Soil-gas behavior and measurement in a carbon-reactive natural analogue; implications for near-surface monitoring

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Monitoring at Carbon Storage Sites

- **Atmosphere**
- **Biosphere**
- **Vadose zone**
- **Shallow groundwater**
- **Seal**
- **Subsurface Monitoring Zone**
- **CO₂ plume**

**Near-Surface Monitoring Zone**
- High background variability and dynamic, many challenges

**Shallow groundwater**
- Moderate background variability, assurance of no damage in USDW

**Subsurface Monitoring Zone**
- Low background variability, early detection, small signals

**CO₂/brine**

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Goals of Vadose-Zone Monitoring:

- Ability for relatively early leak detection.
- Identify and characterize pathways of preferential transport.
- Cost-effective monitoring strategies.
- Provide information useful for remediation and accounting.
Challenges to Near-Surface Monitoring in the Vadose Zone

- CO₂ exists naturally and is spatially and temporally variable and site-specific.

- Discern natural background variations from a leakage signal.

- CO₂ is highly reactive and mobile in the subsurface.

- What is being measured?
Goal and Approach

Use simple fixed gases (CO₂, O₂, N₂, CH₄) to understand the environmental factors affecting CO₂ concentrations at a playa lake natural analogue.
Effects of Vadose-Zone Carbon Cycling

Vadose-zone Carbon Cycling

Produce CO₂
Concentrate CO₂

Consume CO₂
Disperse CO₂

False positives
Mask signal

False negatives
Dampen signal

Biotic
Produce CO₂

Abiotic
Produce, consume, redistribute CO₂

Plant activity
Organics → CO₂

Soil carbonate
Soil moisture

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Natural Analogue - Playa Lake

Organics $\rightarrow$ CO$_2$

Contribute to background variability

CO$_2$ “leakage signal” in case study

Soil carbonate

Dissolution of CO$_2$ into pore water.

Soil Moisture

Above wetting front, soil breathing dilutes CO$_2$

Below wetting front CO$_2$ is concentrated

Contribute to background variability

CO$_2$ “leakage signal” in case study
Natural Analogue - Playa Lake

- Perched Lakes
- Thick vadose zone (~ 60 m)
- CO$_2$-rich (17 vol. %)
- High environmental variability
- High degree of carbon cycling
Study Area

Canadian River

Southern High Plains
Playa Zones

Floor

Annulus

Slope

Moisture
Organic carbon
Soil carbonate
Dynamic Environmental Factors

Water flux
Soil organic matter
Microbial activity
Soil carbonate

<table>
<thead>
<tr>
<th>Gas</th>
<th>Conc. Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogenic CO2</td>
<td>atm - 17%</td>
</tr>
<tr>
<td>O2</td>
<td>0-21%</td>
</tr>
<tr>
<td>CH4</td>
<td>0 - 2.5%</td>
</tr>
<tr>
<td>N2</td>
<td>78 - 95%</td>
</tr>
</tbody>
</table>

Wet condition
Dry condition

Soil carbonate

Pump house
Playa Monitoring

54 permanent gas wells
24 stations
≤ 15 m deep
>1000 real-time gas analyses
  CO₂, CH₄, N₂, O₂

Soil organic carbon
Soil carbonate

Atmospheric parameters

Looking at variability over playa zones

TDCJ Study playa
Soil-gas Well Construction

Soil-Gas Well Design

- ½ inch copper tubing
- PVC surface protector
- Bentonite seal
- Porous sand-pack.

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**Biogenic CO₂ Production**

\[
\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]
What About Denitrification?

6CH₂O + 2NO₃⁻ = N₂ + 6CO₂ + 12H⁺
Chemical Advection

• CO$_2$ dissolves and reacts with soil carbonate.

• Total pore pressure drops.

• Advection occurs.

• Volume % of N$_2$ increases.
Nitrogen Gas Compositions

Weyburn

Cava dei Seici

Playa Lake

Riding and Rochelle, 2005
IEA Weyburn Final Report
CO₂ Dissolution

Soil carbonate absent
Henry’s Law constant-

\[ K_H = \frac{\text{CO}_2^{(g)}}{\text{CO}_2^{(aq)}} \]

Soil carbonate present
Chemical Reaction

\[ \text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^- + \text{Ca}^{2+} \]
Summary: Important Environmental Components and Measurements

Vadose-zone Carbon Cycling

Soil-gas parameters
- $CO_2$, $O_2$, $N_2$, $CH_4$

Soil Organic Content
- Source of microbial $CO_2$
- $CO_2$, $O_2$, $CH_4$

Soil Carbonate
- Enhances $CO_2$ dissolution
- $N_2$

Moisture Fluctuations
- Master variable
# Characterization of “Surface Monitoring Potential”

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>COMBINATION OF EXISTING VADOSE-ZONE CONDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Water Flux Only</td>
</tr>
<tr>
<td>Organics → CO2</td>
<td>negligible</td>
</tr>
<tr>
<td>CO₂ Dissolution</td>
<td>negligible</td>
</tr>
<tr>
<td>Gas Redistribution</td>
<td>high</td>
</tr>
<tr>
<td>Monitoring Difficulties</td>
<td>Soil breathing limited. Caution advised when interpreting surface flux measurements. Surface flux measurements may underestimate subsurface CO₂. Microbial CO₂ input causes overestimation. Carbonate dissolution is a CO₂ sink. Gas advection may cause mislocation of of leak. Complex carbon cycling. Isotope data are necessary to constrain cycling. Soil-gas monitoring is relatively straightforward and will accurately define CO₂ leakage.</td>
</tr>
<tr>
<td>Accuracy of anthropogenic CO₂ estimation</td>
<td>Underestimate</td>
</tr>
</tbody>
</table>
Conclusions

• Water flux, organic matter and soil carbonate can be major factors affecting variability of background CO$_2$ and the fate of exogenous CO$_2$.

• Measuring all fixed soil-gases such as O$_2$ and N$_2$ in addition to CO2 can give information on important vadose zone processes affecting CO$_2$ concentrations.

• One-time measurements of parameters such as soil organic matter, soil carbonate, and moisture flux is a simple way of characterizing a site for its “Surface Monitoring Potential”

• “Surface Monitoring Potential” can give an indication of the sensitivity of the system to exogenous CO$_2$ input.
Thank you!