CO₂ Flux Measurements to Estimate Natural Source Zone Depletion – State of the Practice and Method Validation using Modeling

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Presentation Outline

- Background and purpose
- Field methods for estimation of LNAPL mass loss from CO₂ fluxes and published data
- CO₂ sequestration monitoring tools and selected data
- Results of modeling study using MIN3P-Dusty numerical model

This modeling study is extension of a project being conducted by Golder Associates for the American Petroleum Institute on evaluation of implications of ethanol-blended gasoline on vapour intrusion – API’s support is gratefully acknowledged!

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

Can occur through volatilization, biodegradation and dissolution
Background and Purpose

- CO₂ is the final end product of petroleum mineralization either directly through aerobic respiration or through oxidation of CH₄ from anaerobic processes (methanogenesis).
- Large natural LNAPL losses have been measured relative to depletion achieved through intrusive remediation strategies.
- Losses may be important in reducing the potential for LNAPL mobility.
- There has been limited modeling studies of CO₂ flux and biodegradation processes, including evaluation of gasoline-ethanol blends.
Figure 2.1. Conceptualization of processes governing natural losses of LNAPL (After Sihota et al., 2011).

McCoy 2012 (after Sihota et al. 2011)
Mass Flux and Loss Estimation Methods

- Gradient method
  - Requires accurate measurement of soil gas profile and soil properties (porosity, soil moisture) to estimate effective diffusivity

- CO₂ surface flux method
  - Static trap
  - Dynamic method
Static CO₂ Trap Method

- Static trap that integrates CO₂ flux over time (typically 2-4 weeks)
- Two sorbent elements consisting of sodalime media
  - Bottom element – measures soil CO₂
  - Top element – measures atmospheric CO₂
- Travel blank for QC
- Lab analysis for total carbonate
- Method developed by Colorado State University (CSU)

McCoy, K. 2012. Resolving Natural Losses of LNAPL using CO2 Traps, Colorado State, MSc Thesis
Dynamic CO₂ Flux Method

- Dynamic closed chamber and infrared analyzer (e.g., Li-Cor 8100)
- Successfully used for many studies/applications
- Can take single snap-shot measurements or multi-plexed for multiple measurements over time
- Typically soil temperature and moisture also measured
- Possible disadvantage is that does not integrate temporal variations, but more measurements can be made
- Method developed by University of British Columbia (UBC) for mass loss estimation


Background Correction

- Both static and dynamic methods require consideration of background flux through soil respiration
- Can measure flux at background site with similar vegetation
- Conduct radiocarbon $^{14}$C analysis by accelerator mass spectrometry, $^{14}$C half-life = 5,600 years, fossil fuels depleted in $^{14}$C
- Isotope analysis can also provide insight on source
Selected Published CO$_2$ Flux Data

- McCoy (2012) CSU
  - Comprehensive testing at six sites (N=75)
  - CO$_2$ efflux could not be resolved from background (0.8-9.0 umol/m$^2$/sec) in 28 samples
  - For samples where flux > background, CO$_2$ efflux was 3.3-36 umol/m$^2$/sec (mean = 9.5 umol/m$^2$/sec)
  - LNAPL loss rates = **660-18,000** gal/acre/yr.

  - Natural hydrocarbon losses of 0.1-1 kg/m$^2$/yr for Guadaloape Oil Field (~**130-1300** gal/acre/yr)

- Sihota et al. (2011)
  - Natural hydrocarbon loss of 3.3 g/m$^2$/d for Bemidji oil spill (~**1600** gal/acre/yr)
Background range for different vegetation Western Canada site = 0.2-7 umol/m²-s

Seasonal CO₂ data compares well to FluxNet Data
CO₂ Sequestration Monitoring Tools and Selected Data

- CO₂ and CH₄ of soil gases in real time at 1-Hz.
- Atmospheric O₂ = 20.946%; CO₂ = ~400 ppmv
- O₂ anom. vs CO₂ anom. used to identify deviations from a slope of 1:-1, i.e. the microbial respiration of soil carbon line.
Modeling Approach

Numerical Model Reactive Transport Code MIN3P-DUSTY (developed by Dr. Uli Mayer, UBC)
Model setup: 1-dimensional steady state (infinite source) & transient (depleting LNAPL source) scenarios

Key Model Inputs

- Ethanol Content & Solubility
- Ethanol Degradation Kinetics
- Vadose Zone Moisture Content
- Concrete Foundation Cap
Modeling Approach

- Transport Processes:
  - Diffusion
  - Advection
- Sorption
- Volatilization & Dissolution
- Degradation Reactions:
  - Aerobic: E10 gasoline components & methane
  - Anaerobic: ethanol
Model Domain

