

# Challenges associated with geochemical monitoring of active CO<sub>2</sub> 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<sub>2</sub> 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  
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## 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.)

# Multi-technique approach

## InSAR

Falk Amelung

Kenny Zhao

## Geochemical

Peter Swart

Daniel Riemer

Ben Galfond

## GPS

Tim Dixon

## Modeling and Policy

Caitlin Augustin

## Seismic

Guoqing Lin

Peng Li

# Our geochemical measurements are primarily made using commercially available CRDS instrumentation

- Operating Principles of CRDS
- Challenges with field deployment and application to CO<sub>2</sub> soil-gas surveillance

H<sub>2</sub>O and CO<sub>2</sub> concentration dependence

Methane interference

Response times

Local biogenic variability

Variability in soil organic carbon

Operating temperature

Data connectivity

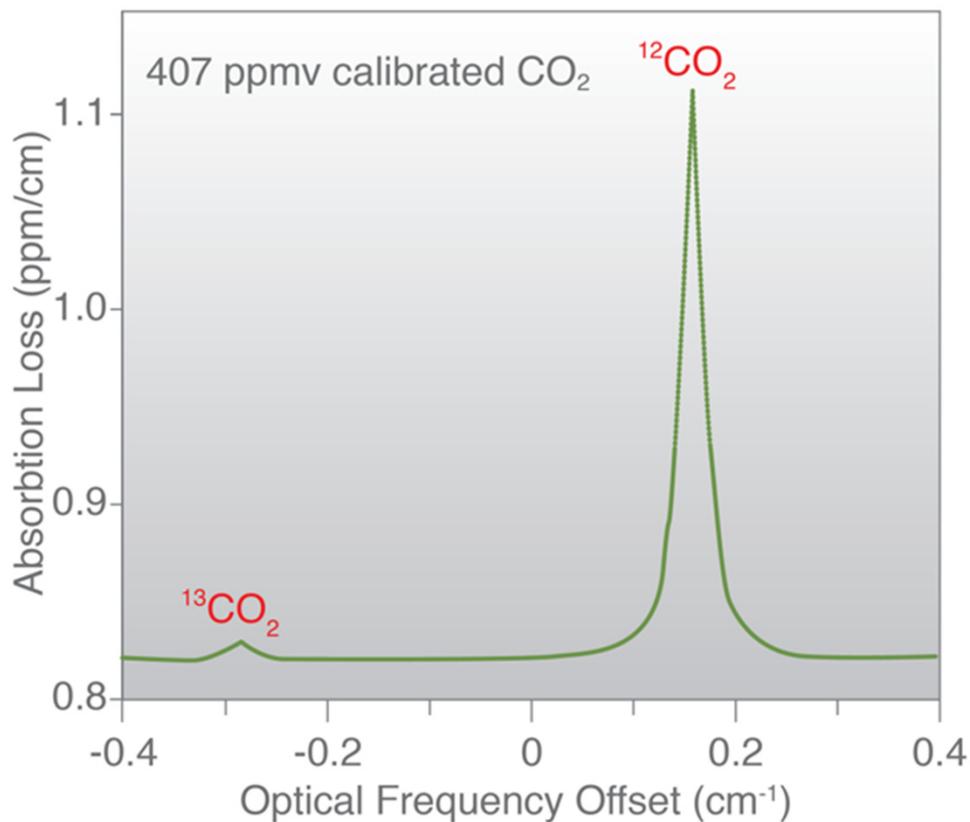
Large quantities of data



- Measured long-term background signals
- Additional geochemical monitoring

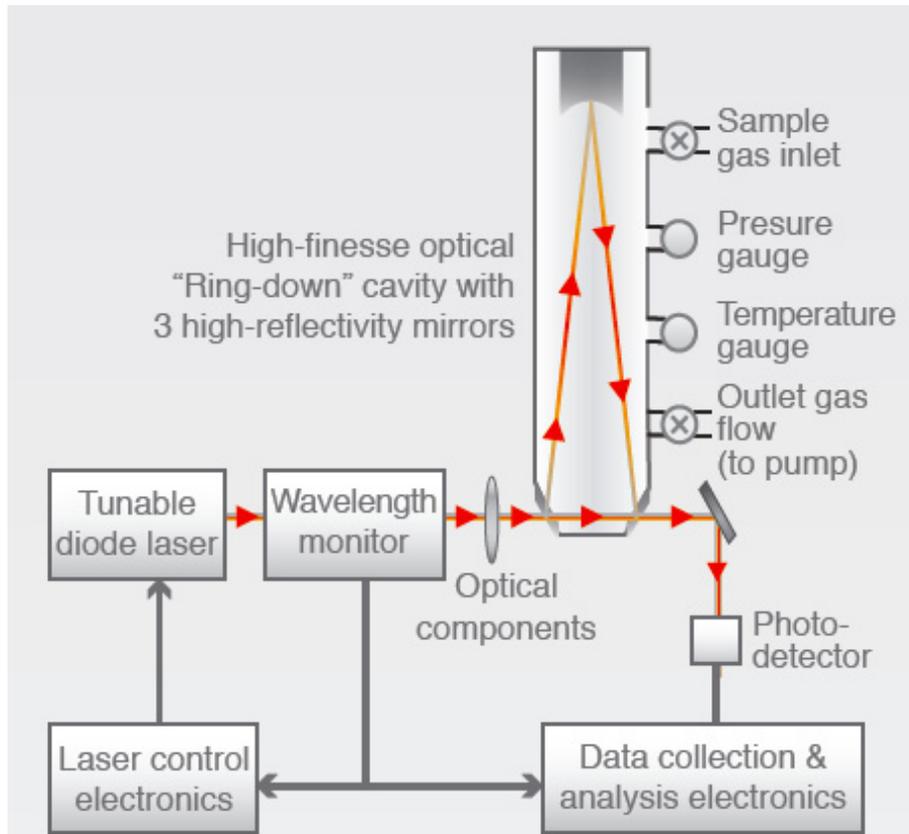
# CRDS uses characteristic IR absorption to quantify concentrations of CO<sub>2</sub> and other gases

Isotopic CO<sub>2</sub> Spectra



- Isotopic substitution slightly changes this wavelength, allowing isotopologue concentrations to be measured.
- A single laser can measure both CO<sub>2</sub> and H<sub>2</sub>O at 1603 nm. A second laser at 1651 nm is required for CH<sub>4</sub>.

