

Interactive comment on “A new instrument for stable isotope measurements of ^{13}C and ^{18}O in CO_2 – Instrument performance and ecological application of the Delta Ray IRIS analyzer” by Jelka Braden-Behrens et al.

Anonymous Referee #2

Received and published: 27 June 2017

This paper describes the testing and use of the new Delta Ray IRIS CO_2 isotope spectrometer during a three-month field campaign. I have serious concerns about the analytical details, as well as the conclusions regarding interpretations of the field measurements. Overall, I am not convinced that this instrument has been put through the necessary rigorous tests.

The authors conclude in the abstract that “1) the new Delta Ray IRIS with its internal calibration procedure provides an opportunity to precisely and accurately measure $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ at field sites” I am concerned with this statement, because the internal

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calibration procedure in the IRIS is never actually described. How are the absorption spectra used to calculate isotope ratios, and how are these modified based on the calibration? This point appears critical for understanding whether the internal procedure is adequate and/or necessary, or for understanding what other post-hoc calibrations may be needed. This is a critical gap in the paper. One cannot simply assume that the manufacturers of the instrument have worked out the details here. There are instruments that are sold that do not necessarily function as advertised, thus it is necessary to validate every step of the way. I would like to see plots and regressions of raw vs. known values for both $\delta^{13}\text{C}$ and $[\text{CO}_2]$ for a number of different standards spanning a broad range of delta values and mole fractions of CO_2 .

The authors mention that they used a post-hoc CO_2 concentration calibration, but it is unclear how often the additional standards used for this were measured (once? Half-hourly?) in relation to their check standard. Note that quadratic relationships may give a better fit as employed elsewhere for other absorption-based CO_2 instruments. Given that this is a methods paper, it would have been very useful to see tests using a broader range of CO_2 mole fraction and isotope compositions in the range of standards, and to see more standards tested. Without this, we cannot validate the linearity of the instrument both in concentration and isotope space. This is a critical deficit of the paper.

Why was the need for a post-hoc $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ calibration not tested or described? Note that many of the other laser-based isotope instruments achieve much higher precision with frequent (e.g. 20 minute) isotope calibrations in the field. This need appears especially critical here given the large (~ 1 per mil) jumps in $\delta^{13}\text{C}$ values observed in the check standards shown in Figure 4. This suggests that there are some serious stability problems that need to be addressed with more frequent isotope calibration. With respect to the second major conclusion of the abstract, “2) even short snow or frost events could have strong effects on the isotopic composition of CO_2 exchange at ecosystem scale” this finding is not new, but also not very well supported by the data

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(e.g. Figs 7 and 8. There are now several multi-year datasets of canopy CO₂ and $\delta^{13}\text{C}$ profiles in temperate ecosystems that have shown similar patterns.

With respect to the Keeling plot intercepts, no data is shown to actually validate the approach (e.g. plots of $\delta^{13}\text{C}$ and $1/\text{CO}_2$ space), nor summary statistics presented for these regressions. This is another serious deficit given the key methodological issues the authors point out in the Appendix, but do not quantify in the text. I don't think the authors present enough information here to rigorously test the hypotheses proposed in the Results/Discussion section. The value of the CANVEG modeling exercise for the overall study was not terribly apparent to me, nor were the questions that it sought to address.

More specific comments: Introduction: there is much excessive detail here that repeats recent reviews, such as the Griffis 2013 paper. Please condense. P1 18: the main constraint is low temporal resolution P4 13: how are these "physically different" air samples if the pump is flowing continuously? P8 5: "A possible reason for this resulting deviation is the range of the gas tanks we used for the instrument-internal concentration calibration, that was approximately 300 to 430 ppm" this logic doesn't make sense to me—this is similar to your other standards P8 6: I am having trouble understanding how your "target standard" could be stable without posthoc calibration yet your five other standards were so variable. P8 9: "Secondly we set the IRIS analyzer's internal referencing procedure (described in Sect. 2.7) to 1800 s which corresponds to an Allan variance of 0.03 ‰ for both δ values and 0.01 ppm for CO₂ concentration." This is unclear to me—are you measuring the standards every 1800 s? For how long? Where are these new Allan variance values coming from? Figure 4: There are apparently large (1 per mil) jumps in measured "target gas" isotope values at several points—these are disconcerting. Are the data shown in this figure the raw values or the calibrated values? If they are the calibrated values, this suggests that the two-point calibration employed here is inadequate

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Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-120, 2017.

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