Gasmet™ FTIR application note

Greenhouse Gas Soil Flux Analysis

KEY WORDS

- Greenhouse gas
- Soil flux
- Nitrous Oxide (N₂O)
- Climate Change
- Chamber
- Soil probe
- Field measurements

PRODUCTS

- DX4015 Portable FTIR Gas Analyzer

OVERVIEW

Measurement of greenhouse gases released from soil and water surface forms an important part of climate change study. It is essential to know the contribution of soil ecosystems on climate change, as well as how the ecosystem reacts to the changes in atmospheric conditions. There are two ways to measure the activity in the soil: either the samples are collected for the laboratory analysis or a portable analyzer is brought to the measurement site.

Figure 1. Gasmet DX4015 multicomponent portable FTIR gas analyzer for trace gas analysis.

The most widely used analyzer in the laboratory is a gas chromatography (GC), which uses different types of detectors sensitive only to specific gas components. The samples are usually collected using syringes to extract the gas from chambers or soil probes, and injected into an airtight container for transportation from field to the laboratory for destructive analysis of GC.
Microbial activity in the soil and, for instance, the melting of permafrost releases greenhouse gases such as methane (CH₄), nitrous oxide (N₂O) and carbon dioxide (CO₂) into the atmosphere. A field-deployable, nondestructive FTIR analyzer is capable of rapid measurements for several gases simultaneously on-site (see Figure 1). There are several advantages provided by the field-based FTIR analyzer, such as the ability to follow the real-time gas concentration changes, and the ability to analyze and study the results as soon as they are collected. With access to online results, the operator can react flexibly to any unexpected situations during measurements, giving researchers the ability and freedom to modify the experimental design whenever needed.

GASMET GREENHOUSE GAS APPLICATION AND DX4015 SPECIFICATIONS

Gasmet greenhouse gas application includes six (6) gas components (see Table 1) with user selected measuring ranges. Calcmet software is able to measure simultaneously up to 50 gases which can be selected from the Gasmet gas library, containing 244 organic and inorganic compounds. In addition, the user can easily configure the analyzer for a new set of compounds or add new gases of interest without an installation of new electronics.

Table 1. Standard greenhouse gas application. Other gases and measuring ranges are available.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Typical range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water vapor</td>
<td>0 - 5</td>
<td>vol-%</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0 - 2000</td>
<td>ppm</td>
</tr>
<tr>
<td>Methane</td>
<td>0 - 15</td>
<td>ppm</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>0 - 5</td>
<td>ppm</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0 – 15</td>
<td>ppm</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0 – 50</td>
<td>ppm</td>
</tr>
</tbody>
</table>

The minimum measurement time is five (5) seconds, in the soil flux application measurement times of 20, 60, or 180 seconds are used to improve signal to noise ratio. Results are displayed as a trend plot of gas concentrations (x-axis) versus time (y-axis). The technical specifications and key characteristics of portable DX4015 FTIR gas analyzer are collected in Table 2 below.

Table 2. Technical details of DX4015 FTIR gas analyzer.

<table>
<thead>
<tr>
<th>DX4015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Temperature (controlled)</td>
</tr>
<tr>
<td>Flow rate</td>
</tr>
<tr>
<td>Water vapor (V/V%)</td>
</tr>
<tr>
<td>Sample cell volume</td>
</tr>
<tr>
<td>Operating time (Bluetooth ON)</td>
</tr>
<tr>
<td>Interface</td>
</tr>
<tr>
<td>Wavenumber range</td>
</tr>
<tr>
<td>Wavelength: Mid-IR region</td>
</tr>
</tbody>
</table>
MEASUREMENT TECHNIQUE

There have been multiple measurement campaigns in demanding field conditions in the Canadian High Arctic areas, where Gasmet DX4015 analyzer have been tested in conjunction with soil probes and chambers. The soil probes were used for below-ground in situ measurements of gas concentrations within soil pore spaces, in which probes were buried into the soil to a set depth.

Each probe consisted of a ring having 12 tiny holes (2 mm i.d.) around the circumference of the tube at different depths (Figure 2), allowing to do measurements up to 500 mm below the surface. Several probes were inserted to undisturbed soil to determine a single soil gas profile.

The volume of the soil probe was lower (112 mL) than the volume of the sample cell (400 mL) of the analyzer which would have caused a huge dilution of signal. Thus, in order to create a large sample volume a plastic reservoir bottle of 1 L was used in between the probe and the analyzer for minimizing the dilution effects from ambient air remaining in the FTIR cell when the analyzer is connected to the closed loop.

