New Methods to Assess and Support Monitoring Natural Source Zone Depletion

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Presentation Agenda

- Introduction to Natural Source Zone Depletion (NSZD) and Carbon Dioxide (CO₂) Efflux
- New NSZD Monitoring Methods
  - Soil flux system (LI-COR, Inc.)
  - CO₂ Traps (E-Flux, LLC)
- Case Study 1 - Large Diesel Release, Colorado
- Case Study 2 - Natural Gas Well Site, Alberta
- Conclusions
Introduction
Visual Representation of NS ZD and CO₂ Efflux
How has CO$_2$ efflux traditionally been monitored?

- CO$_2$ efflux has not been part of the routine of monitored natural attenuation (MNA)
- Typical focus has been on groundwater - electron acceptors, redox parameters, microbiological evidence, and contaminant concentrations
- Theoretical analysis (P. Johnson, ASU, 2009) and LNAPL stability efforts (T. Sale, CSU, 2012) indicate that more degradation is occurring than conventional mass budgeting techniques are accounting for
Why is CO$_2$ efflux monitoring important?

- Current practice does not account for all natural losses and is significantly under-estimating them.
- CO$_2$ measurement at ground surface can be a very cost-effective alternative to groundwater monitoring.
How does CO$_2$ efflux apply to my remedial efforts?

- Can be used at remediation sites to:
  - Delineate subsurface NAPL footprint
  - Monitor natural attenuation processes and estimate contaminant destruction rates
  - Better understand source zone longevity
  - Benchmark remedies and establish endpoints
How can CO₂ efflux be measured?

- CO₂ efflux can be directly measured at ground surface using:
  - Flux Chamber Method (LI-COR, Inc.)
  - CO₂ Trap Method (E-Flux, LLC)

- CO₂ is created by both petroleum- (deep) and ecosystem-related (shallow) decomposition sources
  - Requires quantitative separation technique to isolate NAPL-related loss rates
  - Techniques are available to “correct” the total measured CO₂ efflux values
CO₂ efflux varies with temperature (seasonal), wind, and spatially due to changes in ground cover (i.e., grass, gravel).

**CO₂ efflux monitoring requires a carefully designed and technically sound approach to accurately estimate annual NAPL loss rates across large diverse areas.**
Industry Acceptance for NSZD and CO\textsubscript{2} Eflux

Advocates include:
- ITRC 2009 guidance published to assess NSZD
- British Columbia (U. Mayer and N. Sihota) and Arizona (P. Johnson and P. Lundegard) continue to publish peer-reviewed literature in support of the methods
- Colorado State (T. Sale and J. Zimbron) commercialized the CO\textsubscript{2} Trap technology (E-Flux, LLC)
- Various site owners and consultants are pushing acceptance
  - 11 abstracts submitted on NSZD to Battelle 2014 conference

Provinces/States with known applications
New NSZD Monitoring Methods
NSZD CO$_2$ Flux = Total CO$_2$ Flux - Background CO$_2$ Flux

**Theory**
- Total CO$_2$ flux measured over the NAPL footprint
- Background CO$_2$ flux measured outside the NAPL footprint
- Instantaneous measure

**Equipment**
- Collar (thick-walled 8” diameter PVC with a beveled edge)
- Vented bellows-controlled flux chamber
- Analyzer control unit (including infrared gas analyzer and pump)
- Application software

http://licor.com/env/products/soil_flux/
Soil Flux System - Data Analysis

- Real-time data collection and analysis
  - \( \text{CO}_2 \) concentration measured in return air over preset time period
  - Efflux = slope of \( \text{CO}_2 \) concentration versus time

![Image of data analysis graph with labels: Dead Band Observation]
## CO₂ Trap (E-Flux, LLC)

