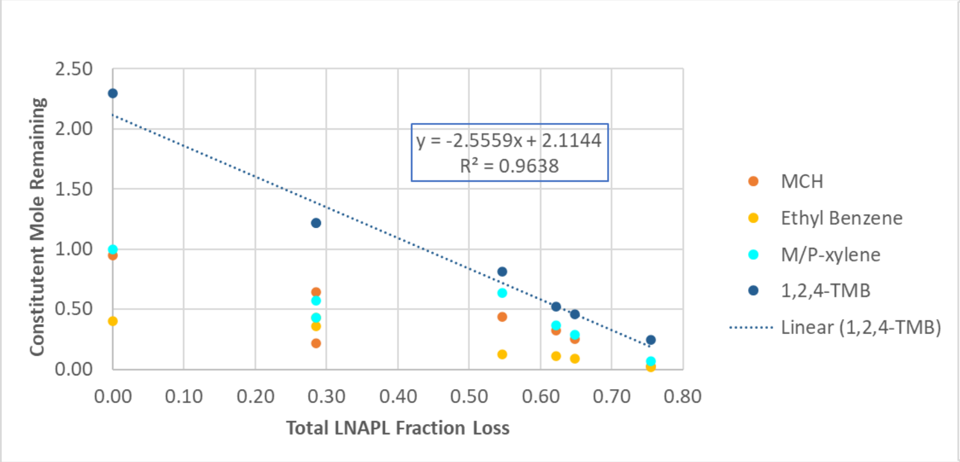


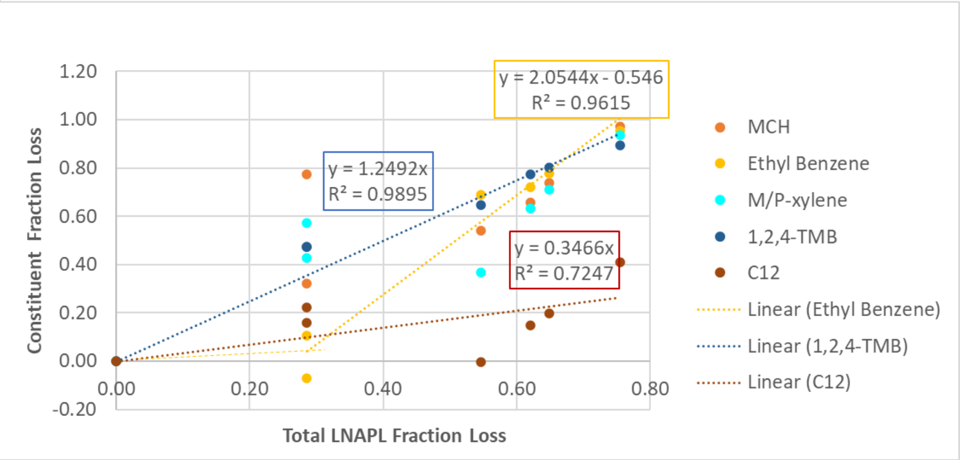




Really restricted by 1993 data for marker……

Preliminary Estimates – 1993 to Present: weathering of LNAPL, but biodegradation?





Constituent Mole Remaining

$= X_{\beta,t} * X_{\alpha,i} / X_{\alpha,t}$

Biomarker Selected: C24

Constituent Fraction Loss

$= (X_{\beta,i} - X_{\beta,t}) / X_{\beta,t}$

Slope >1, constituent is lost at a faster rate than LNAPL is weathering as a whole;

Slope <1, constituent is lost at a slower rate than LNAPL is weathering as a whole;

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NSZD- Supporting Framework

- Build a functional/mechanistic **PHC CSM**
- Hydrogeological CSM and Water Balance
- Historical PHC and Biodegradation Indicators data (Decades, and more recent)
- LNAPL Delineation (*LIF? Shoutout*)
- NSZD: Compositional Analysis, Rates using Gradient Method
- Microbial Communities, soil, groundwater, LNAPL (University of Guelph)
- Stable Isotopes – *Direct evidence of Biodegradation*
- Additional forensics approaches to evaluate sources, and contributions of sources

