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Interactive comment on "Revision of the WMO/GAW CO_2 Calibration Scale" *by* Bradley D. Hall et al.

Anonymous Referee #1

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The paper describes the basis for the revision the Central Calibration Laboratory is making to the WMO GAW CO2 calibration scale. It transparently explains a few issues that are impacting the currently employed WMO X2007 scale and that are the origin of a ca +0.2 ppm correction towards the new scale. An in-depth discussion of involved uncertainties and experimental limits is provided. Experiments and their results are described that were made to verify assumptions (on the influence of CO2 adsorption) and to validate the results (gravimmetric approach). Also results from comparison with NMIs are presented that provide reconfirming evidence for the assumed uncertainties. As the WMO scale has been the basis for all WMO GAW measurements the authors add a section that describes the implementation of the new scale to the measurement community. They offer a straightforward way to implement the scale for data sets where

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Discussion paper

a re-processing based on re-assignments of calibration gases is not assessible and provide information to estimate the associated bias.

General Comment

The topic is extremely relevant as it is the basis for all WMO GAW atmospheric measurements of the main greenhouse gas. It is obvious that the manuscript is based on rigorous work, analytic expertise and good bookkeeping. The quality of this work is exemplary. It is particularly commendable that the authors openly disclose lapses that had been made in the past and are rectified with the scale update and that they provide test results in the supplement material that might challenge their basic approach of a linear extrapolation of the CO2 loss rate to the start of the record. The paper is well written and definitely should be published in AMT.

There are some topics, though, where I would like to ask the authors for further clarification, completion or correction of the manuscript before publication.

Specific comments to the Manuscript text

l. 85: "During a measurement experiment, gas from a cylinder is loaded into the larger of the two volumes (large volume, ∼6 L). After flushing the large volume for 10 min. at 200 mL min-1 and allowing the gas temperature to equilibrate to oven temperature...". For me the reason for the 10 min flushing period that exchanges one third to one half of the large volume is not clear. I have come across the following statement made in Tans et al. 2017: "there may be a component due to gas handling issues on the NDIR system that cannot be resolved. This is still under investigation and will be addressed in a forthcoming paper discussing the scale revision" I have not been able to identify any section in this manuscript that has dealt with such issues. At the 0.01 ppm level pressure regulators are likely to introduce a bias in the CO2 mole fraction. There are certainly standardized gas handling procedures at the Central Calibration Laboratory. Yet, there are little details given in the manuscript.

l. 116 / l. 234: It is not explicitly stated if prior to each manommetric episode the volume ratio was redetermined using the gas expansion technique.

l. 132: Please add a reference to the Suppl. Material Figure S3.

l. 154 / Fig. 4: The text states that Fig. 4 shows the differences between original and updated results (implying that original > updated), the y-axis label is named "X_virial_correction". This seems as a contradiction in the algebraic sign. The text should state this more precisely.

l.160: In l. 235 it is written that the volume ratio changed again in 2014. Is it correct, that the correction function for beta for the period 2014-2016 is the same as 2004-2014?

l.199: It is not explained how the loss correction uncertainty is calculated. A reference to Suppl. Material section 2.4 (l.226) should be made.

l. 247 (Table 1): In the "CO2_primary_all_valid_data_X2019_supplement" file N = 34 x2019 values are listed for AL47-146 instead of N = 35 in Table 1 (one is flagged); for some cylinders the numbers in the Table 1 columns "Avg. (x2019)" and "s.d. (x2019)" are nearly but not exactly those that can be calculated based on the numbers provided in the "CO2_primary_all_valid_data_X2019_supplement" file.

l. 633: There had been a scale identified as X2005. (Tans, P. , Zhao, C. , and Thoning, K.: Revision of the International Calibration Scale for CO2-in-Air: WMO-X2005, 13th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (Boulder, Colorado, USA, 19-22 September 2005) WMO TD No. 1359, Geneva, Switzerland, 19-25, 2011). In this report the bias of old assignments (dating back to 1980) relative to the X2005 scale are presented with assignments from 1980-1995 being low by -0.2 ppm. At the 14th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques in 2007 there has been a similar presentation by Pieter Tans showing X2007 − X2005 differences that indicated smaller mole fraction dependent differences ($\pm$ 0.05

ppm) that appeared stable over time (back to 1988)(see respective slides in Fig. 1-3). This is consistent to Fig. 17 but included many more data points.

