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Biogeosciences Discussions

Interactive comment on "Versatile soil gas concentration and isotope monitoring: optimization and integration of novel soil gas probes with online trace gas detection" *by* Juliana Gil-Loaiza et al.

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Dear Dr. Nicolas Brüggemann and Reviewer #3,

We appreciate the detailed review and the honest comments from reviewer 3 to improve the manuscript. Following, we will address each of the reviewers comments and suggestions, those that required edits to the manuscripts will be addressed and will be noted in each response if pertinent for the editors' evaluation.

1. Does the paper address relevant scientific questions within the scope of BG? Without any doubt reliable protocols for diffusive soil-gas sampling combined with multi-component concentration and isotopic analysis are issues in soil soil ecological research. Indeed, progress in field research about soil-gas exchange requires reduced impact diffusive sampling with good temporal and spatial resolution. Another point are costs, that allow installation with sufficient spatial repetition. Therefore the topic of the paper adress clearly aims and scope of BG. My problem with the paper is, that in the study itself the critical issues are not treated critically and in comparison to existing solutions. The paper lacks a well defined scientific question. It seems to me more than an advertisement for a specific technical solution.

Answer: Thanks to the reviewer for honest comments and suggestions. We consider our research paper to be honest and open about the evaluation and optimization of an open-flow-through sampling system that is not widely used in the field. We have presented the challenges encountered during the evaluation of the system, and shared details of how they were solved. The sampling probes and sample transfer system are not yet commercially available. We hope this study is replicated by other researchers in this field to use and/or compare this probe and system with other instruments to address the challenges in BG noted by the reviewer. Our objective was to optimize and evaluate the versatility of the system under controlled conditions. To clarify the scientific question, we can highlight it in the introduction (in paragraph 6) to read as: "how can diffusive sampling approaches be used to obtain representative soil gas samples, with a return rate that allows high time resolution to capture changes in soil trace gases in response to manipulated environmental conditions." We will highlight also that by answering this question on improving and addressing the challenges of the current system, it will open the possibilities of future studies with sufficient spatiotemporal resolution to analyze soil trace gas dynamics in soil.

2. Does the paper present novel concepts, ideas, tools, or data? Neither diffusive gas sampling, nor the use of hydrophobic porous tubes are novel concepts. The au-

thors use an obviously sophisticated assembly of gas analyzers covering a wide range of isotopic and concentration responses. However, I miss a comparative discussion about the novelty and the advantages of the used equipment. An interesting concept is presented in figure 12-b, where the isotopic signatures of N2O are plotted in a 3-D coordinate system and assigned to specific processes. However, this process analysis is not further discussed and the background of the interpretations are not reported with exception of a literature overview in the supplementary material.

Answer: We agree that the general concept of diffusive sampling approaches and hydrophobic porous tubes are not new. We focus on a novel material for the diffusive probes: sintered PTFE as the hydrophobic porous membrane instead of polypropylene or silicone. From personal experience by the authors and comparing with other experimental set-ups, we have found that sPTFE improves the hydrophobicity, biofouling and physical integrity of the soil probe. These advantages and comparisons were discussed in section "4.6 Implications for sPTFE as a field-based soil probe." However, we argue that the novelty of this submission is not in the probe alone, but its combination with other important developments in open-flow-through sampling scheme and analyzer volume reductions that allow us to sample soil trace gases using high-precision analyzers, with a return rate of minutes/hour for real-time measurements. Specifically, we consider that the novelty and advantages of the described system are the reduction of the sample volume demand of the instrument, ability to control online sample transfer and dilution from the same interface, and a reduction in sampling artifacts. These features allow the possibility of extended measurement periods with no need to transfer samples to the lab, and data acquisition for long periods of time (months/years) become possible. Additionally, the online, real-time and non-destructive sampling increases the possibility of analyzing a wide range of soil gases, including VOCs, isotopologues of various trace gases, including isotopically labeled compounds. Hence, this approach will increase possible experimental studies to understand microbial activity in the subsurface with better spatiotemporal resolution. We appreciate the reviewer's support for the N2O isotope concept presented in Figure 12b, which is inspired by work in pure

culture by the cited references. In this paper, we evaluate this system under controlled conditions to address our questions on whether the approach can sample representative soil gases and under which conditions. The goal of Figure 12b is to demonstrate one potential analysis path enabled by the new soil gas sampling system. As noted by the reviewer, the scope of these experiments already makes the paper quite lengthy, so it is beyond the scope to conduct a detailed scientific analysis of the observed shifts in N2O isotopes shown here.

3. Are substantial conclusions reached? No.

Answer: We kindly disagree. We were able to address the challenges of the soil gas sampling system, successfully obtaining representative samples from different probes measured consecutively, and were able to detect fluctuations in soil gas concentrations and isotopic signature as a response to environmental changes. We describe in detail a general approach to leverage precision gas analyzers for subsurface soil gas studies.

