The integration of the automated EOSENSE soil chambers with the isotopic Picarro CRDS analyzers allows to investigate simultaneously the isofluxes of N_2O, CO_2 and CH_4 from soils.

Measuring isotopic N_2O, CO_2 and CH_4 soil flux with cavity ring-down spectroscopy

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INTRODUCTION

- Stable isotope analysis of N_2O, CO_2 and CH_4 is a valuable tool to better understand production and consumption pathways in soils.
- Here, we present the integration of two cavity ring-down spectrometers (CRDS) for continuous stable isotope analysis of N_2O, CO_2 and CH_4 with 12 automated soil flux chambers.

INSTRUMENTATION

Picarro G2201-*i* analyzer (near infrared)

- Field-deployable analyzer for simultaneous high-precision $\delta^{13}C$ analysis of CH_4 and CO_2.
- Precision (1-σ, 1-hour window, 5-minute averages): $\delta^{13}C$-CO_2 < 0.16‰, $\delta^{13}C$-CH_4 < 1.15‰

Picarro G5131-*i* analyzer (mid infrared)

- Field station deployable
- Precision (1- σ, 1-hour window, 5-minute averages): $\delta^{15}N$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$ <1‰

Field site

The measurements were performed at a long-term field experiment site located at Ultuna, Uppsala, Sweden. The Ultuna trial field has been started in 1956. The soil, a clay loam with 36.5% clay, has been classified as Eutric Cambisol. At the start of the experiment, the soil contained 1.5% total C and 0.17% N and was slightly acidic (pH 6.6).

The overall aim of the field experiment is to study the effects of different organic and mineral fertilizers on soil properties and carbon (C) and nitrogen (N) dynamics. The present chamber set-up is also designed to investigate the effects of different pH-levels in soil on N_2O fluxes, with pH ranging from 4.0 up to 7.5.

Considerations for soil chamber measurements

- The G5131-*i* analyzer (*i*-N_2O) operates in the mid infrared, and therefore, requires more stable operating conditions than a near infrared analyzer. We refer to the G5131-*i* as being field stationary deployable.
- The G5131-*i* analyzer (*i*-N_2O) was initially designed for atmospheric measurements. A priori, soil chamber measurements are challenging because large variations in background gas concentration (e.g. CH_4 and O_2) can require further data post processing.
- In the setup presented here, the chamber measurements were considered as a quasi closed loop configuration since the subsampling line for the G5131-*i* sampled at a low flow (<50mL/min) and sampling was done for less than 15 minutes. Therefore, the pressure change in the chamber was negligible. Alternatively, one could also allow ambient air to mix into the soil chamber to avoid under-pressure. In this case, the small dilution needs to be taken into account in the data analysis, i.e. following the open chamber approach (personal comm. Eliza Harris, University of Innsbruck).

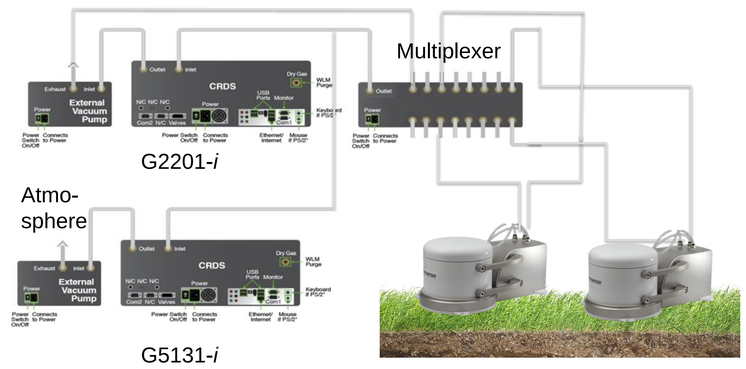

Fig. 1: Schematic illustrating the integration of the G5131-*i* and G2201-*i* analyzer with a multiplexer and a eosAC automated chamber system. The G5131-*i* is subsampling air from the G2201-*i* recirculation loop (also see box on 'Considerations for soil chamber measurements').

