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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 presents an interesting study on the impact of the isotope composition on the specific humidity dependent correction of water vapour isotope measurements with different recent versions (L2130-2140) of commercial cavity ring-down spectrometers from Picarro. It presents results of an elaborate laboratory study on the topic, which is important for measurements conducted in very dry environments such as in polar regions or the lower to mid free troposphere. This study fits well into the scope of AMT and I recommend publication of this interesting and relevant manuscript after the

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Discussion paper

following major comments have been convincingly addressed:

1) To me it is unclear, how the surface correction functions presented here relate to the total uncertainty of the measurements at low absolute humidity (% of total uncertainty). In particular, because in other studies the signal to noise ratio gets rather low in very dry conditions. 1a) Specifically, the dependence of the measurement precision on the absolute humidity is normally considerable with these instruments, a fact that is only mentioned indirectly in one sentence in the manuscript (p.3, l.6). This aspect should be addressed explicitly. Clearly, the amplitude of the correction should be placed into the context of the uncertainty associated with the entire postprocessing framework to be able to judge its significance (including the normalisation to the VSMOW-SLAP scale, where the instrument precision is an important component).

AUTHOR'S REPLY: We agree that this aspect needs to be highlighted more clearly, and we will address this in the revised version with a comparison of the amplitude of the correction and the total uncertainty of the measurements at low humidity, providing explicit values.

1b) The much smaller precision of CRDS measurements at low humidity is also the reason, why previous studies have found that the impact of the isotope composition on the humidity dependence is not significant for older instruments. The latter were characterised by very low signal to noise ratios at low humidity. This point deserves to be mentioned on p. 2, l. 18.

AUTHOR'S REPLY: This point will be mentioned in the revised manuscript.

1c) The errorbars in the Figs with autosampler injections seem unrealistically small to me. Are these small errorbars due to the fact that the authors use the standard deviation of isotope variables averaged over 3-4 injections only, yielding an overconfident measure of uncertainty? A more adequate estimate should be used for the autosampler injections.

AUTHOR'S REPLY: In Figure 1, we now report the standard error of the mean of several injections; it was calculated wrongly 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 number of measurements so that the standard deviation of an individual measurement can be recovered.

2) Unfortunately, the reader is a bit disappointed at the end of the paper to have read this detailed analysis of the isotope humidity dependency with no answer at all to the question to why it exists. The reader thus remains not entirely convinced that the effect is really a spectroscopic one. It could also be related to how the calibration vapour is produced (see Kurita et al. 2012, their Fig. 7).

AUTHOR'S REPLY: In Section 7 we have discussed with respect to two possible causes of the observed isotope composition-humidity dependency, i.e., whether it is an artefact from mixing with water remaining within the analyser, or an instrument behaviour resulting from spectroscopic or other design characteristics. Our work does not support the hypothesis of mixing effect, but points to a likely spectroscopic origin. The spectroscopic effects will be discussed in more detail in section 7 of the revised manuscript. We have tested two vapour generating approaches and found the isotope composition-humidity dependency is a robust feature for both approaches. Kurita et al. 2012 actually stated that they could not conclude from their experiment that the water vapor concentration dependency is related to their vapor production approach; they have rather suggested the concentration effect results are likely from the spectral fitting procedures used, including the removal of interferences in their analyzer (last paragraph of Sec. 3.2.3 in Kurita et al. 2012). We will include this information into the discussion section.

2a) I thus urge the authors to give the reader a bit more insight into what they would

argue the spectroscopic effects are (in particular with respect to pressure broadening effects and baseline shifts, see also Chen et al. 2010, Johnson and Really, 2017).

AUTHOR'S REPLY: Thank you for these references. As requested by all three Referees we will formulate a more detailed discussion of the potential spectroscopic effects in section 7 of the revised manuscript.

2b) For every setup a mean and standard deviation of the isotope variables obtained during dry runs should be provided (ideally in the respective Figures).

AUTHOR'S REPLY: Unfortunately we are not entirely sure what information the referee asks for. We understand it as the isotope composition reported during dry air/N2 measurement only, but do not see directly how it is connected to our results.

3) As mentioned in my pre-review, I appreciate the level of detail that is provided to the reader and the careful analysis that is carried out. However, the paper is currently very long for the simple message it actually conveys and tends to loose the reader, who is interested in transferring the method to his own instrument. It is not clear to me, why the 2D fitting procedure in Section 4 is discussed in such a detail, this part should be put into the Appendix and the procedure summarised in one paragraph of the main text. It is anyway not clear at this stage if the proposed fitting procedure is necessarily the best for all instruments, since it has no physical foundation.

AUTHOR'S REPLY: The proposed fitting function is not chosen on physical basis; it is chosen because it simply fits well with the observations we obtained for the tested instrument. The readers may follow the same steps in establishing a correction surface, but need to check and determine the best choice of fitting function for their specific instrument. This point will be made clearer in the revised manuscript. Also, we will shorten the section and consider moving it partly to an Appendix.

4) I am very critical of the results shown in Fig. 4, because I think that the data suffers from a measurement artefact: 4a) Could the author provide more information about the

temporal resolution of the data points shown in the profiles (1.25Hz?, 0.1Hz?)?

AUTHOR'S REPLY: The raw measurement was taken with a temporal resolution of ∼1.25Hz. But the temporal resolution of the data points shown in Fig. 4 is ∼0.125 Hz. We have plotted every 10th data point for the sake of clarity. We will update Figure 4 with time-averaged data (10 s to 60 s) which should alleviate potential measurement artefacts.

