

## Authors' Comments:

The article has been rewritten substantially in response to the very constructive feedback from both reviewers. There are three substantive changes to the paper. First, new section was added (4.4 "Uncertainty Analysis"), in which all the measurements of the correction factors have been used to construct a Monte Carlo simulation to predict the uncertainty of the water vapor correction under different conditions. This was in direct response to the very useful request by Referee #1. Second, all the figures have been replotted using a common theme to ease in the readability of the article, as requested by both referees. Finally, the language has been tightened to reduce the use of jargon and to improve the reproducibility of the experiments, as requested by Referee #2.

Specific issues raised by each reviewer are discussed below.

## Referee #1

Review of "High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air" by Rella et al.

Submitted to Atmospheric Measurement Techniques

### Summary:

This paper presents a number of tests of the Picarro cavity ring down spectrometer (CRDS) instruments to characterize the transferability and stability of the water vapor correction applied to humid air measurements in order to calculate dry mole fractions. Five different institutions contributed data from their lab and field tests using several different methods. The authors conclude that at relatively low water vapor concentrations ( $\leq 1\%$ ), the manufacturer-supplied correction factors are sufficient to meet WMO/GAW standards and that by doing additional characterization on individual instruments, periodically over their lifetime, this range is extended to  $>4\%$ .

### General comments:

Overall, it is a much-needed publication regarding the use of a popular CO<sub>2</sub> and CH<sub>4</sub> analyzer. Everyone wants to know if they have to dry the humid air, or if not, how often do they need to test the water vapor correction on their individual analyzer. This paper addresses those questions and makes recommendations for instrument calibration based on the humidity levels it is operated in. The subject of this paper is appropriate for publication in AMT and this special issue. However, because so many research groups contributed to this effort, the presentation feels pieced together. The paper could benefit from standardizing the data presentation in the figures and the evaluation metrics used to make it easier to read.

[author response] All the figures are now in a common theme. All the schematics use the same symbols and style; the water correction experimental data is presented using a common theme; and the field data are shown using the same types of plots for easy comparison.

The authors may also consider including a table of the correction coefficients determined for each analyzer. That way other users may easily determine whether their own water vapor correction experiment yielded results that are in the right ballpark.

[author response] This is an excellent suggestion. We have opted to present the data in a graphical format, which we believe is more informative than a tabular format, because of the observed degree of correlation between the coefficients.

More importantly, there are a few questions that they are poised to answer that they don't.

1. What is the variability in calibration coefficients from instrument-to-instrument? Or, if one applies the Chen et al 2010 coefficients to any instrument, how big can we expect the errors to be? This should be included in the conclusions section.

[author response] Another excellent suggestion. This analysis is a central part of the new uncertainty section 4.4.

2. Also, there is one other source of noise that is not really addressed by the authors. That is the uncertainty in the coefficients 'a' and 'b' because of the noise in CO<sub>2</sub> and CH<sub>4</sub> measurements. How well can we expect to measure 'a' and 'b' on any given instrument?

[author response] Agreed. Rather than try to address the possible myriad of individual sources of uncertainty and noise during a single experiment rigorously, we have analyzed the data to quantify the repeatability of the coefficients measurement, when measured on the same instrument on the same day (or within a few days). This analysis is included in the new uncertainty section.

3. How do these recommendations change if the goal is 0.05ppm CO<sub>2</sub> (Southern Hemisphere GAW goal)?

[author response] This assessment has been added to the conclusions.

4. If the correction coefficients do change over time, are they linear? If not, how does one correct the time series?

[author response] The question is a good one, but our limited stability assessment data are insufficient to quantify the linearity of the detected drift if there is any (see Fig.7). Note that the drift in corrected CO<sub>2</sub> and CH<sub>4</sub> due to any potential change of the correction coefficients is a function of the reported water vapor, and the drift is smaller (may not be significant) at lower water vapor concentrations. This is consistent with the uncertainty analysis (see Fig.14) for a single set of coefficients that are determined at the start of life. This also suggests that at higher water vapor concentrations (> 2%) regular

monitoring on the water vapor correction coefficients is required to achieve the WMO recommended target.

