June16th, 2021

Re: Response to Manuscript ID: bg-2020-401

Dear Dr. Nicolas Brüggemann,

We appreciate the reviewers' constructive comments as well as yours. We have carefully addressed each of the reviewers' comments and suggestions in the revised manuscript and believe these edits have improved the manuscript.

Based on the requirements for revised paper submissions, we are including the following documents with the appropriate changes based on reviewers' comments:

- Response to Reviewer and editor taking into account the new page, paragraph, and line number.

- Revised manuscript and Figure Source Files for Resubmission

In order to improve the manuscript as suggested we made the following modifications:

- We added text to address the comments while condensing the manuscript and ending on a balance of fewer words.
- We clarified the questions and hypotheses that motivate this study, highlighting the soil processes studied and their relevance to the soil-atmosphere interactions
- We more clearly distinguished our technical aims and achievements from our process-based hypotheses and results.

Below, please find our response to the fourth reviewers and detailed responses to the editor's comments and the actions we have taken to address each comment. Editor's and reviewer's comments are noted in italic Verdana font, our responses are in Time New Roman font in blue.

Sincerely,

Dr. Laura Meredith
Corresponding author

commentbg-2020-40 1 Review by reviewer #4, Albrecht Neftel

I read with interest this paper and was impressed by the analytical development presented to characterize trace gas composition in the open pore space of a soil matrix. It is a pleasure to see a follow up of the membrane tube technique (METT) that we have developed many years ago.
The presented instrumental setup offers the potential to explore the large variability of microbial and chemical processes in soil that controls trace gas exchange within the soil and between the atmosphere and the soil. It is a milestone to get simultaneously access to continuous data on isotopic ratios of nitrous oxide (δ18O, δ15N, and the 15N site-preference of N2O), methane, carbon dioxide (δ13C), and VOCs.
The paper first presents data from a control experiment from an artificial inert soil imitation to characterize collection efficiency and reproducibility as the gas probing relies on passive diffusion through the porous membrane tube and obviously the gas flow will have a key influence on the measured concentrations.

Secondly data from packed soil core with an embedded sampling tube are presented. An N2O pulse as consequence of an irrigation was traced. The information on the isotopic signature of the N2O concentration in the soil allows to disentangle different production pathways for N2O. This is a valuable information as I most cases the interpretation of the mechanisms leading to an observed N2O flux is a lot of guessing.

We have been aware when we developed the METT system and analyzed the data, that in the best case we got representative trace gas concentrations (at that time we focused mainly on N2O and CO2) in an additional large pore artificially introduced in the soil. These concentrations might not be representative for the most important processes that control the N2O production and consumption as the oxygen concentration is likely higher as in small pores.

I have only a small criticism. The idea of articles in BG is on aspects of the interactions between the biological, chemical, and physical processes in terrestrial life with the geosphere, hydrosphere, and atmosphere. The paper has a very technical focus and presents a toll box what can be measured. The paper would gain in strength if a proposition what relevant question linking the different spheres would be given. I am perfectly aware that this is to moan on a high-level.

Albrecht Neftel

Neftel Research Expertise, Wohlen b Bern, Switzerland

Dr. Neftel,

The authors appreciate your positive comments and the value you've found in our efforts to use isotopic signatures of soil trace gases as real time biomarkers of microbial metabolism, and keep working on improving soil gas sampling methodologies, which build from your work.

Based on your constructive suggestions, we have condensed and focused the paper to better highlight the questions, hypotheses and processes that we studied with our system and how they relate to biogeochemical interactions between the spheres.

bg-2020-401 Comments by Associate

Dear Authors,

*Your paper presents interesting aspects of a non-destructive technique for soil gas monitoring and isotope analysis. I found your paper well written and informative. Two of the reviewers also had a similar impression, while reviewer #3 was more critical. Reviewer #3 recommended "the whole paper should be focused, shortened and reorganized including t**he formulation of a clear scientific question that can be discussed based on hypotheses.** I would suggest splitting up the paper into a physically based sampling optimization part and another, multi component (isotopic) analysis part and possibly th**e process study of the process interpretation by isotopic signatures."** Please follow this recommendation as far as possible.*

In the meantime, I received the review of a fourth reviewer, which could not be uploaded due to technical reasons (included in the attached file). But he also approves your paper and had only a few minor comments.

