Analysis of signal-to-noise ratio of $\delta^{13}\text{C}$ -CO₂ measurements at carbon capture, utilization and storage injection sites

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Abstract

As new regulations from the United States Environmental Protection Agency require monitoring and accounting for Class VI injection wells, determining the efficacy of monitoring techniques is a crucial barrier to wide scale Carbon Capture, Utilization and Storage (CCUS) deployment. The monitoring of CO₂ injection sites to ensure safety and operational success requires high temporal resolution CO₂ concentration and carbon isotopic ($\delta^{13}\text{C}$) measurements. As rapid measurement of $\delta^{13}\text{C}$ is not possible with standard isotope ratio mass spectrometry (IRMS), we have developed a methodology using Cavity Ringdown Spectroscopy (CRDS) with a manifold system in order to obtain accurate rapid measurements from a large sample area over an extended study period. A modified Picarro G1101-i CRDS with updated software and an auxiliary laser allows for rapid and continuous field measurement of concentrations and $\delta^{13}\text{C}$ of carbon dioxide as well as concentrations of water and methane. A manifold system actuated by a 16 position valve allows for an increased sampling region and internet connectivity and software developments permit immediate access to data from a remote location. At a field site in Texas where preparations have been underway for Enhanced Oil Recovery (EOR) operations, we have been able to observe biogenic effects on a diurnal scale, as well as variation due to precipitation and seasonality. Our system has proven field readiness for the monitoring of sites with modest CO₂ flux. These data have been used to improve leak detection thresholds by an order of magnitude over published models.

1. Introduction

Carbon Capture, Utilization and Storage (CCUS), specifically coupled with Enhanced Oil Recovery (EOR), has the potential for rapid and widespread implementation as large-scale carbon emissions reduction strategy (Metz, 2005). While there are economic challenges to the implementation of pure CSS, EOR has been proven commercially viable since 1972 (Crameik, 1972), when 37 million tons of CO₂ were injected into the SACROC unit, increasing recovery of original oil in place by 9% (Langston, 1988). For the commercial and environmental efficacy of this technique and for safety considerations, a comprehensive accounting method must be

developed to ensure sequestered CO₂ remains in the subsurface and environmental impacts are minimized (Bachu, 2008; Wolaver et al., 2013). To validate that the injectant does not migrate to the atmosphere, we have investigated Cavity Ringdown Spectroscopy (CRDS) in an attempt to discriminate between background biological CO₂ emissions and EOR injectant leakage to the surface.

In order to use CO₂ concentrations to detect potential leakage it is essential to discriminate the natural biogenic fluctuations of both soil gas and atmospheric CO₂ concentrations from released injectant, lest natural fluctuation mask small-scale injectant leakage. This can be accomplished by examining the ratio of ¹³C/¹²C of the CO₂ (conventionally reported as δ¹³C) in addition to the concentration and determining what the natural ranges of variation are for a particular site.

A wide range of techniques have been employed to detect inadvertent migration of sequestered CO₂ out of the target reservoir. These include seismic monitoring for micro-earthquakes, GPS and InSAR observation of ground movements due to changes in reservoir pressures (Osmanoglu et al., 2011), geochemical monitoring of fluid composition (Hovorka et al., 2011) and near-surface CO₂ concentration (Furche et al., 2010; Schloemer et al., 2013). The use of multiple parameters to monitor injectant, such as multiple gas species (Beaubien et al., 2013; Romanak et al., 2012) or a wide suite of petrochemical analysis, seismic studies and logs (Hovorka et al., 2011) have offered comprehensive means of accounting for the geophysical and geochemical effects of sequestration. Previous short-term studies using CRDS to identify large CO₂ fluxes in engineered environments have been largely successful (Krevor et al., 2010; McAlexander et al., 2011; Moni and Rasse, 2014), though the simulated flux rates (from around 50 to over 250 μmol s⁻¹ m⁻²) far exceed those used in this study (0.01, 0.1, and 1.0 μmol s⁻¹ m⁻²). At such rates, studies reliant on δ¹³C have had minimal success when monitoring was performed on a monthly schedule (Risk et al., 2013) because of the high biological and meteorological impacts on fluctuations in δ¹³C. The models of Nickerson and Risk (2013) have shown that while such studies are feasible, they would require an isotopically distinctive injectant compared to background biogenic signatures to produce a signal to noise ratio large enough for monitoring purposes. In this study field trials have been carried out to determine if such models are a valid

representation of real-world monitoring, evaluating the field effectiveness of a new stable isotopic monitoring technique and the leakage rates it may identify on a CCUS site.