Specific comments:

P5825, L6: Southern hemisphere target = 0.05ppm CO<sub>2</sub>. [done]

P5829, L4: Please define 'cross-talk'. [done]

P5831, L21: 'Similarly, the range of water vapor...' [done]

P5834, L12: 'The values for r1 and r2 in ambient air were...' [done]

P5835, L11: 'The correction coefficients for Eqn 4 determined...' [done]

P5835, L18: I believe there is an error in the noise equation. It should not decrease with water vapor level.

$$M_{\text{corr}} = \sqrt{[-C_{\text{wet}}(a+2bH)\sigma_H]}$$

[This was indeed an error. We've replaced the approximate equation with the complete equation]

Also note what ambient values of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O are used in this estimate. Assuming 400 ppm CO<sub>2</sub>, 1900 ppb CH<sub>4</sub> and 3% H<sub>2</sub>O, I get values the same as, or very close, to those you list in the text.

[done]

What about the noise in the correction coefficients due to instrument noise in CO<sub>2</sub> and CH<sub>4</sub> during the water vapor correction experiment?

[Noise in the correction coefficients would appear as a persistent bias in the reported dry mole fraction of CO<sub>2</sub> and CH<sub>4</sub>; this is captured in the new uncertainty analysis]

P5837, L6: Figure shows that no switching between wet/dry streams is needed. There are 2 analyzers.

[switching between two streams allows you to cross-calibrate the two analyzers, so that the dry gas stream measurement on one analyzer can be used as the dry gas value in calculating the wet/dry ratio using data from the other analyzer]

P5837, L10: What H<sub>2</sub>O levels were tested?

[0.6-6% H<sub>2</sub>O mixing ratio, see also section 4.2.1]

P5837, L19: Need to mention wet/dry stream switching here.

[done]

P5837, L25: Are 1 or 2 analyzers used in this NOAA implementation?

One analyzer was used.

P5838, L17: LSCE and NOAA used 1 analyzer, MPI used 2.

P5838, L20: Was the dew point generator water acidified?

[no. this info was added to the text]

P5839, L16: Has the wet hydrophobic particulate filter ever been tested for CO<sub>2</sub> effects? Any wet surface has the potential to modify CO<sub>2</sub>.

[not rigorously, other than via the experiments shown here and in the supplemental material. But, we would not expect any issue – because the material is hydrophobic, it does not wet, and should not present a large water surface area to the gas stream.]

P5818, L18: How were all the instruments adjusted to the same water scale? Were they compared against the ‘golden instrument’ used in Chen et al?

[the water scales are not adjusted. This was a hypothetical suggestion that is clarified in the text. At MPI, different analyzers were set up to measure the same gas stream with different water vapor levels, and compared against the CFADS37 analyzer used in Chen et al., 2010]

P5847, L23: This is why you should note the concentrations of CO<sub>2</sub> and CH<sub>4</sub> used in the water vapor correction experiments presented in this paper.

[done in the uncertainty analysis section]

P5850, L6: Comment on the offsets and variability of the comparison.

The offsets can be explained by the uncertainties of the in situ CRDS and flask measurements. The variability is mainly due to unaccounted atmospheric variability. See section 5.1.

P5850, L28: Drift or noise?

[Drift, in the sense that the deviations seem to persist on a multiple data point time scale. I think of noise as being essentially uncorrelated from measurement to measurement. Perhaps this is just semantics, but I prefer the term drift]

P5851, L9: Not biasing under these humidity conditions. Most of these time series comparisons are only done in the 0-1.5% H<sub>2</sub>O range.

[range added]

P5851, L23: Note the temperature and pressure conditions of the Nafion dryer.

[done]

P5851, L27: What water vapor correction coefficients were used in this experiment? Dilution by H<sub>2</sub>O = 0.04-0.15% still needs to be accounted for.

[It is corrected using the default Chen et al (2010) coefficients. The text was changed to clarify this.]

P5853, L14: This is why the data should be H<sub>2</sub>O corrected.

[see above]

P5855, L3: This is a big spread. Comment on the scatter of the observations > WMO.

[done]

P5857, L21: Within compatibility targets up to ~1.2% H<sub>2</sub>O.

[done]

Supplementary material:

Needs some introduction on what you are testing, pH, CO<sub>2</sub>/CH<sub>4</sub> degassing and why. Also where these tests were done. Picarro or NOAA?

