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

Glenn Ulrich and Paul Feshbach-Meriney

- 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

Decreased benzene concentration downgradient of LNA PL Area. Benzene closest to Kill Van Kull or New York Bay: Benzene < detection or GWQS in 21 of 28 wells. Low in other wells (4.5 µg/L median benzene). Benzene C Isotopes Samples

LEGEND:
- SOIL BORINGS (NOT ANALYZED)
- DETECTED ≈ 10X THE STANDARD
- DETECTED GREATER THAN STANDARD
- DETECTED LESS THAN STANDARD
- NON-DETECT
- Benzene C Isotopes Samples
Benzene Concentrations (1995 and 2013) (primary line of evidence)
### MNA Geochemistry (secondary line of evidence)

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

All MNA data from all depths

- Electron acceptor (oxygen, nitrate, sulfate) depletion and reduced products indicate hydrocarbon biodegradation.
Secondary Lines of Evidence:

- Confirms hydrocarbon biodegradation
- High methane associated with LNAPL areas
Plume 10. Sulfate (mg/L)
MNA geochemistry (electron acceptors and reduced products) can’t be used to determine biodegradation of specific hydrocarbons.

Carbon occurs as $^{12}\text{C}$ and $^{13}\text{C}$ (light and heavy isotopes).

$^{12}\text{C}$-benzene is biodegraded at a faster rate than $^{13}\text{C}$-benzene.

Remaining benzene becomes heavier (enriched in $^{13}\text{C}$; less negative value).
Benzene Biodegradation: Continued

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

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)

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

- 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
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
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

Piping for Bioremediation Treatment Delivery Installed in Two LNAPL Collection Trenches

Approx GW Flow
Residual LNAPL Treatment Trenches

Shallow trenches backfilled with long-lasting electron acceptor and nutrient sources

Approx. GW Flow
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

glenn.ulrich@parsons.com
573-762-2410