Finally, I also went through the paper in detail and had only a few comments and technical corrections (see attached file).

Considering all the comments and your responses, I have decided to recommend your paper for publication after major revisions. Please address all comments and provide a point-by-point response.

General comments

Following the editors and reviewers comments, and trying to make the paper more succinct, we: i) we highlighted the questions and hypotheses in the introduction in the last paragraph of the introduction in page 4, and ii) the section from 4.1 to 4.4. Are dedicated to the integration and optimization process of the system, and we merged the discussion sections 4.4 and 4.5 into one called "Subsurface gas measurements to capture and interpret environmental drivers of soil processes" in page 29.

Editor Specific comments:

p. 3, L. 72: „For example, probes larger than 1 m have been used in water": You cite Rothfuss et al. (2013) for this statement, but see Rothfuss et al. (2015), who used 15 cm long pieces of the same microporous PP tubing (Accurel) successfully for water isotope measurements over a period of 290 days.

Thanks for the suggestion. Later in line 73, we mentioned the PP accurel improving the diffusion equilibrium time. In this line we meant to cite Rothfuss et al. (2015). Also we found value highlighting the specific probe and the sampling period. The sentence in Line 73 now will read: "Rothfuss et al. 2015 used a 15 cm PP tubing to measure water isotope for 290 days."

p. 10, L. 221-222: You mention here that the TILDAS you used was also capable of measuring water isotopologues, but you don't present any data. For the readers who are interested in non-destructive analysis of soil water isotopic composition, it would be very interesting to see the performance of your soil probes also for soil water isotopic analysis.

Our controlled optimization experiments were run using a dry silica matrix flushed with dry air from compressed gas tanks, so our soil moisture and water vapor concentrations were low, and not controlled in the experiments that used the water isotope analyzer. We agree with the Editor that this method will be interesting for the hydrological community, and hope to have time in the future to perform the controlled experiments with silica and soil to share useful data with the community.

p. 11, L. 271: Here you mention a surveillance standard of 1,000 ppm N2O. From the following sections it can be deduced that it should read 1,000 ppb here. Please confirm.

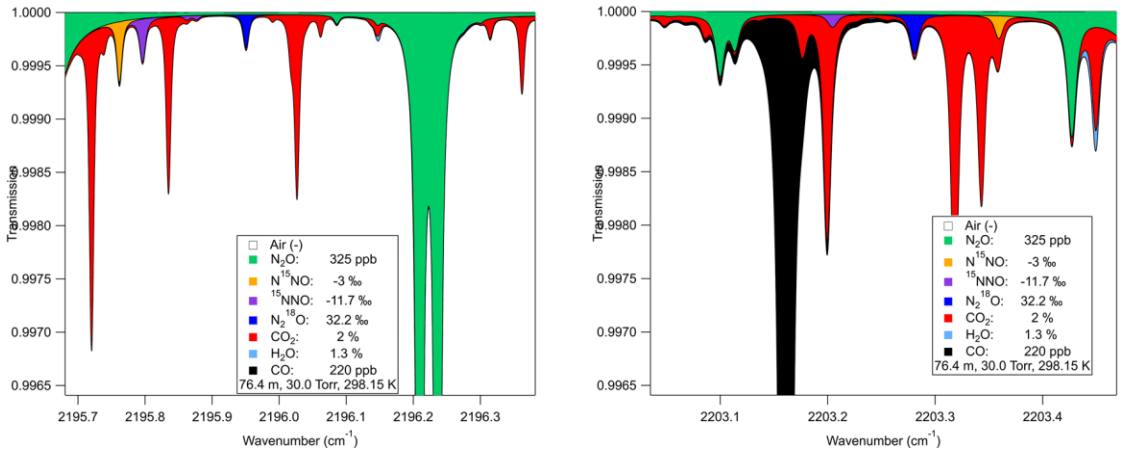
We are confirming that we used the MIT Ref II to make a 3 L surveillance standard of ~1000 ppm N_2O, which was then diluted into a container filled with zero air to produce sampled concentrations of 100 ppb - 30 ppm.

p. 12, L. 284: Use capital delta here: m/Δm.

