PARSONS

Characterization of Natural Biodegradation Using Benzene Carbon Isotopes, LNAPL Characterization and Geochemical Lines of Evidence

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- Background
  - Site conditions
  - Lines of evidence approach
- Results - Natural attenuation and biodegradation of:
  - Benzene and LNAPL in shallow groundwater
  - MTBE in deep groundwater
- Conclusions

Site Conditions and Activities

- 288 acres
- Former terminal
- ~20 LNAPL Plumes
- Geology
  - Fill
  - Peat, silt, clay (former marsh deposits)
  - Upper alluvium
  - Till (low permeability)
  - Lower alluvium
- LNAPL, soil, and groundwater investigations
- LNAPL recovery
- Remediation and redevelopment planning

Natural Attenuation Lines of Evidence Approach

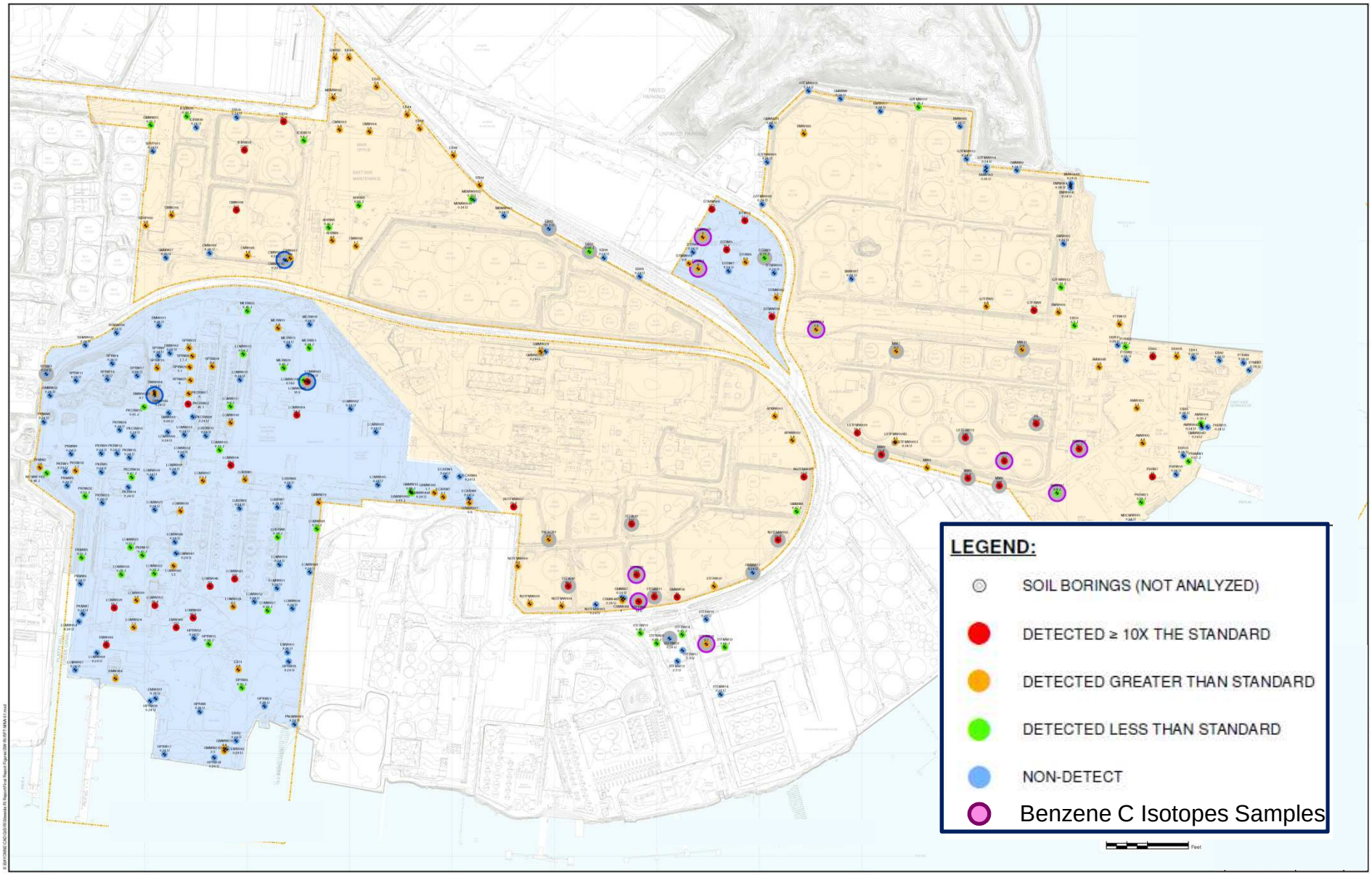
Dissolved Phase

- Primary
  - Stable or shrinking plumes
  - Decreasing contaminant concentration trends
- Secondary
  - Geochemical conditions
- Tertiary
  - Microbiological and/or isotopic studies