RESULTS

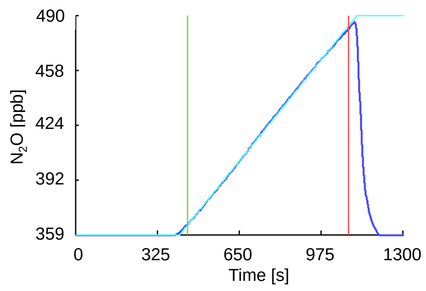

Fig. 2: N_2O emission during <15 min soil chamber closure. The N_2O flux was determined to be 1122.7 nmol/m²/s.

Isotopic signatures	Keeling plot end-members
$\delta^{15}N_{bulk}$	-42.9±1.4‰
$\delta^{15}N_{\alpha}$	-38.1±1.8‰
$\delta^{15}N_{\beta}$	-47.6±1.6‰
SP	+9.5‰
$\delta^{18}O$	-26.4±1.6‰

Table 1: Keeling plot end-members. Note that all *δ*-values are uncalibrated values and the data are meant to illustrate the precision of the isotopic end-member characterization!

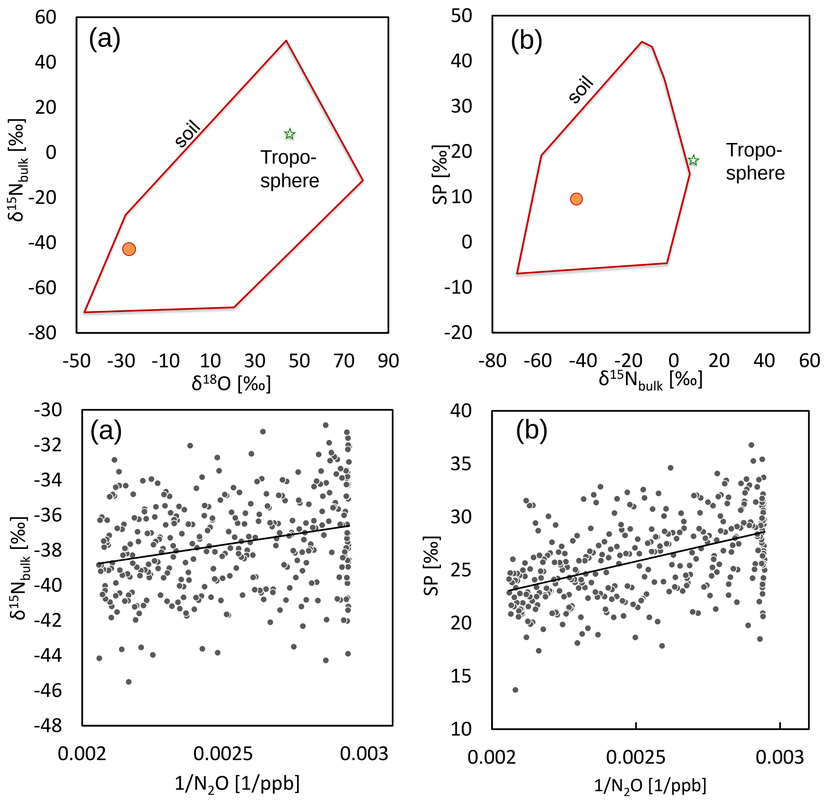

Fig. 3: N_2O Keeling plot end-members (circles) in comparison to soil and troposphere literature data from Toyoda et al., 2015. Note that $\delta^{15}N_{bulk}$ and $\delta^{18}O$ are uncalibrated values, still the isotopic values are reasonable.

Fig. 4: Keeling plots. Note that the $\delta^{15}N_{bulk}$ values are uncalibrated!

CONCLUSIONS

- The Picarro G2201-*i* and the Picarro G5131-*i* analyzer can be operated in parallel to obtain N_2O, CO_2 and CH_4 isofluxes. Please follow the QR code to learn more about the CO_2 and CH_4 carbon isotope data obtained during this study!
- For a ca. 12.5 min soil chamber closure, the N_2O concentration was enriched by 130 ppb (corresponding to a flux of 11227 nmol/m²/s) allowing to determine the $\delta^{15}N_{bulk}$, $\delta^{15}N_{\alpha}$, $\delta^{15}N_{\beta}$, $\delta^{18}O$ end-member with a precision of ±1.4‰, ±1.8‰, ±1.6‰, ±1.6‰, respectively.

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