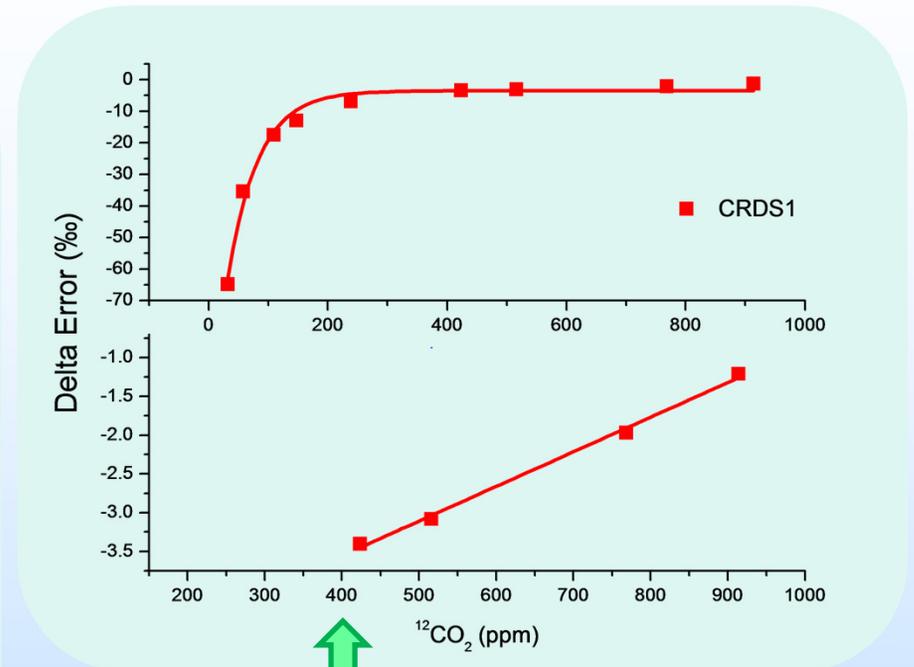
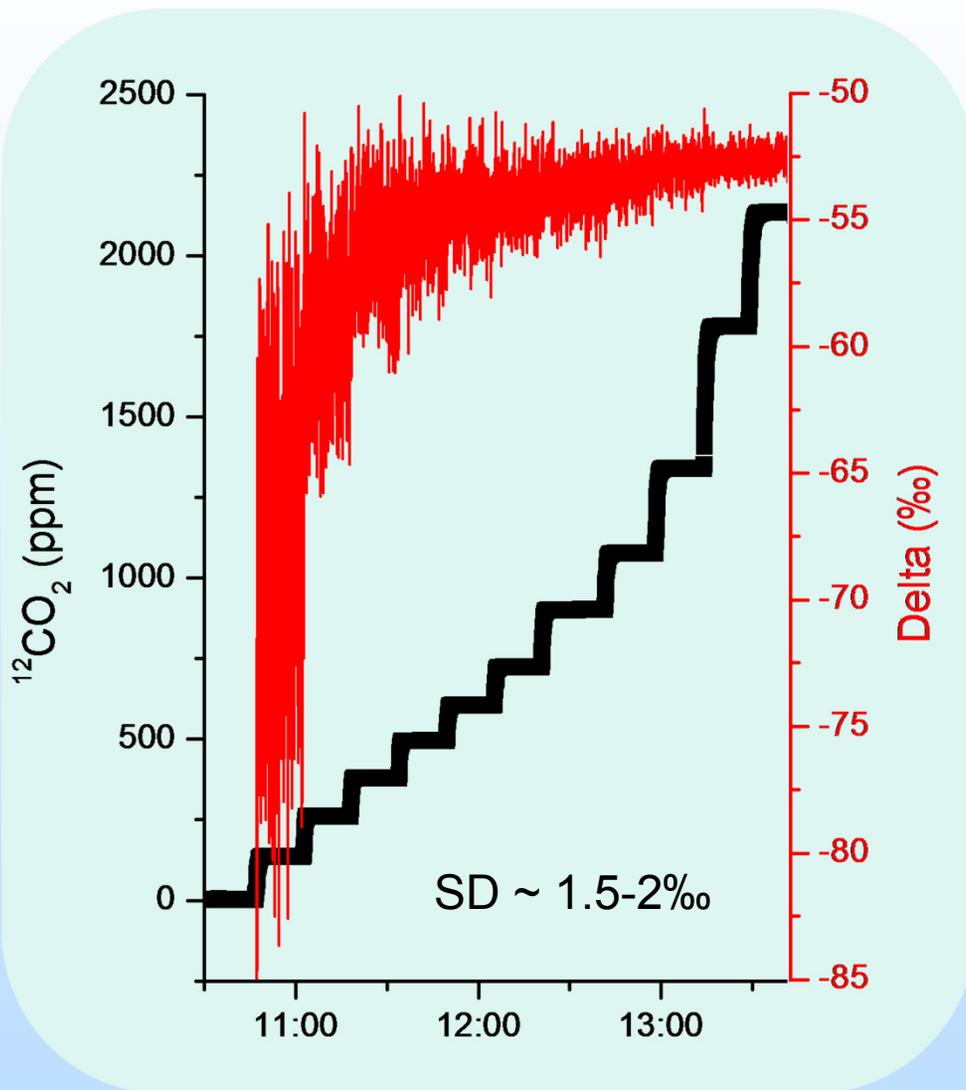
# Multi-pass optical cavity allows for an extended pathlength