- **Concrete foundation (0 - 10 cm)**
- **Clean soil vadose zone (1.0 - 5.0 m) sandy loam**
- **Residual LNAPL Smear Zone (1.0 m)**
- **Free exit (aqueous phase)**
  - No flow (gas phase)

- **Atmospheric conditions**
  - $C_{gases} = \text{constant}$
- **LNAPL saturation = 18\%** (Brost and DeVaul, 2000)

- **Constant / Initial concentrations:** $C_{\text{Ethanol}}$, $C_{\text{Benzene}}$, $C_{\text{Xylene}}$, $C_{\text{Iso-octane}}$

**Gases**
- $Q_{O_2}$
- $Q_{CH_4}$ & $Q_{CO_2}$
Modeling Cases

- **Soil-water content**: Saturation \( (S_w) = 0.1, 0.3, 0.5 \) for E0 and E10 \([D=3 \text{ m}]\)

- **Depth to LNAPL source**: Depth \( (D) = 1, 3, 5 \text{ m} \) for E10 \([S_w = 0.3]\)

- **Ethanol content**: E0, E10, E20, E30 \([D = 3 \text{ m}, S_w = 0.3]\)

- **Capping**: No cap, cap for E10 \([D = 3 \text{ m}, S_w = 0.3]\)

- All cases run to steady state
Biodegradation Rate Parameters

- Biodegradation Model
  - First-order for gasoline components, Monod term for dependence on O₂ availability
  - Dual Monod formulation for methane oxidation
  - Anaerobic degradation of ethanol, first-order with O₂ inhibition term

- Biodegradation Rate Parameters
  - Benzene: 0.79 hour⁻¹; Xylene: 0.79 hour⁻¹; Iso-octane: 42 hour⁻¹; Ethanol: 0.3 day⁻¹ (aerobic) and 0.1 day⁻¹ (anaerobic)
  - Maximum CH₄ degradation rate = 8x10⁻⁸ mol (CH₄)/L(aq)/s; Half saturation constants: 1 x 10⁻⁵ mol/L(aq)

#### Ethanol blended gasoline components and concentrations

<table>
<thead>
<tr>
<th>Hydrocarbon Component</th>
<th>Vapor Phase Mass Fraction</th>
<th>Vapor Concentration (mg/L)</th>
<th>Aqueous Phase Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total</strong></td>
<td>1</td>
<td>200 – 203</td>
<td>89 – 9,089</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.016</td>
<td>3.2</td>
<td>17</td>
</tr>
<tr>
<td>Other aromatics (xylene)</td>
<td>0.072</td>
<td>15</td>
<td>70</td>
</tr>
<tr>
<td>Aliphatics (iso-octane)</td>
<td>0.90</td>
<td>180</td>
<td>1.7</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0 - 0.014</td>
<td>0 – 2.8</td>
<td>0 – 9,000</td>
</tr>
</tbody>
</table>
## Input Parameters

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Source Zone Aquous Ethanol Concentration (mg/L)</th>
<th>Water Saturation, $S_w$</th>
<th>Capping?</th>
<th>Source Depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - E10 Mod $S_w$</td>
<td>3,000</td>
<td>0.3</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>2 - E10 High $S_w$</td>
<td>3,000</td>
<td>0.5</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>3 - E10 Low $S_w$</td>
<td>3,000</td>
<td>0.1</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>4 - E10 capping</td>
<td>3,000</td>
<td>0.3</td>
<td>√</td>
<td>3</td>
</tr>
<tr>
<td>5 - E10 depth</td>
<td>3,000</td>
<td>0.3</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>6 - E0</td>
<td>0</td>
<td>0.3</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>7 - E10</td>
<td>3,000</td>
<td>0.3</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>8 - E20</td>
<td>6,000</td>
<td>0.3</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>9 - E30</td>
<td>9,000</td>
<td>0.3</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>10 - E0 ModSw</td>
<td>0</td>
<td>0.1</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>11 - E0 HighSw</td>
<td>0</td>
<td>0.3</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>12 - E0 Low Sw</td>
<td>0</td>
<td>0.5</td>
<td>-</td>
<td>3</td>
</tr>
</tbody>
</table>
Predicted Depth Profiles – Water Content

baseline

\( S_w = 30\% \)  \( S_w = 50\% \)  \( S_w = 10\% \)
Summary of Key Modeling Results

LNAPL Mass Loss Inferred from CO₂ Flux:
stoichiometry of benzene degradation & LANPL density = 0.8 kg/L

LNAPL Source Loss (gal/acre/yr) \( (S_w = 0.3) \)

E0 Scenario

<table>
<thead>
<tr>
<th>Source Zone Flux</th>
<th>Inferred from CO₂ Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,300</td>
<td>3,100</td>
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</table>

