Comparison of greenhouse gas analyzers - measurements using photoacoustic, laser, FTIR analyzers and gas chromatography

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Abstract

In the last decades, several technologies have been developed to measure greenhouse gas (GHG) concentrations and fluxes. We compared six devices using different measurement technologies: two gas chromatographic systems with a barrier discharge ionization detector (GC-BID) and an electron capture detector (GC-ECD), respectively, a portable GHG analyzer based on laser absorption, a photoacoustic field gas analyzer, and two portable Fourier transform infra-red (FTIR) devices. Absolute concentration measurements agreed well between the non-GC devices for carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4). CO_2 flux measurements under laboratory conditions showed acceptable agreement between the measurement systems. Observed deviations in fluxes were attributed to methodical susceptibilities of chamber measurements rather than to erroneous concentration measurements. We conclude that the less often used photoacoustic and FTIR devices are suitable for studies of GHG fluxes and represent a useful alternative to currently used techniques in the field thanks to their portable character.

Key words: GHG, gas chromatography, laser absorption, photoacoustic analyzer, FTIR

Introduction

During the last decades, several technologies to measure concentrations of greenhouse gases (GHG) as carbon dioxide (CO_2) and less studied methane (CH_4) and nitrous oxide (N_2O), have been developed. The traditional measurements by gas chromatographs (GC) require stable laboratory conditions and frequent calibration (Rapson & Dacres 2014). These systems do not allow for continuous measurements and are labor-intensive due to GC analyses following sampling in the field. More recently, portable online devices based on laser absorption, photoacoustic spectrometry and Fourier transform infrared spectroscopy (FTIR) technologies have been developed. They allow for continuous real-time measurements, particularly suitable to assess soil and tree stem GHG fluxes in the field and less frequent calibration is needed. The tested FTIR devices do not require recalibration at all, only a zero calibration with pure N_2 is necessary before starting the measurement. While the majority of researchers currently use GC and portable laser absorption devices, the photoacoustic and FTIR devices are rarely used for flux measurements of soil gases. However, the use of portable FTIR analyzers is increasing constantly.

To evaluate these so far less frequently used devices (photoacoustic gas monitor and portable FTIR), we compared them with the established systems. We conducted experiments to measure absolute concentrations of GHG, as well as the fluxes of CO_2 from artificial soils with two different GC systems and four different online devices.

Materials and Methods

Six systems were used to measure sub-ambient and ambient concentrations of CO_2, CH_4 and N_2O. A GC with a barrier discharge ionization detector (GC-BID; GC 2010Plus, Shimadzu, Kyoto, JPN; ShinCarbon ST micro column, Restek, Bellefonte, USA; He as carrier gas) and a GC with an electron capture detector (GC-ECD; GC 8000 series, Fisons, Loughborough, United Kingdom; CARBONPLT column, J&W Scientific, Folsom, USA; N_2 as carrier gas) were used as laboratory GC systems. As portable systems we tested a widely used GHG analyzer using laser absorption (Ultraportable Greenhouse Gas Analyzer, Los Gatos Research, San Jose, USA), two Fourier transform infra-red analyzers (DX4040 and DX4015, Gasmet Technologies Oy, FI) and a photoacoustic field gas analyzer (INNOVA 1412 Photoacoustic Field Gas Monitor, LumaSense Technologies, Ballerup, DK). The precision of N_2O measurements using the photoacoustic device is affected by the strong interference with water vapor in the gas samples (Akdeniz et al. 2009; Rosenstock et al. 2013). Therefore, some adjustments had to be made in order to improve the quality of the N_2O measurements. Table 1 gives an overview of the measurements conducted by each tested device.

To compare the GHG concentrations measured by the different systems, an airtight barrel (50 l) was filled with five different sub-ambient to ambient

Table 1. Overview of measurements conducted by the gas chromatograph with barrier discharge ionization detector (GC-BID), the gas chromatograph with electron capture detector (GC-ECD), the greenhouse gas analyzer based on laser absorption, the two Fourier transform infra-red analyzers (FTIR4040 and FTIR4015) and the photoacoustic gas monitor.

	CO_2	N_2O	CH_4	CO_2-FLUX
GC-BID	X	-	X	-
GC-ECD	-	X	-	-
LASER ABSORPTION	X	-	X	X
FTIR4040	X	X	X	X
FTIR4015	X	X	X	X
PHOTOACOUSTIC GAS MONITOR	X	X	-	X

concentrations of CO_2, CH_4 and N_2O. The online devices were simultaneously connected in a closed loop to the barrel, whereas evacuated glass vials were used to take samples for the GC measurements.

CO_2 fluxes from five artificial soils/substrates were measured. Two soil substrates (A and B) were derived from two different agricultural sites, one substrate was made up of compost (C), another one originated from a forest site (D) and another one from a peatland (E). The soil was homogenized and stored in tubs in the greenhouse of the Global Change Research Institute CAS in Brno, CZ.

