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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.

Anonymous Referee #1

Received and published: 16 July 2008

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 conventional 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

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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.

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.)

P9535, L12; "phenomena" not "phenomenon"

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.

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.

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".

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.

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

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

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?

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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.

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.

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.

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!

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

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?

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

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

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.

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

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.

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

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

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