Gas chromatography and photoacoustic spectroscopy for the assessment of soil greenhouse gases emissions

Cromatografia gasosa e espectroscopia fotoacústica para avaliação das emissões de gases de efeito estufa do solo

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ABSTRACT

Assessments of soil carbon dioxide (CO\(_2\)), methane (CH\(_4\)), and nitrous oxide (N\(_2\)O) emissions are critical for determination of the agricultural practices' potential to mitigate global warming. This study evaluated the photoacoustic spectroscopy (PAS) for the assessment of soil greenhouse gases (GHG) fluxes in comparison to the standard gas chromatography (GC) method. Two long-term experiments with different tillage and cropping systems over a Paleudult were evaluated using static chambers. PAS measurements of CO\(_2\) and N\(_2\)O concentrations showed good relationship and linearity (R\(^2=0.98\) and 0.94, respectively) with GC results. However, CH\(_4\) measurements were significantly affected by air sample moisture which interfered on CH\(_4\) detection by PAS. Overestimation of CO\(_2\) and N\(_2\)O concentrations in air samples determined by PAS (14.6 and 18.7%, respectively) were also related to sampling moisture. CO\(_2\) and N\(_2\)O fluxes showed good agreement between methods (R\(^2=0.96\) and 0.95, respectively), though PAS overestimated fluxes by 18.6 and 13.6% in relation to GC results, respectively. PAS showed good sensitivity and was able to detect CO\(_2\) and N\(_2\)O fluxes as low as 332mg CO\(_2\) m\(^{-2}\) h\(^{-1}\) and 21µg N\(_2\)O m\(^{-2}\) h\(^{-1}\). PAS analyzer should be detailed calibrated to reduce humidity interference on CO\(_2\), CH\(_4\), and N\(_2\)O concentrations measurements avoiding overestimation or erroneous determination of soil GHG fluxes.

Key words: no-tillage, conventional tillage, cover crops, INNOVA 1412.

INTRODUCTION

Agriculture is responsible for 5.47, and 84% of the global carbon dioxide (CO\(_2\)), methane (CH\(_4\)), and
nitrous oxide (N\textsubscript{2}O) emissions to the atmosphere, respectively (RICE, 2006). Recent research initiatives are being conducted aiming to identify agricultural practices able to mitigate GHG emissions. However, some concern persists about the methodologies available for evaluation of CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2}O fluxes in the soil-atmosphere interface since intensive labor is required for sample collection and laboratory analysis.

Soil-atmosphere CO\textsubscript{2} fluxes are generally assessed through the balance of soil organic carbon stocks in long-term experiments (BAYER et al., 2006). However, the evaluation of soil CO\textsubscript{2} efflux is an important tool to identify short-term CO\textsubscript{2} fluxes induced by soil tillage and sowing operations or by the incorporation of crop residues into the soil (CHAVEZ et al., 2009), decomposition of soil organic matter and crop residues (PÊS et al., 2011), and the effect of soil and crop management strategies on the improvement of soil organic carbon stabilization (CAMPOS et al., 2011).

The CH\textsubscript{4} fluxes are more relevant in flooded soils where the incorporation of crop residues increases methanogenesis (ZSCHORNACK et al., 2011), but short-term CH\textsubscript{4} emissions could also be verified in aerated soils following manure or nitrogen fertilizer amendments (SHERLOCK et al., 2002; ZANATTA et al., 2010). N\textsubscript{2}O emissions are critical on aerated soils under nitrogen fertilization or inclusion of legumes on the cropping systems (ESCOBAR et al., 2010; ZANATTA et al., 2010).

Most of studies assessing CH\textsubscript{4} and N\textsubscript{2}O fluxes in soil-atmosphere interface are performed by using static chambers for gas sampling and further gas chromatography (GC) analysis (ESCOBAR et al., 2010; GOMES et al., 2009; ZANATTA et al., 2010). Fluxes are then calculated by the linear increase of GHG concentration in the chamber air in a given period (usually < 60min). Although accurate, conjunct analysis of CO\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2}O by GC imposes operational limitations on the number of gas samples that could be feasible collected and analyzed. Therefore, it is very important to have some alternative method for accurate GHG evaluation allowing improvement of sampling frequency and number of experiments, treatments and replicates under analysis.