Thanks for the correction, the line 278 now reads as suggested > 10000 m/Δm

p. 15, L. 345: It is not clear why the 2196 cm-1 region was chosen for N2O isotopocules. There is a more suitable region between 2203-2203.4 cm-1, where all four N_2O isotopologue lines are found at similar transmittance values between 0.9995 (weakest = 15N14N16O) to 0.998 (strongest = 14N14N16O). This would strongly reduce any issues with non-linearity (= concentration dependence). Although there is a relatively strong CO line at about 2203.16 cm-1, its interference at higher concentration can be reduced by removing the CO from the air stream (see Ibraim et al., 2018,
Isotopes in Environmental and Health Studies, 54(1), 1-15. Doi: 10.1080/10256016.2017.1345902

Through simulations and experimental testing, we determined that the 2196cm-1 region is overall a better spectral region for monitoring the N_2O isotopologues (i.e., 446, 456, 546, and 448) in the soil gas matrix. There are fewer interfering or closely overlapping lines, such as from CO_2 which is expected to be present on the percent level. A comparison of those two regions is shown below, with the same vertical scale. CO_2 at 2% concentration would make very strong interference with the 456 and 546 absorptions. The line strengths of the N_2O species are also stronger at 2196cm-1 for the 15N isotopologues. While we agree that a CO scrubber could remove CO spectral interference, it would add complication to the flow scheme.



p. 19, L. 404: What is shown in Figure 6 compared to Figure 4? The data look quite different, but it is not clear to me what was the difference in setup or measurement.

Figure 4 shows the effect of probe sampling on the column by changing the probe flow rate with constant control gas concentration and dilution using System 1 and a single column. We alternated measurement of CO_2 concentration in headspace gas (1 h) and the probe (15 min) . The column CO_2 was depleted after probe sampling and took 1 hour to stabilize. To further clarify this, we added the following to the Figure 4 caption, line 369: ", representing the potential impact of probe sampling on the soil environment". In Figure 6, we evaluated the impact of different total flow rates and dilutions at different percent increments calculating the residence time explaining the dependence on flow probe rate. To clarify this, we added the following to the Figure 6 caption in line 394: ", reflecting the recovered sample vs. true gas concentrations, respectively".

p. 20, L. 419-420: "These concentration and isotopic fractionation results underscore the need to ensure that the probe flow rate is sufficiently low…": Yes, or that the probe is sufficiently long (!) to allow a reasonably high gas flow required for the analyzers, especially at low soil gas concentrations where dilution would compromise the analyzer precision, especially for isotope measurements. This point is missing in the discussion, i.e. to ponder whether the shortness of the probes used bring also a disadvantage (= too strong a dilution of soil gas at higher sample flow rates through the probes), which could be overcome by longer probes.

The Editor raises a good point. We mainly advocate for the use of shorter probes to reduce the sampling footprint of the probe and resolve a smaller region in the soil, but this clearly is a challenge to obtaining a well-equilibrated sample. We argue that in most cases smaller probes are advantageous for increasing spatial resolution and minimizing disruption, but we also recognize that a longer sampling length might integrate over the heterogeneity in soil and be considered an advantage for other applications. To address this, we added the following passage to the discussion on Page 29, Line 590: "In some field applications, it may be more desirable to physically integrate (rather than resolve) variations in soil gas concentrations over a distance (e.g., for a representative concentration) using a long soil probe, which would help release the low-flow demands of the relatively short probes used here."

p. 24, L. 482: It would be good to have an estimate of the precision of your SP values, especially in view of the fact that it is the difference of two isotope ratios. Looking at your Figure 9, it seems as if the SP precision could easily be >10‰, making any strong statement on source processes basically impossible.