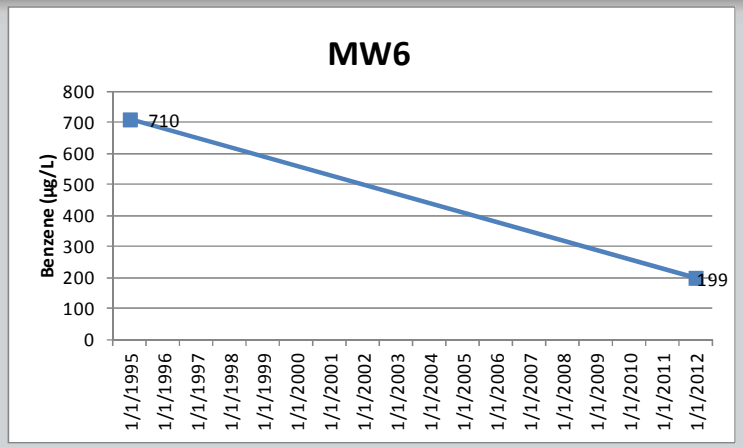
LNAPL

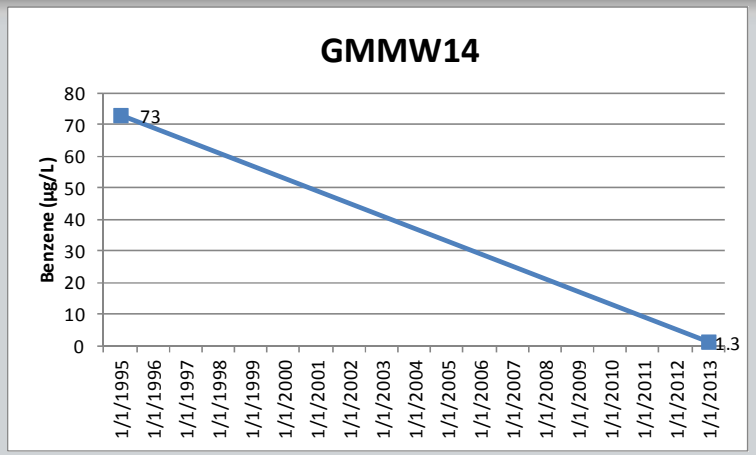
- Compositional changes
  - Depletion of biodegradable hydrocarbons
  - Viscosity and density increases
  - Mobility decreases

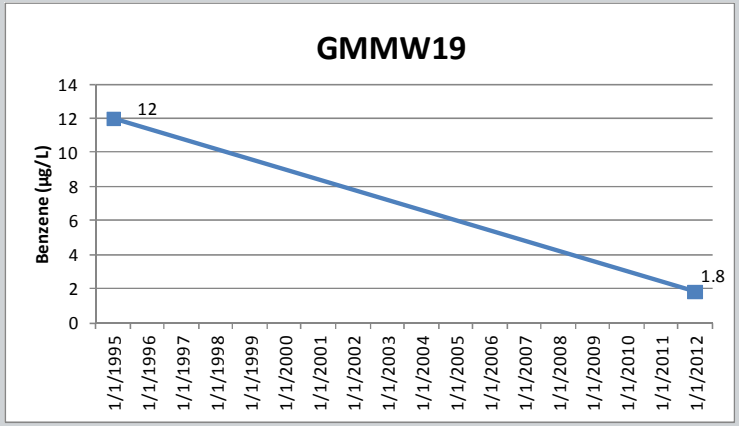
Benzene Concentrations in Groundwater

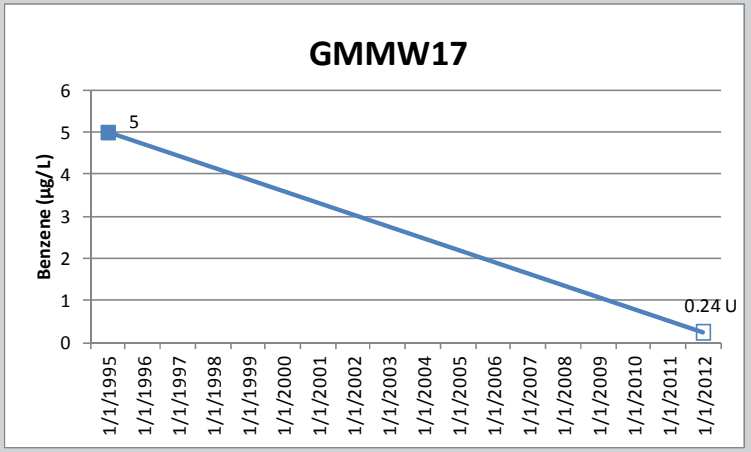


Benzene Concentrations (1995 and 2013) (primary line of evidence)









MNA Geochemistry (secondary line of evidence)

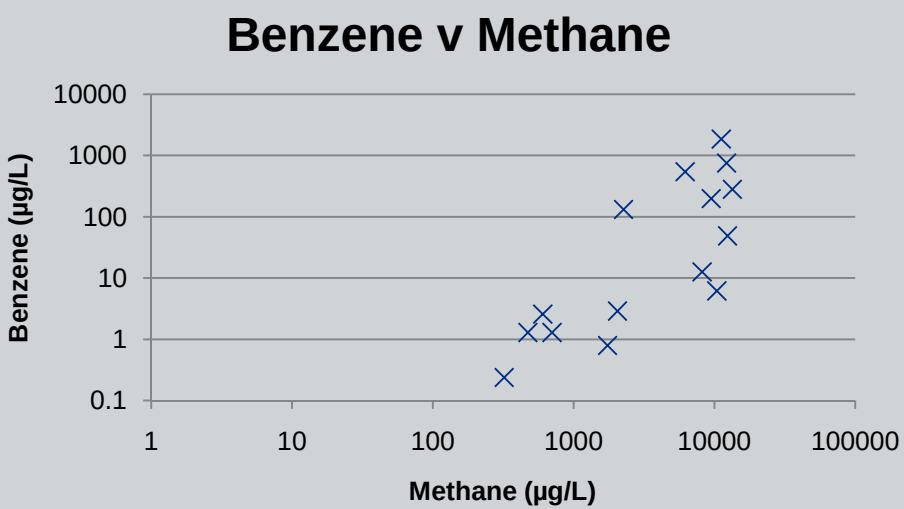
Parameter	Count	Average	Median
ORP (mV)	111	-115	-101.6
DO YSI (mg/L)	62	2.0	0.72
DO 2013-Chemetrics (mg/L)	23	0.4	0.30
Ferrous Iron-Total (mg/L)	256	24.2	9.4
Sulfate (mg/L)	25	62	10
Methane (mg/L)	25	5276	4760