There are few references in the text that do not appear in the reference list, namely:

l. 39 (WMO,2020); l. 126 (Sengers et al., 1971); l. 295 (White et al., 2015)

The references of Keeling et al 1986 and Tans et al. 2011 in the reference list are incomplete:

Keeling, C. D., Guenther, P. R., and Moss, D. J.: Scripps reference gas calibration system for carbon dioxide-in-air standards: revision of 1985, WMO;??, 1986

Tans, P. P., Zhao, C. L., and Kitzis, D.: The WMO Mole Fraction Scales for CO2 and other Greenhouse Gases, and Uncertainty of the Atmospheric Measurements, 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, GAW Report No. 194, Geneva, Switzerland, 152-159, 2011

Specific comments to the Supplemental Material text

1.1 Historical manometric records l. 15: "However, some manometer runs from 1998 and some from 2004 show two CO2 peaks (Fig. S1)". Please either omit CO2 or add "..show apparently two CO2 peaks.".

2.3 Volume Ratio

l. 123/equation (s3): The reader will not know Zhao et al. 1997 by heart. The equation (s3) is not self-explanatory as neither the definition of r1, r2, r3, r4 nor the derivation of the equation is given here. I suggest to shift the reference from l. 123 to below equation (s3) in a form like "(see Zhao et al. 1997 for further description of the volume ratios ri and the derivation of the (s3))."

l. 162-l.166: It is likewise not immediately obvious to the reader why it is relevant provide the uP for the specified pressures. It would help to add to l. 160: "for pressures

attained after expansion during volume ratio measurements r1, r2, r3, r4 as described in in Zhao et al. 1997" and add in each line e. g. l. 163: "On expansion to 19 kPa, (r1), 8 10-6 ..."

l. 171 / l. 190: It is not clear to me if the differences in volume ratio determinations that occur when expansion experiments are made with different gases are only due to uncertainties in the applied virial coefficient or if other experimental aspects are involved in using the three gases. In l. 171 the uncertainty estimate relates to n=3 (which appears to refer to the three data series presented in Fig. S6). The data basis for the larger uncertainty contribution quote 0.03 in l. 190 is not that clear.

l. 183: Table S2: Another column for the counter "i" = 1..4 would be useful.

l. 189: "We add to that uncertainty contributions from temperature probe placement (0.08)". Whereas 2.3.1 has covered this aspect it is not clear how eq. (s4) and (s5) translate to this uncertainty contribution term.

l. 192: In the main manuscript l. 269 only a subset of variables accounting for 0.012% of the uncertainty of the volume ratio is considered to be relevant for drift assessment. It would be useful to have this detailed in here.

2.4 Total uncertainty associated with the manometric measurement

Reference to equation (s8) is made in the lines 209, 219, 228, which should be corrected to (s6).

l. 223 & l. 226: Does the 15% uncertainty represent entirely the uncertainty of slope from the regression fit of the pressure data? The uncertainty of the loss correction depends on the uncertainty in the loss rate and the uncertainty in the time tmax_CO2 - t0. If the uncertainty of the loss rate itself is estimated to be 15% I would expect any further uncertainty in the duration would need to increase this percentage. A typical 0.015 ppm / 4cycles has been stated in the manuscript l. 187. It is not clear why the total loss correction uncertainty remains 15%.

l. 226: In l. 41-51 the potential influence of non-linearity in the CO_2 sorption on the accuracy of a loss rate based on linear sorption behavior is considered. I think it is fair that the authors only consider an upper limit for this and conclude that the conditions under which they could make their experiment were not sufficiently representative for the manometric procedure as to derive any quantitative uncertainty contribution from it. However, I also think it would be fair to mention this here in the uncertainty section. that there is indication for a potential error in the loss rate determination. (something like "A potential bias resulting from a non-linear adsorption at the beginning of the experiment is assumed to be very small and could not be quantified experimentally")

Table S3: Please change Bair and BCO2 to betaair and betaCO2 (same as elsewhere in the manuscript); it is not clear from this manuscript how the beta standard uncertainty estimate of 0.2 is made. Please add the reference.