[done]

Fig S2, right and left panel descriptions are reversed. Explain the addition of dry air and the step change in each droplet experiment. Point out CO<sub>2</sub> degassing on the figure panel.

[done]

Fig 1: List labs that used this setup. MPI, NOAA, LSCE.

[done]

Fig 2: Need legend. Pick a different symbol for the injection T. Same as excess flow now. List labs (MPI/NOAA, empa, lsce, picarro)

[done]

Fig 5: Standardize the label for the CDRS, CFADS, Picarro.

[done]

Fig 7 & 8: CO<sub>2</sub> and CH<sub>4</sub> concentrations used in these experiments?

For Fig. 7, CO<sub>2</sub> was between 380 and 430 ppm, and CH<sub>4</sub> was between 1800 and 2000 ppb. For Fig. 8, CO<sub>2</sub> was between 360 and 390 ppm, and CH<sub>4</sub> was between 1700 and 1900 ppb. This information is now included in the figure caption.

Fig 8: '(without rescaling water vapor)'

[done]

Fig 9: Standardize y-axis labels. LSCE results. Over 20 days and 5 replications.

[done]

Fig 11: Relative to Chen et al would make these comparable with previous plots.

[done]

Fig 12: Comparison of flask measurements with what?

[done]

Fig 13: Flow rates?

[done]

Fig 14: Why is there so much noise in the target tank? 'as well as the difference (grey...'

[clarified in caption]

Fig 15: In histograms, mark zero in red, not the mean. Plot difference vs H<sub>2</sub>O?

[done]

Fig 16: PAL color is hard to see.

[clarified]

Fig 17: CO<sub>2</sub>?

[clarified]

Fig 18: How does this look if the PAL instrument is corrected every 9.5 h or daily, etc. for drift like the WCC instrument?

[This would be interesting, but is outside the scope of this paper]

Fig 19: Mention GAW target for CH<sub>4</sub>.

[done]

Fig 23: legend?

[clarified]

Fig 24: Hourly averages? Dried minus wet or wet minus dried? Scale makes it hard to see trends. Can zoom in on y-axis.

[clarified]

Fig 25: Why not average both at 30s?

[done]

Fig 26: The slopes, not the medians are important here. Medians are the same in all figures (vs H<sub>2</sub>O, CO<sub>2</sub>, time), no extra information is presented this way.

[clarified plots]

## Referee #2

General Comment I am familiar with all the scientists, their work, and the activities of all their associated collaborators, and I am quite familiar with the CRDS technologies. All these scientists have a long track record of advancing our understanding in atmospheric sciences and working collaboratively with larger projects. This is a timely manuscript, and has broad application to your readership. I greatly appreciate all the hard work that has gone into this study and writing this manuscript. I have 3 basic comments, which are easily remedied. First, the science is basically sound, but is not reproducible. I know what the authors meant to say, but do not say it. The large amount of jargon and imprecise writing bogs down the reader. Moreover, there are numerous locations in the text that does not describe the methodology sufficiently enough to make the paper reproducible.

[author response] This observation is excellent. Much effort has been made to improve the reproducibility of the manuscript to address this point.

A key issue is the how the authors choose their averaging times. I know they have Allen's variances, which should use as part of their justifications. Ultimately, the manuscript must be scientifically objective, and make the methodology transparent and reproducible for this sensor to be considered by the research community.

[author response] This point is also important. As it turns out, for 30-second or longer averages, instrument noise is not a dominant factor in the uncertainty of either the determination of the coefficients or in assessing the effectiveness of the correction coefficients. Text has been added to the document to reflect this point.

Second, It is always tricky for good scientists under the employment of a private corporation to publish – in this case, this manuscript does not appear to offer objective, well thought out and reproducible data to support their claims (I know they their intent is to be far and open, but the style of writing is filled with vendor jargon and descriptors that read more often like an advertisement.) It reads far more as an advertisement than objective science, and at time, the results follow the same (lack of) scientific rigor. This should be edited out to make it transparent and accessible by a broader audience.

[author response] The referee raises a very important point, and a valid criticism regarding the language used in the manuscript in certain parts. Any perception by the referee that this paper is intended an advertisement for Picarro is inaccurate. In response to this point, the language has been refined to remove subjective language, and vendor references have been removed when unnecessary.