2. Methods

Equipment: The CO₂ concentration and $\delta^{13}\text{C}$ measurements were made using a modified Picarro G1101-i. As leaked CO₂ from the reservoir would be accompanied by methane, a second laser on an optical switch was added to the unit. This allowed us both to correct for any potential interference, and also served as a secondary indicator of injectant leakage. This was interfaced with a VICI Valco electrically actuated valve (EMT2CSD16MWE) to allow for monitoring of 12 soil sampling locations. Each sampling session lasted 20 minutes, with the first 2-3 minutes of measurement discarded to allow the cavity to flush. As the instrument produced measurements at a frequency of 1Hz, this resulted in over 1000 individual data points per sampling session. These sampling wells were located radially from the central instrumentation site at a distance of up to 150m. A secondary KNF pump (UN726.3 TTP) was used to draw the sample through the lines to the Picarro unit at a rate of approximately 10 sccm. All sampling lines were equal length, 6.35mm OD (4.32mm ID) polyethylene tubes, tested for any fractionation effects and UV/temperature related offgasing before installation. Each well was constructed of PVC shell with a 52.5 mm inner diameter sunk into a hole bored approximately 60cm deep. Sample lines were attached to the top of the chamber using Swagelok fittings and sealed with silicone.

Site Location: The instrument was deployed to the Texas site from January 30, 2012 to October 20, 2012. The site selected is one of three with instrumentation from the University of Miami group located on an active EOR site. During our experimental time frame, active injection only occurred at locations north of our study area in non-communicating fault blocks. The CO₂ was injected at a depth of approximately 1600 m, increasing reservoir pressure, reducing hydrocarbon viscosity, and displacing hydrocarbons from pores as they swell to aid in hydrocarbon extraction. During our study period, injected CO₂ was sourced from a natural reservoir with a $\delta^{13}\text{C}$ of $-2.94 \pm 0.40\text{‰}$ (Zhou et al., 2012). This relatively positive injectant value is ideal for monitoring, as it provides a very clear signal of injectant release compared to atmospheric CO₂

(Troler et al., 1996) and possible biological sources such as plant and microbial activity which generally have much more negative $\delta^{13}\text{C}$ values (Craig, 1953). The site had very limited biological production, as the small amount of precipitation, often delivered in short but intense bursts that may limit uptake, coupled with intense periods of heat made water availability key to plant and microbial activity. Soils often had low amounts of organic carbon, and varied from loamy sand to sandy clay.

Meteorological Data: With the importance of soil moisture in mind, local weather data were obtained from a nearby airport, providing reliable accuracy and high temporal resolution (Figure 1).

Soil Samples: Soil samples for organic $\delta^{13}\text{C}$ analyses were retrieved from each gas sampling position at depths of surface to 0-2.5cm, 2.5-10cm, 10-20cm, 20-30cm, 30-45cm, and 45-60cm. Samples were dried in the lab, then acidified in HCl, filtered, and analyzed by EA-IRMS (ECS 4010 CHNSO Analyzer, Costech Analytical Technologies Inc., and Delta V Advantage, ThermoFisher Scientific) using the method outlined by Oehlert et al. (2012).

Statistical Analysis: Plots of the $\delta^{13}\text{C}$ of the CO_2 against the inverse of the concentration (Keeling plots), were generated for the entire site and for each individual sampling position. This allowed for the $\delta^{13}\text{C}$ of contributing endmembers to be determined (Pataki et al., 2003). Characterization was performed weekly to ensure a reasonable sample size for general analysis, but can be reduced to shorter timeframes for further examination of short-term events such as possible injectant leakages, atmospheric boundary layer variations, or interpretation of anomalous data points. The twelve individual gas sampling locations at the site (Figure 2) allowed for localized atypical behavior to be identified and isolated. Principal component analysis (PCA) of the CO_2 concentration, $\delta^{13}\text{C}$, and variance of $\delta^{13}\text{C}$ values identified and separated out these incongruous measurements. Two eigenfactors were sufficient to account for at least 85% of variability every week of sampling. A biplot of these eigenfactors allowed for atypical sampling locations to be readily identified (Figure 3).