E10 Scenario

<table>
<thead>
<tr>
<th>Ethanol Loss</th>
<th>Source Zone Flux</th>
<th>Inferred from CO₂ Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>19,100</td>
<td>4,400</td>
<td>9,600</td>
</tr>
<tr>
<td>22,500</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

What about CH₄ efflux?
## Modeling Results

<table>
<thead>
<tr>
<th>Scenario</th>
<th>CO₂ Efflux</th>
<th>Predicted LNAPL Loss from CO₂ Efflux</th>
<th>Predicted LNAPL Loss Rates including Ethanol</th>
<th>Predicted LNAPL Loss Rates without Ethanol Contribution</th>
<th>LNAPL Depletion Time including Ethanol</th>
<th>LNAPL Depletion Time without Ethanol Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>units</strong></td>
<td>(mg/m²/day)</td>
<td>(gal/acre/yr)</td>
<td>(gal/acre/yr)</td>
<td>(gal/acre/yr)</td>
<td>(years)</td>
<td>(years)</td>
</tr>
<tr>
<td><strong>No Ethanol</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E0 - Low Sw = 0.1</td>
<td>4.71E+04</td>
<td>6819</td>
<td>7642</td>
<td>7642</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>E0 - Mod Sw = 0.3</td>
<td>2.13E+04</td>
<td>3082</td>
<td>3342</td>
<td>3342</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>E0 - High Sw = 0.5</td>
<td>6.97E+03</td>
<td>1008</td>
<td>1094</td>
<td>1094</td>
<td>69</td>
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<tr>
<td><strong>Ethanol E10</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E10 - Low Sw = 0.1</td>
<td>5.98E+04</td>
<td>8652</td>
<td>13348</td>
<td>7074</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>E10 - Mod Sw = 0.3</td>
<td>6.67E+04</td>
<td>9646</td>
<td>22503</td>
<td>4454</td>
<td>3</td>
<td>17</td>
</tr>
<tr>
<td>E10 - High Sw = 0.5</td>
<td>7.65E+04</td>
<td>11065</td>
<td>35465</td>
<td>6308</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td><strong>Different Ethanol Blends (for D=5 m)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E0  Sw = 0.3</td>
<td>1.28E+04</td>
<td>1850</td>
<td>2006</td>
<td>2006</td>
<td>37</td>
<td>37</td>
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<tr>
<td>E10  Sw = 0.3</td>
<td>6.47E+04</td>
<td>9359</td>
<td>22003</td>
<td>3954</td>
<td>3</td>
<td>19</td>
</tr>
<tr>
<td>E20  Sw = 0.3</td>
<td>9.76E+04</td>
<td>14120</td>
<td>43906</td>
<td>7788</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>E30  Sw = 0.3</td>
<td>1.28E+05</td>
<td>18520</td>
<td>65918</td>
<td>11714</td>
<td>1</td>
<td>6</td>
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<tr>
<td><strong>Effect of Cap</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E10 - no cap Sw = 0.3</td>
<td>6.67E+04</td>
<td>9646</td>
<td>22503</td>
<td>4454</td>
<td>3</td>
<td>17</td>
</tr>
<tr>
<td>E10 cap  Sw = 0.3</td>
<td>1.77E+04</td>
<td>2562</td>
<td>21951</td>
<td>3900</td>
<td>3</td>
<td>19</td>
</tr>
</tbody>
</table>
Effect of Soil Moisture Content (E0)

Mass loss shown is calculated from source mass loss (and not CO₂ flux)
Effect of Ethanol Content

- **Surface Efflux (mg/m²/day)**
  - CO2
  - CH4
  - Benzene
  - Xylenes
  - Iso-octane

- **Volumetric LNAPL Loss Rate (gal/acre/yr)**
  - Total
  - Without Ethanol

March 19, 2014
Effect of Cap (E10)

![Graph showing surface efflux and volumetric LNAPL loss rate with and without cap for CO2, CH4, Benzene, Xylenes, and Iso-octane.](image)

- **Surface Efflux (mg/m²/day)**
  - CO2, CH4, Benzene, Xylenes, Iso-octane
  - Blue diamonds represent no cap, red squares represent cap.

- **Volumetric LNAPL Loss Rate (gal/acre/yr)**
  - Total and Without Ethanol
  - Blue bars represent no cap, red bars represent cap.

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Conclusions

- Innovative new methods (static and dynamic chambers) have been developed for estimation of LNAPL mass loss
- Numerical model enables mass loss to be estimated from CO$_2$ efflux and source loss as check
- For E0 case and $\geq$E10 cases (excluding ethanol component), model predictions fall within range of published losses from field studies
- CH$_4$ flux not accounted for in CO$_2$ measurement method, may be significant for higher ethanol contents
- Future modeling plans to include capillary fringe, loss through dissolution and to conduct more detailed comparison to field site with accurate soil properties
Questions?

Thank-you!

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