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Atmospheric Measurement Techniques Discussions

Interactive comment on "A mass spectrometric multiple soil-gas flux measurement system with portable high-resolution mass spectrometer MULTUM coupled to automatic chamber for continuous field observation" *by* Noriko Nakayama et al.

Anonymous Referee #2

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The study by Nakayama et al. describes a MS-based measurement system that allows the quantification of mixing ratios of the (trace) gases CO2, CH4, N2O and O2. This is a novel approach, and certainly qualifies for a high-ranking journal like AMT.
The authors have conducted both laboratory incubations and field measurements. For both applications, data evaluation is limited to CO2 and N2O since instrument precision prevents flux calculation for CH4 and O2. This is a pity, especially since the authors are i) suggestive of preparing another publication that shows CH4 flux rates

determined in the field and ii) provide the perspective that another data evaluation algorithm could increase precision for O2 measurements so that flux rates could be calculated. For a proof-of-concept study this is a surprising selection of datasets and from studying the manuscript I could not find the reason why the suggested waveform averaging was not applied instead of ion counting for O2. If this is not possible with the given data I have missed the explanation.
For a journal like AMT, the advance for – in this case – determination of soil-atmosphere (trace) gas exchange has to be shown. Even though the manuscript describes progress in making high resolution mass spectrometry field deployable, the benefit of this approach compared to other existing methods is not evident at the moment because

- There are many instruments available for determination of CO2 at low cost. CH4 and N2O exchange between soil and atmosphere has been determined using gas chromatography and, more recently, using spectroscopic methods. With regard to the greenhouse gases, the presented method doesn't seem to reach the precision of existing methods, but the draft stops short of an actual discussion of precision levels (which could for example start with an assessment what precision levels are required for the intended application) for different trace gases and a comparison with available commercial products. For example, determination of the sink strength of upland soils for methane is a challenge at the moment.
- The perspective for O2 flux measurements is missing in my opinion. Figure 4 looks like a dark chamber. Consequently, the authors determine ecosystem respiration. Respiration consumes one mole of oxygen per mole of CO2 released. For this reason, I would expect that linking ecosystem respiration measurement and O2 flux requires similar minimum quantitative fluxes, but they are 3 orders of magnitude apart from each other. The authors don't provide information if there is potential to close this gap or if (and where) they see applications in reach for

the presented O2 flux detection limits.

According to the authors, the largest benefit of the proposed approach is its applicability to practically any gaseous compound. With this potential, selection of a set of mutually complemental compounds seems mandatory, but the strategy behind the (sensible) selection of the compounds CO2, CH4, N2O and O2 remains unclear.
Considering the raised general points, the authors must in my opinion convincingly argue if and how (i.e., application of waveform averaging) determination of oxygen concentrations can be beneficial for soil-atmosphere (trace) gas exchange.
Please find some details below.
Title
ok
Abstract

Introduction
L36-40: This sentence is hard to understand. I guess you mean something like "Both source and sink strength of soils for GHG and O2 are highly variable and depend on . . ."
L58: please replace "mostly lack of" by "lack of"
L63: please change to "flame ionization detector"
L70: please change to recently

Materials and Methods
L168: Please clarify what is referred to with the term analytical precision. LOD, RSD? The unit doesn't comply with RSD definition as ion count or peak area. For LOD, parameter k of equation 1 and 1 sigma don't comply.
L194: accuracy and precision are different quantities. Why is this "definition" necessary?

L201: filled instead of spared; what soil mass was used? Was it sieved, or treated in any way, from which depth did you take a sample?
L202: I suggest changing to production instead of generation.
L203: the term "soil gases" is unclear. Do you mean "initiate production or consumption of CO2, CH4 and N2O"?
L300-302: in other words, there is an experiment that supports your notion that fluxes of N2O, CO2 and CH4 can be determined in the field, but you don't show the CH4-part in the proof-of concept study?!
Results
L266: Please revise terminology. Accuracy is a determined value's deviation from a reference value, precision is reflected by sd.
L270: Why? Please elaborate
L271: Please rephrase the sentence. The meaning is unclear. Are you saying that MDF is not reliable, and, for this reason, you calculated MQF in a reliable way? What is the point in presenting MDF then? Please clarify.
L274: the standard error of the slope can be calculated. Please refer to Crawley's R book section 10.1.5 . Why don't you use the standard error of the slope to calculate the uncertainty of the flux?
Section 3.4: elements of discussion, but actually speculative, and based on a 5 days campaign after tillage.
L335-337: It sounds like the authors could apply another data evaluation method, which could turn O2 measurements feasible. Please clarify why this has not been done.
Figure 7: mean and sd of fitted gaussians would be helpful in caption.
Figure 9: 1:1 line would be helpful
Figure 11: caption doesn't explain dashed lines.

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