

Reviewer 2# Remarks to the Author

1. **Preparation of the calibration gases:** You mixed the gases in N₂. 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 CO₂ 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.

Response: As per the suggestions made by both of the referees, we have conducted another round of calibration by diluting the CO₂ gas using synthetic air (20% oxygen and 80% nitrogen) instead of N₂. Diluting the CO₂ standard gas with N₂ resulted in a standard deviation of 8.1(‰) for $\delta^{13}\text{C}$ values and 4.7 (‰) for $\delta^{18}\text{O}$ values respectively. Diluting CO₂ standard gases with synthetic air resulted in a standard deviation of 6.44(‰) and 6.818(‰) for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ respectively (see Fig.1a-b). With our new calibration curves (see Fig.1 c-d, &Table.1,2), we are able to bring down standard deviation to 0.08(‰) for $\delta^{13}\text{C}$ and 0.04(‰) for $\delta^{18}\text{O}$ (see Fig.2a-b (residual distribution), Fig.3a-d (Corrected $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values)). We will restructure and include new calibration system in the revised version of the manuscript.

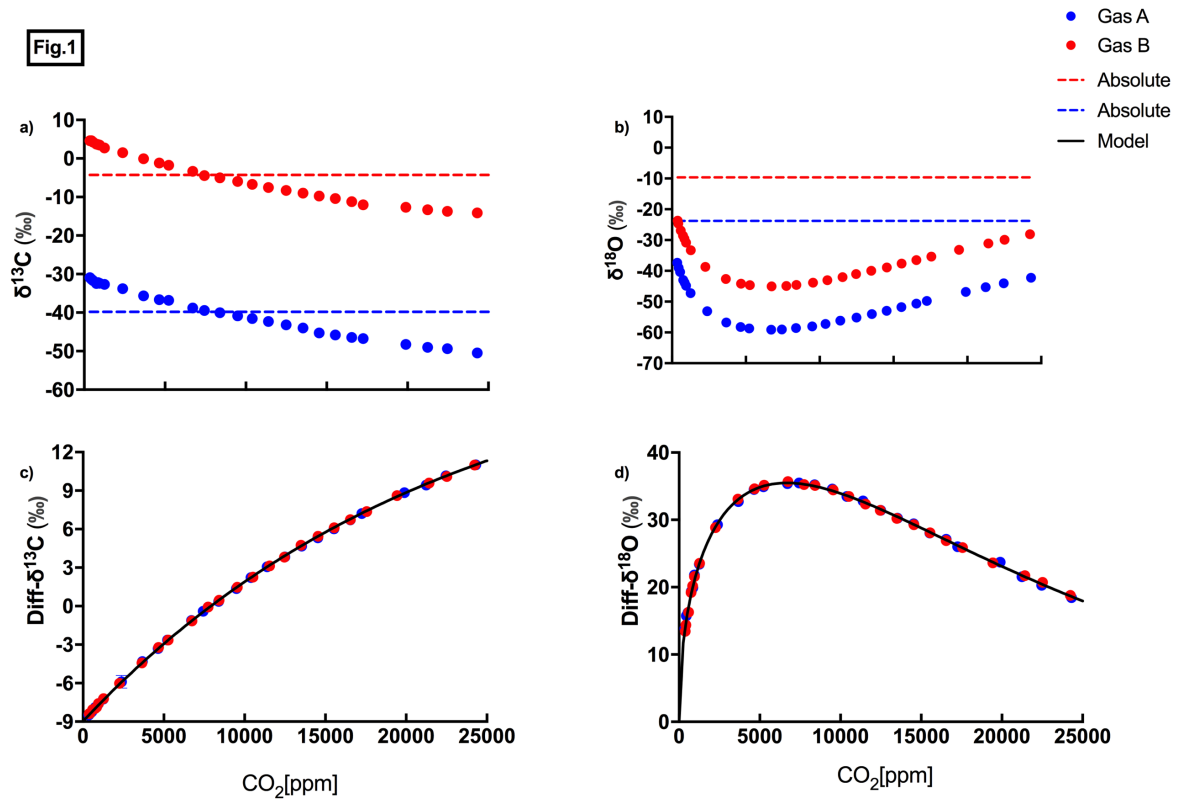


Figure.1: Measured $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 compared to the target values (a,b) when diluted using synthetic air. (c-d) shows the differences from the target values (diff- $\delta^{13}\text{C}$, diff- $\delta^{18}\text{O}$) across a concentration gradient. Red and Blue dots show measured $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ values of two different gases with distinct isotopic signatures, red and blue dashed lines represent the $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ target values of the respective gases calibrated independently by isotope ratio mass spectrometry. Black line denotes model fit for diff- $\delta^{13}\text{C}$, diff- $\delta^{18}\text{O}$ values across changing CO_2 concentration (300 – 25000 ppm).