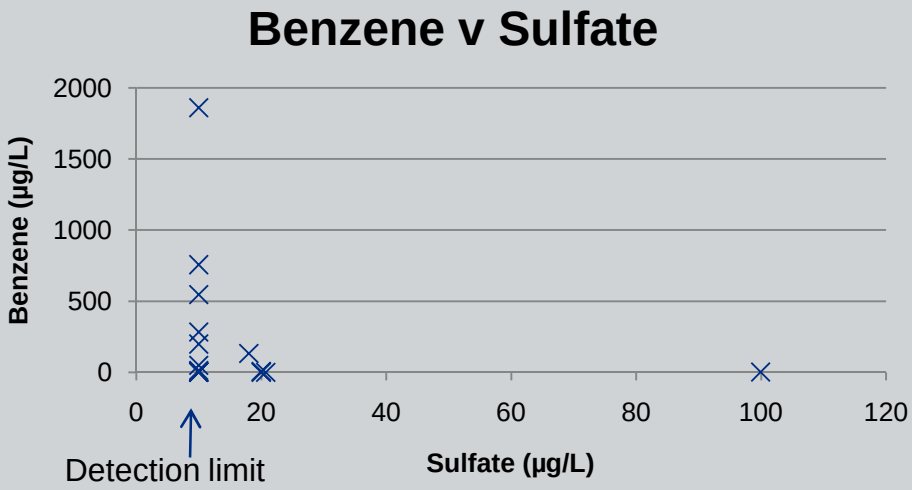
All MNA data from all depths

- Electron acceptor (oxygen, nitrate, sulfate) depletion and reduced products indicate hydrocarbon biodegradation.

Sulfate Depletion and Methanogenesis

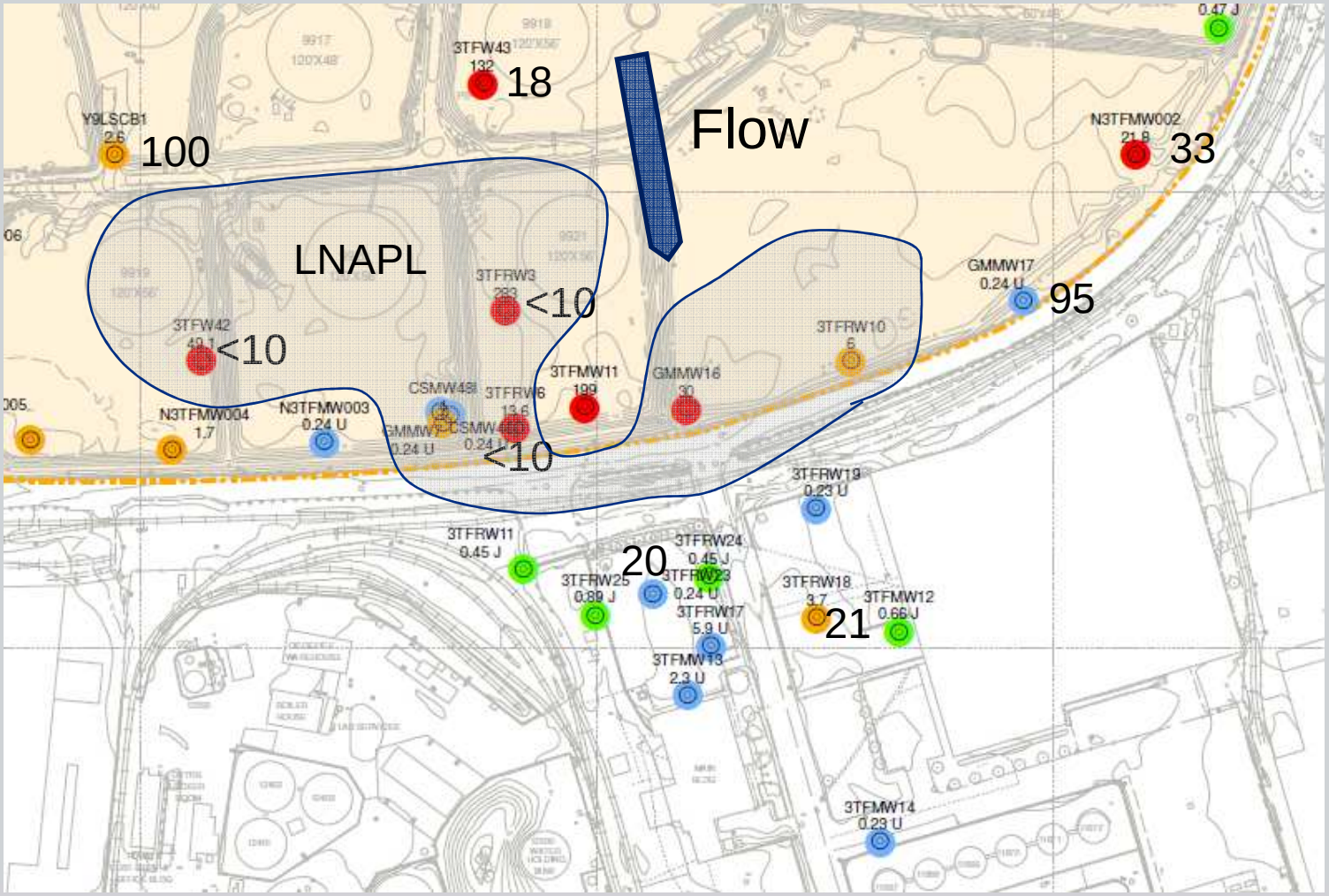
Secondary Lines of Evidence:





- Confirms hydrocarbon biodegradation
- High methane associated with LNAPL areas

Plume 10. Sulfate (mg/L)



Benzene Biodegradation: Carbon (C) Isotope Analysis Background (tertiary line of evidence)

- MNA geochemistry (electron acceptors and reduced products) can't be used to determine biodegradation of specific hydrocarbons
- Carbon occurs as ^{12}C and ^{13}C (light and heavy isotopes)
- ^{12}C-benzene is biodegraded at a faster rate than ^{13}C-benzene
- Remaining benzene becomes heavier (enriched in ^{13}C; less negative value)

Benzene Biodegradation: Continued

Increasing ^{12}C-Benzene

Area	Benzene	Benzene C Isotope Value	D.O.	Sulfate	Iron	Methane
	(µg/L)	δ13C (‰)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Plume 7DT	1.3	-25.5	0.60	< 10	5.29	0.473
Plume 10	13.6	-26.1	0.10	< 10	40.2	12.4
Plume 10	1.3	-26.5	1.0	20.7	1.51	0.702
Plume 7DT	8	-27.2	6.0	18.9	61.2	0.455
Plume 4	757	-27.3	0.10	< 10	71.3	12.2
Plume 4	12.7	-27.7	0.05	< 10	48.2	8.18
Plume 10	283	-27.8	0.20	< 10	44.5	13.4
Plume 4	0.8	-28.4	0.10	< 10	47.7	1.74

