Field intercomparison of four methane gas analyzers suitable for eddy covariance flux measurements

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February 28, 2014
Outline

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4  Discussion and Summary
1 Background

Development of gas analyzers based on laser absorption spectroscopy (LAS) has made sensitive and robust instruments commercially available.

Accordingly, the number of gas analyzers applicable for EC measurements increased.

The comparisons between the gas analyzer are necessary.

This study is to compare and assess the performance of four CH$_4$ gas analyzer and corresponding CH$_4$ flux and it is done during April – October 2010 at fen.
The measurement system of this study

Three-axis sonic anemometer (USA-1, METEK, Germany) (It is shared by the all gas analyzers in this study)

- LI-COR Prototype-7700 (LI-COR Bioscience, USA)
- Picarro G1301-f (Picarro Inc, USA)
- Los Gatos RMT-200 (Los Gatos Research, USA)
- Campbell TGA-100A (Campbell Scientific., USA)
- LI-7000 (LI-COR Bioscience, USA)
LI-COR Prototype-7700

Prototype-7700 is an early pre-production prototype of the open-path methane gas analyzer, tunable diode laser is utilized to create laser beams in the near-infrared region.

Methane concentration is measured by using wavelength modulation spectroscopy (WMS) in order to reduce the effects of mirror contamination.

Picarro G1301-f

- G1301-f is based on wavelength-scanned cavity ring down spectroscopy (WS-CRDS).

- Picarro G1301-f is a closed-path gas analyzer, the analyzer was measuring water vapor and methane concentrations, and sampling line was heated.
Los Gatos RMT-200

- RMT-200 is also a closed-path methane gas analyzer, it is based on the off-axis integrated cavity output spectroscopy (OA-ICOS).
- The tube that sample air to the gas analyzer was not heated but it was situated inside a protective cover.
Campbell TGA-100A

Campbell TGA-100A closed-path gas analyzer is based on TDLAS measurement technique, and the laser was cooled using liquid nitrogen, tube was not heated but the air was dried with a diffusion drier.

Dew point temperature remained at about -15 to -30 °C, WPL terms or spectroscopic corrections were not needed.

This instrument has been widely used in eddy covariance methane flux measurement studies, and is used in this study as a reference for the three new instruments.

Table 1: Characteristics of the four methane gas analyzers and their respective setups

<table>
<thead>
<tr>
<th></th>
<th>Prototype-7700</th>
<th>G1301-f</th>
<th>TGA-100A</th>
<th>RMT-200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyzer type</td>
<td>open-path analyzer enhanced with WMS</td>
<td>WS-CRDS</td>
<td>TDLAS</td>
<td>off-axis ICOS</td>
</tr>
<tr>
<td>Open/closed path</td>
<td>open</td>
<td>closed</td>
<td>closed</td>
<td>closed</td>
</tr>
<tr>
<td>Measured species</td>
<td>CH₄</td>
<td>CH₄, H₂O</td>
<td>CH₄</td>
<td>CH₄</td>
</tr>
<tr>
<td>Sampling height above the soil</td>
<td>2.3 m</td>
<td>2.5 m</td>
<td>2.5 m</td>
<td>2.5 m</td>
</tr>
<tr>
<td>Sampling height above significant structures</td>
<td>1.1 m</td>
<td>2.5 m</td>
<td>2.5 m</td>
<td>2.5 m</td>
</tr>
<tr>
<td>Horizontal sensor separation</td>
<td>10 cm</td>
<td>5 cm</td>
<td>5 cm</td>
<td>5 cm</td>
</tr>
<tr>
<td>Vertical sensor separation</td>
<td>45 cm</td>
<td>25 cm</td>
<td>30 cm</td>
<td>25 cm</td>
</tr>
<tr>
<td>Length of sampling line</td>
<td>–</td>
<td>16.8 m</td>
<td>13 m</td>
<td>15 m</td>
</tr>
<tr>
<td>Flow rate wind speed</td>
<td></td>
<td>10 LPM</td>
<td>14 LPM</td>
<td>12 LPM</td>
</tr>
<tr>
<td>Sample cell volume</td>
<td>open</td>
<td>33 cm³</td>
<td>480 cm³</td>
<td>408 cm³</td>
</tr>
<tr>
<td>Sample cell pressure</td>
<td>ambient pressure</td>
<td>187 hPa</td>
<td>60 hPa</td>
<td>189 hPa</td>
</tr>
<tr>
<td>Connected to dryer</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>System power demand</td>
<td>low</td>
<td>high</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>(solar- and wind-powered)</td>
<td>(grid powered)</td>
<td>(grid powered)</td>
<td>(grid powered)</td>
<td></td>
</tr>
<tr>
<td>Need of maintenance</td>
<td>low</td>
<td>low</td>
<td>high</td>
<td>low</td>
</tr>
</tbody>
</table>

