Evaluating Natural Source Zone Depletion Rates at LNAPL Sites with the Carbon Dioxide Trap
Presentation Contributors

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Presentation Overview

- Basic Concepts
- Field Applications
- Case Study on Use of NSZD Rates
- Findings and Recommendations
Evaluating Natural Source Zone Depletion at Sites with LNAPL

April 2009

Prepared by
The Interstate Technology & Regulatory Council
LNAPLs Team
Definition

“NSZD is a combination of processes that reduce the mass of LNAPL in the subsurface.”

NSZD as a Benchmark

“This document provides a technical overview of natural source zone depletion (NSZD) for LNAPLs, which, when appropriately evaluated, can serve as an objective benchmark by which to compare the relative effectiveness of different remedial alternatives.”
LNAPL Biodegradation and Soil Gas

ATMOSPHERE

- $O_2$: 21%
- $CO_2$: 0.04%
- $CH_4$: 0.0002%

SOIL GAS (LNAPL ZONE)

- $CO_2$: 10-20%
- $CH_4$: 10-50%
- Benzene: 2.5% max
**CO₂ Traps**

Credit: Kevin McCoy/CSU

- Integral CO₂ flux measurement
- 2 sorbent elements
  - Sodalime media
  - Bottom element → soil CO₂
  - Top element → atmospheric CO₂
- Travel blank for QC
- Lab analysis for total carbonate
Correction for Natural Soil Respiration

- Carbon dioxide measurement at background location(s)
- Radiocarbon isotope ($^{14}$C) analysis
  - $^{14}$C generated by cosmic rays, present in characteristic amounts in atmospheric and contemporary samples
  - $^{14}$C half-life = 5,600 years
  - $^{14}$C depleted from fossil fuel carbon
Presentation Overview

• Basic Concepts
• **Field Applications**
• Case Study on Use of NSZD Rates
• Findings and Recommendations
Project Objectives

• Early Applications at Larger LNAPL Sites
• Examine Applicability at Smaller Sites
  – Develop Methodology
  – Determine Rates
  – Assess Significance of NSZD in LNAPL Site Management Framework
## CO\textsubscript{2} Trap Study Sites

<table>
<thead>
<tr>
<th>Location</th>
<th>Fuel Type</th>
<th>LNAPL Zone (acres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kansas City, KS</td>
<td>Gasoline, Some Aviation Fuel and Diesel</td>
<td>22</td>
</tr>
<tr>
<td><strong>West Quincy, MO</strong></td>
<td>Diesel</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>Spanish Lake, MO</strong></td>
<td>Gasoline</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>Kennett, MO</strong></td>
<td>Gasoline</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Basic Scope of Work

• “Snapshot” of LNAPL Intrinsic Bioremediation Rate
• Plant 5 Traps + travel blank
  – 3 locations
  – 1 duplicate
  – 1 background
• Leave in place two weeks
• Analyze for carbon dioxide and $^{14}\text{C}$
• Associated measurements
  – Groundwater temperature
  – Vadose zone oxygen, methane and carbon dioxide
Kennett, MO Site

- MW-12
- MW-18
- MW-17

CO₂ Trap Locations
Monitoring Well Locations
Former UST Pit
Former Fueling Island
Consistent LNAPL
# Kennett, MO Q1 Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>CO₂ Flux Rate (gallons LNAPL per acre-year)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Result(^1)</td>
</tr>
<tr>
<td>TRC-CO2-05</td>
<td>MW-17</td>
<td>819</td>
</tr>
<tr>
<td>TRC-CO2-01</td>
<td>MW-18</td>
<td>1,220</td>
</tr>
<tr>
<td>TRC-CO2-02</td>
<td>MW-12</td>
<td>738</td>
</tr>
<tr>
<td>TRC-CO2-03</td>
<td></td>
<td>480</td>
</tr>
<tr>
<td>TRC-CO2-04</td>
<td>NW of MW-12</td>
<td>2,083</td>
</tr>
<tr>
<td><strong>Average for Three Locations in LNAPL Zone(^2)</strong></td>
<td></td>
<td><strong>1,304</strong></td>
</tr>
</tbody>
</table>