- Benzene biodegradation generally associated with:
  - Less reducing conditions
    - Lower dissolved methane
    - Lower iron
    - Presence of sulfate and/or dissolved oxygen

MTBE Biodegradation (tertiary line of evidence)

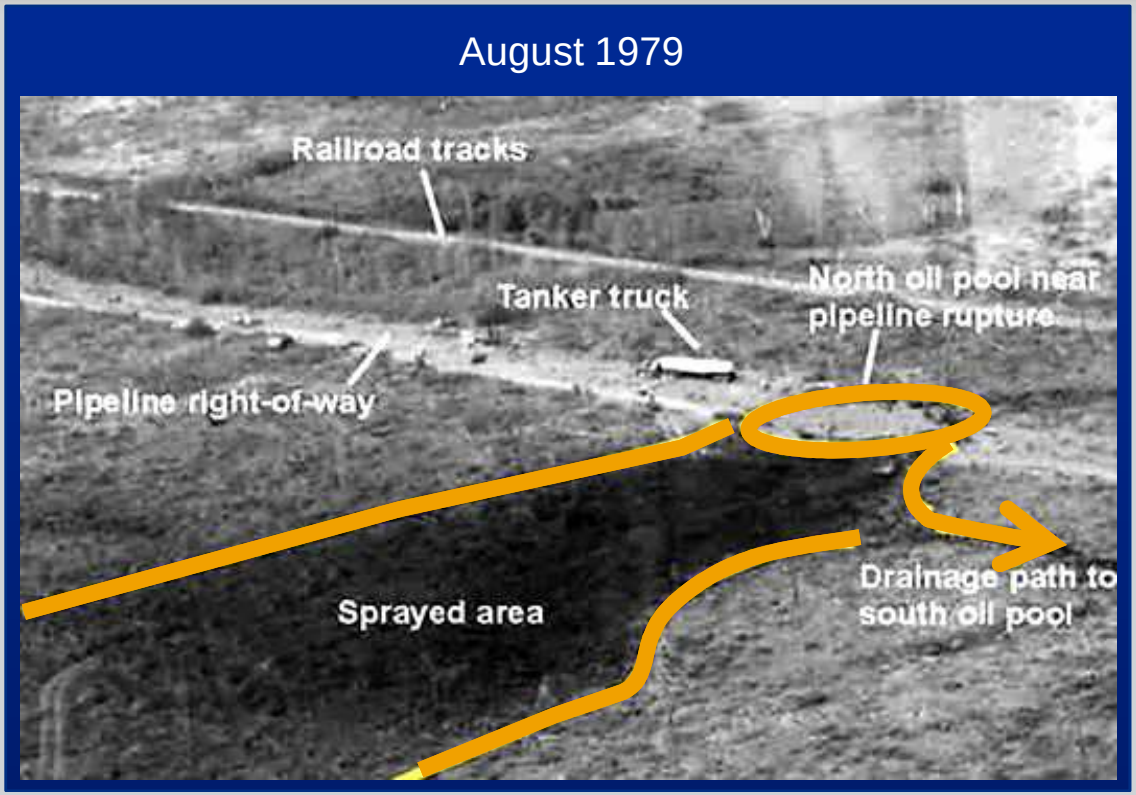
Sample ID	Sample Date	MTBE (µg/L)	TBA (µg/L)	MTBE/ TBA	MTBE δ13C (‰)	Benzene (µg/L)	Alkalinity (mg/L)	Methane (mg/L)	Sulfate (mg/L)	ORP
CMW007I-52.74	5/20/2013	107	1,250	0.1	-8.3	< 0.24	540	10,100	10	-55.7
DMW004I-55.5	5/21/2013	214	666	0.3	-27.1	< 0.24	691	64	57	200.5
LOMW062I-63.0	5/14/2013	9,470	140	67.6	-30.9	18.9	139	4,760	1,010	145.5

- Significant MTBE biodegradation indicated (MW007I):
  - Closer to source.
  - More reducing conditions
  - ~ 80% degradation indicated by C-isotope value

Perimeter MNA Approach - Applicability for Benzene

- Concept
  - LNAPL recovery to extent practicable
  - MNA at perimeter
- Considerations:
  - Benzene
    - Benzene concentrations decrease downgradient of LNAPL plumes.
    - Limited data indicate benzene concentrations are mostly decreasing.
    - Benzene is biodegrading (spatially variable).
  - Monitoring limitations
    - None
  - Receptors Impacted
    - Benzene below GWQS or at low concentrations near surface waters
  - Imminent threat to receptors
    - No
  - Natural remediation of free and/or residual product is not allowed.
    - Enhance natural biodegradation of residual LNAPL after recovery