Length of the exponential decay time is related to the concentration of the absorbing gas



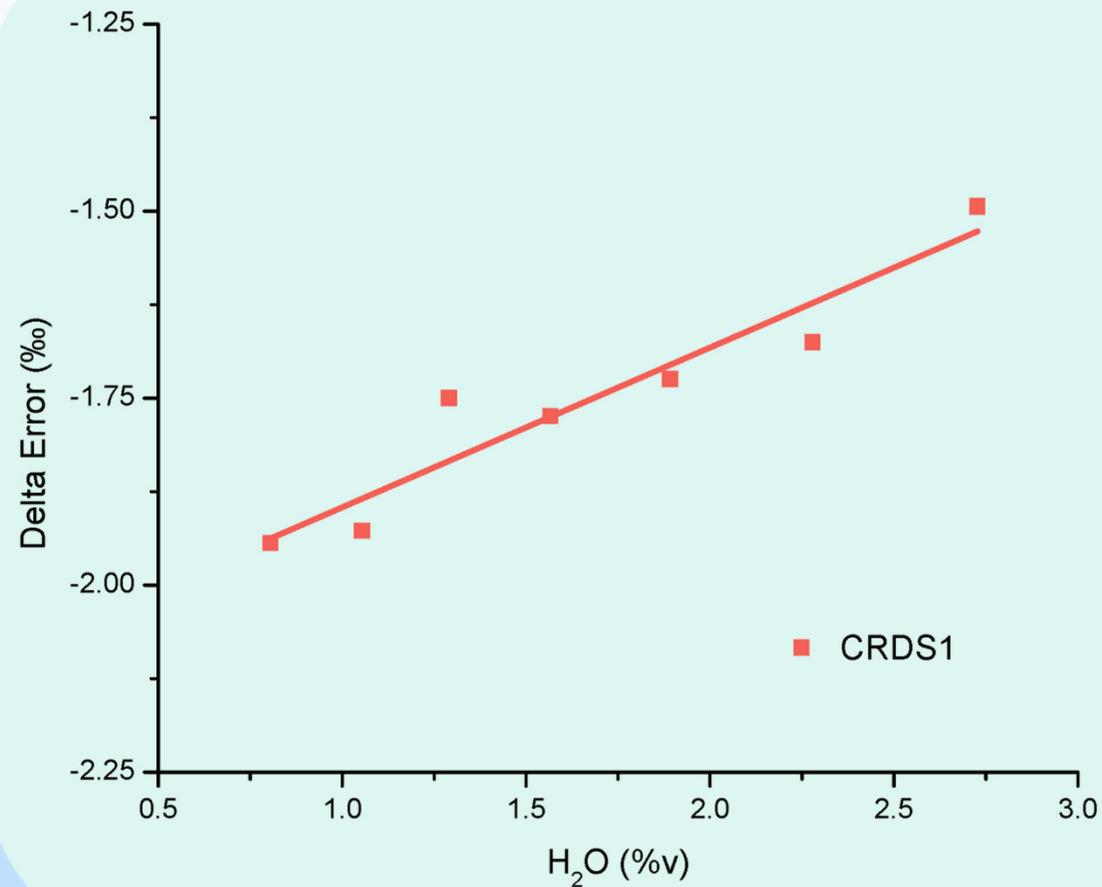
# Measured $\delta^{13}\text{C}-\text{CO}_2$ is dependent on $\text{CO}_2$ concentration and $\text{H}_2\text{O}$ concentration



Atmospheric Background

Also has limitations at higher concentrations (~ 5000 ppm)