The height of sonic anemometer is 2.75m, and below 1.1m of Prototype-7700 is a wooded structure. The filters aperture of G1301-f, TGA-100A and RMT-200 are 1 um, 10um and 0.2um respectively.
2 Materials and methods

2.1 Site description

2.2 Eddy covariance method

2.3 Random error estimations method

2.4 Gap filling procedure
Fig. 1 Aerial photograph of the measurement site. Star marks location of the measurements site, red line and blue lines show average methane flux and amount of obtained methane flux data as a function of wind direction. Dashed lines show where methane flux equals 1, 2 and 3 mg·m$^{-2}$·h$^{-1}$ and amount of data equals 60, 120 and 180 points.

The gas analyzer intercomparison was carried out in Siikaneva fen, Southern Finland.
2 Materials and methods

2.1 Site description

2.2 Eddy covariance method

2.3 Random error estimations method

2.4 Gap filling procedure
Eddy covariance method was used in measuring the vertical turbulent fluxes of trace gases, sensible and latent heat.

\[ H = \bar{\rho_a} c_p \bar{w'}T' \]  \hspace{1cm} (1)

\[ LE = L \bar{\rho_a} \bar{w'}\chi_v' \]  \hspace{1cm} (2)

\[ F_c = \bar{\rho_a} \bar{w'}\chi_c' \]  \hspace{1cm} (3)

Measurements were sampled at 10 Hz frequency, and 30-min averaging time was used in calculating the covariances. For the most part, data processing followed the methodology Described by Aubinet et al (2000).

Data processing

- **Step 1** The high frequency eddy covariance data were despiked by comparing two adjacent measurements.
- **Step 2** The coordinate rotation was applied.
- **Step 3** The mean values were removed from the time series using block-averaging method.
- **Step 4** Time lag between the concentration and wind measurements was corrected.
- **Step 5** Spectral corrections were applied.
- **Step 6** Humidity effect on temperature flux was accounted for.
- **Step 7** Webb-Pearman-Leuning (WPL) terms and spectroscopic corrections were applied.
2.2.1 Spectral corrections

\[ TF_{HF} = \frac{1}{1 + (2\pi f \tau)^2} \]  

\[ CF = \frac{\int_0^\infty S_{wT}^{model}(f) \, df}{\int_0^\infty TF_{HF}(f) TF_{LF}(f) S_{wT}^{model}(f) \, df} \]

Magnitude of signal attenuation can be estimated with correction factor CF.

2.2.2 Effect of water vapor and temperature fluctuations

- Pressure, temperature and water vapor affect the shape and width of the absorption lines used to deduce gas concentration.

- Concentration measurements are affected by air density fluctuations.

- The effect of pressure fluctuations is small according to the test method proposed by Lee and Massam, so atmospheric pressure is assumed constant in this study.

The correction of Prototype-7700 flux data

The Prototype-7700 flux data was corrected for density fluctuations and spectroscopic effects at the same time

\[ F_{c}^{\text{corr}} = A \left\{ \frac{w' \rho_{cm}'}{\rho_{a} L} + B \mu \frac{\rho_{cm}}{\rho_{a} L} \right\} + C \frac{(1 + \mu \sigma) \rho_{cm}}{\rho_{a} c_{p} T} H \]  \hspace{1cm} (6)

The coefficients A, B and C are obtained from look-up tables distributed with the instrument.

A: 0.94~0.99
B: 1.42~1.46
C: 1.21~1.34
The correction of RMT-200 flux data

In a closed-path gas analyzer temperature fluctuations in the sample gas are damped while the gas is transported in the long tube, the spectroscopic effects and density fluctuation caused by temperature fluctuations may be neglected.

