Measuring Isotopic CO_2 and CH_4 Soil Flux with the Picarro G2201-*i*

Introduction

Stable carbon isotope measurements of CO_2 and CH_4 are frequently used to understand the sources and mechanisms contributing to soil gas flux. For example, isotopes of CO_2 can be used to determine the relative contributions of root and microbial CO_2 production to total soil CO_2 flux. Alternatively, in systems where photosynthetic pathways have transitioned from C3 to C4 or vice versa (**Figure 1a**) isotopes can be used to determine relative contributions of carbon from each pathway to total soil respiration. Similarly, methane stable isotopes are used to differentiate biological versus geological sources of soil gas flux (**Figure 1b**) and can also be used to examine the mechanisms of methane production and oxidation. This application note outlines the configuration and use of the Picarro G2201-*i* dual carbon (CO_2 & CH_4) isotope analyzer to differentiate between C3 and C4 respiration sources at a transitional agricultural experiment in southern Sweden.

Figure 1. (a) eosAC chambers coupled to a Picarro G2201-i at the Ultuna site in Uppsala, Sweden (Photo: Muhammad Shahbaz, SLU) (b) Measurements of stable C isotopes near the Daisy Geyser at Yellowstone National Park (Photo: Moyo Ajayi, Vanderbilt University)

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System Setup
Follow Eosense application note **AN0003** for quick setup of your Picarro G2201-*i* with the eosMX multiplexer and eosAC automated soil flux chambers.

Sample Handling

The Picarro G2201-*i* with A0702 recirculating pump has a nominal flow rate of 25 sccm and is optimized to provide recirculation-based measurements. Due to the low flow rate users must consider the total transit time and mixing time required for chamber measurements. Below in Table 1 the estimated minimum times required by tubing length to deliver the sample to the analyzer are shown.

Tubing Length	Volume	Transit Time
10 m	79 cm^3	3 min
20 m	158 cm^3	6 min
30 m	238 cm^3	9 min

Table 1. Nominal transit times for gas to the G2201-i analyzer assuming tubing with a 3.175 mm (⅛") internal diameter and the Picarro A0702 recirculating pump.

Because the required minimum transit times are quite long, users may wish to implement a secondary pump to speed up the sampling process. Eosense recommends a pump with nominal flow rates of less than 1 SLPM (1000 sccm) that is designed for recirculation applications. **Figure 2** demonstrates the configuration of the secondary pump in the system.

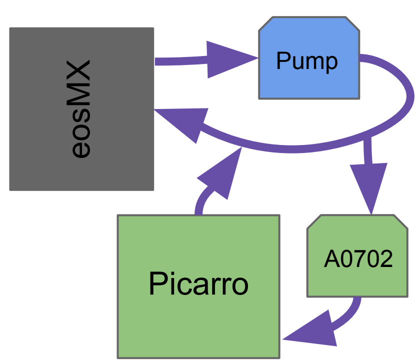

Figure 2. Example diagram of a sub-loop system using an secondary pump to speed up the flow from the eosMX to the G2201-i analyzer. Total system flow rate is the sum of the Picarro pump flow and secondary pump flow.

Field Site and System Configuration

The long-term field experiment ('Ultuna') is located in Uppsala, Sweden and has been used agriculturally (predominantly C3 crops) for at least 300 years prior to the establishment of the experimental trial. Experimental trials were initiated to investigate the impact of various organic amendments, with or without N fertilisation, on soil fertility. From 1956 to 1999, the site was under C3 annual crops, mainly spring barley, oats, rape, beet, mustard and turnip. These C3 crops had an average $\delta^{13}C$ signature of −28.0‰. The $\delta^{13}C$ signature of soil in 1999 was ~−26.6‰. In 2000, C3 crops were replaced by C4 silage maize with root $\delta^{13}C$ signature −12.5‰. Carbon dioxide flux rates at the site are generally low due to low soil organic carbon contents (Shahbaz et al., 2019).

