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Interactive comment on "Impact of isotope composition on the humidity dependency correction of water vapour isotope measurements with infra-red cavity ring-down spectrometers" *by* Yongbiao Weng et al.

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This paper shows detailed tests for the calibration of water isotopic composition vs humidity using Picarro CRDS instrument. Such calibration exercises are important and compulsory efforts to do when working with such instrument to provide records of d18O and dD of the atmospheric water vapor since water mixing ratio strongly varies on the different places (first because of temperature). Several groups are thus performing such exercises and it is interesting to see such results as a basis for discussion.

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For each publication of new d18O and dD records in the water vapor, a methodology section is devoted to the so-called isotopes vs humidity calibration but the present paper is only focused on the method and does not show new records. The question is thus to know if the results displayed here are enough to make a publication by itself, especially since the applicability of the resuts obtained here are not easily transferable to another study and some results are questionable (see below).

AUTHOR'S REPLY: The main novel aspect of the manuscript is that we systematically investigated the impact of the isotope composition on the humidity dependency correction in the water vapour isotope measurements. Previous studies only investigated the humidity dependency for one or more standard waters separately, and not the systematic dependency on isotope ratio. In the revised manuscript, we will bring this important new aspect of our study forward more clearly. We chose AMT as journal for publication because our results are mainly focused on method development. Presenting a new isotope record is not within the objectives of our manuscript.

Despite my mixed feeling on the outputs of the paper, I really appreciate the care given to the description of the measurements and the results. Even if some results seem strange (contrasted dependence to humidity in ascending and descending mode for one standard, figure 9, cf later), they are not hidden or discarded from the study and I really appreciate this honesty in the treatment of the results. As a consequence, I would recommend not to accept the paper in its present form and incite the authors to make more links with previous studies and previous calibration. As an example, they only compare their correction with Bonne et al‘s correction (concluding that their approach was appropriate) while all studies publishing new d18O and dD records in the water vapor have a section on isotopes vs humidity calibration. I therefore strongly urge the authors to discuss other paper dealing with such correction, discuss if it was appropriate given their new results and, if not, discuss the implications in term of uncertainties, signal detection, etc. . .

AUTHOR'S REPLY: While we agree that application to previously published datasets could further demonstrate the relevance of our correction scheme, it is not possible or the objective to directly do so within the present study. This would require subjecting those previously used analyzers to a similar kind of multi-standard characterization at first, as the isotope-humidity dependency is an instrument-specific characteristic. Within the study we compare to the one previously published calibration scheme that approximates our correction scheme (Bonne et al., 2014). As highlighted by the other referees, in the revised manuscript, we will amend the discussion by relating the uncertainty of the correction scheme to the instrument precision at low humidity.

My detailed comments along the text are given below.

- I am quite surprised by the performance obtained at low humidity (below 2000 ppmv). In some cases, the error bars are even not visible on figure 1. By comparison, uncertainties displayed by other studies (e.g. Guilpart et al., JGR, 2017) are at least one order of magnitude larger. I would appreciate that the authors comment and explain such differences. This also has an impact on the outputs of the study. I had the feeling from previous studies that it was impossible / very difficult to perform accurate measurements below 2000 ppmv with a Picarro analyser because of the strong noise in the measurements. The very small error bars displayed on figure 1 do not go along previous studies in this sense.

AUTHOR’S REPLY: In Figure 1, we now report the standard error of the mean of several injections, this was miscalculated in the submitted manuscript. It is correct that at lower humidity, the standard deviation of each injection or measurement interval increases substantially. For the present study, we consider the standard error of the mean, provided by multiple, repeated measurements, to be the most relevant information with regard to fitting the correction surfaces. We also provide the n so that the standard deviation of an individual measurement can be extracted.

- P. 5, l. 28: can you precise what you mean by “the lower precision with SDM measurements” ? Be more accurate, give number. . .

AUTHOR'S REPLY: The number will be added in the revised manuscript.

- P. 6, l. 4: what does it mean "certified down to 200 ppmv" ?

