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Guide to measuring greenhouse gas (GHG) soil fluxes

KNOW WHAT'S IN THE AIR

Introduction to greenhouse gas monitoring

The natural emissions of greenhouse gases (GHGs), such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) can be disturbed by human activities and pose an enormous environmental threat. The measurement of GHG fluxes which exist between soil surfaces and the local atmosphere is critical to understanding the impact that human activity is having on the ecosystem as a whole and key to understanding what best practices can be used to mitigate subsequent human impact on the environment.

In this guide, we will introduce how to measure GHG soil fluxes using a static chamber method. In the static chamber method, a chamber is placed at the soil surface and the chamber accumulates the gases emitted from the surface of the soil. An analyzer, in this case an FTIR analyzer, is used to dynamically measure the soil fluxes accumulated within the chamber.

This guide is aimed at all academics aiming to measure GHG fluxes at soil surfaces.

How to measure GHG fluxes

There have, over the years, been many experimental methodologies developed to measure the flow of gases (fluxes) from the soil into the surrounding localized atmosphere. Today, by far the most common method is the so-called chamber method in which an open chamber is placed on the soil surface of interest to allow the emitted fluxes to accumulate prior to analysis of the gases by a suitable analyzer.

The analysis of the accumulated gases typically falls into two broad practices:

1. Sampling the gases in the chamber using a syringe for subsequent off-line analysis in a laboratory
2. Dynamically measuring the gases in-situ, in real time, using a closed loop arrangement with an analyzer close coupled to the chamber

The popularity of the dynamic in-situ method, apart from the speed and accuracy at which the analysis can be conducted, relates to the ability to make numerous successive gaseous analyses over time allowing data to be easily averaged.

This is in contrast to syringe methods where the methodology is more time consuming and errors can accumulate through sampling anomalies and sample transportation. In addition, the syringe method is fundamentally intrusive to the measurement setup itself ultimately restricting the possibility of analyzing and averaging large simultaneous data sets.

There are numerous types of analytical analyzers on the market today which can be utilized for in-situ dynamic measurements. Available analysis techniques include cavity ring-down spectroscopy, non-dispersive infrared spectroscopy, gas chromatography and the like.

None of these analysis techniques however offer the versatility, practicality and analytical robustness that the technique of Fourier Transform Infrared (FTIR) Spectroscopy offers. Modern FTIR instrumentation offers the portability and robustness to enable an analyzer to be practically taken out into the field, it is not limited to measuring just a few pre-determined gases it can measure a large number of gases simultaneously, FTIR requires no calibration or reference gases, FTIR gives simple concentration results requiring no interpretation and FTIR is above all fast and stable.

This guide is intended to give a practical approach to measuring Greenhouse Gas fluxes out in the research field, using the chamber method in conjunction with a modern Gasmet FTIR gas analyzer. In general, with the correct setup, the correct analyzer and a rigorous systematic approach analyzing GHG fluxes can be a relatively straightforward procedure.

A practical approach: chamber measurements

There are many variations and possibilities for experimental chamber setups. The most common technique is to use a chamber with a circulating loop. In this setup, chamber gases are pulled (pumped) from the chamber, passed through the analyzer then returned back to the chamber in a closed loop. This gives a non-intrusive sampling method which is both simple and less prone to any systematic errors

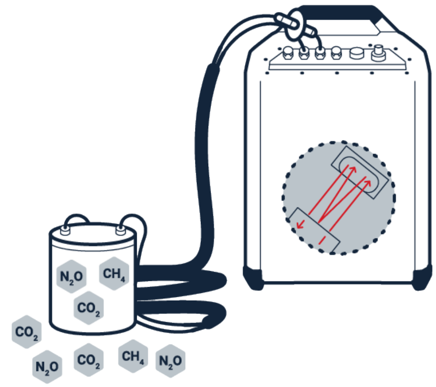


Illustration 1. A chamber for GHG flux measurement placed on the soil surface with a Gasmet FTIR in a closed loop configuration

Typically, each chamber consists of two parts:

> A collar, which can be rectangular or circular in profile, which is sunk into the ground at the point of interest.
> The chamber itself (rectangular or circular) which is placed over the collar and is sealed to the collar with a suitable seal arrangement.