For RMT-200 the spectroscopic effects were corrected by adding water vapor flux multiplied with certain factor $b_{ct}$ to the measured trace gas flux.

$$F_{c}^{SP} = F_{c}^{meas} + b_{ct} \frac{M_{c}}{M_{v}L} LE$$

The instrument specific coefficient $b_{ct}$ was adopted from Tuzson with some modifications, LI-7000 H$_2$O measurements were used to correct RMT-200 CH$_4$ flux data.

The correction of G1301-f and TGA-100A

For G1301-f the corrections were performed using the method and coefficients presented in Chen et al. They use second order polynomial function which describes the effect of H₂O on methane concentration measurements.

Closed-path gas analyzer TGA-100A was connected to dryer and therefore the CH₄ measurements were free of any interference from H₂O and these corrections were not needed.

2 Materials and methods

2.1 Site description

2.2 Eddy covariance method

2.3 Random error estimations method

2.4 Gap filling procedure
The standard deviations of the covariances were calculated according to method proposed by Finkelstein and Sims

\[
\sigma_F = \sqrt{\frac{1}{n_s} \left[ \sum_{p=-m}^{m} \hat{Y}_{c,c}(p) \hat{Y}_{w,w}(p) + \sum_{p=-m}^{m} \hat{Y}_{w,c}(p) \hat{Y}_{c,w}(p) \right]}
\]  

(11)

Absolute value for fractional flux error describing the standard deviations as a fraction of the covariance calculated as:

\[
\text{AFFE} = \left| \frac{\sigma_F}{w' \chi_c'} \right|
\]

(14)

Random uncertainty related to instrumental noise (inst) was estimated with a method proposed by Billesbach.

\[
\sigma_{\text{inst}} = \frac{1}{n_s} \sum_{i=1}^{n} w'(i) \chi_{c \text{ shuf}}(i)
\]

(15)


2 Materials and methods

- 2.1 Site description
- 2.2 Eddy covariance method
- 2.3 Random error estimations method
- 2.4 Gap filling procedure
In this study, methane flux was parameterized using peat temperature by assuming an exponential dependence.

\[
F_{\text{CH}_4, \text{daily}} = ab^{(T_{\text{p, daily}} - 10)/10}
\]  

(16)

\(F_{\text{CH}_4, \text{daily}}\) is the average daily methane flux, \(\text{mg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}\)

\(T_{\text{p, daily}}\) is peat temperature (°C) at 35 cm depth

\[a = 1.88 \pm 0.03\]

\[b = 5.34 \pm 0.22\]

3 Results

3.1 Data coverage

3.2 Spectral characteristics

3.3 Random error estimation

3.4 Systematic error estimation

3.5 Diurnal variation and CH$_4$ flux magnitude
The parameterization is not able to capture the high flux periods, and around day 205 mean daily methane is sudden drop, and Rinne et al (2007) reported similar phenomenon in their study which was carried out at the same site. The CH$_4$ flux measured at MLW also has the phenomenon.

Table 2. Amount of data obtained between 17 April and 17 May

<table>
<thead>
<tr>
<th></th>
<th>RMT-200</th>
<th>G1301-f</th>
<th>TGA-100A</th>
<th>Prototype-7700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data (points)</td>
<td>1178</td>
<td>1173</td>
<td>1141</td>
<td>1045</td>
</tr>
<tr>
<td>Data (%)</td>
<td>82</td>
<td>81</td>
<td>79</td>
<td>73</td>
</tr>
<tr>
<td>Flag 0 (%)</td>
<td>77</td>
<td>77</td>
<td>61</td>
<td>56</td>
</tr>
<tr>
<td>Flag 1 (%)</td>
<td>4</td>
<td>3</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Flag 2 (%)</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Flags 0, 1 and 2 represent data with good, mediocre and bad quality according to criteria proposed by Foken and Wichura.

3.2 Spectral characteristics

Fig. 3 Frequency weighted, normalized cospectra and power spectra plotted against normalized frequency $n$.