To monitor the gas flux and isotopic composition, a Picarro G2201-*i* was installed onsite along with 12 eosAC automated soil flux chambers coupled to the eosMX multiplexer. Each chamber is located on one of four fertilizer treatments (Unfertilized, Calcium Nitrate, Ammonium Sulphate, Calcium Cyanamide), with 3 replicate chamber measurements for each treatment. Chambers are coupled to the system with 30 m of PTFE tubing, and as a result the approximate system purge and gas delivery time is 5-6 minutes (a second analyzer with approximately the same flow is in parallel). For this experiment, each chamber closure was a total of 15 minutes to allow for sufficient gas accumulation. Data was processed using the eosAnalyze-AC software which produces linear and exponential flux estimates, as well as Keeling plots for isotopic CO_2 and CH_4.

Characteristic Flux and Isotopic Data

Shown below in **Figure 3** are two example concentration curves from a single chamber closure. The high precision of the Picarro G2201-*i* analyzer coupled with the high-temporal resolution of data collection means that both linear and exponential fits to the data are very robust. Note that for the Ultuna field site, we observe CO_2 emission to the atmosphere and a CH_4 uptake into the soil, typical of well drained agricultural soils. **Figure 4** shows an example CO_2 Keeling plot analysis performed using the eosAnalyze-AC software.

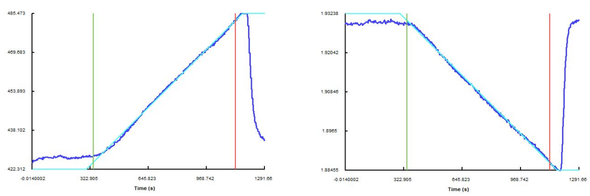

Figure 3. Example CO_2 emission (left) and CH_4 uptake (right) curves from the eosAnalyze-AC software.

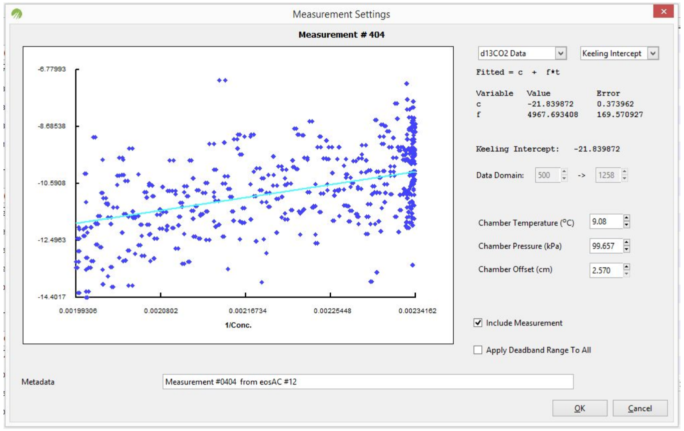

Figure 4. Example CO_2 isotope Keeling plot showing an estimated isotopic value of soil CO_2 flux of $\delta^{13}C$ = -21.8‰.

Comparison of Fertilizer Treatments

In this analysis we chose to focus on one of the three replicates, consisting of four separate fertilizer treatment types (Unfertilized, Calcium Nitrate, Ammonium Sulphate, Calcium Cyanamide). Data presented here is from late-May, 2019, before the sowing of the silage maize crop (bare soil).

Measured CO_2 fluxes ranged between 49 - 70 mg $CO_2/m^2/h$ with linear flux estimates averaging about 14% lower than exponential estimates (**Figure 5**). The highest fluxes were recorded in the unfertilized plot whereas the lowest were in the Calcium Sulphate treated plot. Overall flux magnitudes are consistent with previous site measurements (Shahbaz et al., 2019).

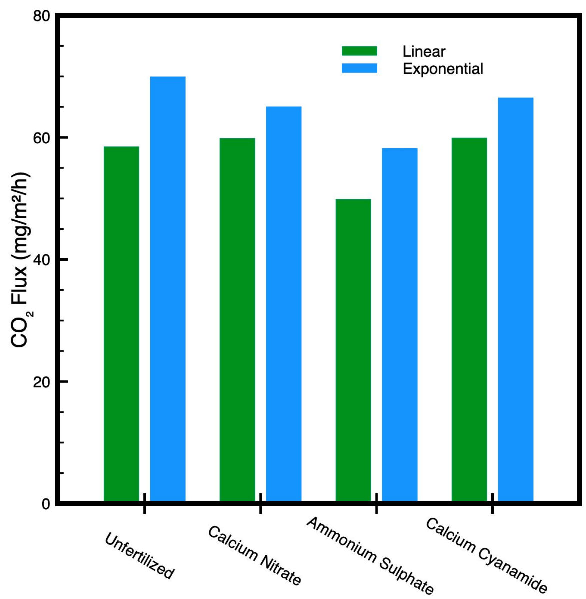

Figure 5. Median CO_2 fluxes calculated using linear and exponential fits from the four treatments over two weeks in late May.