As a result of the large amount of data generated daily, customized processing software was created to condense raw data files. Each 20 minute period of sampling at a given position was individually examined, with early measurements excluded to account for sampler and cavity flushing. The remaining individual measurements were then averaged to provide the CO₂ concentration, $\delta^{13}\text{C}$, H₂O and CH₄ content, and sampling time. Metadata such as number of individual measurements per averaged value and cavity temperatures and pressures were used to ensure consistent instrument operation as well. This processing resulted in a daily data set of about 6 measurements per sampling position, evenly spread across a 24 hour period, for a total of over 70 time averaged entries per day.

Signal-to-noise ratios (SNR) were calculated as specified by (Nickerson and Risk, 2013). They first modeled what the expected background CO₂ concentration and variance would be independent of injection activity, and then simulated three different leakage rates to determine how much of a perturbation would occur. Natural background CO₂ concentrations were modeled based on measurement depth, soil diffusivity, and biological production at depth, according to (Davidson and Trumbore, 1995). Their work shows that while 70-80% of soil CO₂ flux was produced in the top meter of soil, a non-trivial amount is produced at depth. This can be modeled as an exponential distribution, allowing CO₂ concentration at depth values to be predicted. Without consistent soil moisture and temperature measurement sets for our study area, we instead used a representative value for our soil type's gas diffusivity of $1.75 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. This value is dependent on seasonal changes in temperature and precipitation, so while diffusivity likely changed during our study period, the subtropical climate moderated by the nearby Gulf of Mexico would prevent any extreme variations. Using this method to model various seepage scenarios, the SNR value was calculated by dividing the difference of the combined background and seepage model and our measured background values by the weekly standard deviation of our measured data. When CO₂ concentrations exceeded the modeled average, small leakage rates resulted in a negative SNR, indicating that our method would not be able to detect leakage at given rates.

3. Results

Over the 38 week deployment, from January 30, 2012 to October 20, 2012, over 7.5 million measurements of CO₂ concentration and $\delta^{13}\text{C}$ were made. Methane and water concentration measurements determined by the instrument were used to make corrections (Rella, 2011). These data are listed in the supplementary material.

3.1 CO₂ Concentrations

Soil CO₂ concentrations, (Figure 4), generally ranged from 400-550 ppm with the exception of a few high-concentration excursions. The average concentration of CO₂ was 442 ± 53 ppm during the winter and early spring with summer and fall averaging a noticeably higher 512 ± 107 ppm and showing a greater variation during each diurnal cycle.

3.2 Isotopic Values

The average $\delta^{13}\text{C}$ values of the CO₂ ranged from -8 to -13‰ (Figure 5), with only isolated temporary excursions from this range at some locations. During the winter and spring from late January to May, $\delta^{13}\text{C}$ values increased slightly, while during the summer and fall months, June through October, there was a steady decrease in $\delta^{13}\text{C}$.

3.3 Soil Organic Carbon Measurements

Measured $\delta^{13}\text{C}$ compositions of soil organic matter (SOM) are reported in Table 1. Each sampling position followed a trend of increasingly positive $\delta^{13}\text{C}$ values moving from the surface to depth, ranging from -16.9‰ to -25.7‰ at the surface and -15.6‰ to -18.4‰ at depth.

4. Discussion

4.1 Location specific trends

The sampling footprint encompassed approximately 70,000 m², significantly smaller than the size of most injection sites. Notwithstanding the difference in size, we found within our study area that there were location specific trends with different samplers consistently reporting differing CO₂ concentrations and isotopic values. To examine this spatial variability, a soil survey was performed, examining the organic carbon content and $\delta^{13}\text{C}$ of the soils. When coupled with Keeling plots over the same time period, it is evident how variations over short

distances may arise, as when sampled on the same day, there are different trends in the soil bulk $\delta^{13}\text{C}$ values (Figure 6) and the soil gas Keeling intercepts (Figure 7). The soil data indicate that material with more negative $\delta^{13}\text{C}$ values is preferentially found in the south of our sample area, particularly at the surface. This coincides with a topographic low where detrital organic matter has been observed to accumulate. The soil gas Keeling intercepts indicate an opposing trend, with more negative $\delta^{13}\text{C}$ values focused to the north of the sample area, though as gas samples were obtained at a depth of 60cm, most of the variation in SOM has equalized (Table 1).