Few techniques are available for the simultaneous assessment of the three GHG with significant success. Among them, the photoacoustic spectroscopy (PAS) method has been proposed for the conjunct assessment of CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2}O fluxes in substitution to GC. However, this technique is still unprecedented in studies assessing soil GHG emissions in Brazil. Among the main advantages of this method are its sensitivity and linearity for CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2}O concentrations, real-time gas sampling and measurement (avoiding sampling storage and laboratory analysis), and portability (YAMULKI & JARVIS, 1999). Studies assessing soil GHG emissions through PAS have been carried out with success (VELTHOF et al., 2003; LOVANH et al., 2010), although some concern persists when very low GHG fluxes should be measured. PAS analysis could be able to detect N\textsubscript{2}O fluxes of 65.6µg N\textsubscript{2}O m\textsuperscript{-2} h\textsuperscript{-1} (YAMULKI & JARVIS, 1999). However, NT soils without N input could present N\textsubscript{2}O fluxes as low as 13.5µg N\textsubscript{2}O m\textsuperscript{-2} h\textsuperscript{-1} (GOMES et al., 2009). Thus, the objective of this study was to evaluate the efficiency and sensitivity of a PAS trace-gas analyzer on the assessment of soil GHG emissions in static chambers taking the standard GC method as reference.

MATERIAL AND METHODS

This study was carried out in two long-term experiments (30°06'S; 51°40'W; 46m altitude) in Eldorado do Sul, state of Rio Grande do Sul, Brazil. The climate is subtropical humid Cfa according to the Köppen classification, with a mean annual temperature and rainfall of 19.4°C and 1440mm, respectively. The local soil is classified as a Paleudult (U.S. Soil Taxonomy) or a sandy clay loam Acrisol (FAO).

The first long-term experiment was established in 1983 with different cropping systems under no-till (NT). Three treatments (with two replications) were selected with increasing C and N inputs to the soil by crop rotations (winter/summer species): (a) fallow/maize (Zea mays L.), (b) black oat (Avena strigosa Schreb.)+vetch (Vigna sativa L.)/maize, and (c) black oat+vetch/maize+cowpea (Vigna unguiculata (L.) Wlp.) without mineral N fertilization. Further details of the experiment and crop conduction are available in VIEIRA et al. (2009). The second long-term experiment was initiated in 1985 with different soil tillage (NT; and CT – conventional tillage) and cropping systems. For this study, four treatments (with three replications) were selected with increasing soil disturbance by tillage and C and N inputs by cropping systems (winter/summer species): (1) CT with black oat/maize; (2) CT with vetch/maize; (3) NT with black oat/maize; and (4) NT with vetch/maize; without mineral N fertilization. Further description of the experiment and crop conduction was detailed by ZANATTA et al. (2007). Treatments from both experiments were selected in order to provide a wide range of GHG concentrations and fluxes for better methods comparison.

Air samples were collected in static chambers measuring 40x80x40cm (LxWxH) and
mounted over a base with 9 cm of height. The headspace volume of the chambers averaged 70.4 L. The chambers were equipped with three internal fans to homogenize the internal atmosphere before sampling, a probe thermometer for monitoring the air temperature inside chamber and a rubber septum from where air samples were taken through a plastic tube closed by a three-way “luer-lock” valve.

Air sampling was performed in Sep. 22, 2011 (experiment 2) and Sep. 23, 2011 (experiment 1). Chambers were closed and sealed with water to avoid air exchanges between atmospheres inside and outside the chambers. The samples at time zero were collected outside the chamber, while the samples from the atmosphere inside chamber were collected after 15, 30, and 45 min. The samples were collected with 20 mL polypropylene syringes which were stored in a cooler until GC analysis. Immediately after that, the samples for PAS analysis were taken by the trace-gas analyzer INNOVA 1412 (Lumasense Technologies, Denmark). The analyzer automatically pumped 100 mL of air from inside the chambers (or outside chamber at time zero) and performed PAS analysis.

Air samples were analyzed in a gas chromatograph (Shimadzu GC 2014A “Greenhouse”) equipped with three packed columns at 70°C, N₂ as carrier gas at a flow of 26 mL min⁻¹, an injector with 1 mL sample loop for direct injection at 250°C, an electron capture detector (ECD) at 325°C for N₂O detection and flame ionization detector (FID) at 250°C for CH₄. The equipment was equipped with a methanator which catalytically reduced CO₂ to CH₄ for analysis of the CO₂ gas with the FID detector.

The CO₂, CH₄ and N₂O fluxes were calculated based on the following equation:

\[ f = \frac{\Delta Q}{\Delta t} \frac{PV}{RT} \frac{I}{A} \]

Where \( f \) is the carbon dioxide, methane, and nitrous oxide flux (mg CO₂ m⁻² h⁻¹ or µg N₂O or CH₄ m⁻² h⁻¹), \( Q \) is the mass of the gas (mg CO₂ or µg N₂O or CH₄) inside chamber at a given sampling time (\( t \)), \( P \) is the atmospheric pressure (atm) in the inner chamber – assumed as 1 atm, \( V \) is the chamber volume (L), \( R \) is the constant for ideal gases (0.08205 atm L mol⁻¹ K⁻¹), \( T \) is the temperature within the chamber at sampling time (K) and \( A \) is the basal area of the chamber (m²). GHG fluxes were calculated by the angular coefficient of the linear regression adjusted for changes in gas concentrations over time inside chambers.