4. Are the scientific methods and assumptions valid and clearly outlined? The description of the sampling and analysis system is difficult to read and full of technical details that do, however, not focus on critical issues. I clearly miss a list of the requirements that are expected from "a versatile soil-gas concentration and isotope monitoring". Insofar the reader does not really learn, what the authors expect from their equipment with regard to quantification limits, system disturbance, usability in the field, or costs.

Answer: Thank you for the comments to improve the understanding of the manuscript. We consider the technical details important for readers who are interested in developing or improving the gas sampling system from soil subsurface. We consider that we were able to explain in "Results" and "Discussion" the critical issues that we encountered during the evaluation of the sintered PTFE probes the overall sampling system, and the analyzer, including the time response, volume demand from the analyzer, sample equilibration, flow rates, return rate, among others. We will address the concerns about any specific critical issue that the reviewer thinks we have missed.

We agree with the reviewer about the need to highlight why we consider the system versatile for soil gas concentration and isotope monitoring. In particular, this investigation showed that 1) the system has the potential to be used with other gas and isotope analyzers, 2) there was no evidence of any interference during the TILDAS-PTR-MS Vocus inline measurements, and 3) the nitrous oxide analyzer configuration achieved a reduced concentration dependency allowing determination of N2O isotopic measurements over a larger range in concentration. And importantly, the sampling and analysis system is able to capture fluctuations in subsurface gas concentration and isotopologues in response to fairly rapid changes in environmental conditions, with good sampling resolution in space and time.

The reader can find the quantification limits of the instrument in the supplement information on figures S3, S4, S2. These figures are annotated in the manuscript, however, for clarification we can highlight this point directly in the manuscript. Regarding the usability of field deployment, in section "4.7 Considerations for field deployment of the system" and "Conclusions", we stated several considerations for field deployment. This study has been scaled-up, as mentioned previously, to an enclosed ecosystem to measure N2O, CH4 and VOCs from the surface and at different depths, we will share the challenges and considerations based on this experience in its pertinent publication. Additionally, in the future we plan to deploy the system in an agricultural field, which will allow us to share in future publications the challenges faced during a field application.

5. Are the results sufficient to support the interpretations and conclusions? I miss specific scientific interpretations and conclusions with regard to a reference. The extensive report of results is somewhat anecdotal.

Answer: The references we used for N2O and CH4 concentrations and isotopologues are described in the last paragraph in the section "2.2.2 Novel laser spectrometer for N2O and CH4 isotopomers". Also the results were discussed based on dilution corrected and calibrated measurements.

6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? The technical descriptions are very detailed but not in such way, that it could be used to build up a system for measurement in soil columns or even in the field. One of several issues not adressed are power requirements and external conditions to work with the assembly of gas analyzers under field conditions. Neither I found suggestions for low-impact installation of the novel gas samplers or dead volume of the system.. So I have to answer with no.

Answer: We kindly disagree that the system description is not detailed in a way for others to replicate; the diagrams, component information, vendors and part numbers, and operational parameters are given with a level of detail comparable to similar reports, and we would argue with more detail in many cases. If the reviewer has suggestions for experimental details that are necessary to reproduce the system elsewhere, we will consider them. We explicitly describe how the system is used to test specific research questions in soil columns in the lab. Demonstrating a field deployment of the system is beyond the scope of this paper, but we do give specific recommendations for consideration in section 4.7 in the paper. To our knowledge, and in our prior experience publishing on ecosystem- and soil-flux measurement systems, it is not standard practice to list power requirements of sampling systems. As we do not demonstrate field sampling here, we don't list specific field instrument housing or sampling condition requirements, but these are well documented for the analyzers used here (Dual Tracer Gas Monitor, Aerodyne Research, Inc). We also see great potential to integrate lower-cost laser spectrometers and other monitors with these soil gas sampling probes, many of which already have smaller sampling volumes. Here we focus on integration with high sensitivity trace gas analyzers that allow additional compounds to be measured, which are more challenging given flow/volume demands.

We thank the reviewer for the good suggestion to provide recommendations for low-impact installation of soil probes to reduce impacts for dead volume. We can expand the “4.7. Considerations for field deployment” section by discussing that a robust material like sintered PTFE will have the potential to adapt to deployment with devices that will facilitate direct installation in the subsurface, instead of a pre-drilled hole. However, the scope of this study was to evaluate the integration of the system in a controlled environment in the lab; therefore, we placed probes in the empty columns before burying, resulting in this being a non-issue in these experiments. In future studies we will be testing different installation methods in the field.