The absence of an agreement between the $\delta^{13}\text{C}$ of the soil organic material and the value of CO_2 calculated from the Keeling intercept suggests that the decomposition of soil organic matter is either not a significant process, or more likely, that it does not occur evenly throughout the sampling area. More intense microbial activity is expected in the south as a result to the increased availability of both detrital materials and water, and indeed the strongest correlation between SOM and $\delta^{13}\text{C}$ values determined from the Keeling plots is found here. As this soil originates from the same depth as the gas sampler, the $\delta^{13}\text{C}$ of this SOM should approximate that of the released CO_2 . We would thus expect the microbial $\delta^{13}\text{C}$ signature in the southern region to be approximately -21‰ to -22‰. We find that the $\delta^{13}\text{C}$ derived from the Keeling intercepts in this region are -22‰ to -23‰, which while slightly more negative than anticipated, is more positive than the northern region.

The range of $\delta^{13}\text{C}$ values seen in the soil far exceeds the range values calculated from the Keeling intercepts, indicating a large percentage of the contributing CO_2 possesses a reasonably homogenous $\delta^{13}\text{C}$ across the sample area. It is probable therefore that a significant portion of the soil CO_2 is from a source that is not related to the SOM, either derived from atmospheric air entering the soil through the fractured, clay-rich soils, or alternatively, a deep CO_2 source. Each well opening is located 60cm below the surface, and at the time of installation and during periodic testing, this long contact area was found to provide a good seal from atmospheric infiltration. Near the end of this study, a test was performed with large amounts of methane released at the surface and at shallow depths within 20cm of the wellhead, and no measured change in methane was found. As the site was remotely operated and not under constant surveillance, it is possible that the observed fracturing of the top layers of soil under low precipitation conditions not only allowed for atmospheric infiltration of the soil gasses but also

direct access to sampling wells. We feel that this is an unavoidable possibility given the parameters of our experiment, however, should such an event occur at one of our sampling wells and alter that well's behavior, by using PCA we prevent such data from altering our study results.

This illustrates the highly variable nature of isotopic studies in natural environments. Minor topographical changes over short distances can noticeably alter measured values, characteristic of differing origins of measured CO₂. The importance of water availability in the dry Texas climate is critical to the biological CO₂ emitters at our site, and the dramatic temporal and spatial variation they create may be problematic for low resolution attempts at comprehensive leak surveillance.

During the sampling period, data were collected from 12 separate soil locations over a 150 meter radius. Although many of these signals were coherent, some sites showed distinctive behavior either sporadically or on a consistent basis. To eliminate these from the mean signal we performed a PCA analysis (see Methods) on weekly averaged data. Sites which showed unique behavior were then eliminated and a representative site mean obtained. Atypical positions were not common, with 86% of original data retained after filtering. Sampling positions 9 and 10, both located in the extreme northwest of our study area in similarly elevated and dry soils were excluded the most frequently, 20 and 16 times respectively, indicating that soil composition and topography are likely drivers of the behavior.

Typical $\delta^{13}\text{C}$ values of natural CO₂ sources seen in Figure 8 show that at our location, any detected CO₂ signal that positive can be confidently assigned to the injectant. Our study was performed at a distance from the injection site so that we could observe natural variability without anthropogenic influences. Analysis of daily and weekly Keeling plots reinforced that despite CO₂ concentrations becoming elevated later in the study, the source of this additional CO₂ was not from injection activities.

4.2 Temporal trends

Diurnal trends were present throughout the sampling area, with fluctuations between photosynthesis and respiration creating distinct variations in $\delta^{13}\text{C}$ and concentration. Short term meteorological events resulted in noticeable changes in the soil gas composition, and longer term seasonal impacts induced a subtle but noticeable trend in the data, as more negative $\delta^{13}\text{C}$ values occurred during the warm, wetter summer and early fall months consistent with an increase in respiration (Figure 9).

Broad, seasonal climate changes such as temperature have shown to effect soil gas emissions. However, these effects were not apparent on shorter time scales where diurnal trends have vastly greater influence. The remote location and lack of nearby industrial activity explain the lack of influence by wind direction, as the region is fairly homogenous and free of large point source anthropogenic inputs.

An increase in soil respired CO_2 and strong biogenic isotopic signal as a result of precipitation was anticipated. While this was observed, a delay was noted between precipitation and a spike in soil CO_2 concentrations. This could be from the time required for the precipitation to reach our sampling depth and the local microbes to begin metabolizing, or also a result of the precipitation forming an impermeable seal, which temporarily retained gasses in the soil matrix thereby resulting in a delay between precipitation and observed CO_2 concentration spike. These observations are in line with studies on this physical process by Sotta and Jassal (Sotta et al., 2004).

