Picarro G1101-i Isotopic CO2 Analyzer

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Continuous Isotopic CO_2 Measurements by Wavelength-Scanned Cavity Ring Down Spectroscopy: Studies of Exchange Processes in Terrestrial Ecosystems

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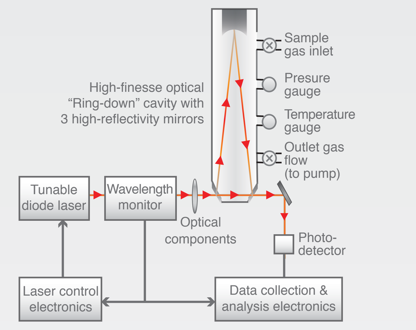
Commercial Gas Analyzer Based on Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS) for Continuous Field Measurements of Carbon Isotopes in CO_2

Introduction:

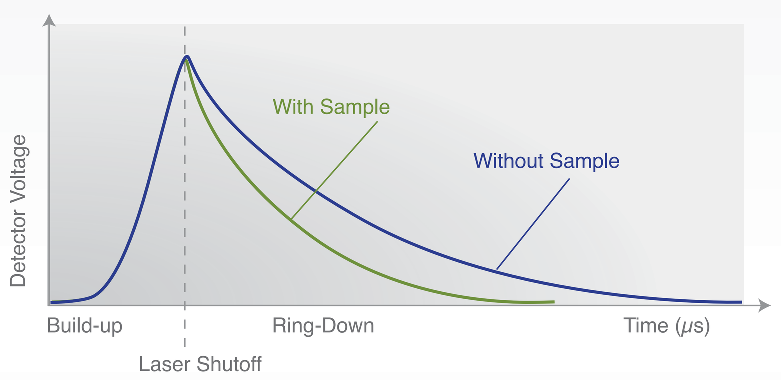
Picarro has developed an isotope analyzer for lab and field measurements of carbon isotopes in CO_2 with the goal of allowing turnkey analysis to be done without the need for flask samples and complex IRMS methods. Here we present a description of the analyzer and its technology as well as recent results from two different collaborators who utilized the analyzer.

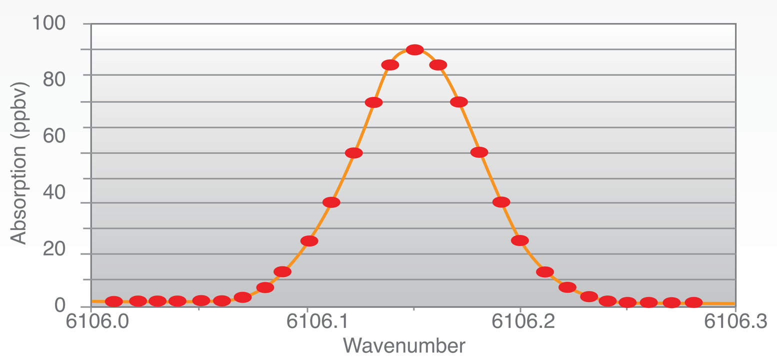


Schematic of Picarro WS-CRDS analyzer showing optical cavity and sample gas flow.

Analyzer Details:

The Picarro G1101-i Isotopic CO_2 Analyzer is a real time, trace gas monitor capable of measuring CO_2 concentrations with parts-per-billion (ppbv) sensitivity and the carbon isotopes (both ^{12}C and ^{13}C) with <0.3 permil precision. The analyzer is based on Picarro's unique Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS), a time-based measurement utilizing a near-infrared laser to measure a spectral signature of the molecule. Gas is circulated in an optical measurement cavity with an effective path length of up to 20 kilometers. A patented, high-precision wavelength monitor makes certain that only the spectral feature of interest is being monitored, greatly reducing the analyzer's sensitivity to interfering gas species, and enabling ultra-trace gas concentration measurements even if there are other gases present. As a result, the analyzer maintains high linearity, precision, and accuracy over changing environmental conditions with minimal calibration required. Precise temperature and pressure control systems designed into the analyzer ensure accurate measurements over long periods of time with minimal use of calibration gases. The analyzer is exceptionally rugged, essentially drift and maintenance free, and requires no consumables, thereby offering significant ease of use and cost of ownership benefits. Easily transportable from site to site, the analyzer can be set up and running within minutes, and require absolutely no sample preparation or drying. The gas concentration is displayed in real-time with no post-processing required, and is continuously archived to the analyzer's internal hard drive. Designed to operate both in laboratories and in harsh environments, it can operate for many months without user interaction. The analyzer can be configured to automatically send out measurement data at regular intervals via the Ethernet or optional modem and can output real-time data in digital format (via RS-232 interface) and via optional analog outputs. Users can connect remotely with the analyzer's internal Windows-based PC and control it through a standard Remote Desktop connection or with similar remote login software. The analyzer can also use its modem or Ethernet connection to automatically synchronize with an atomic clock time service. The software includes a valve sequencer which can manually or automatically control up to six external solenoid valves.