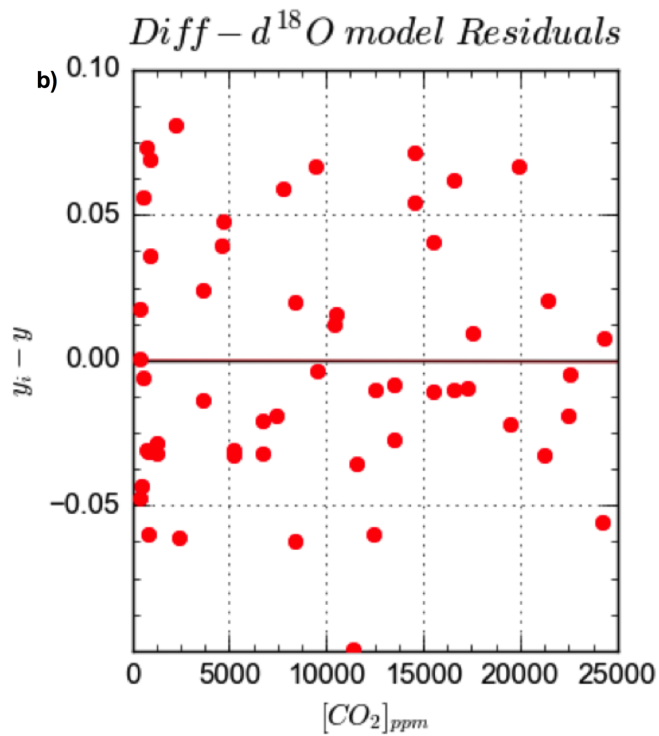
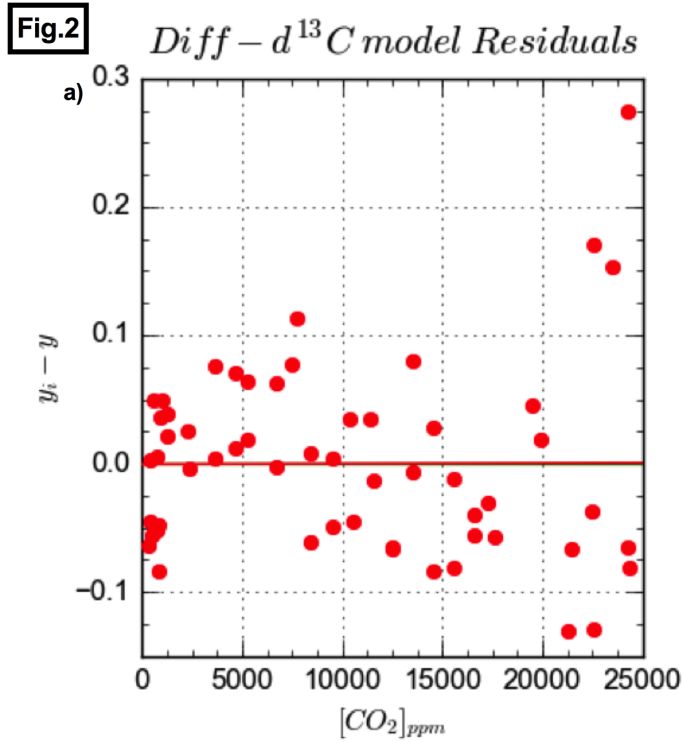


Figure 2: Residual distribution of modeled data for the differences in $d^{18}O$ between measured and target values (diff- $\delta^{13}C$, diff- $\delta^{18}O$) values across changing CO_2 concentration (300 – 25000 ppm).