The authors are better served by having independent analyses done by outside Principal Investigators, at least as first author.

[author response] We respect the opinion of the referee, but we remain comfortable with the reader's ability to judge the integrity of the authors and the merit of their work.



Lastly, the style, tense, voice, and imprecision of the writing does not lend to an easy manuscript to read, understand without the reader asking themselves lots of questions. The style of communication lacks rigor. All these issues have to be made in this manuscript with scientific rigor. Some, not all the issues with writing, are outlined below.

[author response] Substantial effort has been made to clarify the language.

All figures are not consistent publishable graphics. They should be re-worked to provide a storyline with the same graphical resolution, appearance, and consistency of information.

[author response] This has been done.

Specific Comments. P5825, L9 (CRDS) is not needed in the abstract since it is not repeated in the abstract. Abbreviation will be needed in the text

[removed]

P5825, L10 'have led to the development of highly stable and precise greenhouse gas analyzers capable of highly accurate measurements of carbon dioxide, methane, and water vapor.' Highly qualified statement with no citation to back this up. It reads more like an advertisement. Soften the text, or add citation.

[done]

P5825, L11 remove 'compatibility' are these really termed 'compatibility goals' but WMO? If so, they must be italicized or indicated in way that they refer to a specific criteria, otherwise, remove.

[WMO/GAW specifically refers to these goals as compatibility goals. The term has been italicized here.]

P5825, L20 'up to at least 1% water vapor.' Of what? P5825, L22, 23 'least 2% over the life of the instrument,' 2% of what? 4% of what?, unclear.

[This has been clarified]

P5826, L2, 'long-lived species' of what? Gaseous atmospheric constituents? P5826, L5 clause 'due to long-lived greenhouse gases' does not make sense, please check tense/text. Moreover it is redundant to the clause in the previous sentence.

[done]

P5826, L9 add 'globally' to 'of the total radiative forcing globally'.

[done]

P5826, L9 'accounts' to 'accounted', it is past tense, not infinitive tense

[done] P5826, L10 remove 'long-lived greenhouse gases', it is redundant, you have stated as much several times already in the short amount of text.

[done]

P5826, L14, What is 'over their atmospheric lifetimes.', suggest removal.

[clarified]

P5826, L17 add text to 'the magnitude' to 'the magnitude and rate..'

[done]

P5826, L20, 'validation for estimates' confusing text. Do you mean validation of model estimates? because the measurements themselves are 'estimates' not a validation of anything, unless you specifically call out the validation of [what?]. or just remove 'of estimates'.

[clarified]

P5826, L22, 'the atmospheric signals.' is jargon.

[modified]

P5826, L23 'The increasing spatial resolution afforded by these networks is already leading to increased spatial resolution of emissions from global/continental scales' re-ally? Seems either circular logic, or something is missing. Increased spatial resolution of estimates is leading to increased spatial resolution of emissions?

[clarified]

5827, L5 'GC (Gas Chromatography)' flip, Gas Chromatography (GC), ditto on the following lines.

[done]

5827, L6 'dried gas streams' jargon

[modified]

5827, L7 'are only meaningful' why?

[clarified]

5827, L13, again what does 'meaningful data' mean? Unclear

[clarified]

5827, L14 error means lots of things. What type of error? Systematic bias? Is the bias directional always positive in this case (+) or bi directional (+/-)? More description on what type of error this is.

[clarified]

5827,L26 change 'a leaky connection' to 'leaks'

[done]

5829, L4 'cross-talk' jargon, re-write. And elsewhere, re. P5835L26

[done]

5829, L13, 'of highly stable and precise measurements of' is stating it as fact without prove. As such reads more like an advertisement. Careful crafting to the text is needed here.

[clarified]

5829, L15 add text to read 'the models G1301,

...'

[done]

5829, L19 remove 'and described in greater detail in' just reference Crossen 2008

[done]

5829, L20 etc. text describing when sensors were available is not relevant to this paper and should be omitted. It continues to make the paper read more like an advertisement.

[done]

5829, L24 'interchangeably.' Jargon, rewrite.

