Atmospheric
Measurement
Techniques

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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 3 The paper should be published with revisions. Laser based instruments measuring concentrations of gases in the atmosphere have developed rapidly in recent years, with the ability to measure individual isotopologues. At the same time the standards used for calibrating such instruments need to be adapted accordingly to allow for correct calibration, and the paper describes the progresses made. The paper should be improved by: a) improving terminology on quantities and units b) using conventionally used symbols for quantities in a number of equations c) using internationally accepted conventional values for isotope reference materials d) describing the impact of nonequilibrated CO2 in standards and the potential biases that may arise in isotope ratio measurements as a result e) reduction in the number of equations, with references to already published work f) full description of the traceabil-

ity and uncertainty of isotope ratio measurements by both IRMS and Optically based techniques. These should also be propagated through to measurements of mole CO2 mole fractions.

Comment: Page 1 line 14: 'units of mole fraction' is not a correct expression; mole fraction is a quantity not a unit. Correct to 'calculate the mole fraction of each component', expressed in units of μmol/mol

Response: See response to reviewer 2 on this issue.

Comment: Page 1 line 19: same issue as above with the use of 'mole fraction units'. Please correct.

Response: See response to reviewer 2 on this issue.

Comment: Page 2 line 34: correct 'units of mole fraction' also the symbol for mole fraction should be in italics, with normally lower case being used

Response: See response to reviewer 2 on this issue. Also, all symbols have been put into italics. See comments below regarding use of symbols consistent with Coplen (2011) and the IUPAC gold book.

Comment: Page 3 line 9: what is calculated is the mole fraction of CO2 in air, not the ratio. Also 'ratio of moles' is not a correct term. Please correct.

Response: Mole fraction is the ratio of moles of CO2 to moles of air. We leave the text as is to clearly state that we calculate ratios not absolute moles on the manometer. The absolute volumes in the manometer are not nearly as well known as the volume ratios. In all calculations we use the volume ratio rather than the actual volumes.

Comment: Page 4 line 10: 'the number of molecules of CO2 per mole of dry air', is not correct – it is a different quantity (which would be expressed in units of 1/mol) from mole fraction (expressed as mol/mol). Restructure the sentence avoiding this part of the phrase.

Response: This typo has been fixed, should have been "number of moles of CO2 per mole of dry air".

Comment: Page 4 line 13: the authors should reference the fact that they are using the shorthand of the spectroscopy community (e.g. reference to HITRAN, see https://www.cfa.harvard.edu/hitran/molecules.html). Also in this notation the convention is to write isotopologues as 628 and not 826. Please correct.

Response: Reference to HITRAN added and the appropriate corrections to the short-hand notation have been made.

Comment: Page 4 line 21: Equation 1 includes the factor 1000. This is not correct, delete the factor 1000. If needed add a phrase that delta values are often expressed in per mil, where the symbol ‰ means 0.001

Response: The equation and text has been corrected.

Comment: Page 5 line 16 and subsequently: when quoting ranges these need to be written as -7.0 ‰ to -9.0 ‰ Also there needed to be a space between the number and ‰ i.e -9.0 ‰ and not -9.0‰ Please correct

Response: Spaces have been added between values and "‰' symbols. Previous published manuscripts in AMT have expressed isotopic ranges as -7.0 to -9.0 ‰ so we leave these as is to be consistent with other AMT manuscripts unless the editors have a preference. See Griffith et al. 2012 as example.

Comment: Page 6 line 4: depleted in 13C and not _13C. Please correct

Response: Text has been corrected.

Comment: Page 6 Section 3: The authors should use conventional notation in this section, rather than introducing their own. In addition they should differentiate between quantities that are simple ratios and the ones that are fractions. See Santrock (1985) which is referenced in the paper, where the ratio of amounts of substance (abundance

as used by authors) of two isotopes is demoted with the symbol R, whilst a fraction has been given the symbol F. In all cases symbols should be in italics following standard practice.