Collars are important: They ensure that the whole system is consistently sealed to prevent leaks, they offer consistency either for automated arrangements or for arrangements where a single chamber is used in conjunction with numerous collars and they define the area of the surface of the soil to be measured. There are numerous schools of thought as to how deep the collars should be set into the ground, notwithstanding the science they do offer containment of the soil depth profile eliminating migration of any surrounding fluxes.

Chamber geometry appears to have little direct effect on flux estimates as long as adequate air mixing is achieved. Chambers can be made of various rigid materials that don't react with the target gas matrix (e.g. stainless steel, aluminum, acrylic plastic and polyvinyl chloride).

More than one chamber can be used in an experimental setup, allowing topological and geographical spatial data to be acquired. In such a setup one analyzer can be used in conjunction with multiple chambers using an automated multiplexed closed loop arrangement. However, in a simpler arrangement, the same data can be achieved by utilizing numerous spatially arranged collars and a single chamber and single closed loop analysis system. In this instance both chamber and analyzer can be moved from one collar to another.

Commercial, automated chambers and homemade chambers are both equally suitable for Gasmet gas analyzers.

Typical soil flux setup and measurements

1. Sink the collar into the ground to a chosen pre-determined depth. Ideally do this 24 hours prior to analysis. Collars are usually left in place for later use.

2. Consideration should be made of any 'headspace' between the soil surface and the seal of the chamber. Any headspace should be measured and included as part of the volume calculation below.

3. Connect the analyzer to the chamber forming the closed loop arrangement

4. Set the analyzer to measure the gases of interest. Common gases of interest are CO_2, N_2O, CH_4. In this experimental setup we are using an FTIR spectrometer which has the advantage that more gases can be added such as NH3, NO, NO2. Remember that with the FTIR technique samples can be retrospectively analyzed for more gases at a later date.

5. Place the chamber over the collar ensuring a firm fit and tight seal. Consideration should again be made to ensure that any 'headspace' is consistent with the seating of the chamber, i.e. ensure that the chamber is always seated the at the same depth over the collar.

6. Begin analyzing. The rate at which individual gas fluxes pass through the soil surface depends on a host of factors but it is common for enough data to be acquired within a 5-minute analysis window. Within this window, an analysis time of 20 seconds will give 15 datapoints for each gas of interest, enough for any statistical averaging.

7. At the end of the analysis, the FTIR computer will typically have 15 spectra (which can be used for subsequent analysis) and a file of 15 concentrations for each gas of interest.

8. Remove the chamber from the collar, stop the analyzer, and move on to the next site with another collar if necessary.

Data handling

The Gasmet FTIR analyzer is operated using Gasmet's propriety 'Calcmet' software. This software stores data in two distinct ways:

1. Individual **sample spectra** are recorded every 20 seconds (in this case). These spectra contain all analytical data of all measurable gases in the chamber at any time. These spectra can be re-analyzed for more gases at a later date if required thus broadening the

scope of research without the complication of monitoring numerous gases from the onset.

2. A **data file** which contains a matrix of the concentrations of each chosen gas of interest against time (every 20 seconds). This data file is excel compatible and this is the data that we will use to calculate the fluxes of each individual GHG gas.

How to calculate a soil flux

Gas flux is the flow of a gas per unit of area across a soil/atmosphere interface. In our experiment we are using the FTIR spectrometer to measure the individual fluxes for individually speciated gases.

Step 1

To calculate the flux for each gas, consecutive measurements of the individual gas concentrations over time is required. The concentration of each gas component will change with time as long as the chamber is in place. In this instance the experiment lasts for 250 seconds with 13 readings of gas concentrations taken in total.