- The ensemble averaged methane and temperature cospectra and power spectra are shown with black and white dots, respectively.
3 Results

3.1 Data coverage

3.2 Spectral characteristics

3.3 Random error estimation

3.4 Systematic error estimation

3.5 Diurnal variation and CH$_4$ flux magnitude
3.4 Systematic error estimation

Fig. 6. Transfer function determined from measured cospectra

Fig. 7. Diurnal variations of gas analyzers
Table 3. Magnitude of spectral corrections given as percentages of raw uncorrected covariance

<table>
<thead>
<tr>
<th></th>
<th>RMT-200</th>
<th>G1301-f</th>
<th>TGA-100A</th>
<th>Prototype-7700</th>
</tr>
</thead>
<tbody>
<tr>
<td>All data (%)</td>
<td>11.1</td>
<td>5.1</td>
<td>5.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Daytime (%)</td>
<td>12.1</td>
<td>5.8</td>
<td>6.2</td>
<td>-3.6</td>
</tr>
<tr>
<td>Night time (%)</td>
<td>9.1</td>
<td>4.0</td>
<td>4.1</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Table 4. WPL terms and spectroscopic correction given as percentages of the uncorrected raw covariance

<table>
<thead>
<tr>
<th></th>
<th>RMT-200</th>
<th>G1301-f</th>
<th>Prototype-7700</th>
</tr>
</thead>
<tbody>
<tr>
<td>All data</td>
<td>WPL terms (%)</td>
<td>15.3</td>
<td>21.1</td>
</tr>
<tr>
<td></td>
<td>Spectroscopic correction (%)</td>
<td>3.2</td>
<td>0.9</td>
</tr>
<tr>
<td>Daytime</td>
<td>WPL terms (%)</td>
<td>23.9</td>
<td>38.4</td>
</tr>
<tr>
<td></td>
<td>Spectroscopic correction (%)</td>
<td>5.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Night time</td>
<td>WPL terms (%)</td>
<td>4.5</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>Spectroscopic correction (%)</td>
<td>0.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Table 5. Average difference between methane flux obtained from one instrument and mean flux obtained from the four instruments between 17 April and 17 May. (The mean value is 0.415mg·m⁻²·h⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>RMT-200</th>
<th>G1301-f</th>
<th>TGA-100A</th>
<th>Prototype-7700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux (mgm⁻²h⁻¹)</td>
<td>0.448</td>
<td>0.424</td>
<td>0.395</td>
<td>0.379</td>
</tr>
<tr>
<td>Difference (mgm⁻²h⁻¹)</td>
<td>0.037</td>
<td>0.012</td>
<td>-0.017</td>
<td>-0.032</td>
</tr>
<tr>
<td>Relative difference (%)</td>
<td>8.2</td>
<td>2.9</td>
<td>-4.2</td>
<td>-8.6</td>
</tr>
</tbody>
</table>

Table 6. Average difference between methane flux obtained from one instrument and mean flux obtained from the four instruments between 9 June and 29 June. (The mean value is 3.007mg·m⁻²·h⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>RMT-200</th>
<th>G1301-f</th>
<th>TGA-100A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux (mgm⁻²h⁻¹)</td>
<td>3.159</td>
<td>3.104</td>
<td>2.759</td>
</tr>
<tr>
<td>Difference (mgm⁻²h⁻¹)</td>
<td>0.151</td>
<td>0.097</td>
<td>-0.248</td>
</tr>
<tr>
<td>Relative difference (%)</td>
<td>4.8</td>
<td>3.1</td>
<td>-9.0</td>
</tr>
</tbody>
</table>
3.5 Diurnal variation and CH$_4$ flux magnitude

Fig. 8 Median diurnal variation of final fully corrected methane flux obtained from the four methane gas analyzers
4 Discussion and Summary
Concerning the random errors and instrument noise, the RMT-200 and G1301-f had on average the best performance.

Speaking of signal attenuation, the three closed-path instruments had the attenuation generally in the range that can be expected for closed-path design, however, The attenuation was larger from Prototype-7700.

In terms of density and spectroscopic corrections, the open-path Prototype-7700 measurements had large WPL terms as expected for an open-path design.
Summary

- All four gas analyzers performed quite well, and have proven suitable for eddy covariance measurements of methane flux at the study site.

- The observed differences were due to multiple factors, including instrument performance, instrument design, stage of instrument development, experimental setup, data processing, and available data coverage.

- Methane fluxes obtained with the four instruments were not significantly different from each other.

- In terms of field performance, the RMT-200 was the overall best performer, while the Prototype-7700 is a practical choice for measurement sites in remote locations.
The end

Thank you