\(^1\) Values are corrected for \(^{14}\)C

**Duplicate**

**Background**
# Kansas City, KS Q1 Results

<table>
<thead>
<tr>
<th>Event</th>
<th>Sample</th>
<th>Location</th>
<th>CO₂ Flux Rate (gallons LNAPL per acre-year)</th>
<th>Result¹</th>
<th>Corrected for Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Quarter (September 2012)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TRC-CO2-01</td>
<td>MW-14</td>
<td></td>
<td></td>
<td>1,913</td>
<td>1,750</td>
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<tr>
<td>TRC-CO2-02</td>
<td>MW-15</td>
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<td></td>
<td>1,865</td>
<td>1,703</td>
</tr>
<tr>
<td>TRC-CO2-04</td>
<td>MW-15</td>
<td></td>
<td></td>
<td>1,715</td>
<td>1,553</td>
</tr>
<tr>
<td>TRC-CO2-03</td>
<td>RW-219</td>
<td></td>
<td></td>
<td>613</td>
<td>450</td>
</tr>
<tr>
<td><strong>Average for Three Locations in LNAPL Zone</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>1,438</strong></td>
<td><strong>1,276</strong></td>
</tr>
</tbody>
</table>

¹ Values are corrected for ¹⁴C

**Duplicate**

**Background**
# How Many Traps Are Enough?

<table>
<thead>
<tr>
<th>Site</th>
<th>Event</th>
<th>Number of Traps in LNAPL Zone</th>
<th>CO₂ Flux Rate (gallons LNAPL per acre-year)</th>
<th>Result¹</th>
<th>Corrected for Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kansas City, KS</td>
<td>Q1</td>
<td>3</td>
<td>1,438</td>
<td></td>
<td>1,276</td>
</tr>
<tr>
<td></td>
<td>Q2</td>
<td>6</td>
<td>1,091</td>
<td></td>
<td>929</td>
</tr>
<tr>
<td></td>
<td>Q3</td>
<td>6</td>
<td>1,831</td>
<td></td>
<td>1,591</td>
</tr>
<tr>
<td></td>
<td>Average for 3 Events</td>
<td></td>
<td>1,453</td>
<td></td>
<td>1,265</td>
</tr>
</tbody>
</table>

¹ Values are corrected for $^{14}$C
### Summary of Results To Date

<table>
<thead>
<tr>
<th>Site</th>
<th>Event</th>
<th>Number of Traps in LNAPL Zone</th>
<th>CO(_2) Flux Rate (gallons LNAPL per acre-year)</th>
<th>Result(^1)</th>
<th>Corrected for Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Quincy, MO</td>
<td>Q1</td>
<td>3</td>
<td>2,670</td>
<td>2,343</td>
<td></td>
</tr>
<tr>
<td>Spanish Lake, MO</td>
<td>Q1</td>
<td>3</td>
<td>301</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Kennett, MO</td>
<td>Q1</td>
<td>3</td>
<td>1,304</td>
<td>555</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Q2</td>
<td>3</td>
<td>1,288</td>
<td>924</td>
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<tr>
<td></td>
<td></td>
<td>Average for 2 Events</td>
<td>1,296</td>
<td>740</td>
<td></td>
</tr>
<tr>
<td>Kansas City, KS</td>
<td>Q1</td>
<td>3</td>
<td>1,438</td>
<td>1,276</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Q2</td>
<td>6</td>
<td>1,091</td>
<td>929</td>
<td></td>
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<td></td>
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<td>1,453</td>
<td>1,265</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Values are corrected for \(^{14}\)C
CH$_4$ Site Screening

GEM2000
Portable Landfill Gas Analyzer
The GEM™ 2000 portable instrument is designed for analyzing Landfill Gas (LFG) composition and calculating flow. The GEM™ 2000 combines the capabilities of the now discontinued QA-90 for monitoring gas migration probes and the GEM 500 for monitoring gas extraction systems. The GEM™ 2000 is certified Intrinsically Safe and offers improved speed and accuracy. It also measures and displays Sulfur Dioxide content, oxygen, and barometric pressure as well as CH$_4$ LEL (Lower Explosive Limit).

