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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.

Pieter P. Tans et al.

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Comments from referee 1 The manuscript of Pieter P. Tans et al. with the title "Abundances of isotopologues and calibration of CO2 greenhouse gas measurements" is reporting the development of a method to calculate amount of substance fractions for individual CO2 isotopologues, based on XCO2, ïĄď13C and ïĄď18O values. The new method is applied in combination with a new CO2 calibration system, consisting of three laser spectrometer with different technology and sensitivity for isotopologues: CRDS (16O12C16O), OA-ICOS and QC-TILDAS (16O12C16O, 16O13C16O, 18O12C16O, 17O12C16O), to account for isotopic differences among standards. The topic is very timely and of very high interest for a large number of readers of Atmospheric Measurement Techniques involved in atmospheric monitoring of greenhouse gases (especially CO2) and their isotopic composition. The manuscript is a fundamental conceptual and technical description on the WMO CO2 calibration scale and therefore a basic document to define the state of the art. As mentioned by the authors, the developed technique can be applied to other molecules, where isotopologues-specific values are desired or isotopic differences affect analytical techniques. Furthermore, the technique to calculate fractional distribution of isotopologues of CO2 (and other target substances, e.g. CH4, N2O) will be of great benefit for users of optical isotope laser spectroscopy (e.g. Edgar Flores et al., Analytical Chemistry (2017), DOI: 10.1021/acs.analchem.6b05063). The manuscript is very carefully written, concise and clear, and it can be published with very minor revisions. The authors might consider a small number of suggestions to further increase the readability / impact of their work.

Comment: Page 12 Line 5: Eq. 21 + 22: The two formulas for P(826) and P(726) are incorrect as the second denominator is supposed to be squared. Although the mathematical equations are clearly presented, it would be very helpful for the reader to have a sample calculation, for example as a supplementary file, on how to calculate mole fractions of isotopologues (X(626) etc.) from δ13C , δ18O and XCO2. Implementing the equations of the presented manuscript (Eq. 12 – 15 or 19 – 22) on an example from Flores et al. (Analytical Chemistry (2017), DOI:10.1021/acs.analchem.6b05063, e.g. Table 1 mixture 1) results in different mole fractions of isotopologues than given by Flores – please state on the differences in the calculations, and cite the work of Flores at al. in your manuscript.

Response: We agree with the comment and thank the reviewer for finding the error in the equations. The manuscript has been updated to reflect the correct equations for P(826) and P(726) as well as subsequent use of these terms. The corrected equations agree with those of Flores et al. The use of the correct equations does not significantly change the results for total CO2, δ13C, or δ18O because the same mistake was made when deconstructing the total CO2 of the standards into component isotopologue mole fractions and when reconstructing total CO2 from the measured isotopologue mole fractions of the samples. To a large part cancelling out. The differences in total CO2 mole fractions were less than 0.001 ppm. Calculated δ18O values did change by a few hundredths of one per mil but this is less than our analytical uncertainty.

Comment: Page 2 Line 17-20: The role of the world calibration centres (WCCs) to independently verify the implementation of the calibration scales at laboratories of monitoring stations could be mentioned here or elsewhere in the text.

Response: Text has been added to mention the role of the WCC's in helping institutions remain closely tied to the WMO scales. Also mentioned is the use of "round robin" experiments for this.

Comment: Page 3 Line 11: Results of most recent key comparisons (CCQM) with national metrological institutes (NMIs) could be included here. Response: The WMO CO2 scale is being revised to account for biases in the calculations of CO2 mole fraction measured by the manometer and incorporate the increased knowledge of the primary standard values gained through additional manometer measurements since 2007. These biases and the scale revision are being described in an additional paper that is currently in preparation. We allude to that on page 17 line 35 in the current manuscript. The authors would prefer to discuss the results of the comparisons with independent scales in this upcoming paper that is dedicated to the revision of the scale since any bias in the manometer measurements and calculations have a direct impact on these comparisons. We hope to have this publication submitted in summer 2017.

Comment: Page 4 Line 20 (Eq. 1): Multiplication with " x 1000" is frequently used, but should be avoided according to Tyler Coplen, RCM (2011), DOI: 10.1002/rcm.5129.

Response: The equation and text has been corrected. We don't like the x1000 convention, but had included it because many people use it.

Comment: Page 5 Line 32: Scott Marrin Inc. offers "ultrapure air" and "cryogenic ultrapure" air but not "ultra high purity air" please specify accordingly.

Response: The manuscript has been changed to reflect that NOAA uses "ultrapure air" from Scott Marrin.

Comment: Page 6 Line 11: The sub-sentence "... to properly address isotopic issues when..." is colloquial and might be rephrased.

Response: The sentence has been rephrased.

Comment: Page 9 Line 24: Is error the correct wording in this context, or should it be bias? Please check.

Response: Bias is the correct term. The text has been changed.

Comment: Page 11 Line 6: Replace 0.194 with 0.195.

Response: The typo has been fixed.

Comment: Page 14 Line 1-2: Please specify the wavelength region used for the analysis of CO2 isotopologues as different possibilities exist and this might vary from instrument to instrument. Was there any additional temperature stabilization implemented for the optics/electronics of the QC-TILDAS or is the laboratory air-conditioned?

Response: Text has been changed to indicate both analyzers use lines at approximately 2309 cm-1. Both CO2 isotope analyzers are temperature stabilized by the manufacturer, we did not add any additional control since our laboratories are well controlled.

Comment: Page 14 Line 11: What is the reason that δ17O-CO2 cannot be calibrated independently, no IRMS measurements?

Response: The INSTAAR stable isotope laboratory does not have the ability to measure δ17O so our standards have not been calibrated for it. We've added text to make this clear. We therefore have to assume δ17O follows the mass dependent relationship to δ18O. Deviations from this relationship would be small and insignificant when used to assign a total CO2 value to a sample.

Comment: Page 14 Line 35 – Page 15 Line 1: The sentence “The solenoid valve fails to the idle gas . . .” is unclear and might be rephrased.

Response: This sentence is unnecessary so has been removed to prevent confusion.

Comment: Page 16 Line 13-20: The memory effect might cancel out, but it will add to the uncertainty of the isotope analyzers. Has this been quantified? Are improvements possible, such as longer flushing times, or optimization of the flow scheme?

Response: We agree, the memory effect will increase the uncertainty near the ends of the scale. However, the identical treatment of standards and samples should minimize the effect. The residuals of the calibration curve for the 636 isotopologue using a quadratic fit are typically ± 0.0005 μmol/mol. With a linear fit the largest residuals are 0.003 μmol/mol at the ends of the scale. The difference in these residuals indicates the approximate magnitude of the memory effect. In terms of total CO2, assuming the identical treatment corrects for some of the effect, the memory effect is not significant. It would however be important for high precision isotopic measurements. The problem could be resolved by using longer flushing times. However, we feel the extra gas usage, resulting in shorter lifetimes for the standards, is not warranted. The text has been changed to make this clearer.

Comment: Page 18 Line 24: The sentence “Isotopic standards should be calibrated by IRMS measurements” could be valid for the given example but is not a correct general statement, please specify the sentence.

Response: Agreed. We want to make the point that the isotopic measurement results provided by the CCL are not intended to propagate the VPDB scales for scientific studies that require high precision isotopic values. We want to encourage users to continue to have isotopic standards calibrated by techniques and facilities with higher precision than what our system can deliver. Our focus is on making total CO2 measurements that are not influenced by isotopic differences rather than on the isotopic values themselves. The sentence has been reworded to clarify.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/amt-2017-34/amt-2017-34-AC1-supplement.pdf

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