Biogeosciences Discuss., 10, C8144–C8149, 2014
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Biogeosciences Discussions
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Interactive comment on "High temporal frequency measurements of greenhouse gas emissions from soils" *by* K. Savage et al.

Anonymous Referee #2

Received and published: 21 January 2014

This manuscript details a new combination of automated, high temporal resolution sampling technology with laser spectroscopy, to attempt to accurately and precisely quantify three major anthropogenic GHGs, with particular emphasis on N2O and CH4, the predominant gases associated with agricultural systems. The authors 'road test' this technology in two contrasting environments to provide a range of sampling and environmental conditions, and compare their 'high-tech' system with a 'conventional' manual sampling approach in an agricultural crop system to investigate the pros and cons of both with regards to spatial and temporal dynamics.

The paper is of necessity methodology heavy and descriptive, but is sufficiently clear and well-written, with potential wide ranging implications, to be of interest to the general reader of Biogeosciences.

I do have a number of concerns that require further comment and/or addressing prior to potential publication. These relate to: 1) minimum flux detection limits; 2) flux 'acceptance' criteria, and; 3) diel trends. All are important given their influence on the paper's conclusions. I discuss these initially and follow up with specific line-by-line comments.

1) minimum flux detection limits (MDL)

The MDLs for N2O and CH4 are exceptionally low – at least two orders of magnitude lower than I have seen reported elsewhere from similar automated (6-8 daily) GHG sampling systems. Based on this alone, I have to question the approach that generates these values, and by extension the legitimacy of a major conclusion that stems from these values, ie that exceptionally low negative N2O fluxes from the wetland represent a real phenomenon. Questions arising:

Is the approach used by Parkin et al. (2012) for 3-4 point manual sampling systems applicable to your presumably many hundred point automated approach? Please provide further justification.

Does the MDL represent the Method Detection Limit or a more stringent Reliable Detection Limit (reduces expected frequency of false negatives as well as false positives)?

Were the MDLs calculated from the mean and CV of all ambient air hourly measurements over the entire measurement period at the forest site, or was this conducted periodically? If the former, you would expect a very low standard deviation and CV. Would an approach that matches the air sampling time of the automated systems with that of the manual sampling system at the alfalfa site be more appropriate – this along with or separately to a randomized (Monte Carlo) sampling technique of air (or standard [see below]) concentrations would I think be more appropriate?

Indeed, can ambient air be used to determine flux detection limits? Presumably N2O and CH4 concentrations vary over daily and longer time periods at both sites. Using the N2O and CH4 standards that are used to determine instrument precision and accuracy

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would I believe be more appropriate. Could the authors please recalculate using these standards or provide strong justification why this is not more appropriate.

In general please provide greater explanation (including equations and refs) for MDL determination, as these values are important and fundamentally impact the conclusions.

2) flux 'acceptance' criteria

Using CO2 concentration change during chamber closure is a commonly accepted proxy to help to determine the legitimacy of N2O and CH4 concentrations/fluxes from the same air sample. Here, however, I question the 'toughness' of this test and the sole use of a relatively low R2 threshold for CO2 for determining whether the system was operating correctly or not. As the authors are aware/note, although R2 is commonly reported as a means for identifying 'good' or bad' fluxes for N2O and CH4, small positive/negative fluxes of these gases cannot be readily distinguished from zero by its use. Using R2 for CO2 therefore makes sense in this respect, but 0.90 seems a low value. The vast majority of R2s for CO2 fluxes typically encountered are >0.98 – using either manual or automated systems. Perhaps the much larger number of samples (240 over 4 mins?) per chamber closure 'depresses' the R2 value, compared with for example selecting a small number of samples, e.g. 4 (one each at 60, 120, 180 and 240 sec). Irrespective, could the authors justify the specific use of 0.9 as the R2 threshold, given that they have confidence of the previous 'linearity' of CO2 concentration changes. If the R2 values were raised to e.g., 0.95. 0.99, could the authors comment on the resulting percentage of acceptable N2O and CH4 fluxes at both sites and how (if) they alter conclusions.

Although I understand the rationale behind no minimum linear criteria for CO2 with the manual chambers, other factors can of course affect CO2 concentration (e.g. improper vial evacuation, lid/septa integrity, vial storage etc). Could the authors comment on the percentage of manual samples that met the automated sampling CO2 threshold R2 of

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0.9 and higher. Would a consistent approach for both systems be more appropriate – please comment?