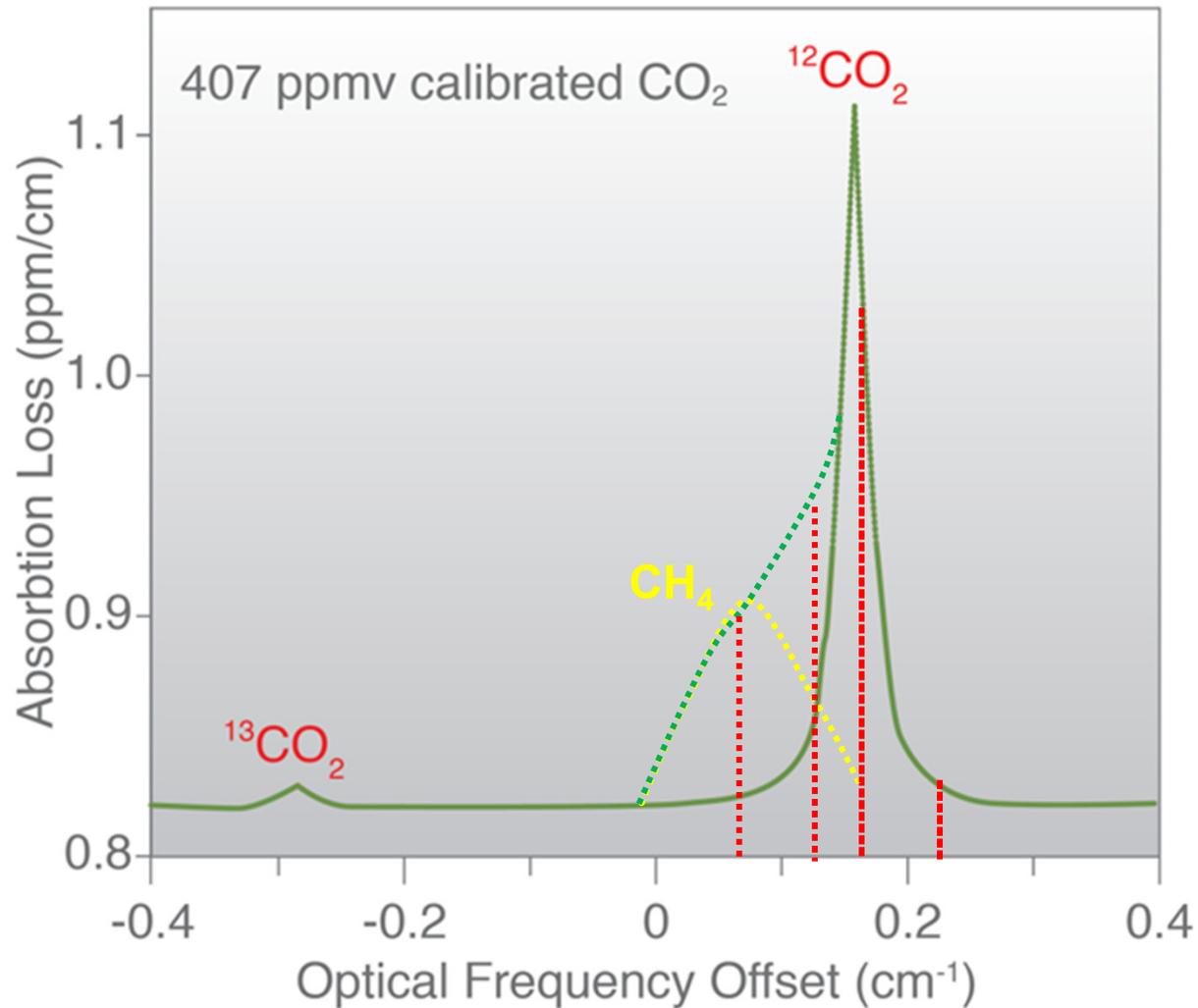
# Measured $\delta^{13}\text{C}-\text{CO}_2$ is dependent on $\text{CO}_2$ concentration and $\text{H}_2\text{O}$ concentration



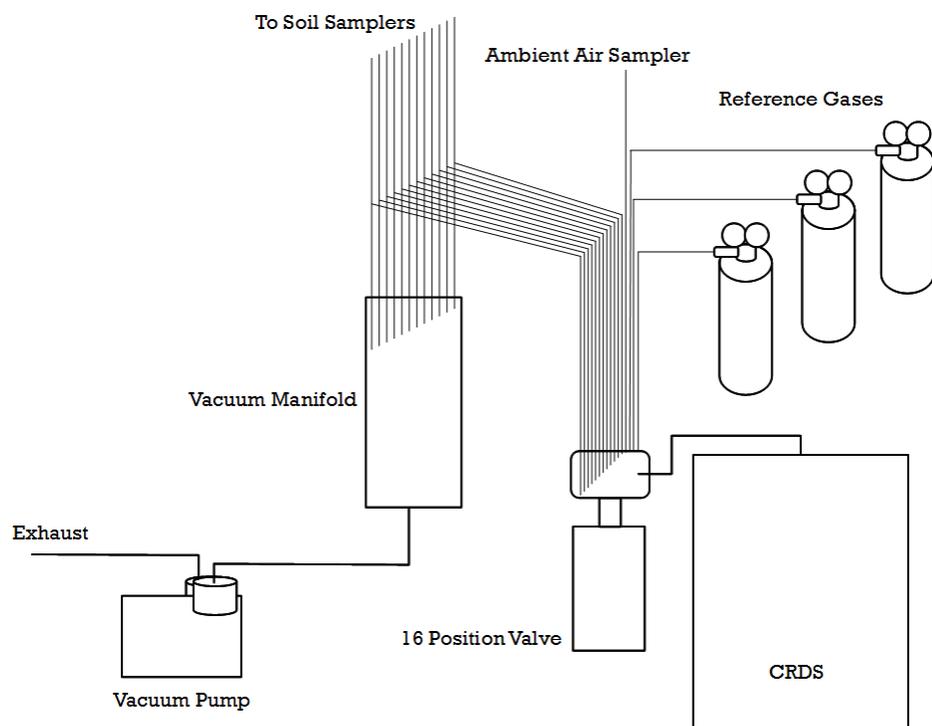
Linear dependency is corrected with software developed by Picarro, using already measured parameters.

