Measurement of N$_2$O and CH$_4$ Soil Fluxes From Garden and Agricultural Soils Using Closed Chamber System Coupled with High-Precision CRDS Analyzer

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Experiment Objectives

Motivation: To evaluate the capability of the new Picarro G2508 analyzer coupled with a static chamber to measure soil fluxes of N$_2$O, CH$_4$, CO$_2$.

• Objective 1: Characterize the sensitivity of the analyzer to other molecular species which may be present in soil emissions.

• Objective 2: Measure agricultural soil samples with a wide range of fluxes in the lab to evaluate the uncertainty of the measurements.
Instrumentation: GHG Analyzer Performance

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Specified Precision: 1-σ of 5 min averages</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>&lt; 5 ppb</td>
</tr>
<tr>
<td>CO₂</td>
<td>&lt; 200 ppb</td>
</tr>
<tr>
<td>CH₄</td>
<td>&lt; 5 ppb</td>
</tr>
<tr>
<td>NH₃</td>
<td>&lt; 1 ppb + 0.05% of reading</td>
</tr>
<tr>
<td>H₂O</td>
<td>&lt; 100 ppm</td>
</tr>
</tbody>
</table>

- Measurement frequency: 7 seconds for each molecule
- Dry mol fraction automatically reported
- Ambient-level reference gas measurements made every two days to check for drift
- Rough calibration prior to experiment: Estimated 1% error
Analyzer Drift Test

**CO₂**

- 2.5 ppm

**CH₄**

- 3.5 ppb

**N₂O**

- 50 ppb
Most likely interfering molecules are the ones which are measured.
1-D CO$_2$ Sensitivity Testing

- **N$_2$O (ppm)**
  - -7.1 ppb per 1000ppm of CO$_2$ 
  
- **NH$_3$ (ppb)**
  - 0.8ppb per 1000ppm of CO$_2$

- **H$_2$O (%)**
  - 400ppm per 1000ppm of CO$_2$ 

- **CH$_4$ (ppm)**
  - Linear Fit of average CH$_4$ 
  
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CO$_2$ (ppm) vs. N$_2$O (ppm)

CO$_2$ (ppm) vs. NH$_3$ (ppb)

CO$_2$ (ppm) vs. H$_2$O (%) 

CO (ppm) vs. NH$_3$ (ppb)
# Measured Sensitivities

Automatic corrections are made within the instrument for $\text{N}_2\text{O}$, $\text{CO}_2$, $\text{CH}_4$, $\text{NH}_3$, $\text{H}_2\text{O}$

Hydrocarbon Sensitivities measured but not corrected

<table>
<thead>
<tr>
<th>Test gas</th>
<th>$\text{N}_2\text{O}$ (ppm)</th>
<th>$\text{CO}_2$ (ppm)</th>
<th>$\text{H}_2\text{O}$ (%)</th>
<th>$\text{CH}_4$ (ppm)</th>
<th>$\text{NH}_3$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_2$ (ppb)</td>
<td>3 E-4</td>
<td>-1.5</td>
<td>-4 E-4</td>
<td>TBD</td>
<td>-1.5 E-3</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4$ (ppm)</td>
<td>-2 E-4</td>
<td>-6.8 E-2</td>
<td>N/A</td>
<td>-2.9 E-3</td>
<td>-5.3 E-4</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6$ (ppm)</td>
<td>-2 E-4</td>
<td>4.7 E-3</td>
<td>1.6E-5</td>
<td>TBD</td>
<td>-7.1 E-4</td>
</tr>
</tbody>
</table>

Not recommended for use in studies using acetylene
Soil Samples from Iowa Plant Zoo

Samples Courtesy of Bernardo del Campo at U of Iowa

- Sample History
  - Samples taken after 15mm rain, capped and shipped to California
  - First measurements taken 4 days after sampling
  - Samples not re-capped between measurements

- Sample types: Molisols from Boone Iowa
  - Biochar: Plot treated with biochar (equivalent of 25 Ton CO$_2$/ha)
  - No Biochar: Plot without biochar
  - Garden: Test garden plot (no biochar treatment)
Experimental Set-up

Chamber

Soil Sample in soil tube

Gas Flow

Perforated tube

5 cm
Add 2.5 minutes to recorded start times for all flux calculations.

