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

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doi:10.5194/amt-2020-408-RC1, 2020 Author Response to Reviewer 2 (RC2)

Thank you for a thorough review. We greatly appreciate the detailed comments and the time taken to check our calculations.

Specific comments 1) Lines 69, 80, 81 – It would be more accurate to use the term "reference gases" instead of "reference materials", as the latter is commonly used for isotopically labelled materials including solids and liquids.

Response: While we would contend that reference material is an appropriate term, we have changed the wording to reference gases, as this term is probably more familiar to the WMO/GAW community.

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2) Line 86 – The brief description of the manometric procedure would be clearer by also stating that the larger volume is pre-evacuated, and its vacuum pressure.

Response: We have made the suggested changes.

The text now reads: During a measurement experiment, the manometer is evacuated to ∼ 5 mtorr and then gas from a cylinder is loaded into the larger of the two volumes (large volume, ∼6 L). The large volume is flushed for 10 min. at 200 mL min-1 and the exit gas stream is monitored by NDIR to ensure a stable CO2 signal. The large volume is then sealed off, allowed to equilibrate for five minutes, and the large volume temperature and pressure are recorded.

3) Section 3.2 - The largest difference from the X2007 scale is allowance for loss of CO2 in the manometer o-rings. Direct tests of the manometric method suggest this process still leaves uncertainty of as much as 0.2 ppm in defining the absolute CO2 scale. It is sobering that uncertainties of this magnitude remain, when other metrics (e.g. network compatibility, scale propagation) can have much smaller uncertainty. The authors address this problem by comparing their manometric data with independent informa- tion, such as from gravimetrically derived scales (which have their own uncertainties), to arrive at a preferred definition of the manometric scale. I agree with their approach, though some questions remain over quantification of the uncertainty. A key point that should be made in the paper is the distinction between total uncertainty in linking the scale to SI units and the component of uncertainty that pertains to maintaining a consistent scale and propagating it to other laboratories. The latter is more important for the CCL's main purpose of aligning CO2 data between laboratories. This concept has been recognised in earlier CCL papers but is not mentioned in this manuscript. Absolute accuracy of the scale is not critical for most applications, and can be revisited in future if the manometer o-ring effect becomes better quantified. Response: We agree that more emphasis should be placed on scale transfer uncertainty. We have added several paragraphs and two tables to the Supplement to document our evidence for scale transfer uncertainty, both with respect to the laser spectroscopic

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system and the previous NDIR system. The brief description of the loss correction uncertainty in supplementary section 2.4 is not clear on whether it includes allowance for possible systematic error (elsewhere given an upper limit of 0.2 ppm) or random error only. This should be clarified.

Response: We have revised the discussion on loss correction uncertainty.

It now reads: For Xloss_correction , we estimate the uncertainty in loss rate at 10% for most measurements, and 20% for those exhibiting a second maxima. We assume that the time corresponding to peak CO2 (t) is known to within one measurement cycle, and that the initial time (to) has an uncertainty of 2 minutes (2-4 measurement cycles). Together, the uncertainty associated with the loss correction is ∼12% for most measurements, and 25-40% when a second CO2 maxima was observed. Although a potential bias resulting from a non-linear adsorption at the beginning of the experiment was observed in separate tests (fig. S3), the magnitude of this potential bias could not be quantified experimentally under conditions consistent with manometric experiments.

A further minor point with the o-ring loss correction is the formulation in section 3.2. If “adsorption of CO2 begins about 1 minute after the liquid nitrogen is removed” and “there was a delay of about 2 minutes between the time the liquid nitrogen was removed and the first data record”, why isn’t the correction applied for an elapsed time of t_max_CO2 + 1 minute?

Response: Apologies. We stated this incorrectly. There is a 3-minute (180 sec) delay in the software, which why we selected 2 minutes for the delay in reprocessing. The text has been revised as: Adsorption of CO2 probably begins about 1 minute after the liquid nitrogen is removed. For many data records, we know that there was a software delay of three minutes between the time the small volume was sealed off (and the liquid N2 removed) and the first data record. While this cannot be confirmed for all records, we include a two-minute delay: t_max_CO2 + 2 minutes (to = 2 min.).

4) Section 6, p 16/17 - Primary standards were analyzed on the laser-spectroscopy

(LS) system 6 times over 3 years. Linear fits to these measurements against their manometric assignments yield residuals for individual standards that are highly consistent across the 6 episodes, and lie in a significantly large range of +/- 0.1 ppm with a standard deviation of 0.05 ppm (Figure 9). It is correctly stated that “variability seen in the residuals relates to the manometer average values”. The residuals are then partly attributed to shorter manometric measurement histories for higher mixing ratio standards. Other sources of variance are implied but not specified. An assumption of the calibration system (manometric + LS harmonization) is that these residuals represent random error in manometric average values. However, the standard deviation is about double that expected based on a 0.1 ppm (1-sigma) manometric uncertainty and the number of measurements listed in Table 1. This suggests some systematic bias between the techniques. Do the authors have any insight into possible causes? My thoughts would be - firstly, can an isotopic bias be ruled out? Data in Table 2 suggest an isotopic bias is unlikely. Could there be sensitivity in either technique to other components of the gas matrix? If so, it is hard to see an unexplained sensitivity in the manometer given the documented evaluation of that technique. Maybe some gas handling bias? Depending on the cause(s) of the bias, has the uncertainty been adequately captured?