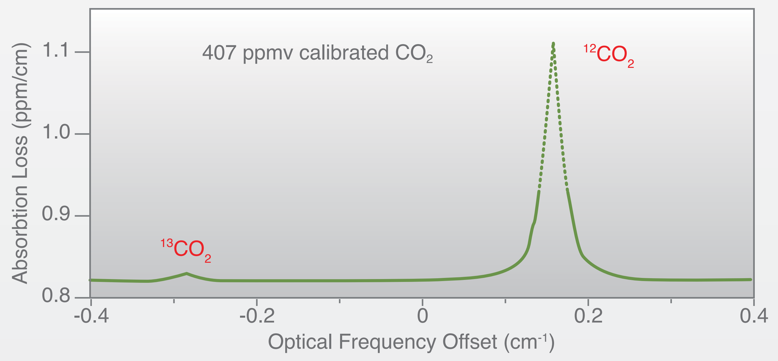


Light intensity as a function of time in a WS-CRDS system with and without a sample having resonant absorbance. This demonstrates how optical loss (or absorption by the gas) is rendered into a time measurement (left). By using a patented wavelength monitor, this measurement is continuously repeated at a number of well-controlled points in wavelength (right). The concentration is determined by a multi-parameter fit to this lineshape and is proportional to the gas concentration.

Wavelength-Scanned Cavity Ring Down Spectrosocpy (WS-CRDS) – How it Works

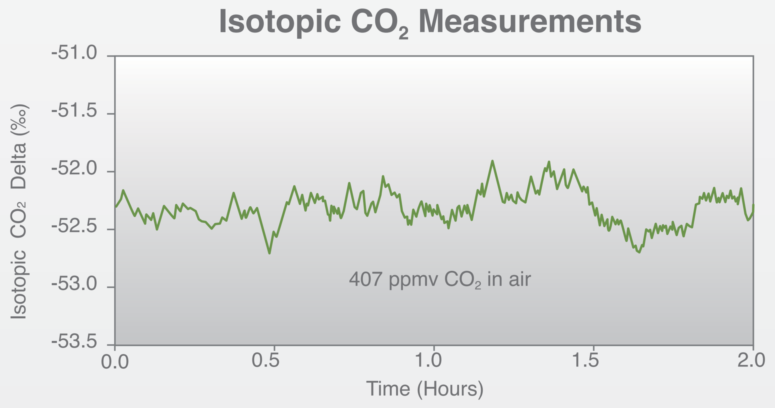
- Light from a tunable semiconductor diode laser is directed into an optical resonator cavity containing the analyte gas.
- When the optical frequency matches the resonance frequency of the cavity, energy builds up in the cavity.
- When the build-up is complete, the laser is shut off.
- The energy decays from the cavity exponentially in time, or "rings down," with a characteristic decay time. This energy decay is measured, as a function of time, on a photodiode.
- The ring down time is measured at several different wavelengths as the laser is tuned across the molecular signature of the analyte gas.
- WS-CRDS is a measurement of time not of absorbance. When the laser is at a wavelength where the gas in the cavity is strongly absorbing, the ring down time is short; when the wavelength is such that the gas does not absorb, the ring down time is long.
- The concentration is proportional to the difference in these ring down times.