Daily data have shown a strong diurnal trend with CO_2 being elevated at night when respiration becomes dominant (Figure 10). Observed $\delta^{13}\text{C}$ values were more negative after sunset by approximately 6‰. The $\delta^{13}\text{C}$ of this additional nighttime CO_2 , based on Keeling intercepts, is between -18‰ to -25‰. Temperature decreases and lack of convection at night also allow for the development of a shallow atmospheric boundary layer. This unmixed layer accumulates CO_2 and increases the concentration in the near-surface atmosphere. This diurnal trending is indicated in our samples of above surface air. This may be due to the physical properties of the soil, which goes through repeated and prolonged dry periods inducing cracks and fissures in the soil surface, promoting atmospheric exchange.

The Keeling intercepts from the various soil sampling positions were recorded and plotted across the weeks to better understand long term trends. During the late winter and early spring months, the intercepts varied widely, commonly decreasing to between -25‰ to -35‰. These negative values match common $\delta^{13}\text{C}$ values of C_3 plants. From late spring into fall (May through September) the $\delta^{13}\text{C}$ values became less varied and consistently fell in the range -20 to -25‰, showing a greater influence from C_4 plants. The superior water use efficiency and greater resistance to high light intensity and increased temperatures of C_4 plants explain why they would have a greater share of photosynthetic activity during the dry, sunny, and hot Texas summers (Downes, 1969; Ehleringer and Monson, 1993). From observation, the majority of plant coverage in the sample area is grasses and small C_4 plants, notably *Paspalum notatum* and *Stenotaphrum secundatum*, with only a limited number of larger C_3 plants.

As discussed earlier, while most sampling positions trend well with one another, there were often location-specific variations due to differing soil and plant compositions. This can lead to patterns where certain locations may manifest diurnal trends of differing magnitudes. Week 7 exemplifies this, as all sampling positions follow similar diurnal trends, with daytime CO_2 concentrations of 375 ppm rising up to near 400 ppm at night under respiration. Positions 9, 10, and 11 all follow the same diurnal cycles, but were generally 10 ppm elevated in CO_2 concentration (Figure 11). These three positions all have very similar soils and plant coverage, and are located in the northern region of the study area; their geographical similarities are mirrored by their CO_2 efflux patterns.

4.3 Signal to Noise Ratio

To calculate the signal to noise ratio necessary, we used the procedure set by Nickerson and Risk, (2013). This allows the evaluation of the effectiveness of CO_2 surface monitoring for CCUS leakage detection. Three leakage rates were used in the model as applied to our study site (Table 2). These rates are conservatively slow and make excellent thresholds for leak detection; at the largest rate of $1\mu\text{mol m}^{-2} \text{s}^{-1}$, a leak would have to extend across an area of 23 km^2 to release 81,064 kg per day, about 1% of what is generated daily by the average coal fired power plant in the USA. While Nickerson and Risk used the modeled monthly deviations of both observed CO_2 concentration and $\delta^{13}\text{C}$ in their calculations, the temporal variation we observed and data density available led us to use a weekly deviation instead. Our results, taken over the

entire study period, fall in line with what is anticipated by Nickerson and Risk for both CO₂ concentration and $\delta^{13}\text{C}$ (Figure 12, Table 3). Week by week, minimum detectable leakage rate, defined as in Nickerson and Risk (2013) by the point when $\text{SNR} > 2$, was seen to vary (Figure 13). As we have established, location, even on the small scale of our 150m radius sampling area, can be a significant factor in measured gas compositions. Using the previously outlined PCA procedure to isolate and remove anomalous sampling locations, we were able to greatly decrease the observed noise of the background biological signature. However, diurnal trends and their varying intensities were still evident in these calculations as noise, rather than a patterned biogenic signal. By separating each 24 hours of measurements into day and night periods, the noise resulting from this diurnal trend has been reduced. The SNR calculated during daylight hours is markedly better than during the night (Table 3). The few times this is not the case, the SNR already greatly exceeds the target ratio of 2. This is primarily as result of the stability of CO₂ concentrations during the daylight hours.

Our resulting PCA-reduced daytime only data shows a large improvement over our initial SNRs (Figure 14). Compared to our initial values and modeled SNRs, we have obtained an order of magnitude improvement. Even at the slowest modeled leakage rate, we were able to exceed our SNR threshold 20% of the time. This shows how background variation, once properly identified, can be refined to produce enhanced monitoring capabilities.