The precision of the SP values (and any isotope measurement) is strongly dependent upon concentration. Therefore there are concentrations for which an SP value would be too noisy to be useful. Here, the measured 15Nbulk and SP precisions were 0.9‰ and 1.6‰, respectively (page 10, line 258), at 325 ppb with an averaging time of 2 minutes. Importantly, barring significant N2O consumption in soil, concentrations are typically larger, from 1-100 ppm, putting the isotopic ratios well below 1‰.

p. 29, L. 611: Also Gangi et al. (2015), mentioned in your reference list, used microporous PP tubing for soil CO_2 isotope measurements, and Rothfuss et al. (2013) and (2015) for soil water isotope analysis, without any problems regarding physical/mechanical stability or loss of hydrophobicity.

Thank you for the recommendation and clarification, we added Gangi, et al, 2015 in our references for PP probes for CO_2 on Page 28, Line 583. Additionally, we will highlight the successful use of PP for water isotopes on Page 28, Line 585 to read: "PP has been successfully used for water isotope analysis (Rothfuss et al. 2013; Rothfuss et al. 2015).."

P. 30, L. 621: From your work, it did not become clear how large the soil volume is that is affected by the probe, which ultimately determines the (reasonable) spatial resolution. This should be taken into account here when talking about cm-level spatial resolution.

From our controlled tests, we are not able to determine whether the impact of probe sampling on soil gas concentrations was a big effect on a small volume around the probe, or a dilute effect over a large volume. This is especially complicated with the controlled tests where we flow control gas through the column, and replenish controlled gas around the probe faster than we would expect in the field. We believe the best test for this would be to install multiple probes in a column to evaluate the reach of probe sampling, which we aim to do in future tests. Here, we could do a back of the envelope calculation:

The gas resides in pore space, so whatever pores are not filled with water carry the soil gas that diffuses into the probe. Typical soil porosities are 40-50%. If we fully exchange, say 20 mL of soil gas for sampling from dry soil, the actual soil volume sampled by the probe is then 20 ml/45% = 44 mL. Note that this is soil moisture-dependent. For wet soil, if the water filled pore space (WFPS) fraction is, e.g. 75%, then the volume of available pore spaces is 75% less, and the footprint of the measurement would increase 4-fold to 176 mL. That value is an upper limit, however, because the water in the pores has the soil gas dissolved in it as well (in equilibrium). To take that into account when calculating the footprint would require knowledge of the Henry's or Raoult's Law coefficients for the analyte species.

For probe dimensions of 1.25 cm diameter and 15 cm long, 44 mL of soil volume corresponds to a region of soil extending ~0.5 cm away from the probe surface. 176 mL corresponds to a region of soil extending ~1.4 cm away from the probe surface.

Technical corrections:

p. 2, L. 38: VOC was defined already in L. 35 on the same page.

It was corrected in Page 1, line 40 to read: "...and VOCs (Abis et al., 2020; Raza et al., 2017)"

p. 15, L. 349: Figure 3, caption: a) and b) have been scrambled and need to be swapped.

The order of the plots (page 15) in the figure were swapped to match the order of the reference in the manuscript.

p. 18, L. 393: Figure 5: What is the unit of time? I assume minutes,

Time units were added to the figure 5, now it is on Pag 17.

please add. p. 19, L. 410: Change 20C to 20°C.

The symbol for centigrade degrees was added to read 20°C in page 18, line 400.

p. 26, L. 514: "a few hours delay"

Thanks to the editor for noticing the mistake. The phrase in page 25, line 513 was changed to read: "In contrast, after five hours,..."

p. 26, L. 515: The formula of dimethyl sulfide must read either C_2H_6S *or* $(CH_3)_2S$.

Thanks for noticing the mistake, the formula was fixed to read C_2H_6S in page 25, line 514.