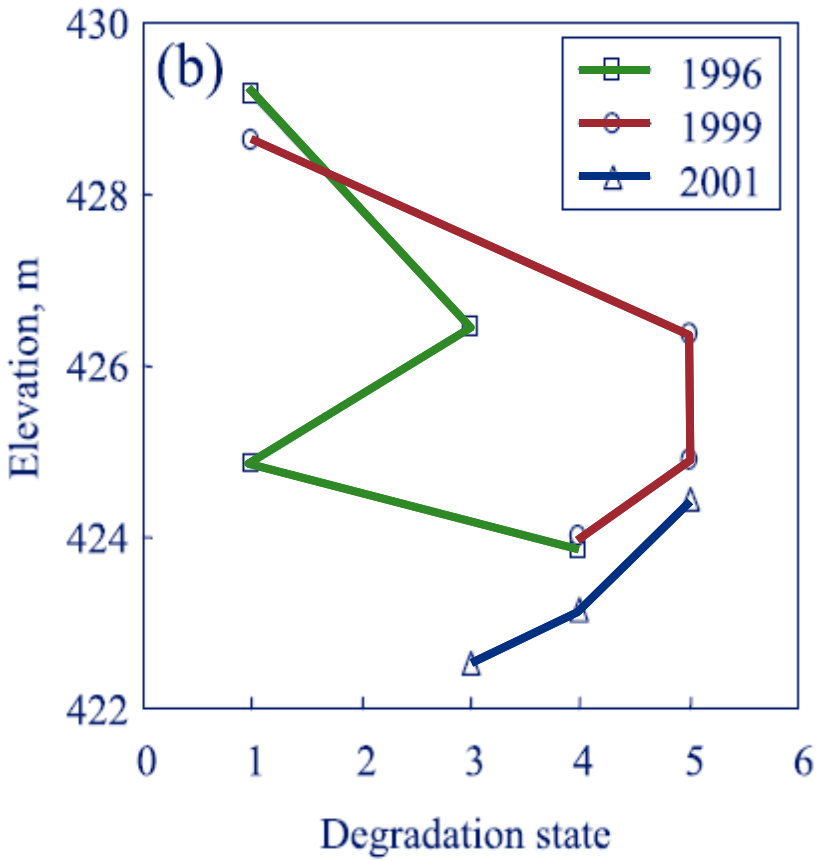
Bemidji: Natural Anaerobic LNAPL Biodegradation Case Study



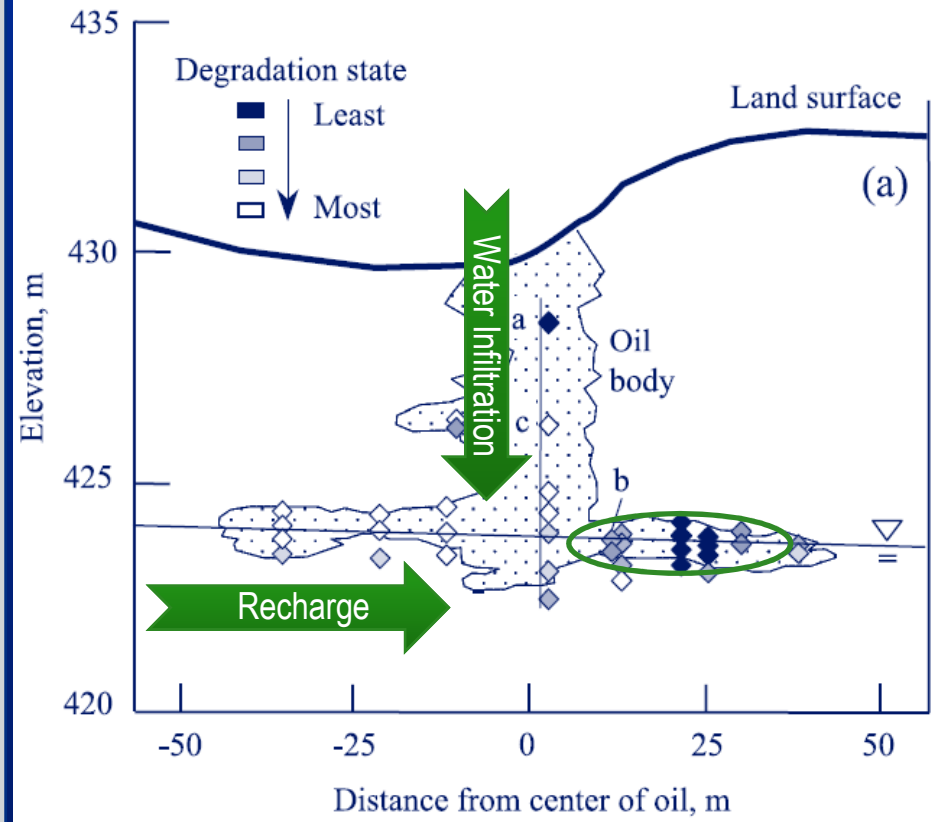
- Long-term USGS MNA research site
- Crude oil release in 1979

Bemidji: Factors Controlling LNAPL Biodegradation

Degree of LNAPL Biodegradation - Temporal



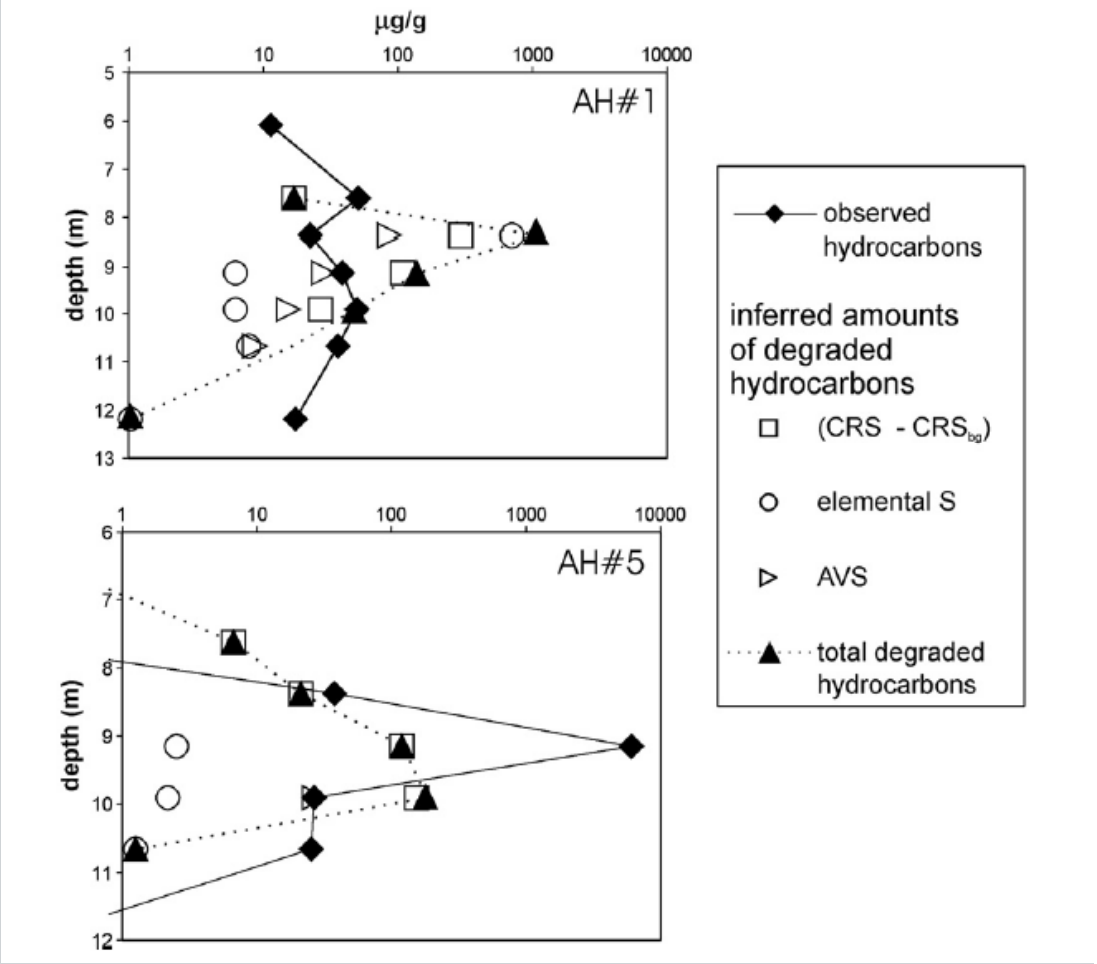
Degree of LNAPL Biodegradation - Spatial



