

Interactive comment on “High temporal frequency measurements of greenhouse gas emissions from soils” by K. Savage et al.

Anonymous Referee #1

Received and published: 16 January 2014

The work of Savage and colleagues presents data from two experiments using an automated static chamber system combined with laser spectroscopy; providing a highly precise measurement system, together with high temporal resolution. Results reinforce the need of high temporal resolution measurements, due to short-lasting pulses, and show diel patterns of the fluxes, both issues being relevant for extrapolation and accounting. Furthermore, the precision of the system allows the confident detection of soil N₂O uptake processes, which usually fall within the detection limit of most of the measurement systems. Finally, the paper makes a comparison between this automatic system and a “common” manual chamber system.

Although the paper is quite descriptive, the topic is of high interest for the journal and provides some useful insights into temporal and spatial dynamics of soil GHG (main

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focus on N₂O and CH₄) fluxes. Unfortunately, the main conclusion I may extract out of this work is that both many replicates and high temporal frequency are needed for reliable estimates of soil GHG emissions.

Overall quality of the paper is good: it is well structured and written, methods are well explained and results and discussion are sound. However, I see a couple of issues requiring further explanations prior to publication. This would avoid misinterpretation of results and make the paper even more useful for people aiming at precise and accurate soil GHG fluxes estimations. Briefly, I think your minimum detectable flux is indeed larger than what you present; recommendations upon diel patterns may be counter-productive and some issues when comparing manual and automatic chambers may be missed in the text. Furthermore, some details of minor importance are commented.

Minimum detectable flux and comparison between manual and automated systems:

The minimum detectable fluxes (MDF) you present are astonishing low! So low, that some clarifications are needed about the procedure to calculate the MDF. I am confident about the reliability of your system, which has a lot of pros and little cons, but I doubt the minimum detectable flux is as low as what you present. Just a rough calculation: the MDF of 0.01 ug N₂O-N m⁻² h⁻¹ corresponds to an increase of approx. 1 ppt N₂O min⁻¹ in the headspace, beyond what the QCLAS is capable of.

First, I am not sure whether the CV can be determined by collecting ambient air (P18287, L5), given the intrinsic variation in the mixing ratios of CH₄ and N₂O of such ambient air before the headspace is closed. This is probably the reason why you end up with different MDF in the two locations, but this does not represent variations in the detection limit, or in the sensitivity of your system, but the stability of the composition of the air.

According to your text, you follow the procedure of Parkin et al (2012) for calculating detection limits. However, this work shows tables to calculate MDF from three and four time points measurements, only, and not 240 points-measurements. Have you run

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your own Monte Carlo simulations to develop your own MDF of the system? If this is the case, what was the influence of the number of points taken on the MDF? This is important since the magnitude of the number of points taken is different according to Parkin (3 to 4) and this paper (240).

However, this is likely the theoretical precision of your measurement instrument, but not of your experimental setup (this is mentioned in the paper from Parkin et al.). You should address the fact that you change the environmental conditions in the chamber headspace (10 minutes though, but they change), you may have sources of uncertainty in the system, due to pressure variations when switching valves, etc.

Diel patterns:

I would be extremely careful with your conclusions. You say the time of day you manually measure (9-12:00) is representative of the mean daily flux. There are a couple of issues here: first, the optimum time is not the same for the three molecules, so that you need a compromise there; second, this morning period is the one with the highest temporal variations in the fluxes. A time gap of 1-2 hours may mean 50 % of difference in the measured fluxes (the 50% is a rough estimate from what I see in Fig 7a), and non synchronized measurements may be biased. When dealing with several plots and limited man power, measurements are usually performed sequentially, so that a group of chambers is sampled within a period of 60-90 minutes (including closing time + preparation) and when this first group is sampled, the next one is sampled in a similar way, so that there is a 60-90 minutes time interval between both samplings. Thus, another solution may be to take the gas samples very early in the morning, or in the afternoon and then apply a correction factor for the under/overestimation. Unfortunately that is usual not that straightforward when working under field conditions.

Comparison manual and automated chamber system:

In your conclusions, I don't think you can say that "manual sampling ... captured transient responses of GHG's to precipitation events. This is not what I see in figure 4.

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Your estimations with manual and automated chambers differ by 300% (26 vs. 9 ug m⁻² h⁻¹) and this is something needing more discussion!

Linking this issue with the MDF one: How can you explain that with the automated system, as much as 9-12 % of your fluxes were below the detection limit (0.01 ug N m⁻² h⁻¹) but, with the manual chambers, only 5% were below the detection limit, which was 70 times higher! To me, this demonstrates there is a source of variation between both methods, potentially leading to a bias when comparing them and this source of uncertainty is not explained by the calculation of the detection limit.

Specific comments:

Flushing: You're flushing your headspace chambers with a total flow of 8 liters during one deployment cycle, which corresponds to 2 times the volume of the headspace. Don't you have pressurization problems? Have you checked this issue?

18284, L24: Did the instrument feature a water broadening correction factor, or only pure dilution was taken into account? Was this correction factor able to eliminate interferences due to changes in water content, so that you don't have a source of uncertainty?

P18278; You focus on soil moisture at the beginning of your abstract, but this is not an issue of major importance in this paper

P18284: Is your laser really cooled to 32°C? Is it a typo, or maybe your thermocube is set at 32°C, but not the laser?

P18285, L26. What do you exactly mean when you write that the instrument is trained on interpreting the N2O gas peak? To my understanding, the instrument makes use of the HITRAN database to simulate size and shape of absorption lines, and this information is used for performing the fitting (with help of the tuning parameters) and estimating the mixing ratio of the target molecule. Therefore, I don't get this "training" issue. I don't know which lines are being measured with this specific instrument. Maybe the strength

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of the CH4 lines is lower? Furthermore, this company usually provides precision according to different sampling frequencies.

P18287, L9: "0.18" instead of "0.180"

P18280, L25. QCLAS corresponds to "Quantum Cascade Laser Absorption Spectrometer".

Fig 1. Replace "cool laser" by "laser cooler" or similar. You say only one chamber is closed at a time, but the graph shows chambers 1 and 2 closed

Fig3, 4 and 5. Please homogenize the X Date axis, the format is not the same across the figures (separator, inclusion of year, etc).

Fig 4. Do not use abbreviations for the experimental site.

Fig 5. Specify where the data come from.

Fig 6d. Scale should be adapted to the magnitude of the values showed, as in the rest of the sub-figures.

Fig 6e. I don't see the line for the mean of the "automated concurrent" seasonal N2O flux.

I see there was some discussion on the units of the fluxes. I recommend to keep them as they currently are.

Interactive comment on Biogeosciences Discuss., 10, 18277, 2013.

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