Isotopic CO_2 Spectra



CO_2 spectrum taken by Picarro analyzer showing the extremely high measurement resolution (0.0001 cm^{-1}). Carbon isotope ratios are calculated by measuring the relative concentrations of the two isotopologues of CO_2.

Isotopic CO_2 Measurements



Data from a Picarro isotopic CO_2 analyzer measuring the isotopic carbon ($^{13}C/^{12}C$) ratio from a constant-concentration (407 ppmv) CO_2 gas stream. The measurement precision is 0.15 per mil (in $\delta^{13}C$ units) in a 5-minute measurement.

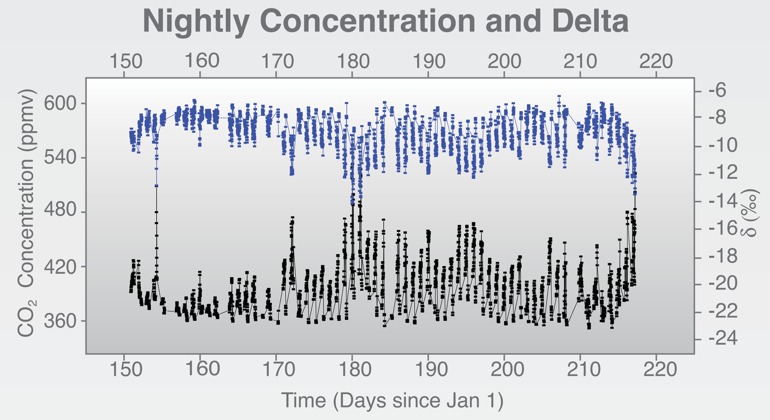
Benefits of the Picarro Analyzer

- Superb sensitivity, precision & accuracy with virtually no drift
- Fast, continuous, real time measurements without interference
- Large dynamic range with high linearity
- Field and laboratory deployable with no consumables
- Installed and operational in minutes
- Rugged and insensitive to changes in ambient temperature, pressure or vibration

Variations of $\delta^{13}C$ in Ecosystem Respiration: Continuous, *in-situ* Measurements in the Pacific Northwest

(T. Rahn, et al, Los Alamos National Lab, Ken Bible, WRCC)

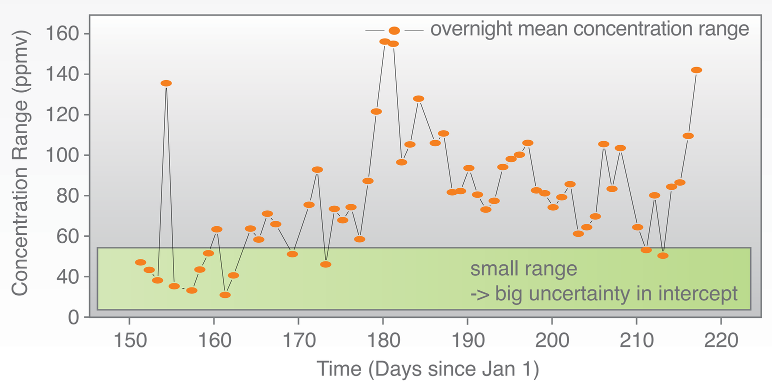
Nightly Concentration and Delta



Concentration and carbon isotope data (nighttime only) over a two month period including data sampled from three different heights above ground level.

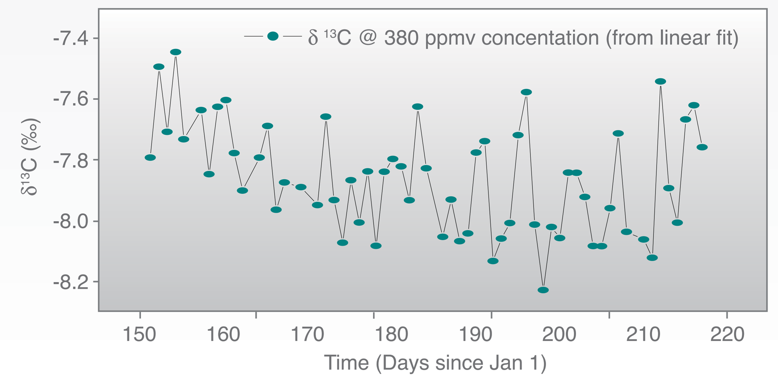
Abstract:

Understanding the interdependencies of sources and sinks within ecosystems and validating models of such systems greatly benefits from fast, continuous, in situ measurements of not only CO_2 concentration, but also isotopic carbon abundances in CO_2. Such high frequency (<5 minute) isotopic measurements help validate carbon transport models of terrestrial ecosystems and are key to developing an overall understanding of the dynamics influencing global atmospheric carbon budget. By utilizing high time resolution instrumentation based on WS-CRDS, the biosphere-atmosphere CO_2 exchange mechanisms can be more carefully examined. This measurement technique achieves precisions of approximately 0.3 per mil with measurement drift that is sufficiently low so as to avoid frequent calibration and can be deployed in remote, unattended locations for long-term, continuous measurements, enabling the observation of diurnal and seasonal trends in the CO_2 exchange processes. We present new data measured at Wind River Canopy Crane, WA, analyzing air within the canopy of an old growth forest. This data was produced using Picarro's recently commercialized WS-CRDS-based CO_2 isotope analyzer.



Mean nightly CO_2 concentration range across different sampled heights. The smaller ranges contribute to larger errors in the intercept on an inverse concentration (Keelling) plot.

Overnight Measurments – Isotope Ratio @ 380 ppmv (‰)

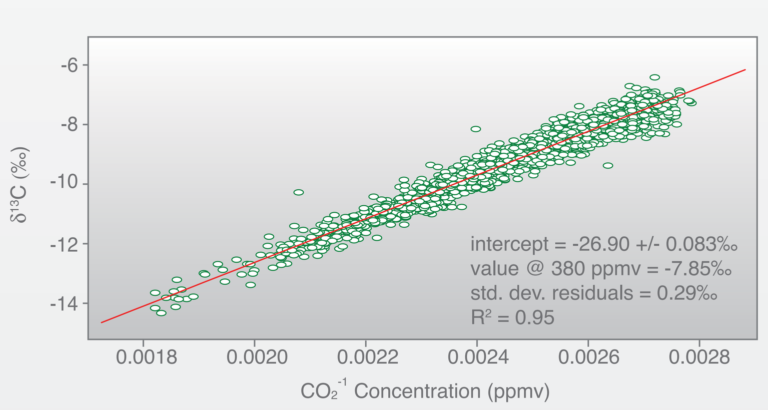


Nightly CO_2 isotope ratio at constant CO_2 concentration over two months.

Measurement Details:

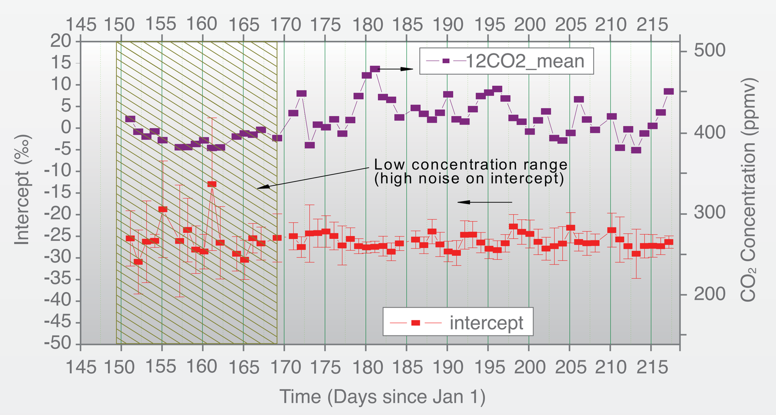
- Data was taken for two months – nearly continuous data from early June through early August
- Analysis of data during the night hours (22:50 – 08:20 local time)
- Each 1 hour period from each of three heights above ground level (0.1m, 10m, 55m) was divided into ~11 minute steps (discarding the first 4 minutes after the valve switch) and the concentration and delta values were averaged over that time period
- Intercept shows a mean value of -26.9 permil over two months
- Variation in intercept from night to night shows excursions of about 5 permil
- Nightly data was compared to local meteorological data (humidity and temperature) but there was no obvious trend of isotope content and humidity as would be expected based on previous work. ($\delta^{13}C$ would be expected to be covariant with moisture – with drier conditions resulting in more positive $\delta^{13}C$ values)
- The lack of correlation between $\delta^{13}C$ and temperature or humidity could be due to a limit on the precision with which the isotope ratio could be measured (if there indeed is a correlation to be observed, albeit small), or perhaps because for this ecosystem, there was not a significant actual variation in $\delta^{13}C$.