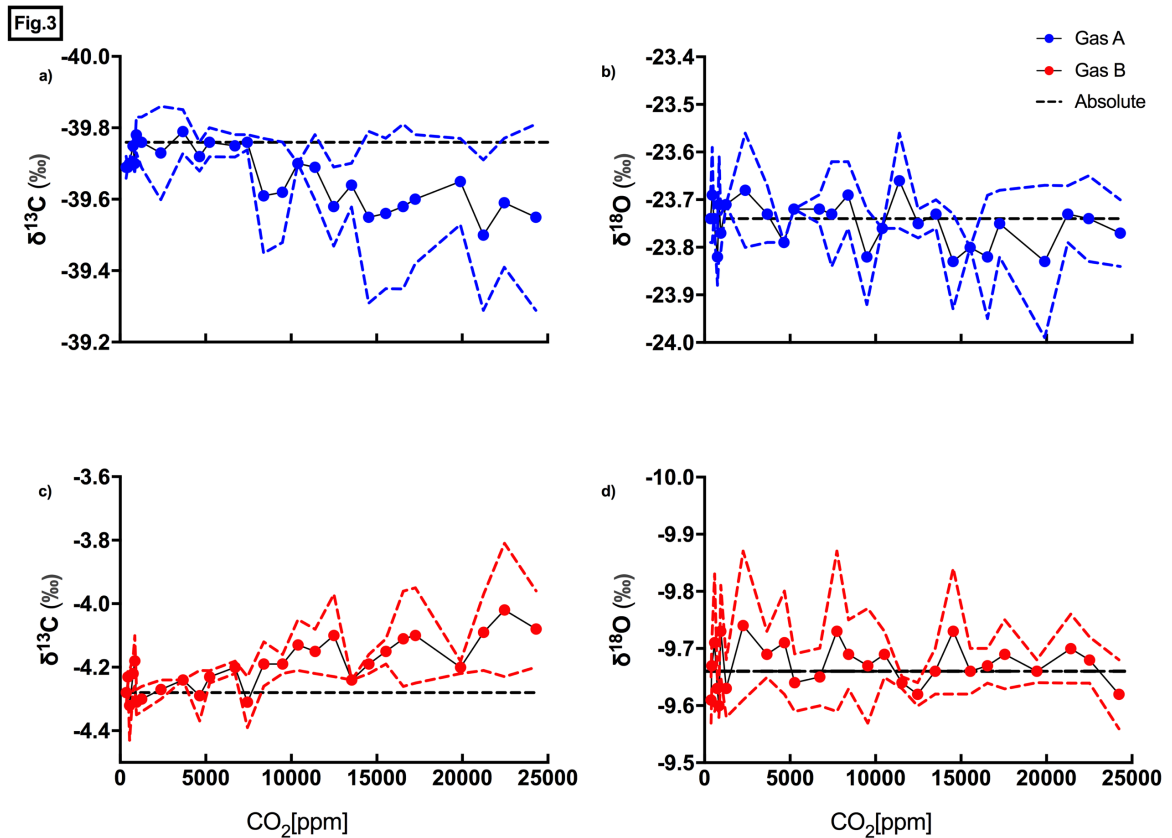


Figure 3: Corrected $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ values of two different standard gases measured after correcting for concentration dependent drift. The dashed lines indicated the target $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ target values calibrated independently by isotope ratio mass spectrometry.

2. 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 vactainers leading to a large scatter for the 18O/16O ratio, in case you used this method?

Response: The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of our inhouse calibration gas standards were measured via cryo extraction and Dual Inlet IRMS. This will be included in a revised version of the manuscript.

3. 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 CO₂ concentration and its C and O isotope values (after line 241)

Response: Subtitles will be added in the modified manuscript.

