

## bg-2020-401 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 ( $\delta^{18}\text{O}$ ,  $\delta^{15}\text{N}$ , and the  $^{15}\text{N}$  site-preference of  $\text{N}_2\text{O}$ ), methane, carbon dioxide ( $\delta^{13}\text{C}$ ), 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  $\text{N}_2\text{O}$  pulse as consequence of an irrigation was traced. The information on the isotopic signature of the  $\text{N}_2\text{O}$  concentration in the soil allows to disentangle different production pathways for  $\text{N}_2\text{O}$ . This is a valuable information as in most cases the interpretation of the mechanisms leading to an observed  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  and  $\text{CO}_2$ ) in an additional large pore artificially introduced in the soil. These concentrations might not be representative for the most important processes that control the  $\text{N}_2\text{O}$  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.

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## bg-2020-401 Comments by Associate 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.

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.

p. 11, L. 271: Here you mention a surveillance standard of 1,000 ppm  $\text{N}_2\text{O}$ . From the following sections it can be deduced that it should read 1,000 ppb here. Please confirm.

p. 12, L. 284: Use capital delta here:  $m/\Delta m$ .

p. 15, L. 345: It is not clear why the 2196  $\text{cm}^{-1}$  region was chosen for  $\text{N}_2\text{O}$  isotopocules. There is a more suitable region between 2203-2203.4  $\text{cm}^{-1}$ , where all four  $\text{N}_2\text{O}$  isotopologue lines are found at similar transmittance values between 0.9995 (weakest =  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ ) to 0.998 (strongest =  $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ ). This would strongly reduce any issues with non-linearity (= concentration dependence). Although there is a relatively strong CO line at about 2203.16  $\text{cm}^{-1}$ , its interference at higher concentration can be reduced by removing the CO from the air stream (see Ibrahim et al., 2018, *Isotopes in Environmental and Health Studies*, 54(1), 1-15. Doi: 10.1080/10256016.2017.1345902

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.

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.

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  $> 10\text{‰}$ , making any strong statement on source processes basically impossible.

p. 29, L. 611: Also Gangi et al. (2015), mentioned in your reference list, used microporous PP tubing for soil  $\text{CO}_2$  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.

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.

Technical corrections:

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

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

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

p. 19, L. 410: Change 20C to  $20^\circ\text{C}$ .

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

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