Dynamic Measurements of Greenhouse Gas Respirations Caused by Changing Oxygen Levels

PICARRO

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Abstract

The necessity for constant monitoring of greenhouse gases (GHGs) is clearly evident now more than ever. Moreover, interpreting and understanding the processes that dictate the production and consumption of these gases will allow for proper management of GHGs in order to mitigate its detrimental climate effects. Presence of oxygen, or lack of it, is the driving force for determining pathways within biochemical redox reactions. Experiments to find correlations between oxygen and greenhouse gases have helped us understand photosynthesis, denitrification and beyond. Within the past few years measurements of O_2 and nitrous oxide have been used over a wide ranging array of disciplines; from studying avenues for redox chemistry to characterizing gas profiles in sputum of cystic fibrosis patients. We present a full analysis solution, based on cavity ring-down spectroscopy, for simultaneous measurements of N_2O, CO_2, CH_4, H_2O, NH_3, and O_2 concentrations in soil flux, in order to better understand dynamics of ecological and biogeochemical processes.

The stability and high temporal resolution of the five-species CRDS analyzer, coupled with a continuous high-precision O2 measurement (1-σ <200ppm) produces a complete picture of biogeochemical processes, for which a multitude of additional research experiments can be conceived. Adding another dimension to explore to help determine the rate at which these greenhouse gases are produced or consumed, allows scientists to further address fundamental scientific questions. Data is presented showing precision, drift and limitations of the O_2 sensor measurement as well as the validity of spectroscopic corrections with the CRDS analyzer caused by changing O_2. Experimental data is also presented to explore correlations of gas flux rates of O_2, N_2O, CO_2 and CH_4 in a plant/soil ecosystem due to differing soil and atmospheric conditions at varying timescales from minutes to days.

Instrumentation

Picarro G2508 CRDS Gas Concentration Analyzer

Â Continuous gas flow at ~240 sccm
Â Continuous concentration measurement of N_2O, CH_4, CO_2 NH_3 and H_2O in air with ppb precision
Â Data rate: Measures all 5 species in < 6 seconds

Completely Integrated Electro-optical O_2 Sensor - PreSens

Â Pressure and temperature stabilized

Peripheral Sensors for Environmental Properties

Â Soil O2 concentration - Apogee S-210
Â Ground Temperature - Apogee
Â Ambient Temperature – Campbell T109
Â Solar Radiation - Licor Li190R

Methodology

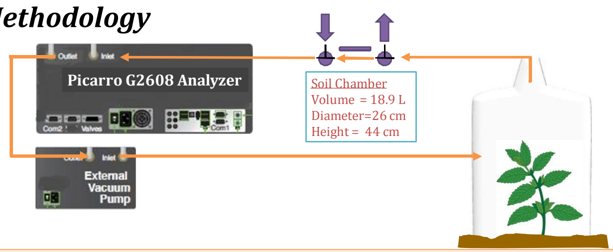
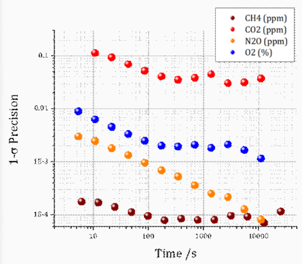


Figure 1: *Back of the Picarro analyzer and vacuum pump showing gas connections to the chamber two three way valves (purple) selected to vent chamber automatically*

Â A closed-loop system using 1/4" Swagelok Teflon tubing and Swagelok fittings recirculates air between the chamber and the Picarro analyzer
Â The chamber was closed for 60 min for each measurement
Â Chamber vented for minimum of 1 hr (later data 2 hrs) to bring chamber closer to ambient concentrations (though full equilibrium never reached)

Analysis

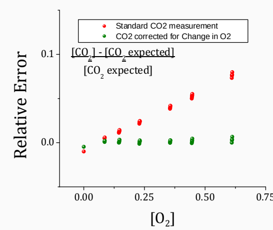
Â Analyzer Stability and Drift – Allan Standard Deviation

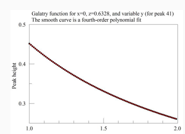


Â Long Term Stability of instrument due to pressure and temperature stabilization allows low long term drift
Â More importantly short term drift is completely negligible allowing for no calibration to be done throughout experiment
Â Maximum Precision for O2 is around 5 minutes averaging and can reach 20ppm