The CO_2 concentration can be seen to rise from a baseline of <400ppm when the chamber is put in place to a maximum of <600ppm when the chamber is removed after ca.5 minutes. This was repeated 3 times to both illustrate and ensure consistency of data.

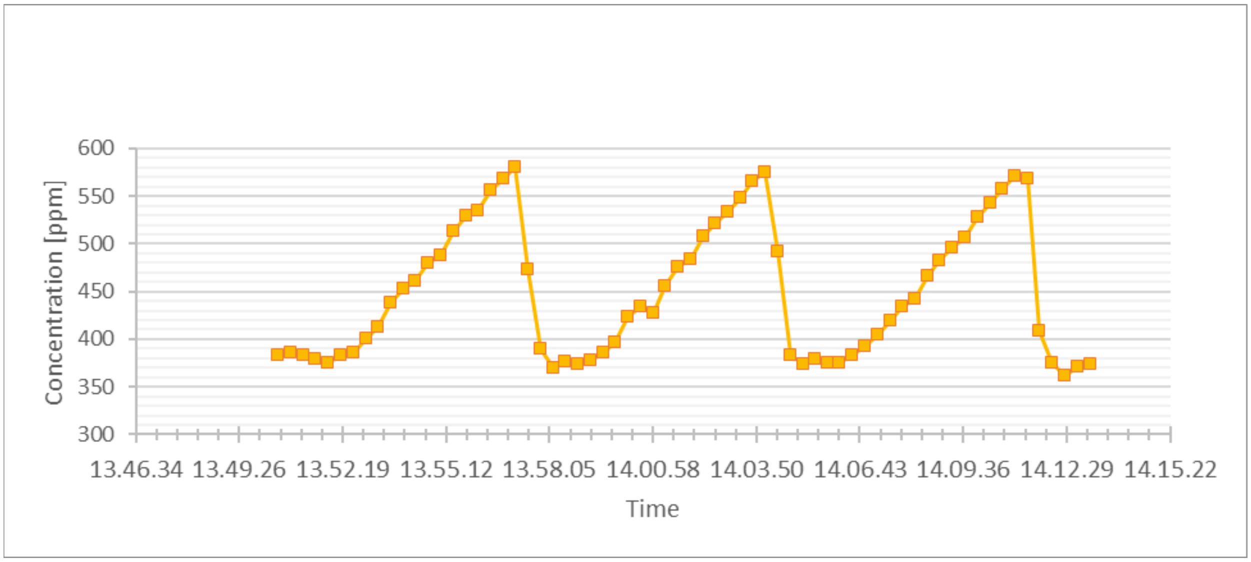


Figure 1. CO2 soil flux data acquired using a closed loop chamber with FTIR analyzer

Step 2

Gas concentration is measured in ppm for each gas species in the chamber at that moment in time Figure 1. We need to convert each gas concentration into gas flux which has the units mol m^{-2} s^{-1}

The following equation is used to calculate the flux (for CO_2 in this example)

$$Soil\ CO_2\ flux = \frac{\eth C}{\eth t} \cdot \frac{v \cdot 10^{-6}}{v_a \cdot \frac{T_2}{T_1}} \cdot \frac{1}{A} \qquad (mol\ m^{-2} s^{-1})$$

where

$\frac{\eth C}{\eth t}$	*is the rate of change of concentration of CO_2 [ppm] with time*
v	*volume of the vessel including cell, sample lines and any headspace (m^3)*
v_a	*molar volume for ideal gas at 273 K = 22.4 x 10^{-3} m^3/mol*
T_1	*air temperature (K)*
T_2	*standard temperature (K)*
A	*Footprint area of the chamber (m^2)*

However, the data shows that the increase in CO_2 concentration with time approximates to a linear increase. So, we can apply a linear regression algorithm to the data.