Figure 2. Typical setup for soil probe measurements. A probe consisting of a hollow steel tube, handle and a pointed tip is inserted into soil to desired depth to sample gases from the zone indicated by concentric circles. Soil gases are allowed to diffuse into the bottle, typically of 1 liter volume, for 24 hours. Measurement is made by connecting the DX4015 FTIR gas analyzer to one of the tubes between probe and bottle for ca. 5 minutes. (After Brummel M.E. & Siciliano S.D., Measurement of CO₂, CH₄, N₂O, and H₂O potential)

Gases inside the probe and in the surrounding soil were allowed to reach the equilibrium by diffusion for 24 hours before sampling by attaching the reservoir bottle to a probe and isolating the gases inside the loop from ambient air. It was investigated that the equilibrium was achieved after seven (7) hours, especially CO₂ ceased the accumulation.
Before starting the measurements of internal gases the analyzer was turned on, allowed to reach the operating temperature (50 °C) and zero calibrated. Then a quick-disconnect in one of the tubes between probe and bottle was disconnected and those ends were connected to the analyzer, creating a closed loop system in which the gas was recirculated between these three components (Figure 2). The measurement interval was adjusted to 180 s and the gas flow rate was 5 L/min. After a 3-min measurement the analyzer was disconnected from the probe and it was flushed with ambient air for at least 120 s before connecting to a next soil probe, whereas the reservoir bottle was flushed for 180 seconds before re-attaching it to the same probe again and allowing to re-equilibrate for 24 hours for further measurements.

Chambers, in turn, were used to examine the gas emissions from soil to the atmosphere. Measurements of the concentrations for gases inside an open-bottom soil chamber placed on the soil over time described the emission rate (flux) per chamber footprint area. The DX4015 gas analyzer and the soil chamber formed a closed-loop system in which the gas sample was circulated through the analyzer back to the chamber (Figure 3). Nondestructive FTIR measurement leaves the gas composition unchanged and in a closed loop like this the concentration increases over time. This enables calculations of greenhouse gas fluxes and the monitoring of diurnal (24 hour cyclic) changes in the production of gases giving the concentrations in parts-per-million (ppm).

Figure 3. Typical setup for soil chamber measurements. A chamber with open bottom receives a flux of gases from the soil underneath the chamber as indicated by concentric circles. Soil gases are circulated through the DX4015FTIR gas analyzer by its built-in pump and sample tubes made from PTFE.

The chambers used for the soil/atmosphere-interface measurements, were opaque or transparent, vented, non-steady state chambers. It should be noted that both types of chambers, home-made chambers and automated chambers, for instance from LI-COR, are equally suitable for the analyzer.

The collars were installed 24 hours prior to the data collection to a depth of 70 mm. Before starting the measurement the chamber was tightly positioned over the collar and the measuring interval of the analyzer was selected to be 60 s to reach the optimal signal-to-noise ratio. The gas exchange between the soil and the
atmosphere is very sensitive even to small disturbances and pressure changes caused by the chamber installation, thus the initial data points were not representative. The changes in gas concentrations were measured over 10 min periods, and after the stabilization of soil circumstances (2 minutes) the accumulation of GHG fluxes was clearly observed.

![Image of measurement campaign](image)

Figure 4. Measurement campaign in the Canadian High Arctic in which DX4015 was used to sample several home-made chambers.

The weather-sealed case of the analyzer protected the instrument for any damage during the measurements, and a laptop running the windows software was field-hardened to protect the measurement data and reduce the risk of data loss. On the field, DX4015 was operated by an external generator.

In addition to gas concentrations for flux calculations, FTIR provided estimates of evapotranspiration (loss of water from the soil by evaporation and transpiration from the plants) by monitoring the water concentration over time in chambers.

More details of the experimental setup can be found from the Dissertation of Martin E. Brumell “Greenhouse Gas Production and Consumption in Soils of the Canadian High Arctic”.
RESULTS

A reference measurement was performed, in which instead of using DX4015 gas analyzer, the samples were collected by syringes and sent to the laboratory for concentration analyses determined by GC. The experiment showed that the results obtained with the FTIR analyzer, integrated with a non-steady state aluminum chamber, corresponds well with the results achieved by the traditional static chamber method where GC was used for concentration analyses.

The pressure inside the cell of DX4015 is maintained at ambient pressure and the temperature is controlled to 50 °C, which facilitated the calculations of converting the ppm volume units to molar equivalents.

ADVANTAGES OF FTIR IN SOIL FLUX MEASUREMENTS

An FTIR instrument is uniquely suitable for field work thanks to its low weight and ruggedness. The DX4015 is field proven in Arctic greenhouse gas monitoring campaigns. This portable analyzer allows to measure simultaneously 50 gas compounds in a single measurement, eliminating the need for multiple instruments. There is no need to do span calibrations, but only zero calibration with nitrogen gas or ambient air. The operating temperature range (0 ... 40 °C) of DX4015 is ideal for field work and the heated sample cell (50 °C) allows to do measurements in higher moisture contents. In addition, Calcmet software allows the user to post-process and re-analyze sample spectra acquired during field measurements.

This analyzer allows researchers to build their own “laboratory” on the field just next to the emission sites and it gives continuous readings of the concentration changes that can be easily followed in real-time. The stability of the analyzer enables productive and efficient field measurements. The small footprint of the analyzer and the lack of carrier gas / purge gas requirement are attractive features also in a laboratory environment.

This application note is meant to be an informative example of typical application where Gasmet analyzers could be used. This is not a technical specification sheet. Information in this document is subject to change without prior notice. Optimal product configuration is application dependent, and exact application details such as detection limits, components included in the application, etc. depend on process and/or measurement site details and may vary. Please, contact your local Gasmet sales representative to get information specific to your needs.