

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.

Anonymous Referee #1

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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. 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

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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 results obtained here are not easily transferable to another study and some results are questionable (see below). 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. . .

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.

- P. 5, l. 28: can you precise what you mean by “the lower precision with SDM mea-

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surements" ? Be more accurate, give number. . .

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

- 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.

- 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"

- 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. 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

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see the added value of such complicated procedure considering 5 standards, some of them being far from the range of values of interest.

- 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.

- 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.

- 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.

- 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).

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

- 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).

- 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

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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.

- 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.

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

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