Concluding Thoughts: Cumulative Effect of NSZD through Compositional Analysis

Direct understanding of NSZD effects on source

Used alone or with other data to identify NSZD behavior

Single or short time frame sampling events

Supports improved targeting of source zone for active remedies

Enables Conceptualization of Site as a whole (vs individual wells)

Continue to Evaluate approach with additional Sites

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Thank you

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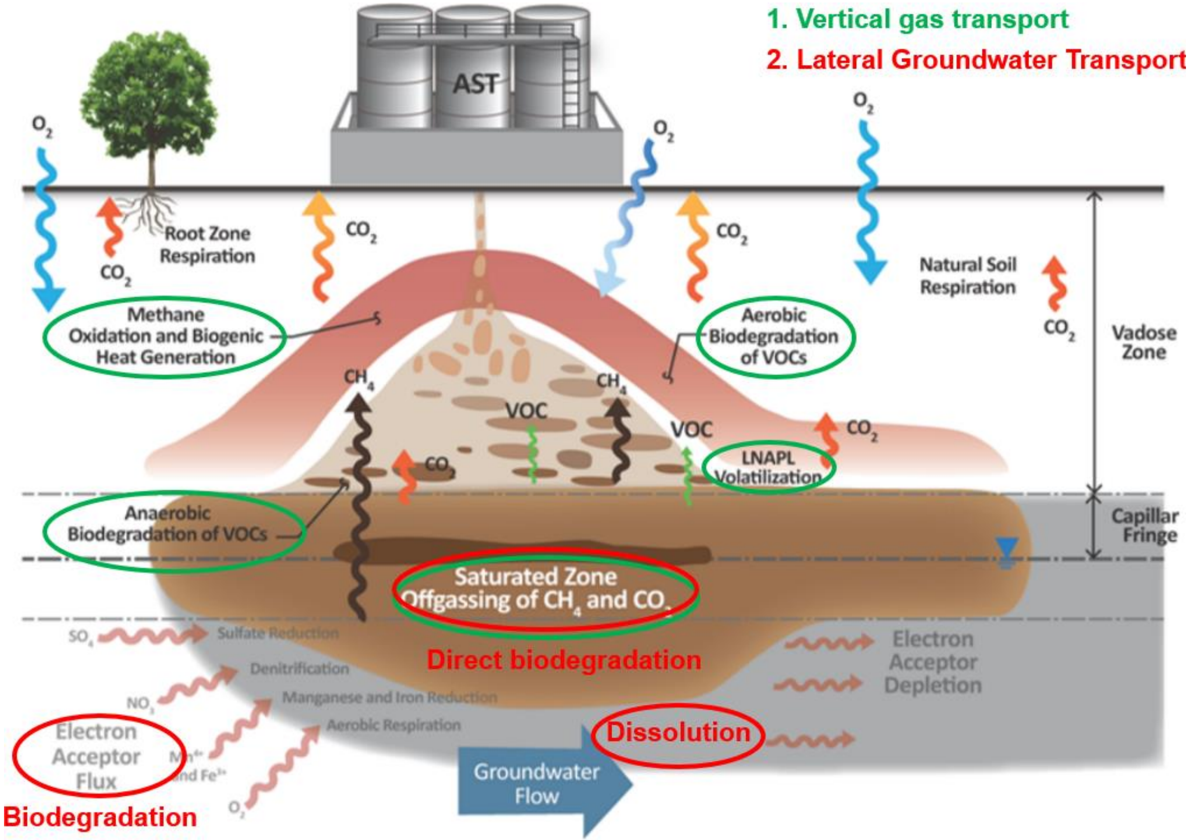