### Theory
- Flow-through sorbent trap method
- Time-averaged CO₂ flux

### Equipment
- Receiver pipe
- CO₂ Trap with dual sorbent pucks
- Vented protective cover
CO₂ Trap – Data Analysis

**Raw Data:**
- **Step 1:** Measure sorbed CO₂ by acidifying sorbent and measuring the volume of evolved CO₂ gas
- **Step 2:** Subtract CO₂ due to travel and background
- **Step 3:** Divide the mass of CO₂ by the cross-sectional area of the column and the period of time the trap was deployed to calculate CO₂ efflux
- **Step 4:** Convert CO₂ efflux to hydrocarbon loss by selecting appropriate stoichiometric ratio between CO₂ and LNAPL petroleum hydrocarbons
  - 2 C₆H₆ + 15 O₂ → 12 CO₂ + 6 H₂O (benzene example)
Case Study 1: Large Diesel Release, Colorado
Conceptual Site Model
Large Diesel Release, Colorado

- WWTP and Waste Oil ASTs
- Approximate Extent of LNAPL
- Thin (<2 ft) Weathered Waste Oil & Diesel Fuel
- DTW On-Site: 18-22 ft bgs
- DTP Off-Site: 6-14 ft bgs
- No Dissolved-Phase Groundwater Plume

- Groundwater Flow
- Property Boundary
- Commercial Area
- Residential Neighborhood
- Sand and Gravel
- Silt and Clay
- Registered private wells appear to pump from deeper aquifer.
- Off-site properties served by municipal water supply
- Not To Scale

30 acres of LNAPL Impacts
**Corrected CO₂ Efflux and Loss Rate Estimates**

<table>
<thead>
<tr>
<th>CO₂ Trap</th>
<th>Total CO₂ Mass (g)</th>
<th>CO₂ Efflux (µmol/m²/sec)</th>
<th>Background Adjusted CO₂ Efflux (µmol/m²/sec)</th>
<th>Background Adjusted LNAPL Loss Rate (g/m²/d)</th>
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<tbody>
<tr>
<td><strong>BACKGROUND TRAPS</strong></td>
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<td><strong>LNAPL LOCATIONS TRAPS</strong></td>
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<td>*</td>
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</table>
Average corrected NSZD rate: 766 g/m²/d
Extrapolated over the entire 30 acre LNAPL body: 219,000 kg/yr
Conclusions and Ultimate Data Use

- Used CO₂ Trap data in conjunction with in-well LNAPL flux data from dye tracer testing to demonstrate LNAPL plume stability
- MNA selected as the sole remedy
Case Study 2: Natural Gas Well Site, Alberta
Site Conditions
Natural Gas Well Site, Alberta

- Natural gas well and compressor station installed on gravel pad in 1996 within a forested and marshy area
- Releases of natural gas liquids/condensate (C6-16) and drilling fluids (C16-50)
- Areas of granular fill underlain by medium-grained sand and interbedded clay and organic materials
- Laser-induced fluorescence survey
  - LNAPL delineated over 1.2 acre
- Focused active remedy over 0.4 acre and natural attenuation for fringe
Project Objectives and CO$_2$ Survey Scope

- Compare natural losses to active removal using multiphase extraction
- Field Program
  - 20 locations – LI-COR 20cm chamber
  - 10 locations – E-Flux 10cm CO$_2$ traps
Field Methods
Natural Gas Well Site, Alberta

- MPE system shut down for several days prior to start of CO₂ survey for re-equilibration of subsurface
- LI-COR collars set ~5-8cm depth with hand tools
- E-Flux CO₂ Traps set ~18cm depth
Decent correlation between LI-COR and E-Flux in grassy areas with loose ground surface soil

Poor correlation between LI-COR and E-Flux in gravelly areas with dense ground surface soil

- Factor of installation depth – deeper ground surface penetration of Traps broke through semi-confining gravel-hard pan and opened a chimney for CO$_2$ escape that was not “naturally” occurring
Results – What did that mean?
Natural Gas Well Site, Alberta