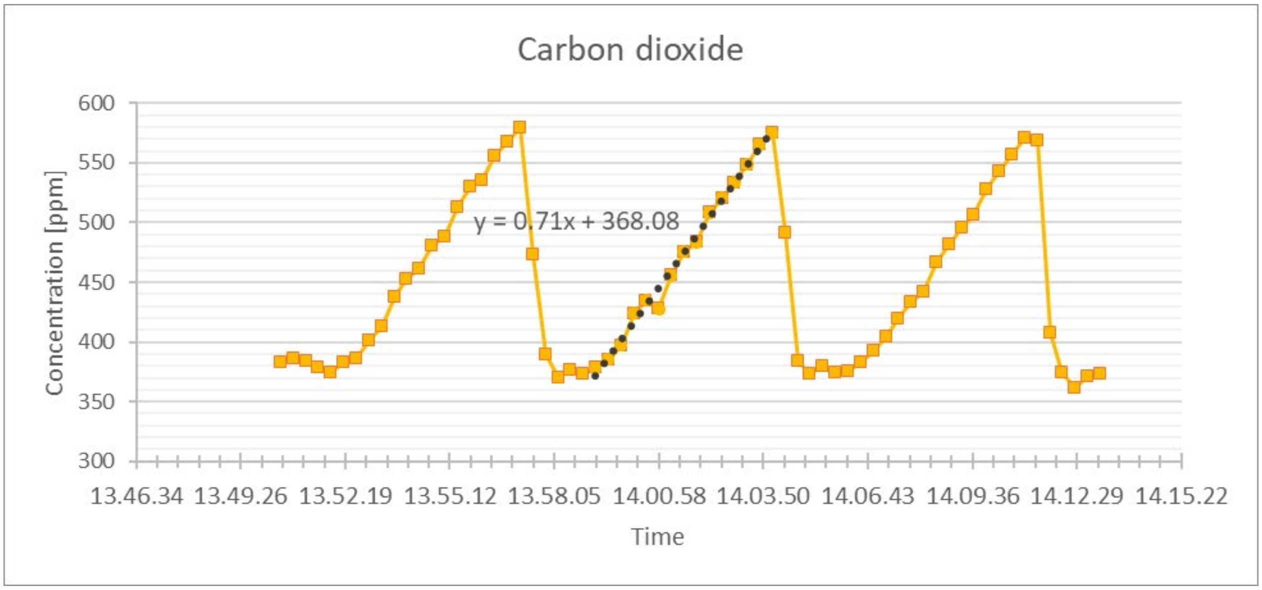


Figure 2. Co$_2$ soil flux data with a linear regression fitted to CO2 concentration

Apply a linear regression algorithm to the data approximates the $\frac{\eth C}{\eth t}$ term to the slope of the line and we can rewrite the equation as

$$\boldsymbol{oil\ CO_2\ \ flux} = \left\{\frac{\boldsymbol{C2 - C1}}{\boldsymbol{t2 - t1}}\right\} \cdot \frac{\boldsymbol{v \cdot 10^{-6}}}{\boldsymbol{v_a \cdot \frac{T_2}{T_1}}} \cdot \frac{\boldsymbol{1}}{\boldsymbol{A}} \qquad (\mathrm{mol\ m^{-2}s^{-1}})$$

Convert the units from $\mathrm{mol\ m^{-2}s^{-1}}$ to $\mathrm{\mu molm^{-2}s^{-1}}$ by multiplying by $\boldsymbol{10^6}$ in the equation giving

$$\boldsymbol{Soil\ CO_2\ \ flux} = \left\{\frac{\boldsymbol{C2 - C1}}{\boldsymbol{t2 - t1}}\right\} \cdot \frac{\boldsymbol{v}}{\boldsymbol{v_a \cdot \frac{T_2}{T_1}}} \cdot \frac{\boldsymbol{1}}{\boldsymbol{A}} \qquad (\mathrm{\mu mol\ m^{-2}s^{-1}})$$

where

$\boldsymbol{C1}$ is the starting concentration of CO_2 [ppm]

$\boldsymbol{C2}$ is the final concentration of CO_2 [ppm]

$\boldsymbol{t1}$ is the starting time of the analysis (s)