Specific comments

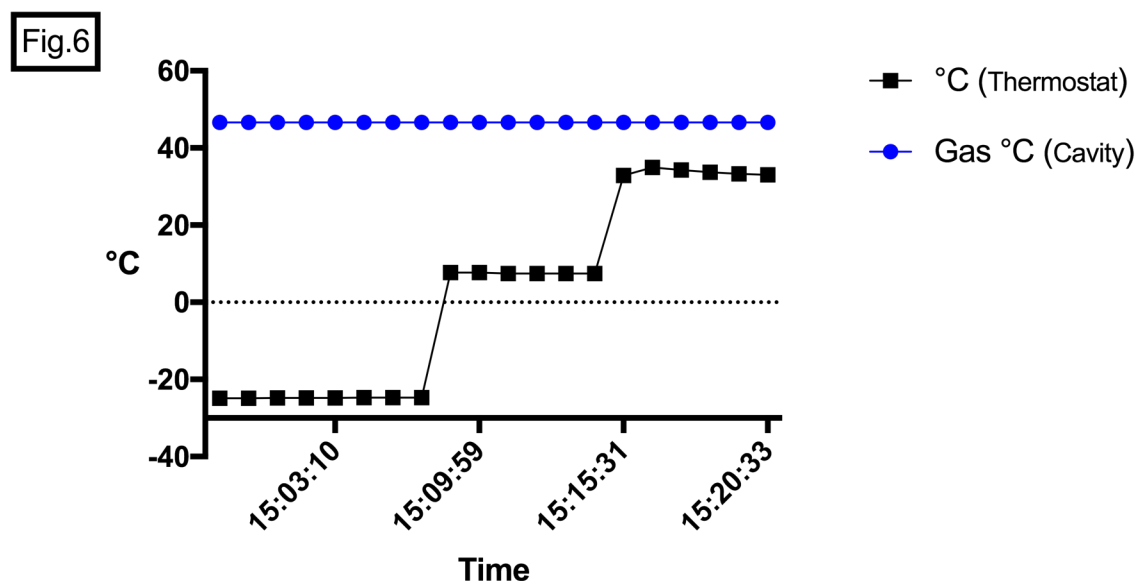
4. Line 140: PTFE or Swagelok filter? Clarify

Response: Swagelok filter (Stainless Steel In-Line Particulate Filter, 6 mm Swagelok Tube Fitting, 15 Micron Pore Size); this information will be added to the revised version.

5. 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.

Response: The filter is a particulate matter filter and not a moisture filter. It can hold very little amount of liquid water and not water vapor. This will be rectified in the revised manuscript.

6. 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.



Response: The reviewer is right, it needs further clarification. We have used a water bath to increase the temperature to higher values than the room temperature. To reduce the temperature below, we immersed gas tubes in liquid Nitrogen kept in an isotherm flask. This information will be included in the revised manuscript.

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

Response: We have used 27 concentration points across the range (300-25000 ppm). For more details see table.3.

Table.3

CO2 ppm	d13C	Stdev data
350.93	-31.28	0.04
453.32	-31.42	0.07
543.73	-31.54	0.07
755.35	-31.87	0.03
852.19	-31.94	0.03
951.99	-32.15	0.03
1257.59	-32.52	0.07
2377.12	-33.86	0.10
3670.33	-35.44	0.03
4651.48	-36.46	0.00
5230.98	-37.13	0.04
6718.14	-38.65	0.02
7441.17	-39.37	0.02
8396.27	-40.13	0.00
9491.37	-41.13	0.00
10390.11	-41.99	0.05
11402.32	-42.83	0.01
12488.75	-43.59	0.07
13531.13	-44.44	0.06
14532.92	-45.09	0.03
15534.13	-45.79	0.01
16547.02	-46.49	0.05
17255.32	-46.97	0.03
19893.50	-48.60	0.01
21237.86	-49.19	0.04
22462.06	-49.92	0.01
24313.08	-50.78	0.05

8. 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.