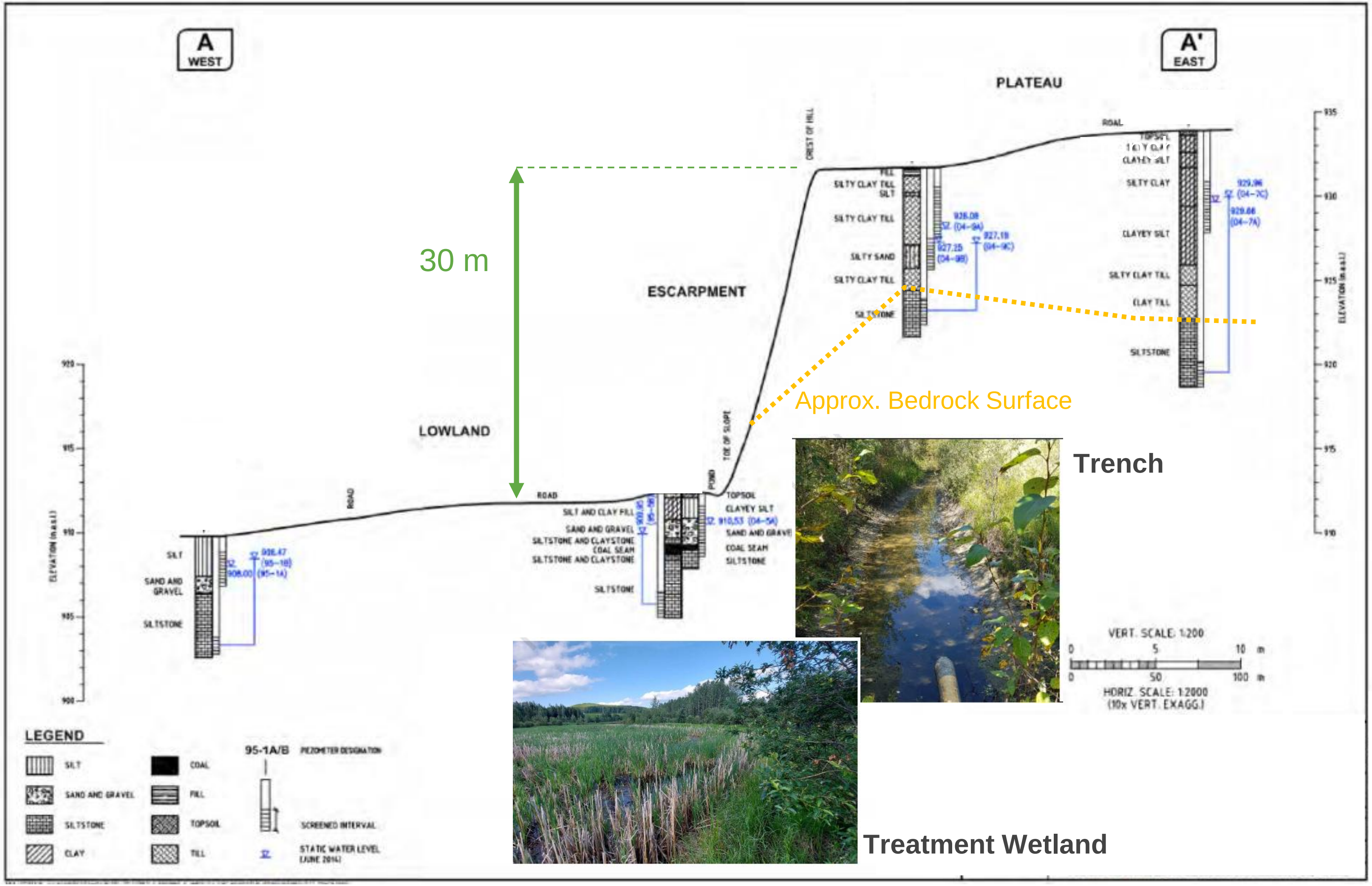
Conceptualisation of LNAPL NSZD processes (modified from API 2017)




A
WEST
A'
EAST
PLATEAU
ESCARPMENT
LOWLAND
30 m
Approx. Bedrock Surface
CREST OF HILL
TOE OF SLOPE
POND
ROAD
SILT
SAND AND GRAVEL
SILTSTONE
SILT AND CLAY FILL
SILTSTONE AND CLAYSTONE
COAL SEAM
TOPSOIL
CLAYEY SILT
SILTY CLAY TILL
SILTY SAND
SILTY CLAY
CLAY TILL
Trench
Treatment Wetland
VERT. SCALE: 1:200
HORIZ. SCALE: 1:2000
(10x VERT. EXAGG.)
LEGEND
SILT
SAND AND GRAVEL
SILTSTONE
CLAY
COAL
FILL
TOPSOIL
TILL
95-1A/B
PIEZOMETER DESIGNATION
SCREENED INTERVAL
STATIC WATER LEVEL
(JUNE 2014)