$\boldsymbol{t2}$ is the finishing time of the analysis (s)

Hence, $\left\{\frac{\boldsymbol{C2-C1}}{\boldsymbol{t2-t1}}\right\}$ **is the slope of the regression**

v volume of the vessel including cell, sample lines and any headspace (m^3)

v_a molar volume for ideal gas at 273 K = 22.4 x 10^{-3} m^3/mol

T_1 air temperature (K)

T_2 standard temperature (K)

A Footprint area of the chamber (m^2)

Calculation of flux from concentration data

As well as the analytical data from the FTIR analyzer, other parameters are required:

1. The volume of the entire closed loop must be calculated. The volume is the sum of the analyzer cell and pipework (0.4L), volume of the interconnecting pipework (0.6L), any headspace between the soil surface and the chamber (0.1), and the chamber volume itself (2.55L).
   v - volume of the vessel including cell, sample lines and any headspace (m^3) = 3.65L

2. Air temperature. Temperature of the air in the actual chamber should be measured with a thermocouple and used to compensate for volume accordingly in the equation. Note it is also common to measure and record the surface temperature of the soil but this is not required for the calculation
   T_1 - air temperature [K] = 273+16= 289K

3. The footprint area of the chamber should be measured. Strictly speaking this should be the internal diameter of the collar
   A - Footprint area of the chamber (m^2) = 0.0189 m2

4. The slope of the regression shown in figure 2.
   $\left\{\frac{C2-C1}{t2-t1}\right\}$ *the slope of the regression = 0.71 ppm/sec*

Substituting into the equation we get

$$\boldsymbol{Soil\ CO_2\ \ flux} = \{\mathbf{0.71}\} \cdot \frac{\mathbf{3.65}}{\mathbf{22.4\ x\ 10-3} \cdot \frac{\mathbf{273}}{\mathbf{289}}} \cdot \frac{\mathbf{1}}{\mathbf{0.0189}} \qquad (\mathrm{\mu mol\ m^{-2}s^{-1}}\ )$$

$$\boldsymbol{Soil\ CO_2\ flux} = \ \mathbf{6.49}\ \boldsymbol{\mu mol\ m^{-2}s^{-1}}\ .$$

Using FTIR technology in GHG measurements

One of the most reliable and effective technologies for greenhouse gas monitoring is Fourier-transform infrared spectroscopy (FTIR). It is the most powerful technology for simultaneous measurements of multiple gases. What is more, its flexibility and versatility make it a very cost-effective and multipurpose tool for measurements of all GHG compounds and much more. FTIR enables all key gas compounds to be measured simultaneously in just seconds.

The following GHGs are typically measured:

Compound	Formula	Unit
Water	H2O	%
Carbon Dioxide	CO2	ppm
Methane	CH4	ppm
Nitrous Oxide	N2O	ppm
Ammonia	NH3	ppm
Carbon Monoxide	CO	ppm