The INNOVA 1412 trace-gas analyzer pumped and confined the air sample in a sealed compartment where intermittent infrared radiation was applied at the specific wavelength absorbed by the gas of interest to be analyzed. The intermittent radiation promotes pulses of temperature and pressure proportional to the gas concentration in the sample which are registered by two microphones. Detailed description of the method is provided by YAMULKI & JARVIS (1999). The INNOVA 1412 trace-gas analyzer used in this study was equipped with UA0982 (center wavelength: 14.1 µm), UA0985 (4.5 µm), UA0969 (8 µm), and SB0527 (5.1 µm) filters for the analysis of CO₂, CH₄, N₂O, and water vapor concentrations in the air samples, respectively (LUMASENSE TECHNOLOGIES, 2009). The detection limits for those gases are 1.50, 0.40, 0.03, and 50 ppm, respectively, for the analyzer equipped with those filters (at 20°C and 1 atm) and with a sample integration time of 5 s for each gas. The equipment was factory calibrated for the above mentioned gases and also for humidity and cross interference among gases. The sample volume (100 mL) was set to ensure the complete flushing of the internal measurement system of the analyzer (60 mL), avoiding contamination between samples. The GHG fluxes were calculated by the same procedure described for samples analyzed by GC.

The comparison of GC and PAS methods for determination of GHG concentrations and fluxes was performed by regressions analysis and the significance (\( p<0.05 \)) of the coefficient of determination (\( R^2 \)) of the adjusted linear equations (SAS INSTITUTE, 2009).

RESULTS AND DISCUSSION

The results of CO₂, CH₄ and N₂O concentrations in air samples collected in both experiments are presented in the figure 1. For CO₂ and N₂O gases, data collected through PAS showed good relationship with GC results (\( R^2=0.98 \) and 0.94, respectively, \( p<0.001 \)). However, PAS overestimated both gases concentrations compared to GC (14.6% for CO₂ and 18.7% for N₂O). CH₄ concentrations determined by PAS showed no correlation with GC results, although previous laboratory studies founded good linearity when comparing both methods (YAMULKI & JARVIS, 1999).

These results could be associated with humidity interference due to the proximity of absorbed wavelength by water vapor (5.1 µm) and the wavelength absorbed by the other GHG gases, especially methane (4.5 µm). Increase of air moisture promotes a linear increase of CO₂, CH₄, and N₂O signal detection by PAS when the analyzer is not accordingly calibrated or configured to compensate this interference (YAMULKI & JARVIS, 1999). This information was confirmed in a
laboratory test with the equipment used in this study (data not showed). The trace-gas analyzer used in this study was factory calibrated for humidity interference for water vapor concentration up to 20.60 mg g\(^{-1}\) in the atmosphere. However, the air samples analyzed in this study showed water vapor concentrations ranging from 13.54 to 32.01 mg g\(^{-1}\). Although the trace-gas analyzer was set to compensate humidity interference, the outrange water vapor concentrations in this study could have promoted overestimation of CO\(_2\) and N\(_2\)O.

Figure 1 - Relationship between CO\(_2\) (a), CH\(_4\) (b), and N\(_2\)O (c) absolute concentrations determined by gas chromatography (GC) and photoacoustic spectroscopy (PAS).

concentrations determined by PAS in relation to GC results, and the lack of relationship between CH₄ results from PAS and GC.

An analysis of air moisture interference on CO₂, CH₄ and N₂O results from PAS and GC analysis is presented in figure 2. Air samples collected at time zero (outside chamber) averaged air moisture content of 15.52 mg g⁻¹, while air samples collected inside chambers (after 15, 30, and 45 min) averaged 25.20 mg g⁻¹ of water vapor concentration in the atmosphere. The higher water vapor concentration in the closed chambers could be result of water evapotranspiration from soil or evaporated from the chamber’s water seal. The analysis of water interference on GHG concentrations was then performed just for the samples collected inside static chambers (15, 30 and 45 min sampling time), where air moisture

