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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long-term field performance of a tunable diode laser absorption spectrometer for analysis of carbon isotopes of CO_2 in forest air" *by* S. M. Schaeffer et al.

S. M. Schaeffer et al.

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Response to Anonymous Referee #1

We thank the referee for helpful comments on the manuscript.

This paper describes an extensive and very carefully managed and calibrated dataset of long-term (2.4 year) measurements of CO2 concentrations and 13C-in-CO2 fractionation in a forest ecosystem in Colorado. It is a very valuable study insofar as it clearly demonstrates the practicality and limitations of long term continuous 13C field measurements using optical techniques - in this case a mid infrared tunable diode laser system. Continuous field measurements of carbon isotopic fractionations have great potential value in many applications, but are not generally practical using the conven-

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tional isotope ratio mass spectrometery techniques. The value of the study comes mainly from the attention to calibration, accuracy and stability of the measurements - there is by contrast only minor coverage of the scientific interpretation of the resultant dataset. This is and presumably will be covered in more detail elsewhere; the paper is already very long and detailed in discussing the measurement methods. In general the standard of language, editorial quality and presentation is excellent. I recommend strongly for its publication subject to the technical revisions and suggestions listed below.

We are working on several continuing analyses regarding scientific interpretation – the current paper is primarily focused on the instrumentation.

P9534, L16: FTIR is not a laser technique: replace "Of the mid-IR laser absorption spectroscopy techniques..." with "Of the mid-IR optical absorption spectroscopy techniques..." (This definition would also cover cavity ringdown methods.)

Changed as suggested.

P9535, L12; "phenomena" not "phenomenon"

Changed as suggested.

P9536, L8: masl is not defined. It is also used as m.a.s.l. later in the paper (P9542, L6). Define on first use and make consistent.

Changed as suggested.

P9536, L21; replace "absorbance" with "absorption". Absorbance is a specific quantity, log(Io/I), and not what is meant here. There are several other instances throughout - search and replace.

Changed as suggested.

P9537, L12: The tubing is actually 1/4 inch. While metrifying the US is to be strongly encouraged, 0.64 cm is actually less accurate than 1/4". Similary line 24, 1/8".

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No change made here. Inches are not SI base units.

P95430, Eq 1. Dimensionally incorrect; as written the x 1000 should be removed, or per mil symbol added. Correct usage is either to add both x 1000 per mil or (now preferred) neither. See IUPAC "Green book" for correct usage.

We’ve added the per mil symbol as requested. Leaving out the 1000 factor is terribly confusing for people that are new to the terminology.

P9541, L15: is the pressure of 300kPa absolute or gauge (ie above atmospheric)?

Absolute, we added this to the text.

P9542, L6: Is this the NOAA Niwot Ridge site? - if so, say so.

We added “or Niwot Ridge” following NWR – NOAA formally calls this site NWR, most people call it Niwot Ridge. Certainly it’s helpful to point that out.

P9543-9544: Statistical analysis - I have a number of comments and concerns: L14: The best way to assess the improvement in a measurement with time-averaging (and deciding what is the optimum time) is to calculate Allen Variance. Can this be added?

We addressed Allen variance in an earlier paper. We added this sentence to be clear “Optimal averaging time for this instrument based on Allen variance is 25-30 s (Bowling et al., 2003), however our selection of inlet heights and flow rates and associated plumbing transients practically limits time averaging to 20 s maximum.”

L19: Discarding all values more than one standard deviation from the mean of 10 is much too strict - in a normal distribution this would reject 33% of all valid measurements, could lead to bias in the calculated mean, and underestimates the true scatter/precision of the measurements. What is the justification for this rejection criterion? I would think 2 or 3 standard deviations would be more appropriate, since this would identify true outliers.

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One could certainly choose other ways to do this, such as selecting 2 or 3 standard deviations. Our justification is that it improved instrument performance. The plumbing scheme was designed to provide an unchanging gas environment during the averaging period. The instrument performance can be spiky (beyond standard white noise) even when the actual mole fractions of the gases are unchanging. The spikes are removed with this scheme. We tried a variety of ways to do this, and settled on the one described in detail in the paper. Our approach does not actually reject any measurements (averages) at this point, – but it does affect the final measured value. Additional QA steps follow for data rejection as described in the text.

L26: Taking the mean and standard deviation of the "histograms" in Fig 2a and elsewhere is not really valid, as they are demonstrably not normal distributions. Quoting most likely value and range or 90% cumulative limits would be more appropriate. See also P9544, L16.

