

Interactive comment on “Evaluating calibration strategies for isotope ratio infrared spectroscopy for atmospheric $^{13}\text{CO}_2/^{12}\text{CO}_2$ measurement” by X.-F. Wen et al.

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Response to the reviewer (E. Pili)

Specific Comments 1) The dependence of the $\delta^{13}\text{C}$ on the CO_2 concentration of each instrument taken separately, for each calibration method, deserves a complete analysis. I wonder why the authors only discussed the difference between 2 instruments or between 2 calibration methods. In Fig. 5 for example, why using the difference Picarro–Los Gatos? Also I think that Fig. 4 might be misleading for some people: it must not be confused with the dependence of the $\delta^{13}\text{C}$ on the CO_2 concentration for a given instrument. There is no practical reality to use the difference Picarro – Los Gatos as

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nobody will run the two instruments at the same time. The difference has little meaning: one instrument may depend on the CO_2 concentration, not the other. Trying to quantify the dependence of the $\delta^{13}\text{C}$ on the CO_2 concentration for each instrument would be of more interest. This may help to understand why different calibration methods may yield similar results for one instrument and not for the other. Indeed, not knowing the mixing ratio seems to be of increasing importance with increasing CO_2 concentration for the Los Gatos instrument (see Table 1).

We agree that in an ideal situation, the concentration dependent behavior should be evaluated against a measurement known to be free of this artifact. Absent of this “absolute” standard, a comparative analysis can still generate good insights, by assuming that one analyzer is accurate and the difference arises from errors caused by the other analyzer. This is indeed the objective of Section 3.4. In response, we have added the following at the beginning of Section 3.4: “Although we cannot conclude which of the two analyzers had better accuracy, comparisons between the two analyzers and between the calibration methods should allow us to gain insights into the problem of error propagation through the Keeling analysis.”

2) Also, Fig. 7 only shows data for the Picarro instrument while the label on the Y axis refers to some $\delta^{13}\text{C}$ difference (with very high values). There must be an error in the Y label and the data for the Los Gatos instrument should be shown equally, as in the other figures, so that the authors are easier to follow.

This error has been corrected. A new figure (Figure 7b) is added for the Los Gatos analyzer. .

Technical corrections 1) P 799, line 9. Air is flowing through a Nafion tubing then through a Drierite-filled cavity. I would recommend using a Nafion tubing embedded in Drierite. This would prevent for potential memory effects and reduce air residence time. What is the dead volume of air in Drierite? Any effect of CO_2 interaction with sorbed moisture?

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This error has been corrected. This was indeed the configuration used in our study. Text is modified as. "Gas was dried by passing through a Nafion gas dryer (PD-200T-12MPS, Perma Pure, Toms River, New Jersey) embedded in a drierite tube before entering the analyzer to prevent water absorption interference. The air residence time in the dryer was about 1s." The dead volume of air in Drierite was about 100ml, and the air from the analyzer's outlet flew through the Drierite for the dryer regeneration.

2) P 800, line 15. $I = 1, 2$. It is not clear that it also means that $i = a$. Please rephrase.

Clarified, and changes have been made. "with $i = 1, 2$ and a standing for standard gas 1, standard gas 2 and sampling air, respectively."; "where R is the ratio of 13C to 12C in the sample air"

3) P. 803, line 19. What is the pore size of the Swagelok filter?

Provided. "with a filter (pore size $2 \mu\text{m}$, Swagelok model B-4F-05, Connecticut Valves and Fittings, Norwalk, Connecticut)"

4) P. 807, Line 6. "Loa" must be replaced by "Los"

Changes has been made.

5) P. 807, Line 7. "The Nafion dryer: : should yield an outlet dew point: : ". It seems that the moisture has not been measured. Please explain why "should yield".

Clarified. "The Nafion dryer embedded in the drierite tube used by the Los Gatos analyzer yielded theoretically an outlet dew point of lower than -35°C or about 300 ppm of water vapor."

6) P. 808, Line 26. Add "Table 2" to (2.00‰ Method 1).

Change has been made.

7) P. 809, Line 3. "by the regression shown in Fig. 6a". Please add ", in the case of the Picarro analyzer."

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Change has been made.

8) P. 809, Line 9. "In Eq. (15), the delta error (d) is : : ."

Change has been made.

9) P. 809, Line 11. Remove "that".

Change has been made.

10) P.809, Line 15. It is not clear where $E=0.15\%$ comes from. Please explain.

With this value, Equation 15 matches reasonably well the regression line shown in Figure 5.

11) P. 809, Line 20. Add "As given in Table 2" in the sentence beginning with "For the Picarro analyzer".

Change has been made.

12) P. 812, Line 11. Typo error: "Agrinie" should read "Agrinier".

Change has been made.

13) P. 817. Fig. 1. Any clue for the bump in the Allan deviation of the CO₂ concentration from the Los Gatos analyzer?

We now state: "The departure of the 12CO₂ Allan variance of the Los Gatos analyzer from the white noise line may indicate sensitivity to environmental temperature (Figure 1b)."

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