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Interactive comment on "Application of a laser-based spectrometer for continuous insitu measurements of stable isotopes of soil CO_2 in calcareous and acidic soils" *by* Jobin Joseph et al.

Anonymous Referee #1

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This manuscript describes attempts to calibrate a laser-based absorption instrument for use in high-frequency measurements of 13C and 18O of CO2 in soil depth profiles, and provides very brief field data from two sites. This type of work is useful in that many investigators use new instruments, such as the LGR instrument described here, without sufficient validation. However, I have some major concerns about the calibration method which the authors can hopefully address in a revised manuscript. In addition, the paper would be much stronger if additional field data were presented, especially along with atmospheric measurements at the soil surface, which are needed to calculate the isotope composition of soil respired CO2 (as opposed to soil profile CO2). At present, it appears that <24 hours of field data are shown.

The authors develop non-linear calibration functions to account for the concentration dependence of isotope ratios but it is not clear to me how these functions might also vary in isotope space (i.e., as a dual function of isotope composition and concentration). For example, fig. 5 shows the correction functions for concentration dependence but does not show how/if these varied as a function of the isotope ratios of the standard gasses, which should all be shown on this figure. Furthermore, Fig 6 and 7 show serious deviations of calibrated vs. true values for both 13C and 18O between circa 2000 – 10000 ppm, of as much as 2 permil, even though those differences disappear at higher values. This deviation is unacceptable given the requirements of analyzing soil CO2, where differences of 2 permil may be highly significant from an ecological perspective. I note that CO2 concentrations < 10,000 ppm are commonplace in most soil profiles, especially in shallow horizons that typically dominate CO2 production, such that capacity for accurate and precise measurements in this lower concentration range is really critical. Even greater variability is shown in Fig 7, which appears to reach 4 per mil. This is not acceptable for natural abundance work.

I am skeptical as to the utility of the exponential calibration function given the unusual trends shown in Fig 4 that do not conform to an exponential curve (residual plots would clearly show violation). A spline fit may be needed and would likely avoid some of the problems mentioned above if it can be shown that the concentration response does not interact with the isotope ratio of the sample gas. Note the analogy from IRMS calibration, where separate calibration functions are typically used to correct for beam area effects and to normalize isotope ratios to the reference materials. A simple offset is very seldom sufficient for adequate calibration. In Fig 7, we need to see how deviations from the 1:1 line vary as a function of isotope composition (what is driving the very large scatter for some observations?). This is another hint that isotope composition and CO2 mole fraction are interacting, implying that more complex calibration functions may be needed (maybe these were used and I am not understanding the method?). Also, it appears that independent standard gasses were not withheld to verify precision independently (i.e., standards that were not used to generate cal curves).

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If this is not the case that should be clarified, and ideally at least one standard would be withheld for validation.

Diluting standard gasses with N2 is not good practice for calibrating measurements of CO2 in air samples due to the phenomenon of pressure broadening. The absence of O2 fundamentally changes the absorption properties of CO2 in an N2 matrix. There is abundant literature on this point, and it becomes especially important for isotope measurements.

Also, basic details about the soils investigated are missing that are necessary to interpret the measured values of 13C and 18O of CO2. For example, what are the carbonate concentrations and isotope ratios in the calcareous soil, and how do they vary with depth? What are the 13C values of SOM? This is a prerequisite for interpreting the soil profile CO2 values. Also, to calculate the isotope ratios of soil-respired CO2, we need measurements of the atmospheric boundary condition. See Davidson 1995 GCA, doi:10.1016/0016-7037(95)00143-3. Note that several recent papers neglected have reported 13C of CO2 from soil profiles using high temporal-resolution optical measurements, these should be discussed or at least mentioned.

I am skeptical as to the validity of the temperature tests employed. Note that we need to know the temperature of the analyte gas itself, which may be substantially different than the temperature of the water bath through which it circulates unless the residence time of the gas in the tubing and the heat transfer properties of the tubing allow for sufficiently rapid temperature equilibration, which may not completely occur if flow rates are high. For example, certain applications require heating of gasses at a sampling inlet to avoid condensation, yet the temperature of the gas at the point of the analysis may be substantially different (e.g. -4 – 40C) for some other optical gas analyzers, and should optimally be controlled within the analyzer cavity itself. Thus, unless the exact temperature of the gas at the point of measurement can be determined, I would not trust the results from the water bath experiment. Regardless, details of the analysis flow rate should be reported (and whether these rates were controlled during sample

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analysesâĂŤMFC’s are mentioned for standards only).

There are numerous issues with grammar, style, and errant capitalization throughout. The figures and tables have a strange mix of fonts (be consistent!) and the legends are compressed. Please follow standard procedures for presenting your MS (provide captions as text in the document, not as images). There is a significant typo in Table 1.

Finally, it should be noted that the useful temporal resolution of the measurements will never actually be 1hz as reported given the Allan variance results.

Was water vapor removed from the analyte gas, and if so, how?

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