Â O_2 Correction and Validity

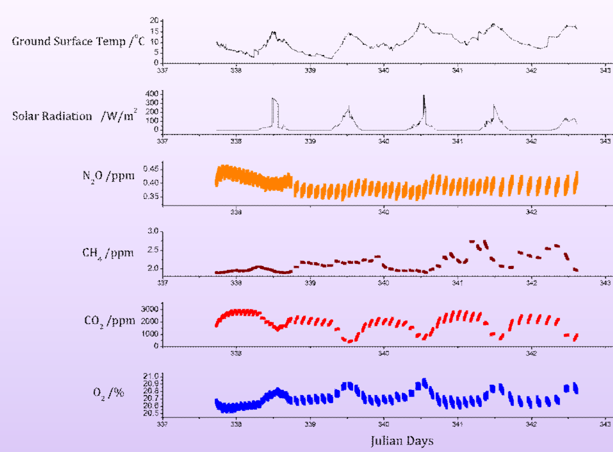
Â Changing O_2 concentration changes shape of aborption feature used for concentration
Â Changes of 5% can cause an influence of more than 0.5% of the concentration measured
Â Changes are small but influence can be seen when data is averaged
Â Current corrections are valid over a range of O2 levels, from nearly 5% to 30% total O_2





*****Background:*** *These deviations stem from spectral features line shape changing and apply to all absorption spectrometers. Figure to the Left shows simulation of changing peakheight because of y-parameter changing. This can be caused by things such as Changing O_2:N_2 ratios.*

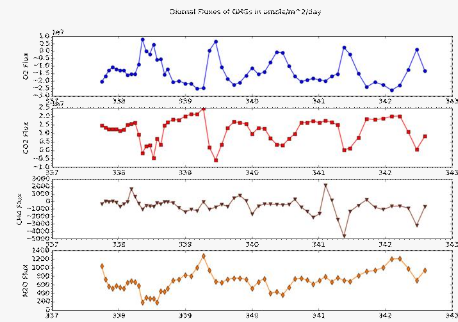
Raw Concentration Measurements for Flux Determination



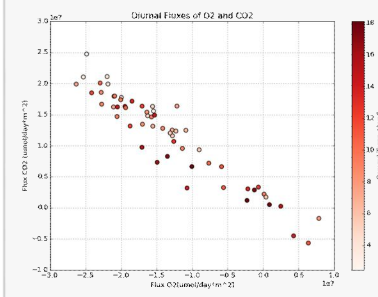
Raw Concentration measurements show diurnal cycles that the CO2 and O2 concentrations follow. Also show that chambers were not fully vented to ambient concentrations, but since the fluxes of CO2 and O2 are large, can still be easily seen

Results

Diurnal Cycles of Plant Ecosystem: Production and Consumption



Above Figure shows the fluxes for all gases measured over the period of 5 days. It can clearly be seen that there is a strong correlation to day and night time, as well as between CO_2 and O_2 All fluxes are calculated in µmole/day/m²



The correlation between CO_2 fluxes and O_2 fluxes is shown to the left. This small single plant ecosystem only has net positive fluxes of O_2 at peak solar radiation, but lower ground temperatures, so microbial activity is not at its height consuming O_2. This can explain the large ground temperatures in the middle where there is a balance of consumption from soil with production of from the plant.
This produced a fitted slope of -0.77 CO_2 flux to O_2 flux.

Conclusions and Recommendations

In this study, we have demonstrated a integrated sensor to a proven instruments in the CRDS Picarro G2508, This new implementation allows automatic corrections to be made within the analyzer due to widely varying O_2:N_2 ratios which can be caused by microbial consumption or plant production. Additionally This O_2 sensor has allowed us to see the changing background matrix to the normal GHGs monitored in soil respiration experiments. We have found the microbial consumption of O_2 can be so large that it can even offset the O_2 production due to a mint plant. Likewise CO2 production due to soil microbes significantly outweighs the consumption of CO_2 from the mint plants, except at the sunniest part of the day in winter at 450 W/m². It should also be noted that , no useful data can be seen in diurnal patterns of the soil oxygen content. soil O2 measurements using the Apogee, which could be due to long response and poor digitization of signal.