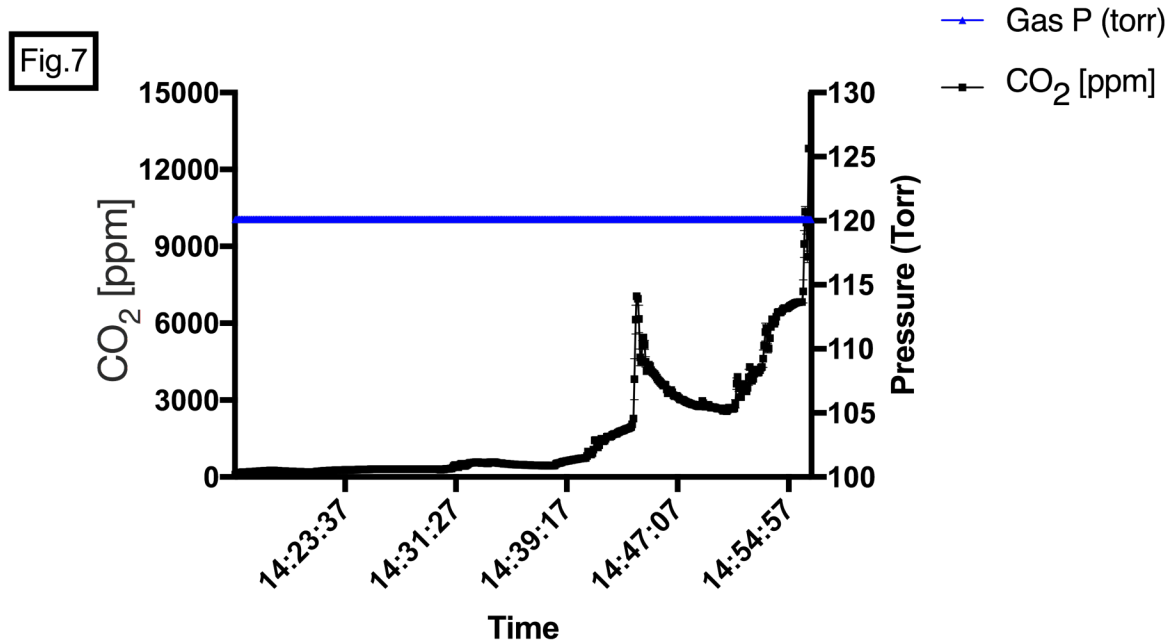


Figure.7: The figure shows pressure inside the optical cavity (blue line) plotted on right y axis and change in CO₂ concentration (black lines) plotted on left y axis. Data was taken while the system is running in a closed loop system with periodic injections of CO₂ gas.

Response: We did not encounter any pressure differences while maintaining a closed loop system. We have cavity pressure data monitored (see Figure.7). We will include this information in the revised version of the manuscript.

9. 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.

Response: We agree with the reviewer. It will be changed in the revised manuscript.

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

Response: Corrected in the revised manuscript.

11. Line 211: replace "... most fitting model ..." with "... best fit ..."

Response: Corrected in the revised manuscript.

12. Line 221: replace “... better...” with “... the needed...”

Response: Corrected in the revised manuscript.

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

Response: We will restructure the sentences in the revised manuscript and let a native speaker do the final language editing.

14. 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.

Response: Corrected in the revised manuscript.

15. Lines 243-245. I can't see that for the top 4 to 12cm. Clarify please.

Response: Yes, for the calcareous soil there was no increase in CO₂ concentration between 4 and 12 cm which is also related to the relative ¹³C depletion in 4 cm compared to 12 cm – both is assumed to be due to mixing in of atmospheric air (having lower CO₂ concentrations and a δ¹³C of approx. -8). We will clarify that in the revised version of the manuscript.

16. Line 246: ...relative to what? Soil δ¹³C_{CO₂} was only slightly enriched, according to Fig.

8

Response: The δ¹³C signal of soil CO₂ at 4 cm depth is enriched compared to the one sampled from 8cm depth and this is visible in Figure.9. We see a constant depletion in ¹³C of soil CO₂ from 80 to 8 cm soil depth – the 4 cm depth does not fit into that trend as we here see compared to 8 cm a slight enrichment.

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

Response: The whole paragraph will be modified by including relevant information from Cerling, 1984, and Bowen, 2004.

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

Response: It seems like there was a pressure dip during the specific time window. It occurred due to a short time technical issue rather than any biological process. It can be that the internal pump was not drawing enough gas into the optical cavity there by creating an under pressure in the cavity which then resulted in aberrant values.

19. 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.

