Challenges associated with geochemical monitoring of active CO$_2$ injection for EOR

Space Geodesy and Geochemistry Applied to Monitoring and Verification of Carbon Capture and Storage – Training Grant
Award # DE-FE0002184

Combining Space Geodesy, Seismology, and Geochemistry for Monitoring Verification and Accounting of CO$_2$ in Sequestration Sites
Award #DE-FE0001580

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U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Infrastructure for CCS
August 20-22, 2013
Accomplishments to Date for Training Grant

– Educating 3 graduate students
– Students are taking courses, engaging in research, presenting at meetings, and writing research proposals
– Instrumentation deployed to field site, with almost two years of geochemical data collected
– All students are within 2 years of graduating (Ph.D.)
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<th>Multi-technique approach</th>
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<td>Peter Swart</td>
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Our geochemical measurements are primarily made using commercially available CRDS instrumentation

- Operating Principles of CRDS
- Challenges with field deployment and application to CO$_2$ soil-gas surveillance
  - H$_2$O and CO$_2$ concentration dependence
  - Methane interference
  - Response times
  - Local biogenic variability
  - Variability in soil organic carbon
  - Operating temperature
  - Data connectivity
  - Large quantities of data

- Measured long-term background signals
- Additional geochemical monitoring
CRDS uses characteristic IR absorption to quantify concentrations of CO₂ and other gases.

- Isotopic substitution slightly changes this wavelength, allowing isotopologue concentrations to be measured.

- A single laser can measure both CO₂ and H₂O at 1603 nm. A second laser at 1651 nm is required for CH₄.
Multi-pass optical cavity allows for an extended pathlength

Length of the exponential decay time is related to the concentration of the absorbing gas.
Measured $\delta^{13}C$-$CO_2$ is dependent on $CO_2$ concentration and $H_2O$ concentration.

Also has limitations at higher concentrations (~5000 ppm).
Measured $\delta^{13}$C-CO$_2$ is dependent on CO$_2$ concentration and H$_2$O concentration.

Linear dependency is corrected with software developed by Picarro, using already measured parameters.
Interference due to excessive and varying methane corrected with additional laser
Field sampling manifold allows consecutive analysis of 12 soil-gas locations and the ambient atmosphere.

- Soil boreholes (45 cm depth)
- Equal length sampling tubes
- Constant flow (~5 mL min\(^{-1}\))
- Reference gases (Concentration + isotopic value)

12 sites placed within ~ 0.1 km\(^2\)
Each site is sampled every 20 min.
We observe a background biogenic signature and diurnal cycle.

**CO$_2$ concentration range above background ~400 ppm**

**Daily $\delta^{13}$C-CO$_2$ range ~8‰**
Soil organic carbon isotopic signature varies with site location and depth in the soil column.

SD of averages of all sites is +/- 1.7‰
SD range of individual sites 1.1 - 3.3‰
Long-term soil-gas background signals show variability between sample sites and broad excursions occurring over periods longer than several days.
Averaging over all soil-gas sampling locations still shows high variability in both concentration and isotopic signature.
Atmospheric measurements often show elevated CO$_2$ concentrations consistent with meteorological changes.
In support of the CRDS soil-gas and atmospheric measurements we collected additional geochemical and meteorological data

- Study of soil organic carbon across sampling area and at various depths
- Stable isotopic study of all plant life in area, both as biogenic input and potential long-term isotopic marker
- Collect and analyze discrete gas samples on GC-IRMS for carbon isotopic values, and GC-MS for trace gas composition
- Full meteorological analysis, including temperatures, wind direction, back-trajectories, precipitation, and soil temperature
Timeline of Geochemical Efforts

Soil samples
Plant samples
Discreet Soil Gas samples

CRDS install

Discreet Soil Gas samples

Soil samples
Plant samples
Discreet Soil Gas samples

2012

CRDS Failure #1 – Power issues, operating system corruption
CRDS Failure #2 – Pump and inlet valve failure

2013

CRDS failure #1

CRDS failure #2
Summary

• CRDS is a robust technology allowing the measurement of CO$_2$ concentration and isotopic signature

• CO$_2$ concentration and isotopic signature variability is dominated by vegetation, microbial activity, and atmospheric connectivity with the soil

• To develop a capability of quantifying leakage from EOR or sequestration sites will require a good understanding of the “background” environment

• Our background measurements using multi-location soil-gas CRDS show limitations of conventional flask based sampling.