Response: When we developed our methods we were not aware of the Santrock paper. While responding to the reviewer's comments we consulted IUPAC guidelines for notation (Coplen reference), but the Santrock paper does not follow them. The IUPAC recommendations have "R" for the isotope-number ratio and "r" for the isotope-amount ratio relative to the most abundant isotope, even though numerically R=r. Similarly, they have "X" and "x" (again, X=x numerically) for the isotope-number fraction and isotope-amount fraction. Because we prefer to think in terms of amounts with the unit of moles we changed our notation to r and x for the isotopic ratio and the isotopic amount fraction respectively, and we use bold-face type for easier readability. IUPAC recommends the same "x" symbol for general amount of substance fractions, and "y" specifically for gases. We will call these "mole fractions". We will use the '"y" in this paper for the CO2 mole fraction in air because we like to distinguish total CO2 from isotopologue-amount fractions.

Comment: Page 6 line 16: the equations should be numbered. The conventional symbol for an isotope ratio is R and not r.

Response: "r" is correct. See above.

Comment: Page 6 line 19: These are just fractions not 'redefined ratios'. The equations should be numbered

Response: We have changed the text to read "we use" rather than "we re-define".

Comment: Page 7 line 1: Often in papers VPDB-CO2 is shortened to VPDB, when a statement is included explaining this. PDB is not used as a shorthand for VPDB, because it actually denotes the original PDB scale. Use VPDB if a short had notation is required.

Response: Shorthand "PDB" has been changed to "VPDB".

Comment: Page 7 line 3: (equation 4a) The value used for 13RVPDB is not the one recommended by the IAEA nor the WMO CCL for CO2 isotope ratios. A value of 0.01118 should be used see you reference Brand et al (2010). Similarly the values for 17R and 18R are not the same as for the Brand et al (2010) reference. Internationally accepted conventional values should be used- please correct.

Response: We now use (13C/12C)VPDB = 0.011180 but we did not use (17O/16O)VPDB-CO2 = 0.0003931 from Brand et al. because it is inconsistent with [(17O/16O)VPDB-CO2/((17O/16O)VSMOW] = [(18O/16O)VPDB-CO2/(18O/16O)VSMOW]0.528

Comment: Page 7 line 13-15: This sentence is not necessary if equation 1 is corrected.

Response: We leave this sentence in because many people assume all "δ" values have been multiplied by 1000 to read as permil. We want to be explicit that the δ values in the equations are in small numbers.

Comment: Page 7 line 22: 'approximate the abundance as mole fraction' should be corrected to 'calculate the mole fraction'.

Response: We prefer 'approximate' to re-iterate that the equations are not exact.

Comment: Page 7 lines 19 onwards: The ratios measured in IRMS together with the convention already mentioned on Page 4 line 26, can be solved exactly to then calculate atomic isotopic abundances, and with simple probability theory (see Ref 1 in Santrock (1985)) and knowledge of the total CO2 mole fraction calculate the mole fraction of any of the 12 CO2 isotopologues in the gas. This section would be improved by replacing with reference to the Santrock(1985) paper and reference there in.

Response: We do not follow the reviewer's recommendation because our paper would be harder to read if one has to go to another paper to follow ours, and furthermore because Santrock is focused on a different issue, namely 17O corrections for mass

spectrometers.

Comment: Page 8/9 entire section: Whilst providing a nice description of probability theory, how is this any different from the Santrock paper in describing the distribution of isotopes among molecules at equilibrium is accurately described by a simple probability function, and reference 1 therein? The current text could simply be replaced by a reference. However, what the authors have not discussed and does not seem to be treated in this paper is that these equations are only exact when the gas is in equilibrium. The procedures used for making the WMO standards, especially historically, are likely to lead to a non-equilibrated gas i.e. by mixing two CO2 gases together with different isotopic compositions the resulting mixture does not have the distribution of isotopologues that would be predicted from the average atomic isotopic abundances of the mixture. The effect of this both for the spectroscopic and mass spectrometric methods applied in the paper should be evaluated and commented upon in order to confirm the authors' conclusions.

Response: Our description on p. 8-9 is more general than Santrock's. If the reviewer refers to thermodynamic equilibrium, it plays no role in our treatment. CO2 as well as its isotopic ratios are not in equilibrium in the atmosphere because the atmosphere is imperfectly mixed and sources/sinks of CO2 occur in different places and times and come with different isotopic ratios, including pure isotopic exchange not associated that any net source/sink of total CO2 (Tans et al, 1993). Even inside reference gas standards there is no full equilibrium. So what? Approximate thermodynamic calculations have been carried out to estimate fractionation factors between different species and phases (liquid, gas, solid) when isotopes are exchanged. Those fractionation factors could be kinetic or equilibrium factors. We take those fractionation factors as given, derived in most cases empirically from measurements. We measure what is in the atmosphere relative to what is in the standards, and differences of isotopic ratios are expressed in the standard delta notation, with uncertainties. That is as exact as it gets.