- Segregate data sets into grassy and gravelly areas
- CO₂ efflux:
  - Low in MPE areas
  - Highest in LNAPL core outside MPE influence
- NAPL loss rates up to 5.7 g/m²/d
LI-COR measurements used in gravel and E-Flux $^{14}$C corrected results used in grassy areas

Geospatially-weighted average mass loss rate estimated to be 1,900 kg/year across LNAPL footprint

Establishes a good basis for an endpoint to MPE operation

Follow-on efforts to ascertain long-term monitoring protocol and better refine estimates of NSZD
Conclusions
Approximate Deployment Costs (Alberta example)

- **LI-COR soil flux system**
  - Rental ~$1,700/month
  - 20 beveled 8” PVC collars ~$300
  - Five site visits over 2 weeks (1 hr drive time each way, 8 hrs onsite/visit, 2 field technicians, $75/hr) – install collars and perform four rounds of daily measurements
  - $9,500 ($500/location)

- **E-Flux CO₂ traps**
  - Supply and CO₂ and ¹⁴C analysis of 10 traps ~$18,000
  - Two site visits, start and end of 2 week deployment period (install and retrieve/ship traps, 1 hr drive time each way, 4 hrs onsite, 1 field technician)
  - $18,900 ($1,900/location)
Role of CO₂ Monitoring at Your Site

- CSM development
  - Estimate amount of NSZD currently occurring
  - Delineate LNAPL footprint

- Line of evidence
  - Use estimate to compare NSZD to active treatment remedies (e.g., Colorado example)
  - Evaluate the value of active remediation
  - Credible active remedy showing substantive NSZD is at work
    • active remedy is in place with minimal remediation costs

- Compare efficacy of remedial actions
  - Compare pre- and post-site conditions to evaluate efficacy of installed remedies (e.g., biosparging)
Applicability of CO$_2$ Efflux Monitoring

- Most suitable for petroleum sites with:
  - Identified NAPL within unconsolidated geology
  - Predominantly pervious ground cover and effective atmospheric exchange
  - Planned or existing MNA remedy component
  - Active remedies approaching/at asymptotic recovery limit
  - Enhanced bioremediation remedies looking for cost-effective monitoring technology

- Useful to projects in all stages of remediation from initial characterization to remedy optimization
# CO₂ Efflux Monitoring Method Comparison

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<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tbody>
<tr>
<td>Soil Flux System (LI-COR)</td>
<td>• Less susceptible to soil cover density</td>
<td>• Snap shot in time only - need for repeat measurements</td>
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<tr>
<td></td>
<td>• Quick measurements – can do more of them</td>
<td>• Measurement variability and need for background correction</td>
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<tr>
<td></td>
<td>• Real-time data</td>
<td></td>
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<tr>
<td>CO₂ Trap Method (E-Flux)</td>
<td>• Time averaged CO₂ flux</td>
<td>• More affected by soil cover density</td>
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<td></td>
<td>• Less labor intensive</td>
<td>• Analytical cost</td>
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<tr>
<td></td>
<td>• Ability to use ¹⁴C radio isotope to correct for background</td>
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<td></td>
<td>• Simpler math to get results</td>
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Conclusions

- CO$_2$ efflux monitoring technologies offer a less invasive and less labor intensive alternative to traditional methods

- More accurately account natural losses, improve understanding, and provide a more technical sound benchmark for remedy evaluation
Conclusions

- These methods provide data to more accurately quantify NSZD and are gaining ground toward regulatory acceptance.

- Technology selection and the field program require careful consideration of data objectives, logistics, site conditions, and ultimate data use.

**These CO₂ efflux methods are a significant improvement in source zone monitoring. Their technical-defensibility, application ease, and cost-effectiveness could lead to replacing traditional methods and gaining a broad industry acceptance as a best practice.**
Questions?
Thank You For Your Time

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Interstate Technology and Regulatory Council (ITRC), 2009. Evaluating Natural Source Zone Depletion at Sites with LNAPL. April.