Keeling Plot – Nighttime Measurements



Keeling plot of all nightly concentration and isotope data for all three sampled heights. The line's intercept yields the delta value of the additional CO_2 (i.e., respired canopy or soil CO_2) added to the stable nighttime atmosphere.

Overnight Concentration and Keeling Plot Intercept



CO_2 concentration range plotted with the corresponding intercept and its associated relative error. The shaded area shows relatively higher errors in the intercept due to a smaller range of concentrations with which to calculate the Keeling plot intercept.

Conclusions and Future Work:

By combining this high-resolution isotopic CO_2 data with existing models of the global carbon budget, these models can be further examined to test their sensitivities to currently held assumptions about the role of photosynthesis, plant respiration and other effects on the relative isotopic abundances of carbon in CO_2.
This initial analysis has helped validate the precision and long-term drift requirements for this and similar applications and has given real-world targets for improvement goals of the analyzer itself.

Such precision and drift improvements have already been implemented by Picarro and we expect the data which continues to be taken at the Wind River site to be significantly improved going forward. Such improvements will undoubtedly produce higher-resolution data and will likely allow observation of subtle effects to be discerned (e.g. evidence of moisture stress via the isotopic data) that were not definitively observed in this initial campaign.

Continuous Measurements of Carbon Isotopes in Soil-Respired CO_2: Fractionation in Non-equilibrium Diffusive Environments

(D. Risk, N. Nickerson, St. Francis Xavier University)

Abstract:

Continuous $\delta^{13}CO_2$ monitoring of soil has been instrumental in validating recent modeling efforts that describe isotope dynamics in diffusive environments where equilibrium has not been established. We see that true isotopic equilibrium is likely rare because of the time it takes for all isotopologues to equilibrate. This results in a range of dynamic fractionations (frequently several permil) that in soil environments are a result of changes in the CO_2 production rate, gas diffusivity, and air-filled porosity. This effect is seen to some extent in most natural and disturbed environments and also as a direct consequence of sampling. Researchers have not previously been sensitive to these transient fractionation effects which can lead to misinterpretation of data. More work is needed in this area but initial modeling efforts and continuous measurements have yielded promising results.

Dynamic Fractionation

- Present in non-steady-state diffusive environments
- Result of gas transport dynamics
- Problem: Are most systems at isotopic disequilibrium? Most theory is for steady-state.

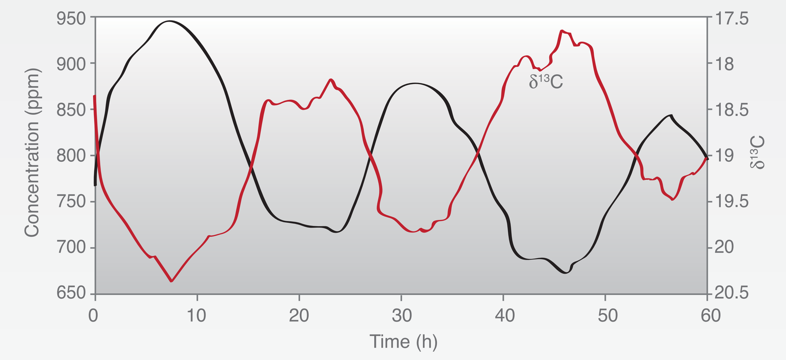
Data for validation of new theory and model:

Risk, D., L. Kellman (2008) Isotopic fractionation in non-equilibrium diffusive environments. Geophysical Research Letters, 35, L02403, doi:10.1029/2007GL032374.
Nickerson, N., D. Risk , Physical Controls on the Isotopic Composition of Soil Respired CO_2. Submitted to JGR-Biogeosciences

Advantages of Picarro Analyzer for this Work:

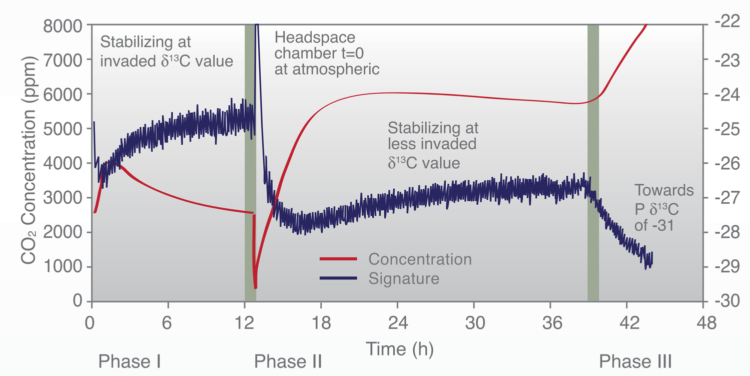
- Not possible to capture rapid changes with IRMS
- Repeat sampling adds further disequilibrium
- Quickly capture dynamic $\delta^{13}C$ behavior in systems assumed to be at steady-state

Diurnal Changes in Soil CO_2 Production: How do they affect isotopic equilibrium?



Soil chamber measurements of concentration and isotope ratio subject to in CO_2 production rate only. Raw delta data with 30 min smoothing.

Isotopic Equilibration in a Disturbed System:



Soil chamber measurements of concentration and isotope ratio subject to apparatus in different configurations. Raw delta data without smoothing.

Phase I: Column (6" diameter) of soil with both ends open to the atmosphere. The Picarro analyzer is sampling soil gas from the middle of the column.

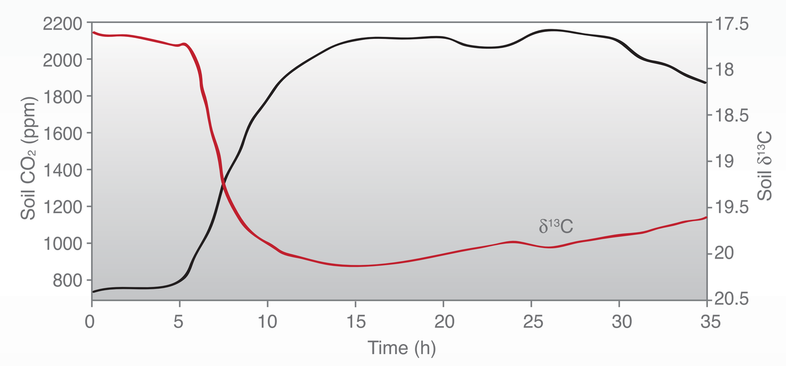
Phase II: Top end of the column capped, Picarro analyzer sampling the headspace that was created by the cap.

Phase III: Bottom end is capped with Picarro analyzer still sampling at the top. The reason for the changes in the data between Phases 2 and 3 results from creating a closed system where CO_2 is being produced, increasing the concentrations and decreasing the $\delta^{13}C$ to near what would be expected from CO_2 production.

Other Dynamic isotopic tests completed with Picarro G1101-i :

- Changes in system $\delta^{13}C$ by wetting and diurnal temperature variation
- Changes in system $\delta^{13}C$ by simple changes to an apparatus
- Tested bias in isotopic sample capture methodologies – tested all soil-based methods
- Tested bias imposed by common data processing techniques
- Data strongly validates new theory and model

Changes in Soil Moisture: How do they affect isotopic equilibrium?



Soil profile measurements of concentration and isotope ratio in a soil subjected to a simulated rain event at 5h. Raw delta data with 30 min smoothing.

Conclusions and Future Work:

- Instrument is well-suited to dynamic work
- Produced measurement data within 30 mins. of unpacking the box
- Exceptional stability up to and outside of measurement range

The observed trends in concentration and isotopic content are consistent with steady state and new non-steady state theoretical models. The ability to conduct continuous (rather than discrete flask sample) measurements has allowed much more straightforward verification of the behavior of these systems in comparison to existing theory. Additional work needs to be conducted in theory verification for a variety of variables including soil porosity, soil drying, step, slow and diurnal changes in gas production rates.