# Interference due to excessive and varying methane corrected with additional laser

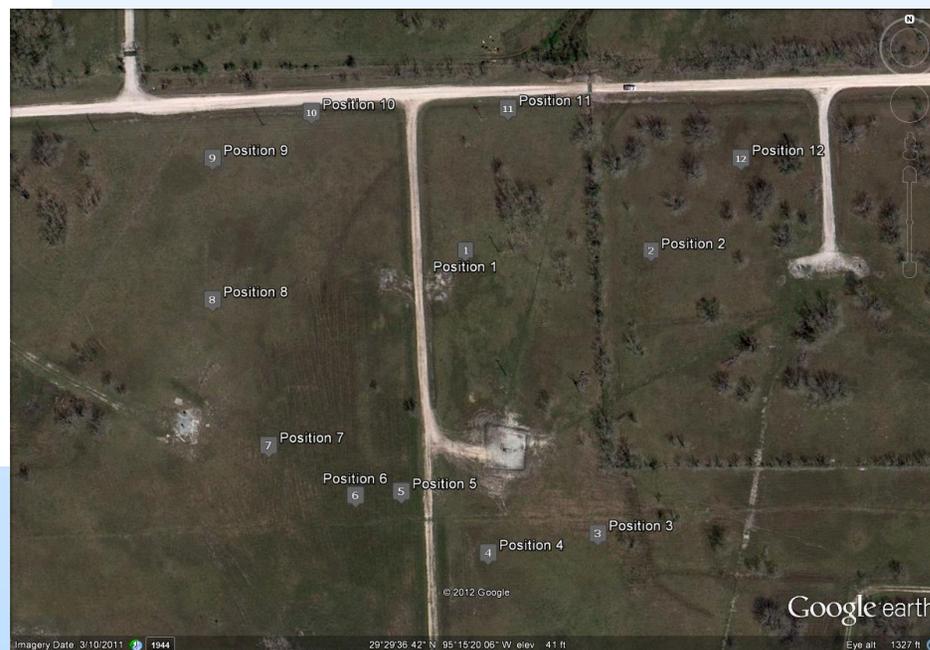
## Isotopic CO<sub>2</sub> Spectra



# Field sampling manifold allows consecutive analysis of 12 soil-gas locations and the ambient atmosphere

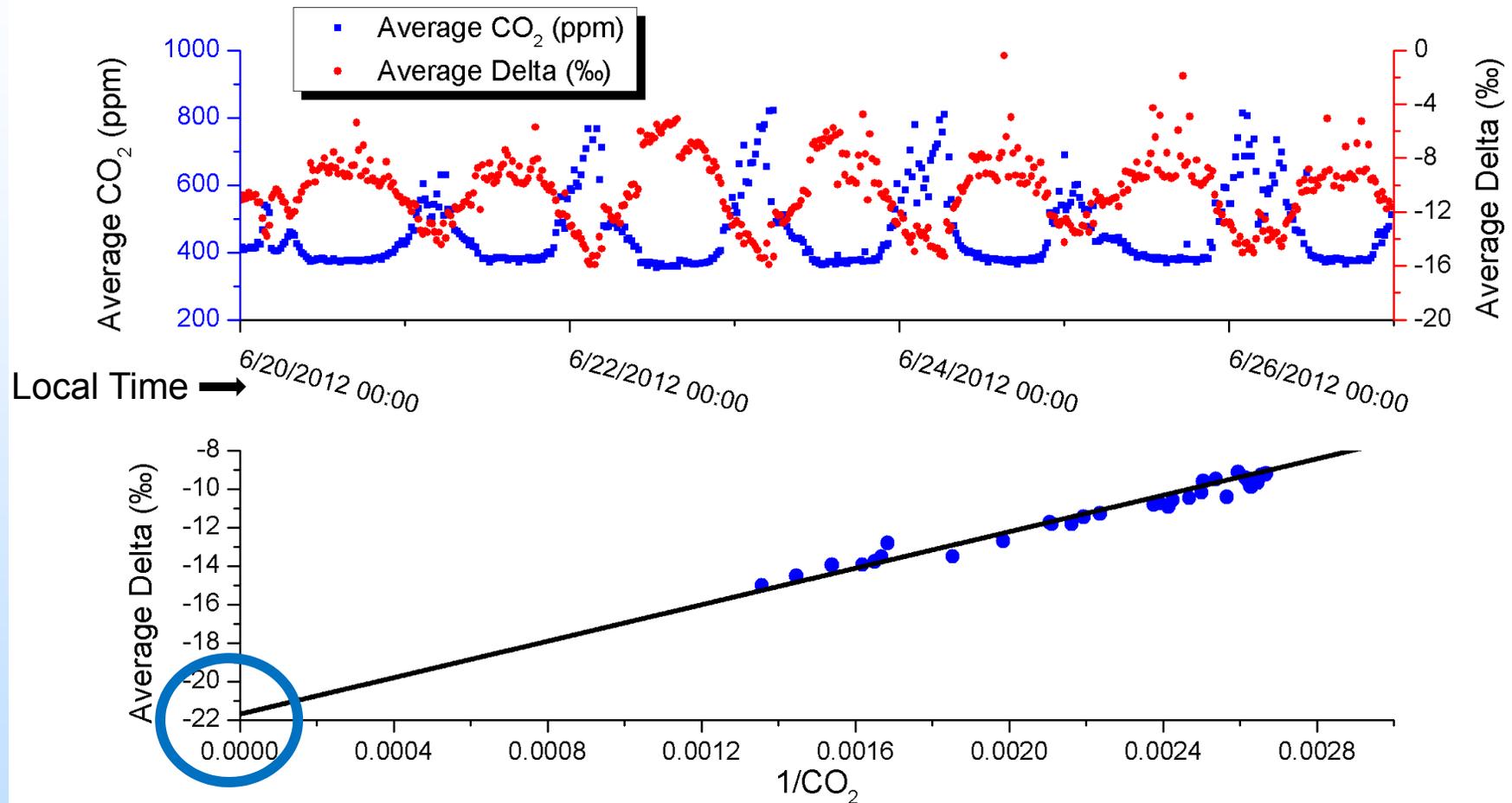


12 sites placed within  $\sim 0.1 \text{ km}^2$   
Each site is sampled every 20 min.