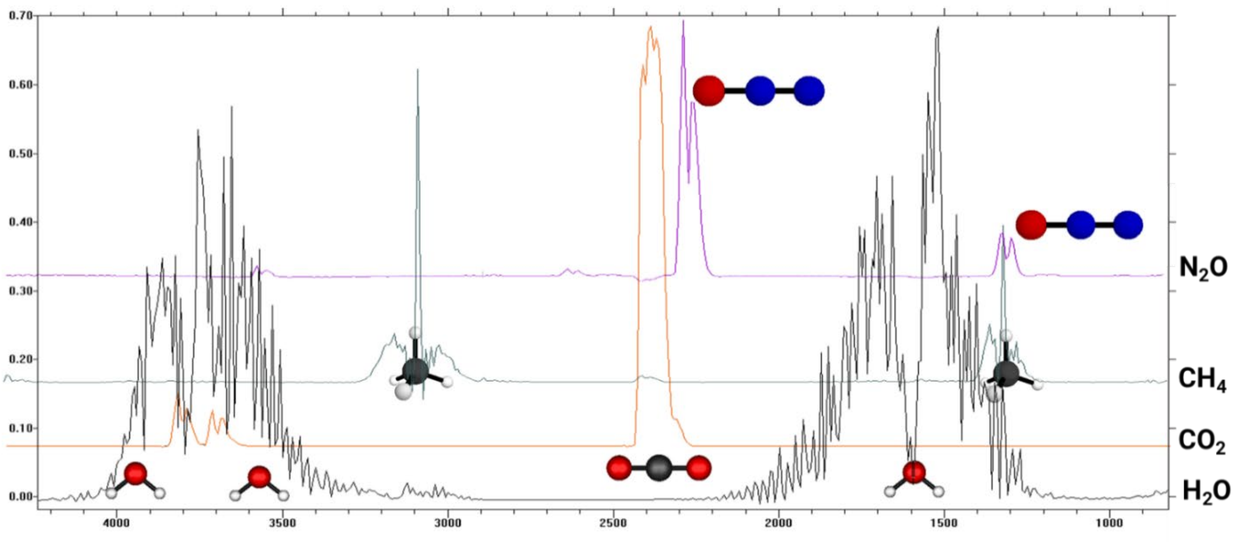
In addition to the gases listed in the table, FTIR technology allows you to measure VOCs, sulphur compounds or any other inorganic or organic compounds. Check Gasmet Spectrum Library tool on the website or download the Gasmet FTIR spectrum library smartphone app (for iOS and Android), to see the list of gases that can be measured and analyzed by FTIR.

How infrared FTIR works

Nearly all molecules can be identified by their characteristic absorption spectrum as each molecule absorbs infrared radiation at their characteristic frequencies. Every molecule has a unique combination of atoms, which produces a unique infrared absorption spectrum. The exceptions are noble gases and diatomic molecules such as N_2 and O_2, which do not absorb IR light, H_2S is also infrared inactive. IR absorption spectrum can be thought of as a fingerprint unique to each molecule.

The infrared spectrum is a plot of infrared absorption against wavenumber. According to Beer-Lambert law, the absorption (peak height) is directly proportional to concentration, and in this way the IR spectrum can be used to determine concentrations of gases in the sample.

Below is an illustration of typical greenhouse gases in an FTIR spectrum. Individual gases are identified by the shape and position of absorptions and quantified by the height of absorptions.



Main benefits of FTIR for measuring GHG fluxes:

> **Multicomponent capability** – FTIR is the only technology that measures such a wide range of gases simultaneously. All key GHG compounds such as N_2O, CH_4, CO_2, H_2O, CO and NH_3 can be measured.

> **High precision and fast acquisition times** – FTIR analyzers can accurately measure very low-level concentration changes in the chamber. This means that a workable dataset can be acquired in a very short timescale and hence any (time dependent) secondary effects that can affect the analysis are minimized: This is shown by the linearity of the data.

> **Futureproofing your research** – FTIR is a very versatile technology. The number of measurable gases is unparalleled, and the system is easily configurable to measure new compounds without need for hardware changes. As all compounds are measured from the

same spectral data, ten spectral data can be re-analyzed at a later date for other gases expanding the scope of research.

> **Proven technology** – large number of successful research projects all around the world, all the way from the Artic and to the Amazon, by our customers worldwide.

> **Reliability** – FTIR is extremely accurate and robust technology. It isn't sensitive to changes in surrounding conditions, such as changes in weather.

Gasmet analyzers for flux measurements

The development of portable, robust, battery-powered soil flux analyzers by Gasmet Technologies has enabled reliable onsite analysis of GHGs. These analyzers are compatible with any type of chamber and can be used for different measurements in various ecosystems and soil types with varying GHG emissions:

- Natural ecosystems such as forests, arctic soils, wetlands, water bodies and geothermals
- Agricultural soils
- Animal emissions such as manure and livestock

Gasmet provides two field deployable non-destructive FTIR based soil flux analyzers for continuous multicomponent gas analyses: GT5000 Terra and DX4015. These robust gas analyzers enable the measurement up to 50 different gas compounds simultaneously. Both soil flux analyzers are ideal for field work and also capable of taking samples from several chambers automatically.

