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Atmospheric Measurement Techniques Discussions

Interactive comment on "Abundances of isotopologues and calibration of CO_2 greenhouse gas measurements" *by* Pieter P. Tans et al.

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Comments from referee 2 Recommendation: Publish - minor revisions General comments: The manuscript "Abundances of isotopologues and calibration of CO2 greenhouse gas measurements" is well written and reports on a method and a new calibration system to account for differences in isotopic composition between primary CO2 reference standards. This is an important development and essential for addressing biases introduced from measurements sensitive to specific isotopologues. The authors point out that these developments can be applied to other molecules. Application to CH4 and N2O would be of further benefit to users of optical spectroscopy. This work is a valuable contribution and of significant interest to the atmospheric monitoring community. The document defines the state of the art for the CO2 calibration scale and it is important that this information is in the public domain. I recommend publication subject

to the following minor suggestions for revision:

Comment: The section on calibration and system performance refers to measurements of delta13C and delta18O made at INSTAAR on the primary and secondary standards using IRMS. What was the reference used for these measurements and are these traceable to VPDB?

Response: The measurements by INSTAAR are traceable to VPDB. The INSTAAR scales were set using NBS-19 and NBS-20 carbonates and VSMOW, GISP and SLAP waters. Text has been added to clarify. Also, text has been added addressing the effects of the differences between INSTAAR and JRAS.

Comment: The term "mole fraction" and "amount of substance fraction" are used interchangeably throughout. One of these terms should be used for consistency. The second sentence of the abstract mol/mol is the unit and should replace mole fraction. This also applies to the fourth paragraph of the introduction.

Response: We have changed the text to be more consistent with terms. It was our understanding from Schwartz and Warneck (1995) that "amount of substance fraction" was the quantity and "mole fraction" was the unit. It seems this reading was wrong and the IUPAC compendium of chemical terminology (the Gold Book) lists "mole fraction" as a synonym of "amount of substance fraction". We use amount of substance fraction in the first instance with mole fraction in parenthesis and then mole fraction for the rest of the document.

Schwartz, S. E., Warneck, P., Units for use in atmospheric chemistry (IUPAC recommendations 1995). Pure and Appl. Chem., 67, 1377-1406, 1995.

IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: http://goldbook.iupac.org (2006) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins.

Comment: I would suggest keeping all y-axis values on the left hand side of the figure and increasing the size of the interval (perhaps 3 y values per chart). It is not clear whether the bars on the data represent standard deviations or uncertainties. Is there any contribution from the change in composition in the CO2 reference standards to the trend observed in figure 2? Is it assumed that the changes in CO2 reference standards is negligible compared to the long term reproducibility of the facility?

Response: We find the y-axis labels easier to read when alternating sides so leave them this way. The error bars are the standard deviation of the 8 measurements per calibration episode. Text has been added to clarify. I don't think the apparent trend is significant. Subsequent measurements have shown step changes possibly due to regulators or subtle variations in the stability of the response of the instruments but not a significant trend in the target tanks. We updated the plot with more data collected since initial submission to make it clearer. We also include the standard deviation of the replicate calibration episodes for each tank individually in the caption. The reference tank is not used as a point in the calibration curve. It only corrects for slow drift between calibration episodes. Changing the reference tank does not affect the measurement results. The reference tank is in effect being calibrated while the calibration curve is being determined.

Comment: Figures 3 and 4 present the comparability of measurements at INSTAAR and the new calibration system. The offset of non-depleted tanks is attributed to the extrapolation of the calibration at INSTAAR. Is there any data to support this statement?

Response: The offsets of depleted tanks is roughly consistent with the INSTAAR offset from JRAS described by Wendeberg et al. (2013) and is contributed to scale contraction at INSTAAR. Text has been added to clarify.

Comment: Assuming uncertainties are symmetrical, the values presented throughout the manuscript (e.g. ± 0.007 μmol/mol in the caption to figure 2) do not require the ± sign.

Response: We leave the ± symbol in to prevent confusion and re-iterate that they are symmetrical ranges.

Comment: The caption to figures 5 and 7 are missing the term mole fraction (e.g. “The top panel shows the INSTAAR delta13C values as a function of CO2 mole fraction.”)

Response: We leave the text as is to be succinct.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/amt-2017-34/amt-2017-34-AC2-supplement.pdf

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