We used the same flux chamber type as Maier et al. (2017) consisting of a collar and a lid for all online measurement devices. The PVC collars (15 cm inner diameter, 9 cm height) were installed the day before the first measurement. Each soil was measured twice by each system on two consecutive days. The chambers (volume 1.8 l) were connected via the mobile lid to the online devices in a closed loop. Chambers were closed for 7 minutes. Flux calculations were carried out by robust linear regression analysis according to Hutchinson & Livingston (2002).

Results and discussion

CO_2 concentrations measured by the different gas analyzers agreed well among the online devices (Figure 1-a). However, an offset of around 70 ppm was observed for the GC-BID (GC_A) what can be attributed to a quality problem in the used calibration gas. Concentration measurements of CH_4 and N_2O agreed well between all devices studied (Figure 1-b, 1-c). An offset of up to 0.18 ppm for CH_4 was measured by the GC-BID. Operated this way, the gas monitor provided similar results as the FTIR devices and the highly sensitive GC-ECD (GC_B) system even for sub-ambient N_2O concentrations.

CO_2 fluxes from the different soils measured with the tested online systems agreed well overall (R^2=0.97). Relative deviations from the mean fluxes ranged

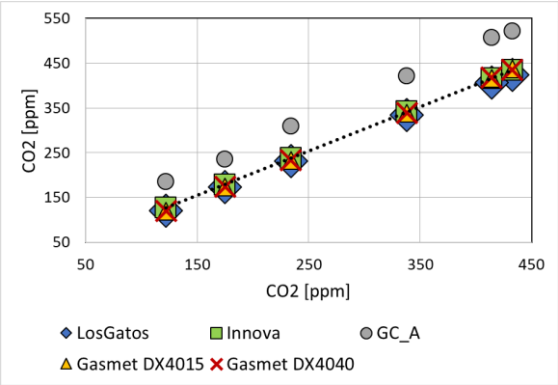

Figure 1-a. Concentrations of CO_2 measured by the different gas analyzers. The black line represents the 1:1 line of the mean concentrations measured by all devices.

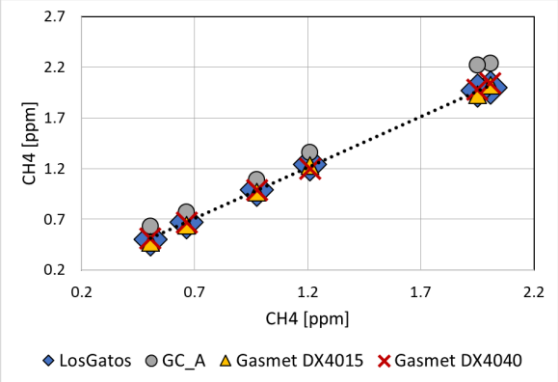

Figure 1-b. Concentrations of CH_4 measured by the different gas analyzers. The black line represents the 1:1 line of the mean concentrations measured by all devices.

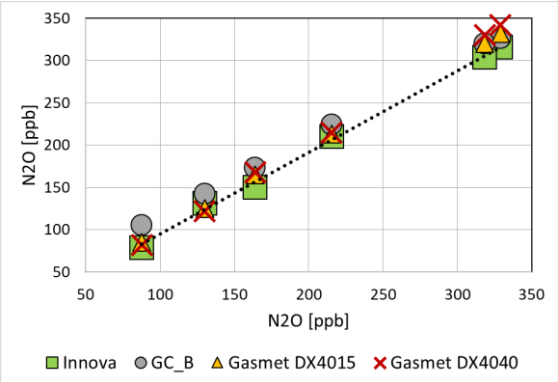

Figure 1-c. Concentrations of N_2O measured by the different gas analyzers. The black line represents the 1:1 line of the mean concentrations measured by all devices.

from -40 to 59 % and were much higher in soils with low flux rates. However, 78 % of all measurements deviated less than 20 % from the mean. High deviations are probably a result of methodical susceptibilities of chamber measurements, since concentration measurements by all devices proved to be reliable. During the laboratory measurements, soil and air temperature as well as ambient CO_2 concentrations were changing, possibly affecting the measured fluxes. Moreover, differences in sampling intervals and flow rates between the devices may affect the net soil CO_2 flux and therefore the comparability of flux measurements. All this indicates that small modifications in original conditions and sampling design may have severe influence on the results of GHG flux measurements. Therefore, it is necessary to follow a strict routine while performing flux measurements and to verify the results by comparing them against results obtained by other measurement systems. Differences in N_2O and CH_4 flux measurements between the systems could not be analyzed because the temporal variability in the measured fluxes was too high even between the repeated measurements with the same systems.

Conclusion

We proved CO_2, CH_4 and N_2O measurements based on FTIR devices to be reliable compared to established devices using gas chromatography and laser absorption. The agreement between CO_2 flux measurements conducted by the online devices was good if methodical weaknesses of chamber measurements are considered. In order to improve the quality of GHG flux

measurements, a strict routine and verification of the results by comparing them to other analytical systems are necessary.

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