Response: While some residuals seem larger than one might expect after averaging over 20 years, the standard deviations of the manometric histories are ∼0.1 ppm. And because the volume ratio is partially common to all measurements, one cannot assume complete independence. Most residuals are 0.05 ppm or less, which is encouraging. However, the 521 ppm cylinder is something of an outlier with a residual of 0.1 ppm. We also wonder if gas handling may have some impact, e.g. the manometric analysis uses considerably more gas than NDIR or laser-spectroscopy. A typical manometric experiment consumes ∼10L of gas (not counting flushing of regulators beforehand). Could this influence how CO2 interacts with surfaces in the regulator, or the valve and neck of the cylinder (e.g. in the vicinity of the thread lubricant)? Perhaps. We do not have sufficient information to address these issues, but perhaps with modern high precision analytical methods these issues can be explored more thoroughly. We do not think isotopic differences are a significant factor, but it is also true that the 521 ppm cylinder is the most isotopically different, and contains the largest “spike” of CO2 injected on filling (in the 1990s). Nevertheless, the value of defining a scale based on a large number of standards is that some of the effects should get averaged out.

5) There is no mention in the manuscript of gas handling effects or uncertainties, in particular regarding regulators. Are the author satisfied that the techniques referred to here are not subject to any significant gas handling effects, and/or can uncertainties be quantified? It was noted by Tans et al., 2017 that “Although 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.” Some comment on the current understanding of gas handling uncertainty is desirable.

Response: We have added some text on this topic, although we do not have sufficient information to draw definitive conclusions. We added the following, along with supporting data in two tables.

"One aspect of the scale transfer not represented by TT (target tank) results is any impact that changing regulators would have since regulators are not typically removed from TT’s to prevent damage to the cylinder valve fittings. For normal calibration services, a regulator is installed and conditioned following standard protocols (ref https://www.esrl.noaa.gov/gmd/ccl/reg.guide.html). Comparisons of pre- and post-deployment value assignments of standards used at NOAA sites, while complicated by drift issues during use, align with the expected reproducibility based on TT’s. Regulators remain an issue requiring further investigations as the CCL attempts to improve calibration services."

Technical comments 75 – replace viral with virial - fixed 106 – fix inconsistent cold trap temperatures shown in the caption and figure legend – fixed 178 – replace were with where - fixed 377 – What is the basis of the NIST CO2 scale - gravimetric?, yes it is gravimetric, we added this to the text 393, SM 193 – should read “Zhao and Tans (2006)” - fixed 394 – “JCGM, 2008” needs a reference or link – we added a proper reference 405 – should read “N2O is sufficient” - - fixed 444 – “function of XCO2” - fixed 504 – “one analysis record” - fixed 521 – “due to the use” - fixed 681 – The Guenther and Keeling reference needs more information to be accessible. It does not appear to have further traceability de- tails other than being a “technical report” but can be accessed online at https://scrippsco2.ucsd.edu/assets/publications/guenther_manometric_analysis_cdiac_report_2000.pdf

Response: We replaced this citation with Keeling et al. 2012, which is accessible on the SIO website. Keeling, R. F., Guenther, P. R., Walker, S., and Moss, D.: Scripps Reference Gas Calibration System for Carbon Dioxide-in-Nitrogen and Carbon Dioxide-in-Air Standards: Revision of 2012, Technical Report, March 2016, Scripps Insitution of Oceanography, La Jolla, CA, 2012.

688 – Keeling, C.D., Guenther, P.R. and Moss, D.J., Scripps Refer- ence Gas Calibration System for Carbon Dioxide-in-Air Standards: Re- vision of 1985. Environmental Pollution Monitoring and Research Programme No. 42, Technical Document WMO/TD-No. 125, 1986. https://scrippsco2.ucsd.edu/assets/publications/keeling_scripps_ref_gas_calibration_system_revision_1986.pdf

Response: We made the change to WMO/TD-No. 125 and added the URL

707 – 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, Report of the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, other Greenhouse Gases, and Related Measurement Techniques, 7–10 September 2009, GAW Report No. 194, WMO TD No. 1553, 152–159, 2011.

Response: Updated as suggested

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SM 51 – “as a way” - fixed

SM 209, 219, 228 – replace s8 with s6 – fixed

Additional changes to manuscript: We updated Table 2, now showing values to 3 decimal places, since this is how values are used for scale propagation.

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