Comments to the manuscript MS No.: soil-2018-9

Title: Application of a laser-based spectrometer for continuous insitu measurements of stable isotopes of soil CO2 in calcareous and acidic soils

Authors: Jobin Joseph et al.

A) Summary:

This methodological paper describes the use of a laser spectrometer to measure the CO_2 concentration in the soil and its C and O isotope ratios from biotic (respiration) and abiotic sources. The authors suggest a new method to capture the soil-CO_2 with gas permeable, hydrophobic tubes, which were buried in different soil depths, to distinguish the different CO_2 origins. The released soil CO_2 was measured with an Off-Axis Cavity Output Spectrometer (OA-ICOS). As the measurements were done for a concentration range between 400 and 25´000 µmol/mol the authors described their calibration method of the laser instrument, an essential task when measuring such a wide concentration range. The authors then present and interpret their first results.

B) General comments:

This is a highly relevant contribution where the authors address an important issue regarding the measurements of CO_2 and its isotopic ratio over a large concentration range. The results demonstrate the importance of a careful calibration of the instruments, given the apparent nonlinearity between concentration and isotopic ratio. The manuscript is fairly well prepared, the objectives are clear although some passages in the text need clarification (see below). Besides, there are some methodological points and questions regarding the interpretation as indicated below that must be addressed before publication.

General points:

Preparation of the calibration gases: You mixed the gases in N_2. This will cause some shifts in your absorption spectra and will result in a shift of your isotopic values as it was shown in Bowling et al. (2003). Tuzon et al., (2008) address the calibration process in detail and it is recommended to consider this paper in this study. If the possibility is still given, it might be worth it produce new reference gases with synthetic CO_2 free air (20% oxygen and 80% nitrogen) then repeat the calibration of the instrument, compare the results and reassess the results. I am aware that this is an unusual request and almost too much to ask for but it would be worth it.

How did you calibrate the gases, via gas bench-IRMS or via cryo extraction and Dual Inlet IRMS? If you used the gas bench method how did you handle the problem with the septa of the vacutainers leading to a large scatter for the $^{18}O/^{16}O$ ratio, in case you used this method?

It would be worth to **insert subtitles** in chapter 3: e.g.
3.1 Instrument calibration and correction (after Line 192)
3.2 Variation in soil CO_2 concentration and its C and O isotope values (after line 241)

Specific comments

Line 140: PTFE or Swagelok filter? Clarify

Line Lines 141-142: what kind of a filter is this to prevent moisture from getting into the device? What device do you mean? Normally moisture isn´t captured with a filter but much rather with a water trap. But usually commercially available gas is very dry making a water trap dispensable.

Lines 145-146: If you intend to produce a gas with a temperature range from minus! -20°C to +40°C a **water** bath is certainly not the right choice. Please clarify. Either you used a different cooling liquid or you never went below 0°C

Line 156: Please indicate the concentration steps for the calibration.

Line 187: How was the pressure regulated in this closed loop? For a proper operation of the laser instrument, the pressure in the cavity cell must be as constant as possible, since only slightest changes in pressure can mimic a change in concentration of all gas species.

Line 204: To prevent misunderstandings it is better to write D-δ or Diff-δ instead of $\Delta\delta$, since Δ is used for discrimination (fractionation) in the isotope literature.

Line 206: rewrite "… *The mathematical model with the most fitting to*…" write "…*the mathematical model with the best fir for* …"

Line 211: replace "… *most fitting model* …" with "… *best fit* …"

Line 221: replace "… *better*…" with " … *the needed*…"

Lines 223 – 231: A native English speaking person should reassess these lines.

Lines 226- 227: It would be more correct to say: " We assume that these ***deviations*** were instrument specific and the **fitting parameters** have to be adjusted for every single device.

Lines 243-245. I can´t see that for the top 4 to 12cm. Clarify please.

Line 246: …relative to what? Soil $\delta^{13}CO_2$ was only slightly enriched, according to Fig. 8

Lines 242-272: For this whole paragraph it would be worth to read the paper of Cerling, 1984, and Bowen, 2004 (see recommended literature).

Line 250: No specific pattern…Actually the pattern for δ^{18}O is quite similar to that of the δ^{13}C, except for this sharp decline at around 2:00, (which is less visible for the δ^{13}C time course) . The authors should comment that, what could be the cause?

Line 254: It would be highly beneficial for this statement if you had the δ values of the soil organic matter for the respective soil depths.