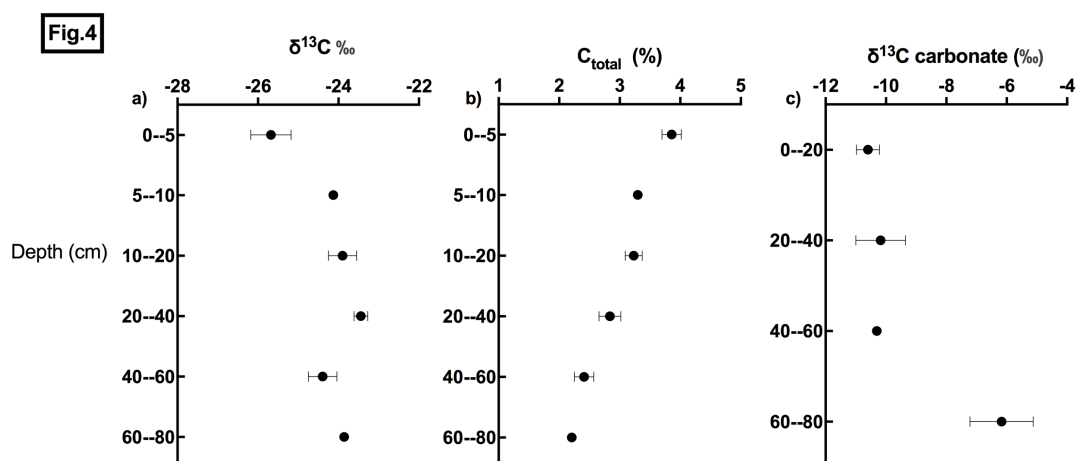


Figure.4: Bulk $\delta^{13}\text{C}$ (a), bicarbonate $\delta^{13}\text{C}$ (c) and % of total carbon (b) in soil across a depth profile of (0-80 cm).

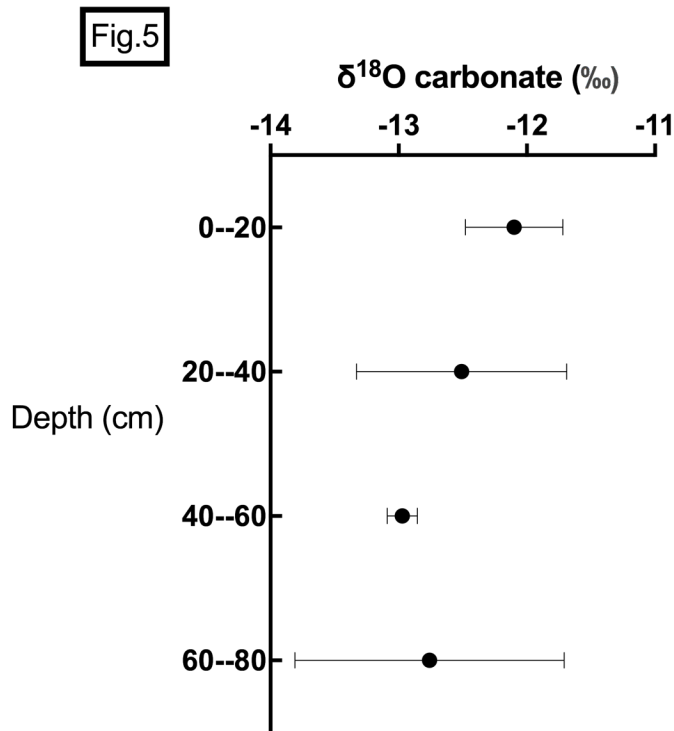


Figure.5: bicarbonate $\delta^{18}\text{O}$ in soil across a depth profile of (0-80 cm).

Response: We have measured soil samples for bulk $\delta^{13}\text{C}$, bicarbonate $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ values and also % of total carbon in the soil across a depth profile of (0-80 cm) for the calcareous soil (See Fig.4a-c and Fig.5). We observed a slight increase in $\delta^{13}\text{C}$ values for bulk soil in deeper soil layers (See Fig.4 a,c). Moreover, also the carbonate $\delta^{13}\text{C}$ gets more positive in the 60-80 cm layer. Since total organic carbon content decreases with depth it can be assumed that CO_2 derived from carbonate weathering having less negative $\delta^{13}\text{C}$ more strongly contributed to the soil CO_2 in this depths (especially since we see an increase in soil CO_2 concentration with depth). This is accordance with the laser-based measurements which shows a strong increase in $\delta^{13}\text{C}$ of soil CO_2 in the deepest soil layer leading us to the hypothesis that this signal is indicating carbonate derived CO_2 .

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

Response: Corrected in the revised manuscript.

21. Lines 269-272: Are you sure that the $\delta^{18}\text{O}$ values of the soil CO_2 are referred to VSMOW? It looks more like VPDB. Please check that! Then, compared to the $\delta^{18}\text{O}$

values close to the soil surface CO₂ the $\delta^{18}\text{O}$ 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.