With these data, we can use the Nickerson and Risk model solved for leakage rate rather than SNR to find the minimum leakage rate needed to exceed our SNR threshold (Figure 15). Leaks in the .02 to .03 $\mu\text{mol m}^2\text{s}^{-1}$ range are consistently within our detection capabilities. These data are crucial moving forward, as it will allow construction of optimized sampling mesh densities and consequently create a framework for the scientifically robust monitoring of CO₂ injection sites.

5. Conclusions

Identifying a leak at a carbon storage site requires careful examination of both concentration and $\delta^{13}\text{C}$ data. Sampling positions identified as atypical under PCA may reflect a localized injectant emission event, while statistically significant increases in CO_2 concentrations or changes in $\delta^{13}\text{C}$ may reveal a site-wide release. Keeling plots allow for the isotopic identification of any additional CO_2 to find if it is consistent with the $\delta^{13}\text{C}$ of the injectant. If so, in scenarios such as ours where no other natural or anthropogenic sources share the same isotopic fingerprint, a leak has occurred. Additional measured parameters such as CH_4 concentration may also provide additional confirmation of emission events. At field locations injecting CO_2 with a highly negative $\delta^{13}\text{C}$ overlapping biogenic values, leak identification will be more difficult, as an injectant release may not alter the background $\delta^{13}\text{C}$ value. In such a scenario, a well-constrained background CO_2 concentration variation is necessary for identifying leakage.

Our field tests measuring CO_2 concentration and $\delta^{13}\text{C}$ isotopic values have shown that for our field site, such a monitoring method is an order of magnitude more sensitive to a leakage signal than previously anticipated in modeled studies. Further studies at future CCUS sites with varying biological and soil conditions will help show how successful this technique may be at other injection locations. Effective monitoring of surface gases at CO_2 injection sites requires high temporal resolution CO_2 concentration and carbon isotopic measurements. Both spatial and temporal variations were found to introduce variability into our measurements that would adversely impact our SNR and thus our monitoring efficacy. By filtering our data to reduce this false noise signal, the SNR we achieve exceeds published models by nearly an order of magnitude. While further work in identifying optimal instrument deployments is needed, with our methodology, off-the-shelf components can now be used to create a highly capable monitoring system, providing a new tool in the effective monitoring of CO_2 injection sites.

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8. Figures

- Table 1 Soil organic carbon isotopic composition at given sampling positions and depths. Surface level depletion and heterogeneity is evident.
- Table 2 SNR of CO₂ concentration monitoring at given leakage rates
- Table 3 Signal to noise ratios of day and night concentration measurements
- Figure 1 Temperature and precipitation recorded during our study period. Rainfall events are seen to be clustered, with prolonged drier periods. Temperatures for most of the study fall in the 20-30 C range.
- Figure 2 Sampling positions for this experiment. Instrument is centrally located proximal to Position 1
- Figure 3 Example of PCA analysis performed on one week of data. This allows for sites with similar characteristics to be categorized, and outliers excluded.
- Figure 4 Measured CO₂ concentrations across all 12 soil gas sampling positions during the study period, with each position averaged daily.
- Figure 5 Observed isotopic values of all 12 soil gas sampler positions during the study period, with each position averaged daily.
- Figure 6 Average $\delta^{13}\text{C}$ of top 60cm of soil, interpolated across sampling area by kriging
- Figure 7 Keeling intercept values at time of soil organic carbon sample collection, interpolated across the sampling area by kriging
- Figure 8 Carbon isotopic values of natural CO₂ sources as well as injectant from Jackson Dome. Adapted from (Schidlowski, 1992; Trumbore and Druffel, 1995)
- Figure 9 Averaged CO₂ concentrations and isotopic values of all soil gas sample locations during the study period.
- Figure 10 Diurnal trending of CO₂ concentration and $\delta^{13}\text{C}$. Plot includes all soil CO₂ samples at locations found coherent by PCA.
- Figure 11 Diurnal trends seen in Week 7 show location bias, with positions 9, 10, and 11 having higher concentrations
- Figure 12 Signal to noise ratios of various leakage rates during our study period.
- Figure 13 Minimum rate of injectant leakage for SNR to exceed 2
- Figure 14 Signal to noise ratios of each week of filtered data for given leakage rate scenarios. Red dotted line indicates SNR=2 threshold.