GT5000 Terra – Compact ambient air FTIR analyzer

The GT5000 Terra has a high sensitivity sample cell for lowest possible detection limits, true multicomponent capability and a built-in-pump, which means that there is no need to use a separate sampling system. This portable gas analyzer is also lightweight (9.4 kg), splash-proof (IP54 rated) and battery powered providing unparalleled portability.

The sample cell of the GT5000 Terra is at ambient temperature providing low energy consumption for maximum battery life while also minimizing warm-up time of the analyzer.

The analyzer is operated with Gasmet's own Calcmet software either on a Windows tablet or laptop. This software collects, stores and visualizes the FTIR spectra of the sample gas, and identifies and analyzes the concentrations of gas components. You can control GT5000 Terra remotely with Calcmet software via built-in Wifi or Bluetooth. The software comes in two versions, Calcmet Easy for accessible on-field work and Calcmet Expert for further analysis with advanced tools.

Key benefits of choosing GT5000 Terra

Bring lab to the field. Ideal choice for environmental researchers on the move, offering lab-quality results in the field with precision, portability, and low detection limits.

Future-proof operation. Ability to measure tens of gases simultaneously in low and high ranges. Same device can be used for future research needs, including additional gases and extended ranges, without any hardware changes.

Ready when you are. Practical analyzer requires no sampling preparation, recalibration by the user or special expertise to use or maintain. Simply start measuring and focus on the results.

Designed for GHGs. Used for environmental research by hundreds of researchers worldwide for high impact publications. With a quick lead time and adaptable chamber compatibility, the entire lifecycle process is optimized.

DX4015 – Portable FTIR analyzer for humid conditions

Gasmet DX4015 is a portable FTIR gas analyzer for ambient air analysis. The DX4015 includes a built-in-pump, which means that there is no need to use a separate sampling system. The analyzer can be powered with 12 VDC from for example an external battery, so it can easily be used in field conditions where main power is not available. The sample cell of DX4015 is heated to 50 °C, which allows measurements in conditions where high humidity is expected and provides temperature stability in changing conditions.

The DX4015 is operated with Gasmet's own Calcmet software running on an external laptop computer. The software provides a flexible and easy-to-use interface for taking measurements and viewing online results.

Key advantages of DX4015

- Portable
- Quick and easy set-up
- Built-in pump
- Heated sample cell for humid air applications
- Possibility to use external battery power
- Simultaneous measurement of all gases

Conclusion

FTIR gas analyzers are unparalleled in GHG soil flux measurements thanks to their ability to measure multiple gases simultaneously, their high precision and rapid data acquisition, and capability to future-proof research by allowing spectral data to be re-analyzed for additional gases. Furthermore, FTIR is a well-established and dependable technology that has been successfully utilized in numerous research projects worldwide.

Gasmet solution

If you'd like to learn more about our solutions for various flux measurements and how our expertise can support you in your research, head on over to our website.

LEARN MORE

Customer Testimonials

University of Padua

Professor Francesco Morari *of the University of Padua and Dr. Gemini Delle Vedove of the University of Udine used the DX4015 with an automated multiplexed chamber system for their studies on GHG soil effluxes in croplands*.

How was the DX4015 beneficial to your research project?

We used Gasmet's DX4015 gas analyzer to monitor continuously GHG's emissions from the soil in shallow water table conditions. While many studies of GHG emissions in shallow water table conditions have been carried out in organic soils, there is not much, if any, previous research regarding shallow water table conditions in mineral soils.

What unique capability does the DX4015 provide your research?