All sites showed a consistent methane sink which was highest under the Ammonium Sulphate and Calcium Cyanamide fertilizer treatments (**Figure 6**). Other research by Hartmann et al. (2011) showed fertilization had a transient effect on methane oxidation, however their conclusions were that moisture had a significantly larger impact. Given the varying soil textures among the four treatment plots at the Ultuna site, this may also be the explanation for the results shown here.

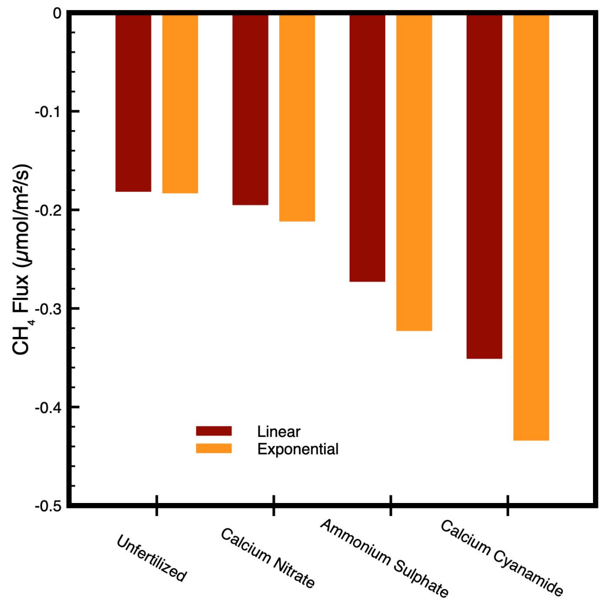

Figure 6. Median CH_4 uptake for each treatment calculated using the linear and exponential flux models.

Carbon isotopic values ($\delta^{13}C$) for all plots ranged from between -22.0‰ to -24.1‰, shown in Table 2. Using a simple linear isotopic mixing model, we estimate that the total C3 soil carbon respired as CO_2 during the fallow period at the end of May ranges between 67-82% with the lowest being in the Calcium Cyanamide treatment and the highest being in the Ammonium Sulphate treatment. Since no vegetation is present during this period of the year we assume C4 carbon that is being respired represents Maize organic matter (roots, stem and litter) that has has accumulated in the 20 years since the transition to C4 crops.

Site	Soil Flux $\delta^{13}C$	C3-C %
Unfertilized	-23.0‰	75%
Calcium Nitrate	-23.0‰	75%
Ammonium Sulphate	-24.1‰	82%
Calcium Cyanamide	-22.0‰	67%

Table 2. Isotopic CO_2 flux values estimated using Keeling plot intercepts for each of the four treatment types. The right hand column shows estimated C3 carbon (C3-C) respired calculated using a simple linear mixing model with $\delta^{13}C_{C3}$ = -26.6‰ (year 2000 soil estimate) and $\delta^{13}C_{C4}$ = -12.5‰ (maize).

Conclusions

The combined Picarro G2201-i, eosMX multiplexer and eosAC automated chamber system allowed us to pinpoint differences in both CO_2 and CH_4 fluxes amongst fertilizer treatments. We determined the CO_2 isotopic composition of soil respiration in real time using Keeling plot analysis. By applying a simple linear mixing model to the data we estimated proportions of C3 and C4 carbon in total soil respiration and how that proportion varied among the treatment plots.

These C isotopic measurements will be used to determine respiratory losses of old C (from C3 plants) and more modern C (C4 plants) from soils at Ultuna resulting from fertilizer treatments, which will help researchers understand how to improve the long-term fertility of agricultural soils.

References

Shahbaz et al. (2019), Science of the Total Environment, 658, 1539-1548.
Hartmann et al. (2011), Plant & Soil, 342, 265-275.

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