[done]

5829, L24 'This family of instruments has been adopted throughout the greenhouse gas measurement community, and a great deal of work has been done to establish their performance under humid sample gasconditions.' Reads like an advertisement, rewrite.

[done]

5830, L3, 'These analyzers are all based upon cavity ring down spectroscopy (CRDS), an all-optical technology that de-livers high stability and precision in a compact, field deployable package.' Reads like an advertisement without backing up these statements with evidence/data/etc.

[done]

5830, L8, 'precision' and accuracy? Both? Why just precision?

[The long path length enables high precision measurements. High accuracy requires a chain of traceability to reference standards. High accuracy measurements are certainly possible with these analyzers, but it takes more than just the long path length being discussed at this point in the paragraph.]

5830, L10 'control system' what is it controlling, otherwise it is just jargon.

[clarified]

5830, L15 'control loops' jargon, rewrite.

[done]

5830, L16, now we are delivering 'accurate' measurements without a definition?

[clarified]

5831, L8 please define 'meg' for those not familiar with this nomenclature

[done]

5831, L18, 'the CRDS instruments models described in this manuscript.' Advertisement, omit, or rewrite

[In issues where spectroscopy is of crucial concern, as it is here, it is important to highlight not only which spectral lines are used, but also whose spectral analysis algorithms are being employed. The spectroscopic behavior of this instrumentation is inextricably linked to the vendor who manufactured the instrument. Identifying who built the spectrometer is of necessary scientific value.]

5834, L7 'validation measurements.' I do not think this is what you mean. Calibration? Or validation of what? Calibration coefficients? Performance? Inter comparability?

[clarified]

5834, EQ2 what are x and y? empirical coefficients?

[clarified]

5834, L14, '1.5 %.' Is the +, -, or +/-?, unclear

[clarified]

5835, L17, what 'additional noise'? Inherent electronic noise? Precision? Over what averaging period? Something is missing here. Otherwise it is just jargon without qualifying what you mean by 'noise'

[clarified]

5835, L19, 'using the manufacturer guaranteed noise specification of 0.003% for water on the 5min measurement.' Reads like an ad-vertisement. Rewrite

[done]

5836, L9, add text 'but with variable humidity.'

[done]

5837, L3, 'LI-COR model 610)' needs manufacturer's location

[done]

5837, L14 'neighboring dry air measurements' rewrite. I know what you mean, but it is imprecise writing, please change.

[done]

5838, L1, webpage address is sloppy writing, please provide the manufacturer, their location, and model to ensure reproducibility of this experimental design.

[done]

5838, L15, 'perhaps the most straightforward implementation of a test method to determine the correction coefficients' seems like a very subjective statement. Needs to be re-worked

[clarified]

5838, L20, 'how is 'equilibrium state' being tested? What are the criteria for 'equilibrium state'? otherwise this is not testable or reproducible.

[clarified]

5839, L1 'Further, the method is somewhat cumbersome and therefore difficult to implement in a field setting.' Seems to contradict the first sentence in this section

[clarified]

5840, L12, 'stainless steel Swagelok filter' imprecise writing, please state the fitting then in parentheses name the manufacturer, their location, and model number, otherwise this is no reproducible, nor consistent with standard scientific writing and notation.

[done]

5841, L11, 'Experiments usually take 1–2 h.' why? Seems to be relevant, otherwise this experiment is not reproducible

[clarified]

5841, L15, 'two mass flow controllers' make, location, model?? 5842, L1, 'overall stability' defined as what? Otherwise it is just a word and not reproducible.

[clarified]

5842, L5 remove 'highly'.

[done]

5843, L15, “golden” remove

[done]

5843, L16, “calibration” why in quotes? Is this a calibration or not? If not, what does this mean. Be very specific and concise in your writing.

[clarified]

5843, L19, ‘shipped by Picarro’ remove, it is advertisement.

[done]

5844, L19, ‘an excellent stability over time,’ subjective judgment, in the results tell the reader what the difference is? What is the stability, not tell us that it is excellent. Imprecise and subjective writing that is not appropriate.

I could not edit much more because of the repeated poor use of language, imprecise writing, and lack of reproducibility. The remaining part of the manuscript should be reviewed, edited and re-written. Watch tense throughout

[we have worked through the rest of the text to address these concerns]

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 5823, 2012.