Previously, a closed dynamic system with 12 automated chambers was used to monitor continuously soil respiration (CO_2 soil efflux) every 2h. N_2O soil effluxes were seldom monitored connecting the automated chamber system with an auto-sampler, to collect air samples in 20 ml vials that were then analyzed later in the lab using a gas chromatograph. This methodology is expensive and limits the accuracy and the precision of the measured effluxes. We substitute the auto sampler with DX4015 gas analyzer using the existing pneumatic circuit. The data of DX4015 were time matched with the operations made by the multiplexed chamber system. In such way we were able to measure continuously simultaneously and on-site the GHG soil effluxes and up to 50 other gases. Now we are able to save time and costs and, above all, to monitor from 12 sensors (chambers) sudden changing soil effluxes of trace gases like CO_2,

N_2O, CH_4 and NH_3. To our knowledge such apparatus is unique at the moment and it allows a strong and cost-effective improvement in the research of GHG and other gases soil emissions.

How was the experience of working with Gasmet?

Thanks to collaboration with Gasmet and Ital Control Meters technicians we found an easy and efficient solution in matching the automated chamber system with the DX4015 analyzer. When we encountered set-back due to faulty laser, Gasmet and the local retailer were all very collaborative. The spare part was changed quickly without any additional costs to us, and we were soon able to continue. We've been happy with the collaboration and we're in the process of buying another portable gas analyzer from Gasmet.

University of Oklahoma

Rajen Bajgain*, a post-doc student from the University of Oklahoma, has been using the Gasmet DX4015 for his studies.*

How was the DX4015 beneficial to you research project?

The analyzer was used in understanding the contribution of nitrogen (N) addition to CO_2, N_2O, CH_4 emissions from grasslands. We observed temporal variation in CO_2, N_2O and CH_4 fluxes of key N sources: urine and chemical fertilizer in grazing pasture.

What unique capability does the DX4015 provide your research?

The DX4015 was very helpful to measure major green house gases from soil with one analyzer at one time. Most of the other commercially available analyzers are capable to measure either only CO_2 and CH_4 OR N_2O. With Gasmet FTIR gas analyzer, the DX4015, we are able to measure all the key compounds, up to 50 gases simultaneously.

Why is it important to be able to measure multiple GHGs in your research?

Management practices and climate change are changing the soil environment which result in harboring different microbial community. It is important to measure all the gas compounds from the soil because varying soil conditions affects gas emissions. We must be able to measure all gases regardless of the soil conditions.

The Allerton Project, UK

Jenny Bussell*, a Soil Scientist at The Allerton Project, UK has been using the Gasmet DX4040 for agricultural research.*

How was the DX4040 (the predecessor of GT5000 Terra) beneficial to you research project?

We've been using the analyzer to understand how changing management strategies affect green house gas emissions from agricultural systems. We've been investigating if shifting to reduced cultivation systems is beneficial for reducing greenhouse gas emissions from soils, particularly CO_2 and N_2O.

What unique capability does the DX4040 provide your research?

The main benefit for us is the ability to simultaneously measure different green house gas emissions directly from the soil. This means we can measure how CO_2 and N_2O are affected by management, but also how changes in soil temperature and moisture affect gas fluxes, because we can repeatedly measure the soil within our plots as the weather and seasons change.

Why is it important to be able to measure multiple GHGs in your research?

If we are going to change agricultural practices in order to reduce green house gas emissions, we need to fully understand how all the green house gasses respond. CO_2 production often reduces when cultivation is reduced, but with reduced cultivation there is a risk of increased compaction and anaerobic conditions, which favor N_2O production. In order to tackle climate change and reach targets of net zero emissions we need to fully understand how management affects all green house gas fluxes from the soils to find the best solution with the lowest environmental impact.

Buy with confidence – As your potential gas analysis partner, we offer a complete solution for your gas measurement needs. Our very own technology ensures laboratory grade results, ease of use and reliable, high quality products.

Mutual trust and years of expertise – We strive to provide a smooth partnership for every step. We walk you through the whole process from consultation to first measurements, and all the way to service and support.

Local support – Our global multi-disciplined teams and vast distributor network ensures that professional and fast service and support are available to you locally.

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