Figure 2 - Absolute concentrations of CO₂ (a), CH₄ (b), and N₂O (c) determined by gas chromatography (GC) and photoacoustic spectroscopy (PAS) and the relative PAS/GC concentrations of CO₂ (d), CH₄ (e), and N₂O (f) as affected by air moisture inside static chambers.
concentration exceeded the PAS analyzer humidity interference calibration point. Also, variation of GHG and water vapor concentrations in samples collected outside chambers (time zero) was too small to perform such analysis. Weak but significant relationships between air moisture and CO₂ concentrations were noticed for both PAS and GC results (Figure 2A). For CH₄, PAS results showed strong relationship with water vapor in the air sample, while GC results were not affected by sample moisture (Figure 2B). PAS-CH₄ results indicate that the trace-gas analyzer used in this study was misreading water vapor as CH₄, providing the discrepant results showed in the figure 1B. To solve this issue, detailed humidity interference calibration above 20.60mg g⁻¹ water vapor concentration should be performed for this analyte. On the other hand, N₂O results from PAS and GC analysis showed no relationship with air moisture (Figure 2C). These results could indicate that air moisture didn’t affected N₂O measurements by PAS or at least the treatments effect were by far superior than humidity interference for this gas.

However, when the relative PAS/GC difference (percentage difference between PAS and GC results) were analyzed for its sensitivity to sample moisture, fitted linear equations showed that PAS-CO₂ and N₂O results were also affected by humidity interference (Figure 2D,F). Thus, explaining the cause of PAS overestimation in relation to GC results. The higher slope of the linear equation between relative PAS/GC difference and air moisture fitted for N₂O also agree with the higher overestimation for N₂O concentrations verified in figure 1C in relation to the overestimation verified for CO₂ (Figure 2D and 1A). These results indicate that even for CO₂ and N₂O PAS analysis were being affected by air moisture out of the calibration range and further humidity interference calibration should be performed at higher air moisture levels (at least 32mg g⁻¹). Relative PAS/GC difference for CH₄ (Figure 2E) showed the same pattern observed in the figure 2B, since air moisture interference was more pronounced for this gas in PAS analysis.

The sensitivity of each GHG analysis method was assessed by the coefficient of determination (R²) of the linear equation describing the increase of GHG concentrations inside static chambers with time. Since PAS-CH₄ concentrations were erroneous and GC-CH₄ fluxes were too low in both experiments, this comparison was performed only for CO₂ and N₂O (Figure 3A,B). Both PAS and GC showed good sensitivity in all the range of CO₂ fluxes observed (PAS: 332 to 871mg CO₂ m⁻² h⁻¹), with R² always higher than 0.99 (Figure 3A). For N₂O, GC showed R² higher than 0.90, while PAS showed R² above 0.81 (Figure 3B) at N₂O fluxes ranging from 21 to 855µg N₂O m⁻² h⁻¹. R² lower than 0.90, but still highly significant, were noticed for PAS results when N₂O fluxes were lower than 252µg N₂O m⁻² h⁻¹. Previous study reported that PAS analysis could be able to detect N₂O fluxes lower than 11.6ng N-N₂O m⁻² s⁻¹ or 65.6µg N₂O m⁻² h⁻¹ with acceptable R² higher than 0.70 (YAMULKI & JARVIS, 1999). In the present study, PAS were able to detect N₂O fluxes as low as 3.7ng N-N₂O m⁻² s⁻¹ or 21µg N₂O m⁻² h⁻¹ with R² higher than 0.81. Thus, indicating the high sensitivity of this method for soil GHG emission assessments.

The comparison of CO₂ and N₂O fluxes determined by PAS and GC are presented in the figure 3C,D. PAS showed good relationship with GC results (R²=0.96 and 0.95, respectively, p<0.001). However, PAS overestimated both gases fluxes in relation to GC (18.6% for CO₂ and 13.6% for N₂O). Lower interference of sample moisture on PAS-N₂O than PAS-CO₂ measurements (Figure 2A,C) resulted in lower overestimation of N₂O than CO₂ fluxes determined by PAS. Comparison of CH₄ fluxes determined by PAS and GC methods was not performed due to humidity interference errors of PAS-CH₄ measurements. PAS showed to be an efficient method for the assessment of soil GHG fluxes in substitution to GC. Further studies considering accurate calibration of the trace-gas analyzer for humidity interference should be carried out to confirm these results.

CONCLUSION

PAS showed good relationship and linearity with GC on the assessment of soil CO₂ and N₂O fluxes in static chambers. However, PAS overestimated soil CO₂ and N₂O fluxes by 18.6 and 13.6% in relation to GC. Detailed calibration of PAS analyzer for humidity interference on CO₂, CH₄, and N₂O measurements should be performed to avoid overestimation and errors on GHG concentrations and fluxes analysis. PAS showed good sensitivity and was able to detect fluxes as low as 332mg CO₂ m⁻² h⁻¹ and 21µg N₂O m⁻² h⁻¹.

ACKNOWLEDMENTS

The authors would like to thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) (process n. 477603/2011-4), Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS), and PECUS Research Network from EMBRAPA for their support to this research.
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