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Atmospheric Measurement Techniques
Discussions
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Interactive comment on “Abundances of isotopologues and calibration of CO_2 greenhouse gas measurements” *by* Pieter P. Tans et al.

Anonymous Referee #3

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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 non-equilibrated 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 traceability 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.

Specific comments: 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 Page 1 line 19: same issue as above with the use of ‘mole fraction units’. Please correct. 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 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. 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. 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. 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 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 Page 6 line 4: depleted in 13C and not δ13C. Please correct 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. Page 6 line 16: the equations should be numbered. The conventional symbol for an isotope ratio is R and not r. Page6 line 19: These are just fractions not ‘redefined ratios’. The equations should be numbered 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. 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. Page 7 line 13-15: This sentence is not necessary if equation 1 is corrected. Page 7 line 22: ‘approximate the abundance as mole fraction’ should be corrected to ‘calculate the mole fraction’. 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. 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. 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

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measurement uncertainty of this realization should be described as well as any known bias form the WMO Scale for CO2 in air(JRAS).

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. 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 reported 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. Page 16 line 14: no information on the uncertainty for the standards is given. Please add this. 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. 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. Page 26 Table 1: The currently internationally accepted conventional values for VPDB should be clearly identified in this Table.

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