System volumes: 387–493 cm$^3$
Flux Measurement & Analysis Methods

• Measurement:
  – Closed path measurements
  – Minimum 15 min closed chamber
  – Minimum 10 min chamber flush (open) between measurements

• Analysis
  – Response time of 2.5 min added to recorded chamber close times
  – Linear fits using different measurement durations tried
  – Four min of concentration data provided the best uncertainty
  – Chi-square fitting (linear only) used to model slope & uncertainty
    • Assume unknown measurement uncertainty
    • Assume the same standard deviation for all measurements
    • Variance:
      \[ \sigma^2 = \sum_{i=1}^{N} \frac{(y_i - y(x_i))^2}{(N - M)} \]
Flux trends over time

CO$_2$ Flux (kg/ha/yr)

- Biochar A
- Biochar B
- No Biochar A
- No Biochar B
- Garden A
- Garden B

Hours after soil sample uncapping
Flux trends over time

CH$_4$ Flux (kg/ha/yr)

Flux (kg/ha/yr)

Hours after soil sample uncapping

- Biochar A
- Biochar B
- No Biochar A
- No Biochar B
- Garden A
- Garden B
Flux trends over time

N$_2$O Flux (kg/ha/yr)

Flux (kg/ha/yr)

Hours after soil sample uncapping

-10

0

10

20

30

40

50

60

70

Biochar A

Biochar B

No Biochar A

No Biochar B

Garden A

Garden B
### Flux Comparison

<table>
<thead>
<tr>
<th></th>
<th>Range of Fluxes (kg/ha/year)</th>
<th>Repeatability 1-sigma (kg/ha/year)</th>
<th>Uncertainty of Flux (model) (kg/ha/year)</th>
<th>Fluxes (kg/ha/year)</th>
<th>Uncertainty of Fluxes (SE) (kg/ha/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>-3.9 - 40</td>
<td>0.34 – 1.9</td>
<td>0.1 – 1.9</td>
<td>6-120¹</td>
<td>2.4 - 24¹</td>
</tr>
<tr>
<td>CO₂</td>
<td>7,900 - 205,400</td>
<td>320 – 1,700</td>
<td>2,800 – 74,600</td>
<td>0 - 96¹</td>
<td>4.8 - 12¹</td>
</tr>
<tr>
<td>CH₄</td>
<td>-2.7 - 1.6</td>
<td>0.013 – 0.34</td>
<td>0.3 – 1.7</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

¹Ventera et al 2010 SSSA (Minnesota Corn field using GC)
Conclusions & Next Steps

• Conclusions
  – Uncertainty and repeatability of the flux measurements were encouraging compared to GC measurements
  – We have only scratched the surface..

• Next investigations:
  – Effect of changing oxygen concentration
  – Compare measurements with GC, PAC, IRGA in Iowa
  – Other potential interfering species (small molecules which absorb in MIR)
Thank You.
Additional Material
1-D CH₄ Sensitivity Results

The sensitivity of CH₄, N₂O and NH₃ was less than the specified measurement precision over 100 ppm CH₄, see NH₃ graph (below, green) for example.

.07 ppm per ppm of CH₄

0.001 ppb per ppm CH₄
• $\text{N}_2\text{O}$ has essentially has zero cross talk to other molecules because it is so weak in NIR, except $\text{NH}_3$
1-D NH₃ Sensitivity Results

-0.1 ppm per ppm of NH₃

0.1 ppm per ppm of NH₃

10 ppm per ppm of NH₃

-0.1 ppb per ppm of NH₃

10 ppb per ppm of NH₃
N$_2$O Allan Standard Deviation

Instrument performance results from the analyzer used in this experiment
CO₂ Allan Standard Deviation

Instrument performance results from the analyzer used in this experiment
CH$_4$ Allan Standard Deviation

Instrument performance results from the analyzer used in this experiment
NH₃ Allan Standard Deviation

Instrument performance results from the analyzer used in this experiment
Ambient N$_2$O Thermal Sensitivity Test

Instrument performance results from the analyzer used in this experiment

- Sensitivity is < 0.02 ppb per °C
- Effect over 30 °C change in ambient temperature is < 0.6 ppb
Ambient CH₄ Thermal Sensitivity Test

Instrument performance results from the analyzer used in this experiment

- Sensitivity is < 0.007 ppb per °C
- Effect over 30 °C change in ambient temperature is < 0.2 ppb
Ambient CO$_2$ Thermal Sensitivity Test

Instrument performance results from the analyzer used in this experiment

- Sensitivity is $< 0.5$ ppb per °C
- Effect over 30 °C change in ambient temperature is $< 15$ ppb
Zoom in on time response

\[
\begin{align*}
\text{CO}_2 & \\
\text{CH}_4 & \\
\text{N}_2\text{O} & 
\end{align*}
\]