Table S3 is providing an overview of the various variables' uncertainty contributions and their effect on the total result of the manometric measurement. What I find incoherent and confusing, is to include the contents of the lowest three rows. As I understood the "Repeatability" is a standard error derived from the total set of manometric measurement results that have been made between 1996 and 2016 that define the X2019 scale. These measurement results are subject to the overall uncertainty involved in the manometric procedure (ïА¿0.079 ppm according to l. 229). In l. 238 it is explained that the episode results are deemed to be independent. Therefore, I would expect the scatter of the episode mean results to be in line with the estimated uncertainty (which is the case). What does not seem proper to me is to add the "Repeatability" term as an additional uncertainty contribution. It would appear more coherent if the Table S3 only contained the compilation of the manometry uncertainty terms (omitting the last three rows beginning with "13C,18O") and another table compiled the uncertainties associated with the measurement of a 400 ppm air sample. This latter then should include the standard error of the manometric measurements and the uncertainty of the scale transfer measurement including uncertainty associated with the stable isotope compo-

sition (note: this is discussed in the main paper but not mentioned in any part in the Suppl. Material document; a reference to section 6 of the paper would be helpful). The column "Approx. Relative contribution (%)" could be part of both tables, but should sum up to 100% in each of the tables.

2.5 Total uncertainty, including scale transfer

l.   237:   I   would   assume   "The   manometer   repeatability   from   up to 10 episodes" to be the average of column "Episode_std" in the "CO2_primary_all_valid_data_X2019_supplement" file, which is 0.077.   Instead the authors take the s.d. (x2019) from Table 1, i.e. the standard deviation of the entire set of individual manometric measurements per cylinder. Therefore, please add for clarity: "The manometer repeatability from all individual manometric mea-surements made within up to 10 episodes is... 0.10 ppm (see Table 1 column "s.d.(x2019))". These represent measurements done over a period of 20 years with parts of the system having been replaced throughout this period and operators having changed. As episodes are also considered independent perhaps a change of the term "repeatability" to "reproducibility" would appropriate.

l. 239: The volume ratio value is also a critical component. I might have missed it but having read the paper it is not clear to me if the volume ratio value used for each episode is the result of an individual redetermination valid for the respective episode, or if the volume ratio numbers are the same for all episodes within the respective periods where the volume ratio was nominally the same 1996-1999, 1999-2004, 2004-2014, 2014-present. In the first case the uncertainty of the volume ratio determination would add to the scatter, in the latter case it would not (only changes of the manometry apparatus from episode to episode would). This should be stated somewhere in the manuscript.

l. 241: Which exact calculation results in 0.039 ppm? I could only get this result when dividing the values from Table 1 "s.d.(x2019)" by the square root of "Nep(x2019)"

the number of episodes, and averaging this for all cylinders listed in Table 1. This seems inconsistent to me: either the s.d. of the cylinders' episode means (16th column in the "CO2_primary_all_valid_data_X2019_supplement" file) should be divided by "Nep(x2019)" or else the "s.d.(x2019)" divided by the square root of "N(x2019)". Both would yield a smaller values, in the first case 0.028 ppm, in the latter 0.021 ppm.

l. 242ff: There has been changing analytical instrumentation over time as is described in section 9 of the manuscript. It should be repeated in l.242 that the uncertainty contribution from scale transfer with laser spectroscopic techniques does only apply to these and not to NDIR measurements. It would be good to have a statement here if the X2019 scale transfer uncertainty estimate for assignments that were made by NDIR before November 2016 remains as it has been estimated previously for the X2007 scale (0.034 ppm, k=2; https://www.esrl.noaa.gov/gmd/ccl/co2report.html). l. 247f: I cannot fully follow how Table S4 col. 3 is calculated. According to Table S3 for 400 ppm it should be $(0.079^2+0.039^2+0.01^2+0.01^2)0.5$ which is close to but not exactly 0.093 ppm.

Specific comments to the file "CO2_primary_all_valid_data_X2019_supplement"

Header: please add the formula how "Episode_unc" is computed. For me that is not obvious. It would be helpful if the "Cylinder#" would be harmonized with Table 1 "Cylinder" Cylinder 101 xdate has been filled out incorrectly for the June 2015 episode.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2020-408, 2020.

Fig. 1. Tans et al 2007: old assignments - X2005

Fig. 2. Tans et al 2007: X2005 - X2007 (times series)

Fig. 3. Tans et al 2007: X2005-X2007 (mole fraction dependence)