An Evaluation of Natural Source Zone Depletion Versus Active Remediation Rates

IPEC 22 November 2015

Nicholas Mahler
Tom Palaia
Rebecca Rewey
Drivers and Objective

• Measurement of natural source zone depletion (NSZD) rates (aka loss rates) of petroleum hydrocarbon LNAPL is an emerging science
  – To receive broader support, it is important to ground-truth the results
• To provide perspective, a survey consisting of 51 diverse sites/systems was performed to improve understanding of rates of remediation (in consistent units) for various petroleum remediation approaches
• This presentation will compare NSZD remediation rates to active remediation systems, and show that measurements of NSZD rates are comparable
Agenda

• Conceptualization of LNAPL in Subsurface
• Overview of NSZD
• Rates of NSZD as Measured by CO$_2$ Efflux
• Rates of Active Remediation
• NSZD vs Active Remediation Rates
• Conclusions
LNAPL Setting

- LNAPL exists in 4-phases

- Pore fluid profile often at $<$30% pore volume

HC = hydrocarbon
LNAPL Quantification

• Integrating specific volume over an area provides an estimate of the volume of LNAPL in the subsurface
  – A 1-ft mobile LNAPL smear zone profile with specific volume of 0.05 ft³/ft² roughly equates to 16,000 gallons of LNAPL per acre (gal/ac)

• Removal of 5,000 gallons from this area, reduces the in situ LNAPL volume by 30%
  – Reduces in situ LNAPL pore fluid saturations in smear zone profile to a maximum equal to the residual LNAPL saturation
  – Non-recoverable, immobile fraction will remain in situ
Natural Source Zone Depletion - Petroleum
Natural Source Zone Depletion - Petroleum

• LNAPL is degraded by the intrinsic processes of volatilization, dissolution, and biodegradation

• Results in significant and measurable losses of source material
Carbon Dioxide (CO₂) Efflux Measurements

• Estimated NSZD (aka LNAPL loss) rates based on stoichiometric conversion of sitewide CO₂ efflux measurements

• 8 diverse sites (E-Flux CO₂ Traps – 3 sites and LI-COR® 8100A soil flux system – 6 sites)
  – Total of 86 CO₂ trap and 290 LI-COR® event-locations

• Site conditions included:
  – Natural gas well site
  – Operating gas plant and compressor station
  – Pipeline
  – Terminal
  – Railyard
  – Remote maintenance camp

• Urban and rural areas with predominantly pervious, but variable ground cover

• Consolidated and unconsolidated subsurface soil
Example Results from a NSZD Evaluation

- Collected CO\textsubscript{2} efflux measurements
- Corrected for background
- Performed stoichiometric conversion
- Plotted NSZD rates
- Integrated the results to estimate a sitewide NSZD rate
- Sites with multiple rounds of measurements were seasonally adjusted to estimate an annual rate
Summary of NSZD Rates

NSZD Median = 700 gal/ac/yr

Site Number

Note: Recall a site with LNAPL specific volume of 0.05 ft³/ft² contains 16,000 gals/ac.
Summary of NSZD Rates

- Recall: 1-ft mobile LNAPL smear zone profile with specific volume of 0.05 ft$^3$/ft$^2$ roughly equates to 16,000 gallons of LNAPL per acre (gal/ac)

- Removal of 700 gallons per acre equates to less than an inch removal, with the same assumptions
Assessment of Comparable Rates of Remediation

- Surveyed projects to compile real site monitoring data

- 43 systems

<table>
<thead>
<tr>
<th>Method</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNAPL Skimming</td>
<td>6</td>
</tr>
<tr>
<td>Groundwater drawdown-enhanced Skimming</td>
<td>5</td>
</tr>
<tr>
<td>Bioventing/Biosparging</td>
<td>4</td>
</tr>
<tr>
<td>Soil Vapor Extraction</td>
<td>5</td>
</tr>
<tr>
<td>Air Sparging/Soil Vapor Extraction</td>
<td>10</td>
</tr>
<tr>
<td>Multiphase Extraction</td>
<td>13</td>
</tr>
<tr>
<td><strong>Total Number of Active Systems in Survey</strong></td>
<td><strong>43</strong></td>
</tr>
</tbody>
</table>

- Sites in survey include a variety of:
  - petroleum products
  - source zone dimensions
  - remedial design bases
  - operation and maintenance routines (i.e., zones, pulsing, etc.)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Median</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment Area Size (acres)</td>
<td>2.0</td>
<td>0.1 - 108</td>
</tr>
<tr>
<td>Total Volume Removed (gallons)</td>
<td>4,500</td>
<td>18 - 6,000,000</td>
</tr>
<tr>
<td>Mass Removal Rate (pounds/year)</td>
<td>7,339</td>
<td>4 - 5,000,000</td>
</tr>
<tr>
<td>Years of Operation (years)</td>
<td>5.0</td>
<td>0.6 - 24</td>
</tr>
<tr>
<td>Remediation Rates (gallons/acre/year)</td>
<td>1,057</td>
<td>0.1 - 11,790</td>
</tr>
</tbody>
</table>
Active Remediation Rate Survey Results
Comparison of Median Rates of Remediation

- Survey indicates that NSZD rates fall within the range of other remedial approaches
Evaluation of Early and Late Stage Rates

- Midway into remediation, NSZD may become stronger than some remedies

Note: 10 of the 13 MPE systems had no difference in early and late remediation rates, thus were excluded from this early/late data sets
Approximate Efflux Monitoring Costs

- **LI-COR soil flux system**
  - Rental ~$1,700/month for the first month and ~$900/month for subsequent months
  - 20 beveled 8” PVC collars ~$300
  - Mobilization, 8 hrs onsite/visit, 2 field technicians – install collars and perform four rounds of daily measurements
  - ~$500/location

- **E-Flux CO₂ traps**
  - Field components (~$320/location)
  - CO₂ and ¹⁴C analysis of traps ~$1,700/location
  - Two site visits, start and end of 2 week deployment period (install and retrieve/ship traps, 4 hrs onsite, 1 field technician)
  - ~$2,000/location
Conclusions

• In general NSZD rates measured using CO$_2$ efflux methods are reasonable
  – They fall within the spectrum of the surveyed remedial systems (~200-4,000 gal/ac/yr)
  – Are consistent with plausible rates of remediation for sites with >10,000 gal/ac present in the subsurface

• NSZD rates are significant and are competitive with remediation rates of some active systems

• There appears to be a point during remediation when the effectiveness of active remediation may fall below NSZD
  – The NSZD rate is a useful metric for optimization of active remediation
Thank You

Nicholas Mahler
Nicholas.Mahler@ch2m.com
(720) 286-3103