Bekins et al; 2005 (with permission)

Canada Site: Natural LNAPL Biodegradation

- Well site in Canada
- Gas condensate in silty clay aquitard
- Iron sulfides account for degradation of up to 1,000 mg/Kg hydrocarbon in capillary fringe

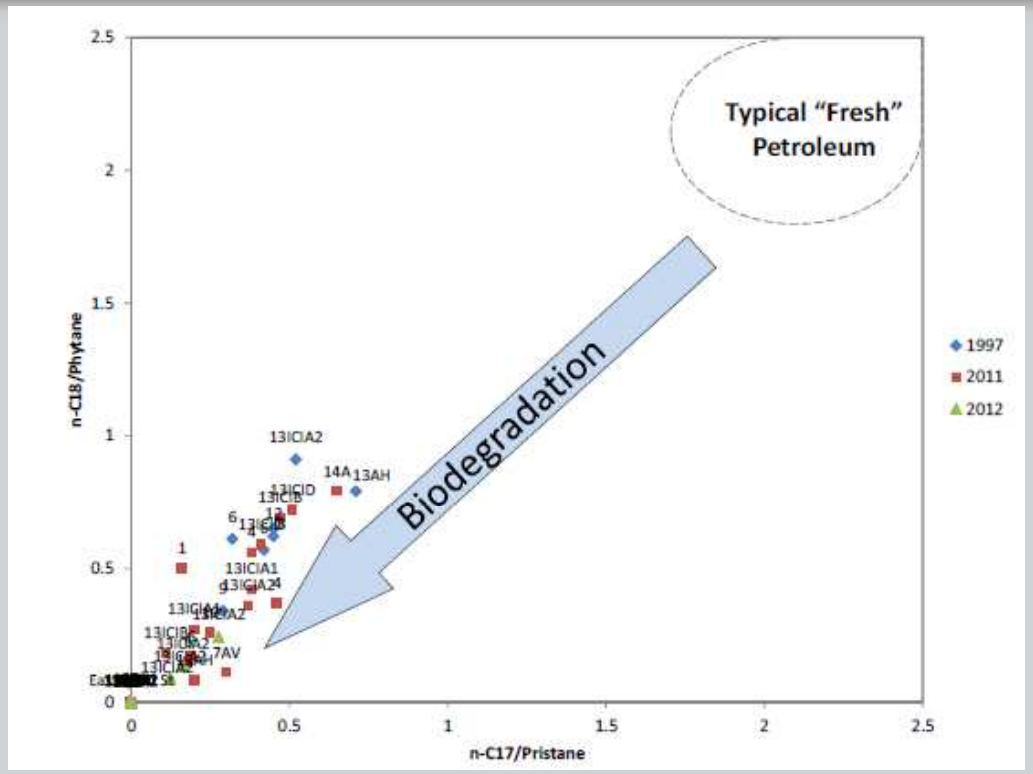


From Stempvoort and Kwong; 2010 (with permission)

Natural Anaerobic LNAPL Biodegradation - Oil Reservoirs

- Anaerobic biodegradation of crude oil common in shallow reservoirs
- Increased biodegradation towards oil/water contact
- n-alkanes and smaller hydrocarbons biodegrade more rapidly
- Up to 50-60% oil mass loss
- Oil viscosity and density increase, mobility decreases

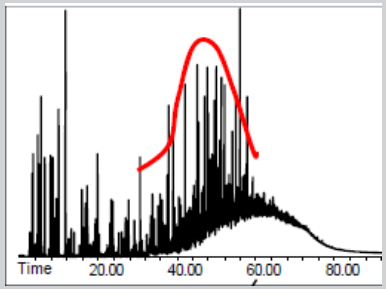
This Site: Natural Anaerobic LNAPL Biodegradation