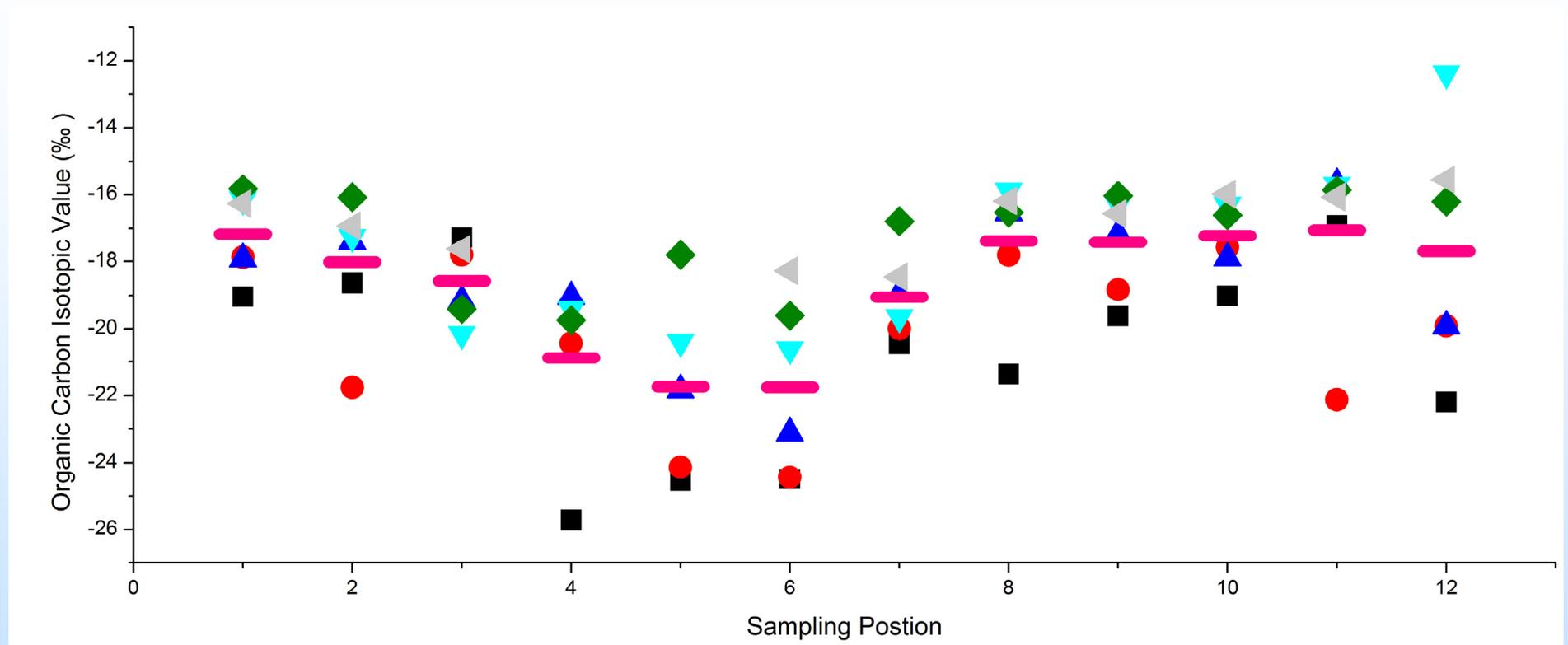
Soil boreholes (45 cm depth)  
Equal length sampling tubes  
Constant flow ( $\sim 5 \text{ mL min}^{-1}$ )  
Reference gases (Concentration + isotopic value)

# We observe a background biogenic signature and diurnal cycle



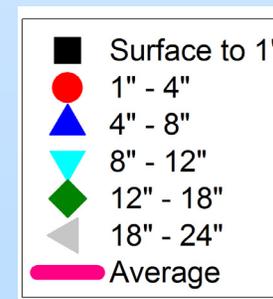
CO<sub>2</sub> concentration range above background ~400 ppm  
Daily  $\delta^{13}\text{C}-\text{CO}_2$  range ~8‰