Mean, standard deviation, and higher order moments (skewness, kurtosis, etc.) are useful metrics for all distributions, not just normal distributions. In fact, comparison of these moments is a common way to show the differences in the distributions.

Eq. 2: Should the denominator here be (n-2) since 2 degrees of freedom are used up in the linear regression? Since n=4, this will significantly affect the calculated RMS error.

Perhaps – however, this would simply scale all the RMS error calculations together by a constant multiplier. As discussed, we use the RMS error only as a metric for poor performance, and making this change would not influence data rejection.

P9544,L18-27. Here the rejection of "true" outliers is more correct. After the heavy filtering of L19 above, it isn’t clear to me how any outliers remain at all!

The “heavy filtering” merely removes spiky instrument performance in a subset of a 10-s period. It does not catch other problems, which clearly remain in the

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data set (Figure 2). Hence more QA/QC is needed.

P9545. L13-14: "The mean difference between ..."

Changed as suggested.

P9547, L1: "offsets" would be better described as "drifts", since these data seems to imply a slow drift (changing offset) over time. Is this assumed to be linear in time?

We changed this to “systematic offsets or drifts”. We make no assumptions about linearity, we have not used these measurements to adjust our final values, only to report on the possibility of problems as interpreted from our measurements.

P9547, L15: "greater" is ambiguous, does it mean a larger (lower precision) or smaller (higher precision) number?

Good point – we changed this to “worse”.

P9547, L20: See above - I believe the sigma(10) provides an unrealistically low value for the precision because of the 1-sigma rejection criterion.

Agreed – if one questions the validity of the calculation of sigma, then one should also question the validity of our estimates based on precision that follow. However, we are very explicit about the way we have arrived at this estimate of precision. Other groups have reported very high precision for the Campbell TDL, and we don’t feel the instrument performs as well as these studies indicate (the relevant papers are pointed out in the text). We prefer to let our work stand on the openness and detail that we have provided, and let people decide for themselves what is most appropriate.

P9548. L15: One obvious possible cause for the flask/laser disagreements is that they are sampled over different times, and if the signal is changing in time, disagreement is to be expected. This is not mentioned until later (P9549) and presented as a "surprise effect", but it could have been predicted in advance. It would be good to mention this

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effect here.

The discussion of this possible cause (P9549) comes only 15 lines later in the text, so we left it as is.

P9548, L24: -6.5per mil at night - no data at this value to be seen on Fig 4b.

No idea where that came from – must have been an earlier version with different figures. The text was changed to “Observed PFP flask values for δ13C ranged from -9.6 to -8.0 ‰ during the day and from -10.2 to -8.0 ‰ at night”.

P9549, L5: "Histogram plots" Fig 4c and 4d are true histograms, but Fig 2a and 2b are also referred to as "histograms" but plotted as continuous distributions. These should be made consistent. Also Fig 3.

Actually these (Figures 2, 3, and 4) are all histograms (frequency distributions), except for 2c and 2d which are cumulative distributions. There is a very large amount of data on these plots, and the bins are narrow. Figure 4 is plotted in bar form and the others are not (perhaps this is the reviewer’s point?). We have changed the use of “histogram” to “frequency distribution” throughout.

P9551, L10 etc. I recognize that data interpretation is not the main point of this paper, but an example of a Keeling-type plot would be very useful here as an illustration of the power and precision of the continuous measurements. This is something every isotopically-aware reader can relate to.

Figures 5 and 6 were added to provide material that most readers can relate to (even those that are not isotopically aware). There are dozens of papers (many cited in the text, including Bowling et al. 2005 and Schaeffer et al. 2008 from this same forest) that show Keeling plots and how they are useful.

Figures: generally as presented are quite small and hard to read. Should be enlarged for publication.

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We are happy to work with the publishing staff on this.

Fig. 2: See earlier commentsa on formatting of histograms - use convetional column/ bar format. Dashed line in (c) and (d) cannot be seen in my PDF. Fig 3: dashed lines not visible. Fig 4: Adding labels for the time periods (March-April, Aug-Sept, etc) beside each frame of the plot would be helpful for readability, there is plenty of space

We tried this, but the bar form of the histograms is hard to read on Figure 2. The dashed lines in 2c and 2d are apparent in the discussion paper we viewed on the web, but we’ll keep an eye out on the proofs. The time periods are clearly labeled in the caption of figure 6 (I suspect the referee means figure 6 and not figure 4).

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9531, 2008.

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