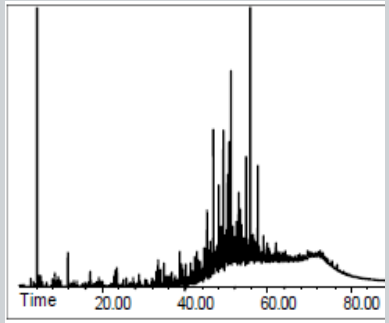


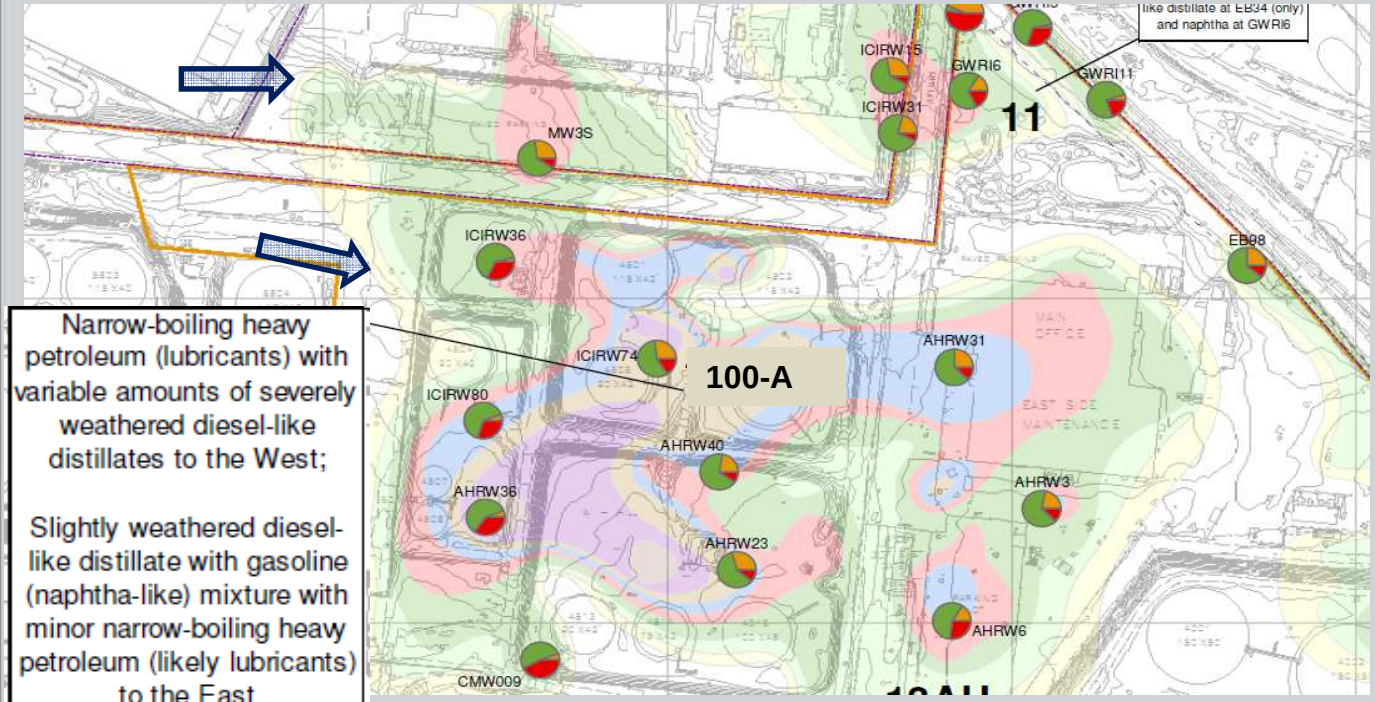
- LNAPL across the site is weathered due to biodegradation
  - Preferential loss of n-alkanes relative to branched alkanes
  - Preferential loss of toluene relative to benzene in less weathered LNAPL
  - Less LNAPL biodegradation in middle of LNAPL plumes

This Site: Spatial Variability in LNAPL Weathering

- Severe LNAPL weathering observed within upgradient position of LNAPL plume 100-A.
  - Consistent with increased LNAPL biodegradation upgradient at Bemidji site.







Narrow-boiling heavy petroleum (lubricants) with variable amounts of severely weathered diesel-like distillates to the West;

Slightly weathered diesel-like distillate with gasoline (naphtha-like) mixture with minor narrow-boiling heavy petroleum (likely lubricants) to the East

LEGEND:

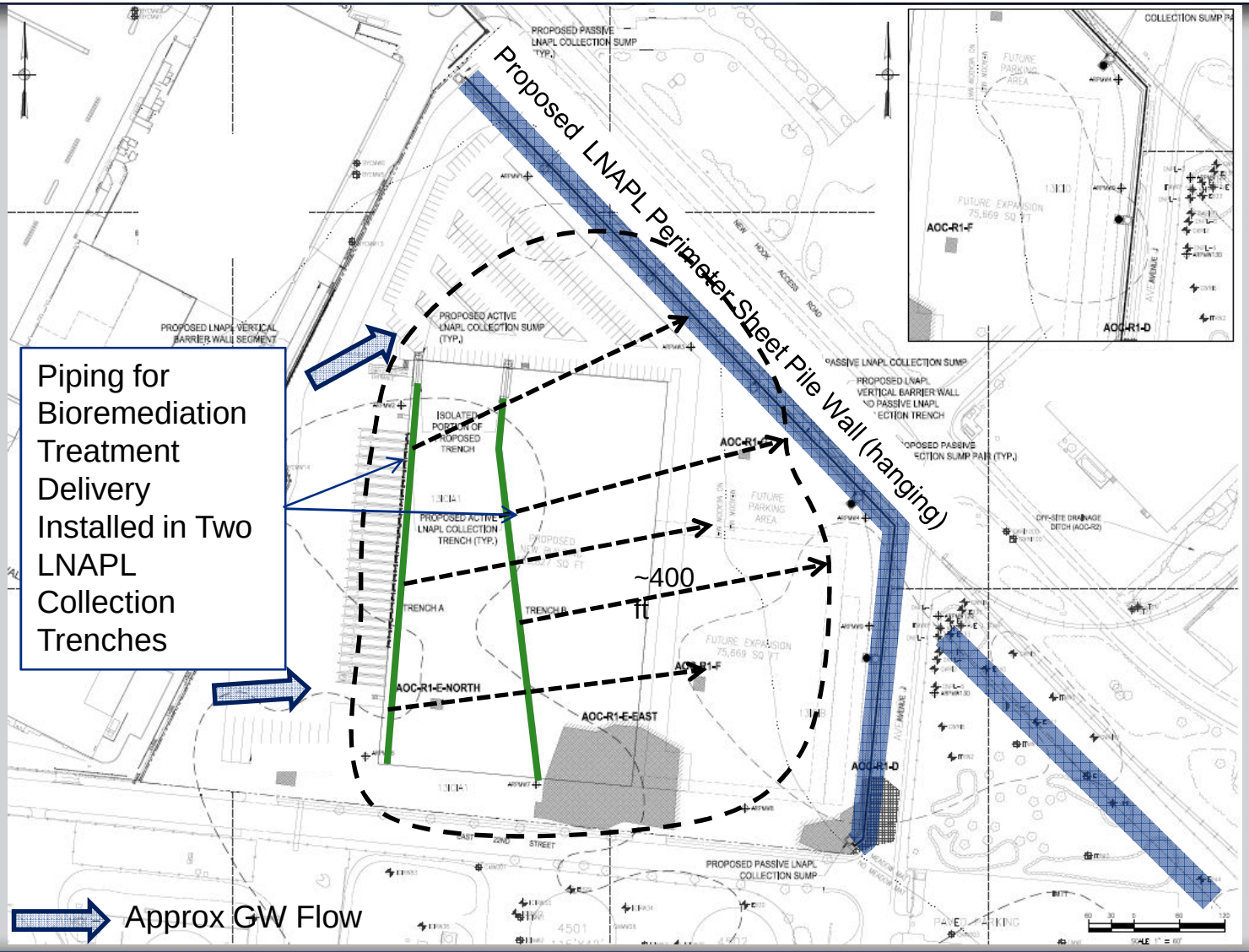
GRO (C4 - C10)