7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution? The paper is more a technical description or even an advertisement of a specific setup but not mainly a scientific paper. It is not fully clear what is new (the use of PTFE instead of PE porous tubing?) or the use of an assembly of different laser-gas analyzers? Several literature references seem to more be an enumeration than a than a critical review.

Answer: We appreciate the author’s comments to help us improve the paper by clarifying what we consider it has been an improvement in the soil gas analysis methods. As we have seen in other BG papers, we pose specific technical scientific questions that we answer with a series of controlled experiments, for example:

a. Pirk, Norbert, Mikhail Mastepanov, Frans-Jan W. Parmentier, Magnus Lund, Patrick Crill, and Torben R. Christensen. 2016. “Calculations of Automatic Chamber Flux Measurements of Methane and Carbon Dioxide Using Short Time Series of Concentrations.” Biogeosciences 13 (4): 903–12.

b. Pape, L., Ammann, C., Nyfeler-Brunner, A., Spirig, C., Hens, K., and Meixner, F. X.: An automated dynamic chamber system for surface exchange measurement of non-reactive and reactive trace gases of grassland ecosystems, Biogeosciences, 6, 405–429, https://doi.org/10.5194/bg-6-405-2009, 2009.

We consider that the original contribution lays on the methodology evaluated and the improvements in the use of sintered PTFE material as a low reactive soil probe, in-

novation in the analyzer, precision in controlling sample transfer, and consecutive soil gas measurements from one sample with low volume demand. This work overcomes previous challenges to integrating the relatively high sample volume demand of many state-of-the-art trace gas analyzers (e.g., laser spectrometers but also online mass spectrometers) with diffusive soil probes for high resolution sampling both in space and time, instead of requiring significant compromise between the two. Therefore, the system required several modifications and changes during the evaluation process. Our approaches and elements of the system, including probe material, are not exactly the same as other systems in our literature references, and in this study we utilize trace gas instrumentation that has not previously been coupled to subsurface probes; therefore, we have not found a succinct and accessible way to compare directly with other soil gas sampling systems, as each system takes a different approach to address requirements of the analyzer and application. This resulted in the use of sintered PTFE that decreases reactivity of the material while being in contact with soil and changes in the soil environment like increase in moisture or biofouling, keeping its integrity and hydrophobicity with different matrices. Additionally, we consider this system is novel because it is the first online, realtime system quantifying subsurface soil gas N2O isotopes including site preference. The soil probes system soil has potential to be evaluated with low-cost analyzers, or to take high-precision analyzers to the field to measure a wide range of soil gases and isotopologues with a high spatiotemporal resolution. Respectfully, we consider that this is not an intercomparison paper, the strength of this paper is a sample transfer and probes approach that can be translated to other applications and a system that open the possibilities to evaluate in situ microbial activity from soils by measuring N2O isotopologues and a wide array of other trace gases including volatile organic compounds.

8. Does the title clearly reflect the contents of the paper? In principle yes.

9. Does the abstract provide a concise and complete summary? Yes, including the weaknesses of the scientific substance.

10. Is the overall presentation well-structured and clear? Too extensive, too complex, lacking structure and conciseness.

Answer: In organizing the manuscript, we took great care to structure the paper in specific, labelled sections/subsections and tables. In the resubmission, we will look for places where we can condense and clarify our presentation.

11. Is the language fluent and precise? Yes.

12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Yes

13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? For publication the whole paper should be focused, shortened and reorganized including the formulation of a clear scientific question that can be discussed based on hypotheses. I would suggest to split up the paper into a physically based sampling optimization part and another, multi component (isotopic) analysis part and possibly the process study of the process interpretation by isotopic signatures.

Answer: We appreciate the suggestions to improve the paper. We can clarify the scientific question and the hypothesis. Our objective with this paper is to show the sampling optimization, as well as the versatility of the system. Therefore, we consider that the test with soil columns and isotopic analysis shows the potential of the system to study soil trace gas dynamic. Part of the process is to demonstrate the capabilities of this system in real soil to show what possibilities are available for others to replicate and apply in different, more complex settings. We also feel it is important to demonstrate the system in real soil so it is clear that it can be deployed in natural ecosystems.

14. Are the number and quality of references appropriate? Yes.

15. Is the amount and quality of supplementary material appropriate? Some parts of the supplementary material should be used in the main text. I miss in both, the paper and the supplementary material a listing of quantification limits of the equipment.

Answer: Thanks for the suggestions, we can highlight the precision and limitations in the text of the paper instead in the supplemental material. But here, we aim to balance the reviewer's concern for brevity vs adding more content to the main text. We checked that the precision and limitations are clearly referenced in the paper (Figures S3, S4, S2.). Or if the editor considers that the paper can be improved by moving figures and tables to the main paper, and specifies which content, we will do so.

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