485 Figure 15 Minimum leakage rates needed to exceed SNR threshold of 2

Table 1.Measured $\delta^{13}\text{C}$ composition of soil organic matter (SOM)

Position	Depth (cm)						Average
	0-2.5	2.5-10	10-20	20-30	30-45	45-60	
1	-19.0	-17.9	-17.9	-16.2	-15.8	-16.3	-17.2
2	-18.6	-21.8	-17.4	-17.3	-16.1	-16.9	-18.0
3	-17.3	-17.8	-19.2	-20.2	-19.4	-17.6	-18.6
4	-25.7	-20.4	-19.0	-19.4	-19.8	-	-20.9
5	-24.5	-24.1	-21.8	-20.4	-17.8	-	-21.7
6	-24.5	-24.4	-23.1	-20.6	-19.6	-18.3	-21.8
7	-20.5	-20.0	-19.0	-19.7	-16.8	-18.5	-19.1
8	-21.4	-17.8	-16.5	-15.9	-16.5	-16.2	-17.4
9	-19.6	-18.8	-17.2	-16.3	-16.0	-16.6	-17.4
10	-19.0	-17.6	-17.9	-16.3	-16.6	-16.0	-17.2
11	-16.9	-22.1	-15.7	-15.7	-15.9	-16.1	-17.1
12	-22.2	-19.9	-19.9	-12.4	-16.2	-15.6	-17.7

Table 2.

Leakage rates used in the model as applied to our study site

Seepage rate ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	SNR (CO_2 Concentration)
0.01	1.2
0.1	1.7
1	2.2

Table 3.

Initial calculated signal to noise ratios						
Week	Leakage rate ($\mu\text{mol m}^{-2} \text{s}^{-1}$)					
	Day			Night		
	0.01	0.1	1	0.01	0.1	1
1	0.6	8.0	82.4	2.5	32.9	336.6
2	3.3	43.5	445.8	2.4	39.7	412.3
3	1.7	21.7	222.0	0.9	17.9	187.3
4	2.2	27.7	282.5	0.9	15.6	162.6
5	1.7	20.0	202.7	0.6	11.8	123.3
6	3.4	37.2	374.7	1.0	13.6	139.7
7	14.0	125.8	1244.2	19.3	187.7	1872.4
8	1.2	15.2	155.3	0.0	8.7	95.3
9	1.6	17.6	177.7	0.0	7.3	80.7
10	1.2	15.8	162.4	-0.1	10.0	110.7
11	1.3	15.4	156.0	-0.1	6.4	71.3
12	3.1	33.0	332.2	0.3	12.4	133.0
13	3.6	35.8	357.8	1.1	16.5	170.7
14	1.6	17.4	174.6	-0.2	6.8	76.4
15	3.0	32.1	322.6	0.2	11.4	123.5
16	1.2	14.2	144.2	-0.6	7.2	84.9
17	1.1	11.7	117.8	0.3	8.9	95.0
18	0.3	3.9	40.4	-0.3	1.3	17.3
19	1.2	14.5	147.6	-0.1	7.1	78.6
20	1.7	18.0	180.8	0.0	8.6	94.7
21	3.2	31.	317.1	-0.4	6.2	72.2
22	1.5	16.3	164.2	-0.2	9.4	105.4
23	0.4	7.1	73.5	-0.8	5.0	61.8
24	1.2	14.0	141.9	-0.5	7.4	85.7
25	0.7	9.5	97.5	-0.5	5.6	66.2
26	0.7	8.7	89.5	-0.6	5.4	65.9
27	1.1	13.1	132.9	-0.4	7.0	80.7
28	-0.1	3.5	39.5	-1.0	4.4	57.8
29	-0.2	2.9	33.3	-0.6	4.0	50.1
30	1.0	11.7	118.8	-0.4	5.1	59.7
31	1.1	11.9	120.0	-0.4	4.9	57.7
32	0.5	6.7	69.5	-0.8	3.1	42.1
33	1.5	16.3	164.4	-0.3	5.5	63.2
34	0.5	7.7	79.3	-1.3	3.5	51.8
35	0.9	11.9	122.1	-0.6	4.6	57.1
36	0.3	6.7	70.4	-0.6	3.7	47.2
37	2.6	26.6	266.5	0.2	10.1	109.0
38	0.5	9.3	97.7	-0.6	4.5	56.0

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15