AUTHOR'S REPLY: According to manufacturer specification of Option S0508 (optimised performance during low humidity conditions, calibration to 200 ppm H2O), the instrument has an optimized performance during low humidity conditions compared to regular instruments (down to 200 ppmv instead of 1000 ppmv). This is a feature that the manufacturer has customized according to our order. The exact details of the calibration procedure have not been made available. We will provide additional information in the revised manuscript.

- On figure 1, it would help the reader to have the isotopic value (at least d18O or dD) for each standard to see directly the influence of isotopic composition on the isotopes vs humidity relationship.

AUTHOR'S REPLY: We will add d18O values to the legend of Figure 1.

- Everywhere in the paper, I do find that the term "bias" (e.g. on p. 8) is not used properly. Bias with respect to what ? Indeed, in all studies dealing with d18O and dD in the water vapor, there is a correction for isotopes vs humidity. This effect is well known and taken into account so I would not call it a bias. This is a classical procedure to correct for this influence especially for studies dealing with low humidity. If there is a bias, then, it is perhaps linked to the method used by others to correct for this effect if they considered only one standard and did not adjust the uncertainty bars properly. However, this is not discussed in the present manuscript. I encourage the authors to avoid using bias (which is misleading in my opinion) but better use the term "isotope (humidity relationship" or "isotope-humidity correction")

AUTHOR'S REPLY: We agree with the reviewer and will replace the word 'bias' by a more neutral expression such as 'deviation' throughout the revised manuscript.

- The section "correction framework" is a bit problematic. First, it implies that the readers should use such a frame but we can wonder if it is correct and if it is useful. The reason why we can wonder if it is correct is that in figure 9, the authors show huge difference (actually opposite) dependencies of isotopic composition to humidity for descending and ascending humidity during the calibration method. This strongly questions the validity of the conclusions presented here. Also, the fact that the error bars for low humidity are so small are questionable since previous studies have shown much different figures.

AUTHOR'S REPLY: It is correct that the fits to standard MIX appear with an opposite sign for upward/downward calibrations. However, this opposite sign is only observed for standard MIX, which has a very limited number of data points. We will therefore repeat the experiments with more data points for this standard to confirm or reject this finding. All other standards only show some small hysteresis effect, but no sign reversal. In the revised figure, we will report the correct standard error of the mean, which will show as larger error bars (see above).

The reason why we can wonder if it is useful is that the author show that the correction performed by Bonne et al's using only the two standards bracketing the isotopic composition of the water vapor isotopic measured in their site is appropriate. Such approach (Bonne et al.) is actually a classical method used by many authors since SDM are equipped for performing calibration with two standards. I thus do not see the added value of such complicated procedure considering 5 standards, some of them being far from the range of values of interest.

AUTHOR'S REPLY: If the instrument is deployed in ambient conditions with widely varying humidity and isotope compositions, such as during aircraft measurements, characterisation across the entire range of measurement conditions is needed. Comparing with the approach in Bonne et al 2014, our approach provides new values in three perspectives. First of all, our approach provides a more accurate solution by actually being able to partly capture the non-linearity of the humidity response functions on a large spread of isotope compositions since we use five laboratory standards. Using two standards, the approach by Bonne et al 2014 (hereafter Bonne2014) assumes a linear dependency between the two response functions in order to correct the humidity dependency for other isotope compositions. Secondly, our finding that the isotope composition-humidity dependency is a robust instrument behaviour does not support Bonne2014's hypothesis that the contrasting humidity responses of their two working standards is likely an artefact of residual humidity in the dry air dried by Drierite. Finally, we show that using a dry gas cylinder (or a more advanced drying system) can preclude the possible influence of residual humidity in the dry gas and thus lead to a more accurate humidity response function.

- It is also difficult to follow the authors when they propose equations 4 and 5 to fit the dependency to humidity and to isotopic composition. Since there is not any physical mechanism to explain the dependencies observed here, there is no reason why there should be a particular format for the fitting equations.

AUTHOR'S REPLY: It is correct that the proposed fitting function is not chosen on physical basis, it simply fits well with the observations we obtained for the tested instrument. The readers can choose to follow the same correction framework, but need to check and determine the best choice of fitting function according to the observations for their specific instrument. These points will be made clearer in the revised manuscript.

- Figure 4 is without error bars so that the comparison between the correction method can not be done. The authors should present a calculation of these error bars and use them for the comparison.