Line 264: It would be more accurate to say: "…*is assumed to be the dominating source of soil* CO_2…"

Lines 269-272: Are you sure that the $\delta^{18}O$ values of the soil CO_2 are referred to VSMOW? It looks more like VPDB. Please check that! Then, compared to the $\delta^{18}O$ values close to the soil surface CO_2 the $\delta^{18}O$ values in -80 cm depth are surprisingly high relative to the topsoil. Soil surface water is more prone to be enriched, due to soil surface evaporation processes, than water close to ground water. The authors should comment on that.

Lines 281-283: Here it would be valuable to have more information on the soil structure. Isn´t the acidic soil less compact and dense than the calcareous soil and therefore the diffusivity would be higher in the acidic soil. Its higher CO_2 concentration could as well be a result of a higher microbial activity due to its higher organic content. It would be interesting to see soil respiration data for these soils. Maybe the authors can comment on that

Lines 285-287: Again are these $\delta^{18}O$ values really referring to the VSMOW scale? Then somehow your calculation between the $\delta^{18}O$ of the soil water and that of the CO_2 is strange. If you add 41‰ (oxygen fractionation between water and CO_2) to -10‰ ($\delta^{18}O$ of the soil water) that would result in ca. 31‰, but you indicate -10‰. Please clarify.

Conclusion: The first 8 lines are more a summary than a conclusion. Focus on the main outcome of your study, which is the non-linear response of the δ-values versus CO_2 concentration. This is a strong demonstration for how **essential** a careful concentration vs. Isotope ratio calibration is especially when the system is used for such a wide concentration range. Then it would be interesting if your tube-soil-CO_2-capture method is reliable and highlight the advantages and disadvantages versus other methods. You practically ignored this method in the discussion. It would be interesting to know more about your experience with it. In that light what do you conclude from your first results?

Figures:

In all Figures, where you plot $\delta^{18}O$ values, check whether you used the VSMOW or VPDB scale.

Fig. 1: the expression "water bath" is misleading better to use an expression like "gas thermostat system" or something alike. Clarify whether you used PTFE (brand, type, producer etc.) or Swagelok filters.

Fig 5 and Fig 6: it would be better to use D-δ or Diff-δ instead of Δδ

Fig. 8: Indicate in the figure legend that this is a "… **Time course** of the evolution of …" with the specific time resolution.

Fig. 9: Indicate in the figure legend that you display "…**Daily? averages** of CO_2 concentration and isotope values in depth profiles…"

Literature worth reading and potentially including:

About laser spectrometer calibration and application

Bowling D. et al., (2003) Tunable diode laser absorption spectroscopy for stable isotope studies of ecosystem–atmosphere CO_2 exchange Agricultural and Forest Meteorology, 118, 1-19.

Tuzson B. et al., (2008) High precision and continuous field measurements of d^{13}C and d^{18}O in carbon dioxide with a cryogen-free QCLAS. Applied Physics B – Lasers and Optics; 92, 451–458, DOI: 10.1007/s00340-008-3085-4

Nelson D. et al., (2008) New method for isotopic ratio measurements of atmospheric carbon dioxide using a 4.3 µm pulsed quantum cascade laser Applied; Physics B – Lasers and Optics, 90, 301–309 (2008); DOI: 10.1007/s00340-007-2894-1

Sturm et al., (2012) Eddy covariance measurements of CO_2 isotopologues with a quantum cascade laser absorption spectrometer. Agricultural and Forest Meteorology 152, 73–82.

Wehr R., S.R. Saleska (2015) An improved isotopic method for partitioning net ecosystem–atmosphere CO_2 exchange. Agricultural and Forest Meteorology 214-215 (2015) 515–531.

Wehr R. et al., (2016) Seasonality of temperate forest photosynthesis and daytime respiration. NATURE | VOL 534 | 30 jUNE 2016

About isotopes in soil CO2

Kato et al., (2004) Seasonal variation of the oxygen isotopic ratio of atmospheric carbon dioxide in a temperate forest, Japan. GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 18, GB2020, doi:10.1029/2003GB002173

Cerling TE (1984) The stable isotopic composition of modern soil carbonate and its relationship to climate. Earth and Planetary Science Letters, 71 (1984) 229-240

Bowen G. (2004) An integrated model for soil organic carbon and CO_2: Implications for paleosol carbonate pCO_2 paleobarometry. GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 18, GB1026, doi:10.1029/2003GB002117