DRO (C10 - C25)

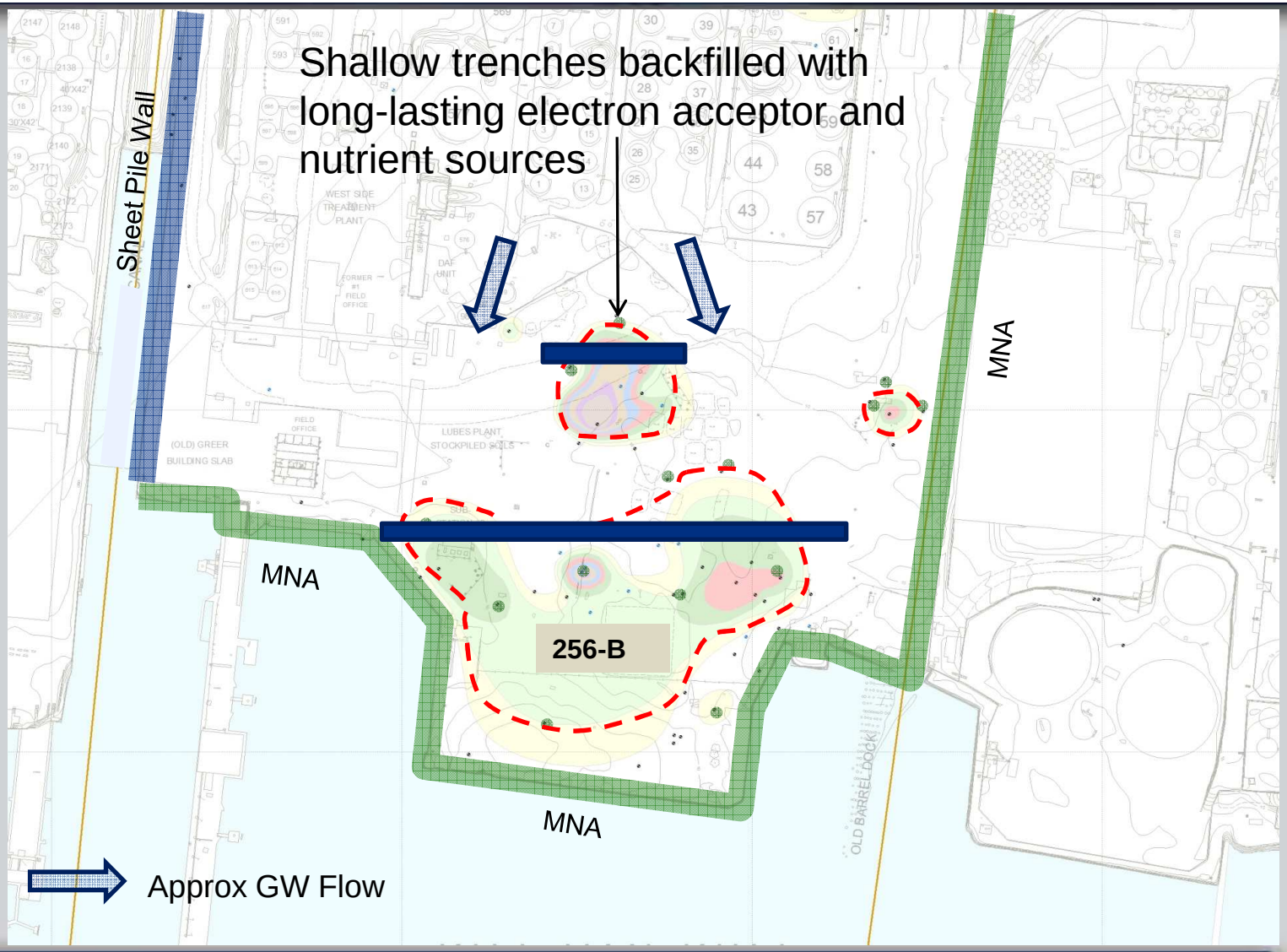
RRO (C25 - C44)

Groundwater Flow

Planning for Enhanced Anaerobic Biodegradation of Residual LNAPL



Residual LNAPL Treatment Trenches



Conclusions

- Primary, secondary, and tertiary lines of evidence collectively provide good indicators of benzene/MTBE biodegradation
- Data support a perimeter MNA approach for petroleum
  - Petroleum hydrocarbons are biodegrading
  - Benzene is biodegrading (spatial variability)
  - Low benzene concentrations downgradient of LNAPL Areas
  - Mainly decreasing benzene concentrations
- Data support enhanced anaerobic biodegradation of residual LNAPL
  - Anaerobic LNAPL biodegradation is occurring
  - Higher benzene concentrations in LNAPL areas
  - Electron acceptors depleted and less evidence for benzene biodegradation in LNAPL areas
- Delivery systems to enhance residual LNAPL biodegradation can be installed

Thank You

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