AUTHOR'S REPLY: Error bars will be included in revised Figure 4.

- P. 12, l.19 to 26: I am not really impressed by such discussion. In all studies dealing with such measurements, the authors chose a standard with an isotopic value close to the one of the measurements to be performed.

AUTHOR'S REPLY: We will rephrase to clarify that, in the cases when the range of

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isotope compositions is known in advance, and proper standards can be chosen, there is no direct benefit from using our characterisation method. However, in the case of a previously unknown range of isotope ratios, or strongly varying conditions, a comprehensive characterisation provides advantages and should be preferred. Unknown ranges are particularly likely for atmospheric measurements of vertical profiles, or over a wide area from moving platforms.

- Similarly, I am moderately impressed by the fact that the correction is smaller for the measurements performed on the ship. It is obvious from figure 1 that the effect discussed here is not important for this humidity range. One sentence can easily replace section 5.2 (the results can also be omitted from this manuscript).

AUTHOR'S REPLY: We will shorten the discussion at this point in the revised manuscript, but would like to keep the ship measurements as a contrasting example to emphasize the point made in the comment directly above.

- Section 6.3 can be summarized in 2 sentences (the tables already explained the methods and the results can be summarized in one sentence).

AUTHOR'S REPLY: We will shorten the section in the revised manuscript.

- Figure 8 shows that there is a significative effect of the carrier gas (considering the error bars). Also, I am surprised to see larger error bars here. So what is the conclusion? Could the authors end up with an estimate of the error bars after their corrections given the uncertainty on the determination of the isotopes vs humidity depending on the carrier gas and sequence of humidity variations (ascending or descending).

AUTHOR'S REPLY: We confirm as found in previous studies that a change in the carrier gas induces a different isotope-humidity dependency. Our results are most relevant for measurements in ambient air, and we will therefore attempt to shorten the discussion of N2 in the revised manuscript. We will also attempt to provide more information on the errors after correction with our proposed isotope-humidity dependency correction scheme, as requested by Referee #3.

- Figure 9 is really rising many questions on the validity of the conclusion of this study and should be given extreme care if this manuscript is revised. It shows opposite evolution of isotopes vs humidity for different sequence of humidity variations. I am surprised that the authors did not try to understand deeper what happened here because it is central to their entire study. I would really urge the authors to repeat their measurements and see if they can repeat this opposing behaviour for different ways of varying the humidity. If this is a solid feature, then, there may be an explanation and it should be investigated. If this behaviour is indeed true, the correction proposed here is not be correct or at least error bars in the reconstruction should take it into account. In any case, the authors should comment more on this surprising result and on its implication. Actually, it is a very interesting result and it should definitively be investigated more to make progress on the isotopes vs humidity relationship in picaro instrument.

AUTHOR'S REPLY: We agree with the referee that the contrasted dependence to humidity in ascending and descending mode for the standard MIX needs corroboration. As mentioned above, there are currently not sufficient data points for both the ascending and descending branch at low humidity to make definite conclusions, and we will repeat this experiment. This uncertainty in the dependency behaviour has been addressed in Sect. 6.5. It is possible that for a standard that is close to a turning point in the correction surface, hysteresis effects with opposing sign may become visible within the range of uncertainty, but we will await the repeated experiments before further discussion.

- I find that a background humidity of 60-80 ppmv (p. 17) is quite high when discussing measured values at 500 ppmv. It is quite surprising that you could not obtain lower values with dry air.

AUTHOR'S REPLY: The background humidity of 60-80 ppmv is not from the carrier gas, but from the remaining moisture in the system (including vaporizer chamber, analyzer chamber and the filter surface in between). The background humidity in the analyzer when measuring the dry carrier gas is <10 ppmv. The discussion will be made clearer in this respect in the revised manuscript.

- Section 7 started well. We really would like to understand this dependence to isotopic composition. Unfortunately, the discussion is really short and disappointing.

AUTHOR'S REPLY: The discussion will be extended based on the input of all referees. Regarding the spectroscopic effects, also taking into account the fact that we are working with commercial instruments, it is not certain that we will be able to go far beyond indicating potential factors within this manuscript.

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