Comment: Page 11 lines 21-23: The scale on which INSTAAR is measuring CO2

isotope ratios should be described, as well as the conventional values used for its scale. Is it its own realization of the VPDB or VPDB-LSVEC scale? The measurement uncertainty of this realization should be described as well as any known bias form the WMO Scale for CO2 in air (JRAS).

Response: A great advantage of our method is that it uses multiple standards covering a range of values to create a scale. "Scale contraction" can result from having a single standard reference, and mass spectrometer measurements have suffered from that. We do not have such "contraction" because we have a real scale over a range of interest instead of a single point so that we can create for any analyzer a response curve. We have added this to section 6. The INSTAAR offset from JRAS has been included in the discussion. The offsets are attributed to scale contraction at INSTAAR (Wendeberg et al. 2013 and personal communication with Slyvia Michel) The differences are not significant for the total CO2 calculations and our calibration strategy is largely immune to scale contraction at INSTAAR since all of our secondary standards are close to ambient isotopic composition where the effect is minimal.

Comment: Page 11 Entire Section: Several papers have been published describing approaches for calibrating optical system for isotope ratio measurements (Wen et al, Atmos. Meas. Tech. 2013 and Flores et al. Anal. Chem 2017) with the latter including uncertainty estimation of calibration procedures. The authors reference neither, nor do they provide a description of the uncertainty of their calibration or measurements procedures. A reference to previous descriptions of calibration procedures and an assessment of the measurement uncertainty should be added, which would then allow propagation of the uncertainty into mole fraction values.

Response: We only became aware of Flores when the first review of our paper came in. We were not aware of the Wen et al paper.

Comment: Page 12 and 13: The equations on these two pages are difficult to follow. It is not clear to the reviewer why the sum of all isotopologues is not included in the re-

ported total CO2 mole fraction value. Accurate measurement of the 626 isotopologue, together with its isotope ratios and the assumed distribution of isotopes would allow the mole fractions of all other isotopologues to be calculated and their sum added to the 626 mole fraction to give total CO2.

Response: All isotopologues are included in the total CO2. Dividing the sum of the measured isotopologues (x626, x636, and x628, plus x627 calculated using the δ17O to δ18O relationship) by the sum of the probabilities for the 4 major isotopologues corrects the sum for the unmeasured rare isotopologues. The probabilities used in the equation are determined for the unknown sample based on it's measured isotopologue mole fractions. Generally they are very slightly different than the sum of the probabilities assuming VPDB values but we calculate them anyway. Text has been changed to clarify.

Comment: Page 16 line 14: no information on the uncertainty for the standards is given. Please add this.

Response: The uncertainty of the manometric method used to assign the primary standards was given on page 3. It has been re-stated in this section to clarify.

Comment: Page 17 line 10 and 11: It would be useful to know if INSTAAR are using a second reference material to control scale contraction effects to substantiate this conclusion.

Response: INSTAAR is not using a second reference material to control scale contraction. The published INSTAAR vs JRAS offsets has been referenced as evidence that scale contraction at INSTAAR is the cause of the offsets seen between NOAA and INSTAAR when measuring highly depleted tanks.

Comment: Page 17 lines 22-23. Reproducibility and uncertainty appear to be used as synonyms, which they are not. The author's should differentiate between the reproducibility and uncertainty, and an estimation of the measurement uncertainty would

help in this respect.

Response: This was unintentional word choice. Text has been added to clarify that reproducibility is one component of uncertainty. Even without a full uncertainty budget the reproducibility estimate shows the δ13C and δ18O calibrations are not applicable as standards for high precision CO2 isotopic measurements. Full uncertainty calculations for the CO2 scale will be in an upcoming publications describing the revision of the WMO CO2 scale since the largest terms in the uncertainty budget is related to the manometer measurements.

Comment: Page 26 Table 1: The currently internationally accepted conventional values for VPDB should be clearly identified in this Table.

Response: See response to previous comment on values for reference materials.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/amt-2017-34/amt-2017-34-AC3-supplement.pdf