# Soil organic carbon isotopic signature varies with site location and depth in the soil column

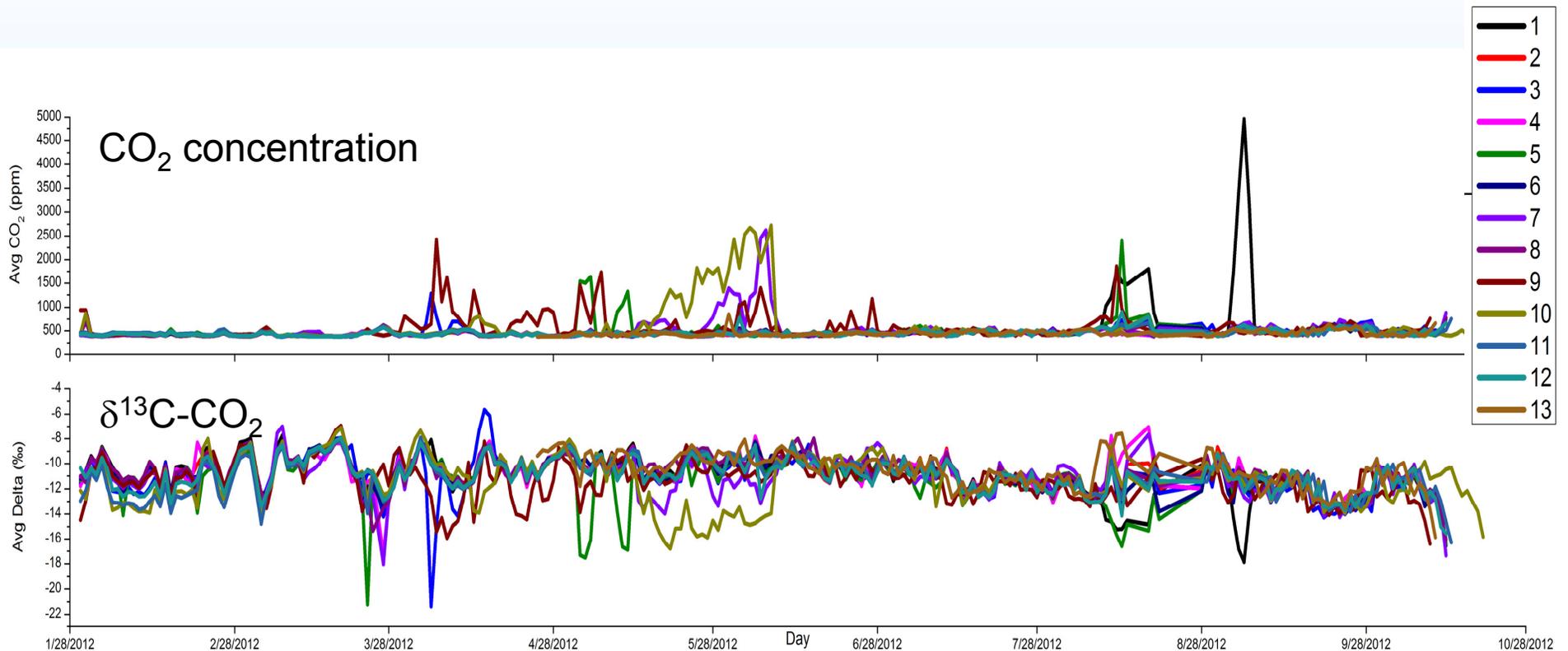


SD of averages of all sites is +/- 1.7‰

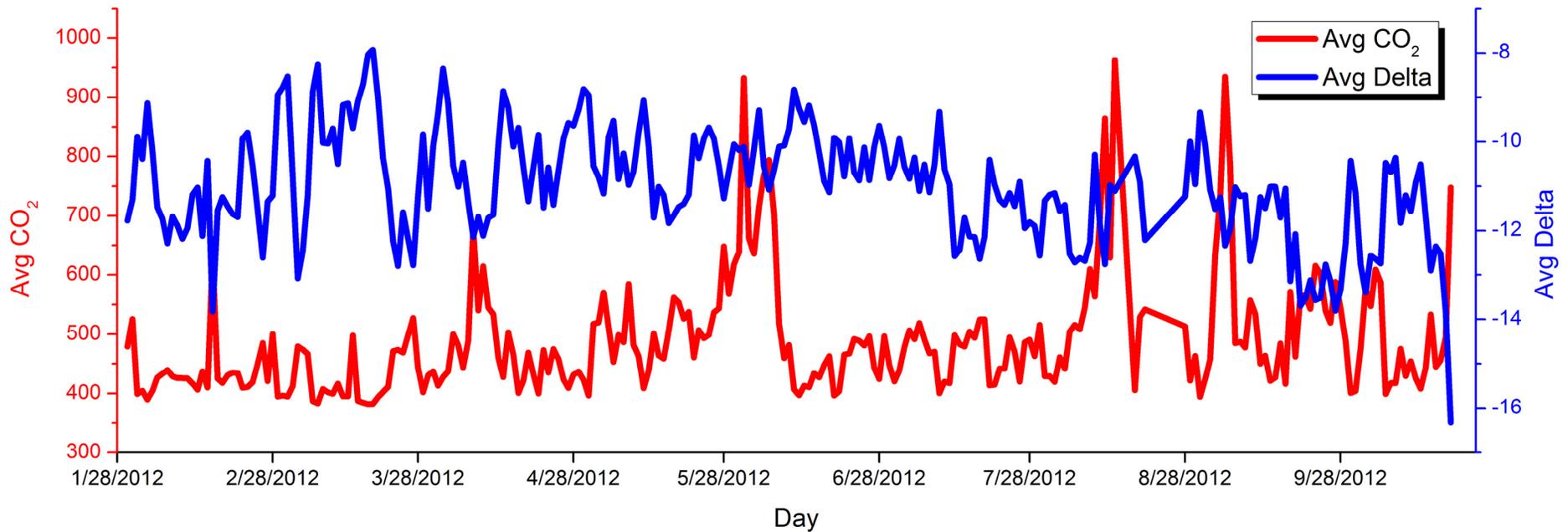
SD range of individual sites 1.1 - 3.3‰



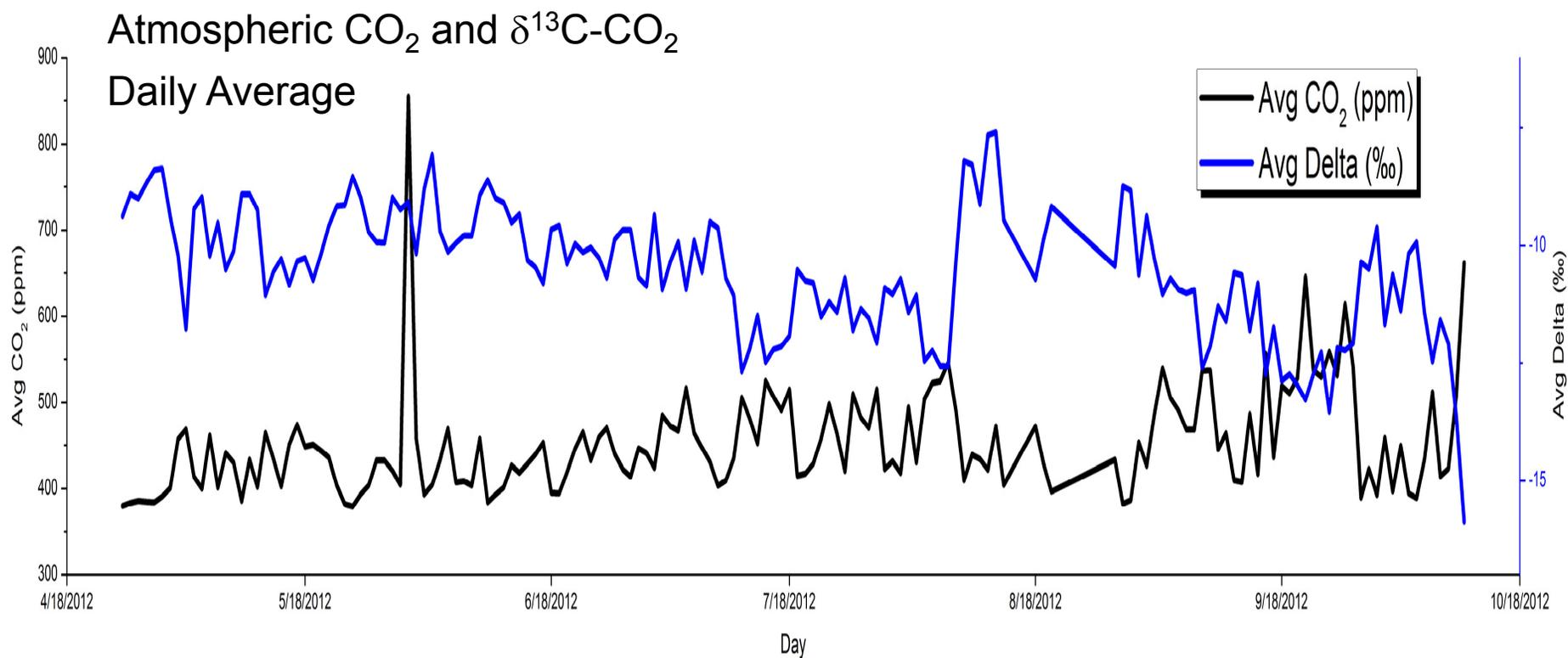
Long-term soil-gas background signals show variability between sample sites and broad excursions occurring over periods longer than several days



Averaging over all soil-gas sampling locations still shows  