Response: $\delta^{18}\text{O}$ values are reported against VPDB and not VSMOW. We will clarify that in the revised manuscript. When we assume that in 80 cm soil depth a relatively large part of the CO₂ derives from carbonate this could explain the strongly enriched ^{18}O signal. We, however, need then to assume that the oxygen in the CO₂ is not in full equilibrium with the precipitation influenced soil water. As mainly microbial carbonic anhydrase mediates the fast equilibrium between CO₂ and water in the soil and the microbial activity is low in deeper soil layers (e.g. Schmidt MWI, Torn MS, Abiven S, et al. Persistence of soil organic matter as an ecosystem property. *Nature*. 2011;478(7367):49-56. doi:10.1038/nature10386.) we can speculate that in deep layers with a significant production of carbonate derived CO₂ a lack of full equilibration might be the reason for the observed $\delta^{18}\text{O}$ values..

22. 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 CO₂ 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

Response: Calcareous soil sampled from our study site was gravel rich and less compact. while the acidic soil was more fine, homogeneous and compact. It is sound to consider gas diffusivity in calcareous soil (in our study site) higher in comparison to the acidic soil.

It is highly likely that it is due to an increased microbial activity in the acidic soil. We have soil respiration data for the acidic but not for the calcareous soil so we cannot make a comparison.

23. Lines 285-287: Again, are these $\delta^{18}\text{O}$ values really referring to the VSMOW scale? Then somehow your calculation between the $\delta^{18}\text{O}$ of the soil water and that of the CO₂ is strange. If you add 41‰ (oxygen fractionation between water and CO₂) to -

10‰ ($\delta^{18}\text{O}$ of the soil water) that would result in ca. 31‰, but you indicate -10‰. Please clarify.

Response: $\delta^{18}\text{O}$ values are reported against VPDB and not VSMOW. Will be corrected in the revised manuscript.

24. 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?

Response: We agree with the reviewer regarding the fact that the calibration procedure is not well discussed and needs to shed more light into it. We will certainly consider this suggestion and modify the discussion and conclusion parts by including more details and knowledge gained from calibrating the Laser spectrometer in the revised manuscript.

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

Response: Yes, we will check and correctly indicate the reference in a revised manuscript.

26. 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.

Response: “This correction will be made in a revised manuscript. And we used Swagelok filter (Stainless Steel In-Line Particulate Filter, 6 mm Swagelok Tube Fitting, 15 Micron Pore Size)

27. Fig 5 and Fig 6: it would be better to use D- δ or Diff- δ instead of $\Delta\delta$

Response: Diff- δ will be used instead of $\Delta\delta$ in the revised manuscript.

28. Fig. 8: Indicate in the figure legend that this is a “... Time course of the evolution of ...” with the specific time resolution.

Response: Will be included in a revised manuscript.

29. Fig. 9: Indicate in the figure legend that you display “...Daily? averages of CO2 concentration and isotope values in depth profiles...”

Response: The data displayed is an average of measurements taken over 4-hour time period. Will be corrected in the revised manuscript.

Table.1

Equation	$y=a*(b-\exp(-c*x))$				
Standard Error	0.07468171				
Correlation Coeff.(r)	0.999941				
Coeff.of Determination (r^2)	0.99988246				
DOF	54				
AICC	-294.6349				
Parameters					
Value	Std	Err	Range	(95%	confidence)
a	31.007446	0.214984	30.576428	to	31.438463
b	0.713759	0.002376	0.708995	to	0.718522
c	0.000043	0	0.000042	to	0.000043
Covariance Matrix					
	a	b	c		
a	8.286768	0.088333	-0.000018		
b	0.088333	0.001012	0		
c	-0.000018	0	0		

Table.2

Equation	$y=a*(b^x)*(x^c)$				
Standard Error	0.04365503				
Correlation Coeff.(r)	0.999981				
Coeff.of Determination (r^2)	0.99996128				
DOF	51				
AICC	-337.04644				
Parameters					
	Value	StdErr	Err	Range (95% confidence)	
a	0.851623	0.003025	0.84555	to	0.857697
b	0.999928	0	0.999928	to	0.999928
c	0.477819	0.000472	0.476871	to	0.478767
Covariance Matrix					
	a	b	c		
a	0.004803	0	0.000745	-	
b	0	0	0		
c	-0.000745	0	0.000117		