3) diel trends

The correlation between diel patterns of N2O and soil temperature appears to corroborate previous studies. Blackmer et al. 1982 however note that "neither the amplitudes nor the times of minima and maxima in these patterns can be predicted solely from soil temperature".

The diel patterns, particularly for N2O and CO2 may also be partially/primarily temperature artifacts associated with the warming/cooling of the sampling tube and chamber air. This appears to be corroborated by the better synchrony between air temperature patterns and N2O and CO2 diel patterns, as compared with soil temperature patterns, which have peak/trough lags of $\sim$ 4 hours (depth of N2O production questions arise?). I would therefore urge greater caution about this relationship, and reflect this in the narrative.

In relation to this, what (if any) was the temperature differential between chamber air and external air during chamber closure (I realize chamber closures were very short) – was this (and any pressure differences) tested?

Specific comments

18281, L 25-26: How deep were automated chambers deployed into the peat/moss? Did the positioning of the chambers reflect the variability of the well/poor drained site? Were the same five automated chambers in the same conformation deployed here as in the alfalfa field (not clear from narrative)?

18282, L 26-27: Could the authors please provide more specific dimensions for the manual sampling chambers. I cannot find chamber height, diameter, deployment depth information in the manuscript or in Phillips et al. 2009 cited in 2.3.

18282, L 13: Were the collars inserted into soil to their full depth (5.1cm)? Given the

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precision needed to achieve a gas tight fit between the collars and the chamber tops using only gas pressure, what tests have been carried out to ensure no (or minimized) leakage from these systems?

Can the authors describe the 'connections' used (material, dimensions, vendor etc) that allows air flow from and to the chambers and the analyzing equipment – I don't see this mentioned in the text or in Figure 1.

18282, L 21: Were individual automated chambers sampled at the same time during each hour throughout the measurement periods, or where they randomized within each hour?

18282, L 27: Were non-linear models tested – assume short closure period precluded their use?

18284, L 28: Was atmospheric pressure measured locally or derived from altitude?

Could the authors include a flux calculation equation for clarity?

18285, L 6: In relation to vial preparation, could the authors also comment on their practice of evacuation, as opposed to over pressurization that allows leak detection and avoids contamination during sub-sampling (eg Rochette and Eriksen-Hamel 2008. Soil Sci. Soc. Am. J. 72:331-342)?

18286, L 11: How was this particular model chosen to represent diel fluxes – were others tested? The model peaks/troughs for N2O (Fig 7a) seem shifted wrt measured N2O fluxes (earlier in morning and later in afternoon).

18287, L 18-19: Please see general comments on MDL for automated system.

18289, L 13-16: Please see general comments on MDL for automated system. The range of N2O fluxes noted equivalent to $\sim$ 0.1 to 0.3 g N2O-N ha-1 day-1 are, as previously noted, exceptionally low to consider as 'real'. Despite this, and assuming similar uptake throughout the year, could the authors comment on this sink strength at

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a broader scale?

18290, L 9-12: It is difficult to see this apparent good agreement between one manual sampling event and the equivalent automated sampling event from Fig 3a-c. I suggest formalizing the correlation or consider removing/revising this assertion.

18292, L 12-15: If manual sampling was able to “characterize much of the transient GHG responses” then how can it also “miss many of these responses”. Seems contradictory, please clarify/revise.

Section 3.6 and 3.7: Could the authors please include a few more citations in these sections, by comparing their results to a relatively small, but important number of previous publications that have investigated comparisons between automated and manual sampling systems (eg Smith et al. 2001. Global Change Biology, 7, 933-945.), determined suitable manual sampling regimes based on automated systems (eg Parkin et al. 2008 J. Environ. Qual. 37:1390-1395) and investigated diel N2O cycles and their drivers (eg Blackmer et al. 1982. Soil Sci. Soc. Am. J. 46:937-942, Alves et al. 2012. Soil Biology & Biochemistry 46 (2012) 129-135, and Smith et al 1998. Atmospheric Environment Vol. 32, No. 19, pp. 3301-3309).

Figures

Fig. 1. As reproduced it is very difficult to read and interpret. Consider font size increases and revisions of schematic for clarity. Please also make clearer the sampling connections between the chambers and the analytical equipment in the ‘enclosure’

Fig 3. Consider removal of red symbols for manual sampling. See specific comment above.

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