high variability in both concentration and isotopic  
signature



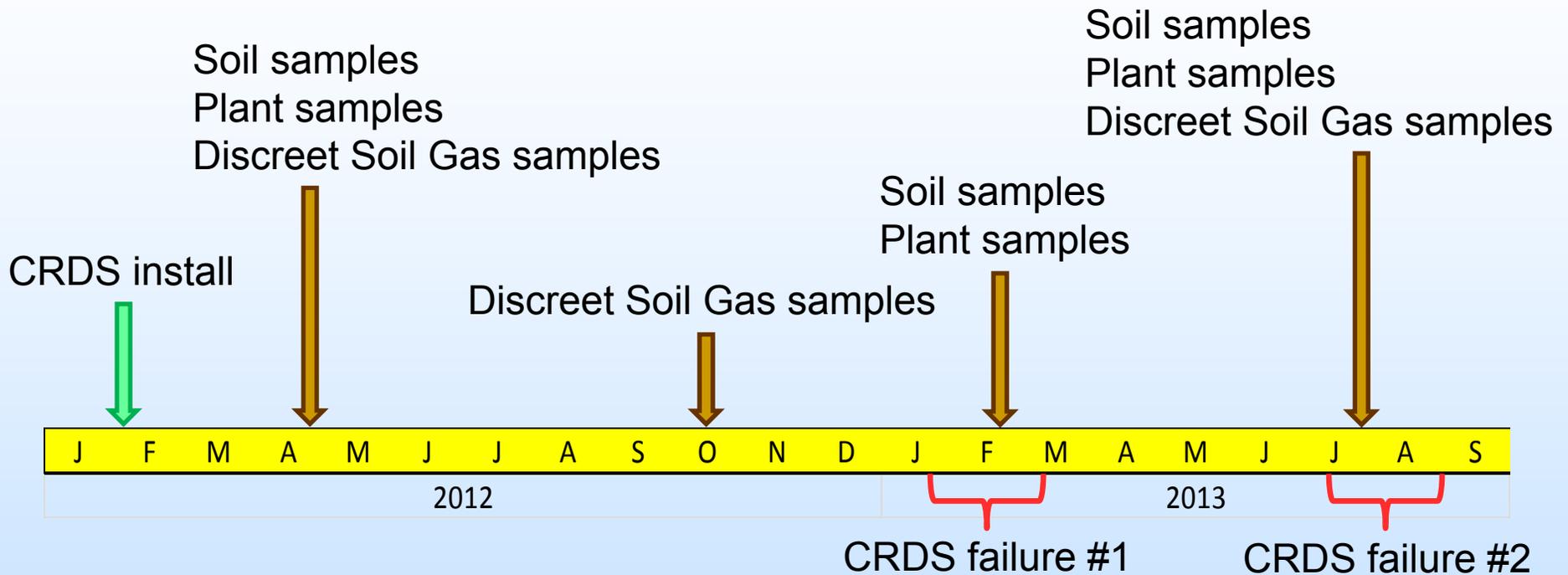
# Atmospheric measurements often show elevated CO<sub>2</sub> concentrations consistent with meteorological changes



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



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

# Summary

- CRDS is a robust technology allowing the measurement of CO<sub>2</sub> concentration and isotopic signature
- CO<sub>2</sub> 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.