A New Screening Method for Methane in Soil Gas Using Existing Groundwater Monitoring Wells

by Kenneth P. Jewell and John T. Wilson
Presentation Overview

- Basic Concepts
- Field Applications
- Case Study on Use of NSZD Rates
- Findings and Recommendations
LNAPL Recovery Requirements

- Congress passed Subtitle I of the Solid Waste Disposal Act (1984)
- EPA adopted rules establishing requirements for UST systems (1988)
  - Requirement to “remove free product to the maximum extent practicable as determined by the implementing agency” (40 CFR 280.64)
- “How to Effectively Recover Free Product at Leaking Underground Storage Tank Sites” (EPA OUST, 1996):
  - “The soil will retain a significant portion of the product, but as this portion is immobile, it does not contribute to that portion termed “free product”
Missouri LNAPL Recovery Requirements

- **Missouri Risk-Based Corrective Action (MRBCA) Process for Storage Tank Sites (February 2004):**
  - “LNAPL must be removed from the environment to the maximum extent practicable.”
Soil Coring to Determine LNAPL Saturation
Petro-Physical Core Testing

- Core logging
- Pore fluid saturation testing on 18 soil samples (% of pore space occupied by LNAPL)
  - Maximum: 12.3%
  - Average: 6.1%
- Imbibition testing performed on two soil samples to determine residual saturation:
  - 19% to 26%
Conclusion of Petro-Physical Investigation

• No mobile/recoverable LNAPL in 18 samples from six locations
• If recoverable LNAPL exists at the site:
  – It occurs in thin seams and/or intermittent pockets
  – Relatively low volume
Carbon Dioxide Trap Locations

[Map with labeled locations TRC-CO2-6, TRC-CO2-7, TRC-CO2-8, TRC-CO2-9, TRC-CO2-10]
## West Quincy NSZD Rates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Result$^1$</th>
<th>Corrected for Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRC-CO2-10</td>
<td>Near RW-5</td>
<td>911</td>
<td>584</td>
</tr>
<tr>
<td>TRC-CO2-6</td>
<td>Near MW-8</td>
<td>327</td>
<td>0</td>
</tr>
<tr>
<td>TRC-CO2-7</td>
<td>Near PW-9</td>
<td>1,100</td>
<td>773</td>
</tr>
<tr>
<td>TRC-CO2-8</td>
<td>Near RW-4</td>
<td>5,939</td>
<td>5,612</td>
</tr>
<tr>
<td>TRC-CO2-9</td>
<td></td>
<td>6,060</td>
<td>5,733</td>
</tr>
<tr>
<td><strong>Average for LNAPL Zone</strong></td>
<td></td>
<td><strong>2,670</strong></td>
<td><strong>2,343</strong></td>
</tr>
</tbody>
</table>

$^1$ Values are corrected for $^{14}$C
Cumulative Mass Removal Recovery vs NSZD

- **Recovered Product**
- **Natural Source Zone Depletion**

Graph showing the cumulative mass removal recovery versus NSZD over time from 1/1/2005 to 1/1/2011.
Multiple Lines of Evidence for Assessing LNAPL Recovery Endpoint

- Recovery reached asymptote
- Baildown testing yielded transmissivity values consistent with endpoint values for hydraulic/pneumatic methods
- Petrophysical data showed little or no mobile LNAPL remaining
- Mass removal from recovery operations was far less than mass removal from NSZD
Presentation Overview

• Basic Concepts
• NSZD Measurements Using the Carbon Dioxide Trap – Project Summaries
• Case Study on Use of NSZD Rates
• **Findings and Recommendations**
Findings and Recommendations

- Traps are an effective tool for quantifying NSZD rates
- Trap applicability at UST sites may be limited by paving
- Assess vadose zone gas composition prior to applying traps
- Perform $^{14}C$ analysis
- For smaller sites, use a minimum of three locations within LNAPL zone
- Based on limited data, temporal variability:
  - Within a factor of seven at individual locations
  - Within a factor of two considering site-wide average
How to Use NSZD Rates

• LNAPL NSZD rate estimates that do not account for vadose zone processes will woefully under-estimate the actual rate.

• The NSZD rate can serve as a benchmark:
  – *Is installation of a free product recovery system warranted?*
  – *What is the cost-effectiveness of any active remediation?*
  – *Once installed, how long should the remediation system be operated?*
LNAPL Recovery Implications

• Requirement to “*remove free product to the maximum extent practicable as determined by the implementing agency*” (40 CFR 280.64, 1988)
  – Assumption: Any free product posed a particularly significant hazard; e.g., migration to nearby sewers

• Things we have learned since 1988:
  – “Free product” is a small fraction of total LNAPL, particularly with an aged release
  – “Accumulation in a well” does not equal macro-scale mobility
  – NSZD rate will often far exceed rate of free product recovery
For More Information

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