4b) In my opinion, a flow rate of 35 sccm is very low (if not too low) for performing precise and high resolution aircraft measurements given the Picarro cavity size. With this flow rate and a cavity size of 35 ccm, the air sample in the cavity volume is exchanged only once per minute. The response times of d18O and d2H have been shown in earlier studies to be different with an up to 10s slower response of d2H than d18O at such low flow rates. This difference in response time can lead to an artificial lowering of d-excess in a downward profile with the d2H lagging behind the d18O signal. Before publishing such very low values of d-excess (-40 ‰) at the upper edge of a cloud layer as naturally occurring, the data quality also in terms of other instrument setup characteristics (response time, precision) should be carefully checked.

AUTHOR'S REPLY: The flowrate of the instrument was about 35 sccm, and it was connected with short tubing to an inlet tube providing ambient air with a much higher flow rate of about 8 slpm. We are aware of the very low values of d-excess in the profile shown here. This is potentially an artefact due to the dephasing of d18O and dD profiles. This aspect will be explained more in the revised manuscript, while also emphasizing that we do not attempt an interpretation of the isotope data in terms of atmospheric processes in this manuscript. Nonetheless, the low values of d-excess will not affect our discussion of the impact of the different correction schemes. We will state more clearly that our aim is to use this data profile to demonstrate the impact of the dependency correction schemes rather than focusing on the physical interpretation of the dataset itself. To this end, we consider omitting the profile of the d-excess from the manuscript.

4c) Errorbars (2D) are indispensable for being able to show that the differences between the correction scenarios are actually larger than the measurement uncertainty (total uncertainty). The precision of L2130 instruments at 1000 ppmv is usually around 10‰ (d2H), 1-2 permil (d18O) and 10-15‰ (dexcess).

AUTHOR'S REPLY: We had excluded the error bars for clarity of the figure, but will include reference error bars in the revised figure to allow for a comparison of the correction to measurement uncertainty.

Minor comments and typos: 1) Title: "Impact of the isotope composition. . ."

AUTHOR'S REPLY: Will be done in the revised manuscript.

2) P.1, l.1: isn't the main point here that measurements can be performed in remote areas in general and specifically on mobile platforms?

AUTHOR'S REPLY: Will be changed to "in remote areas, on platforms such as ship and aircraft"

3) P.1, l.4 and other locations: I think the wording "humidity" or "humidity dependency" is a bit unprecise. The authors should choose what they like best, but they should avoid any confusion with an effect that would be relative humidity dependent. A clear definition at the beginning of the manuscript would be helpful and I would suggest always adding "absolute" or "specific "humidity" everywhere in the abstract.

AUTHOR'S REPLY: We have changed "humidity" to "absolute humidity" at several places where the term "humidity" alone could lead to confusion. We will use the term "absolute humidity" consistently throughout the manuscript.

4) P.1, l. 7: of the measured water vapour

AUTHOR'S REPLY: Will be done in the revised manuscript.

5) P.1, l. 8: humidity correction at low absolute humidity

AUTHOR'S REPLY: Changed to "at low absolute humidity".

6) P. 1, l12 and L17 replace "cold" by "dry". The temperature of the environment is not the relevant factor in this technical study.

AUTHOR'S REPLY: Replaced by "dry (often also cold)" and equivalent throughout the manuscript.

7) P. 2, l. 19: likely an artefact

AUTHOR'S REPLY: Will be done in the revised manuscript.

8) P.2, l. 29: the masking came mainly from the lower precision of the older versions of the CRDS instruments

AUTHOR'S REPLY: We will emphasize the lower precision from the older versions of the CRDS instruments. However, we also think that the characterisation method (number of standards used, dry gas supply, etc) is another important factor. Therefore we will state both factors in the revised manuscript.

9) P. 3, l. 19: Eq. 1: missing factor 2 for the H216O concentration in the denominator. Or alternatively write the equation for the atomic ratio.

AUTHOR'S REPLY: Because laser spectrometry measures the absorption intensity of the isotopic water molecules, we use the definition of molecular isotope ratio here. Therefore the factor 2 is not needed. We will make it clear that we are using the definition of molecular isotope ratio in the revised manuscript.

10) P. 5, l. 3: here the "measurement uncertainty" is mentioned but it is unclear what the authors mean. The uncertainty of the estimated drift?

AUTHOR'S REPLY: We will replace the "measurement uncertainty" with "the uncertainty associated with the estimated drift".

11) P. 5, l. 22: a humidity step

AUTHOR'S REPLY: Will be done in the revised manuscript.

12) P.5, l. 27: with the SDM

AUTHOR'S REPLY: Will be done throughout the revised manuscript.

13) P. 5, l. 29: again not clear what "measurement uncertainty" is, I would rather say that this is the uncertainty associated with the estimated drift.

AUTHOR'S REPLY: We will replace the "measurement uncertainty" with "the uncertainty associated with the estimated drift".

14) P.6, l. 21: replace "may have" by "have": the type of dry gas supply has an influence that's a fact, there are several studies showing this: Aemisegger et al. 2012 is one but several others show this as well: Casado et al. 2016, Johnson and Rella 2017 including other greenhouse gas CRDS studies (Chen et al. 2010, Nara et al. 2012, Long et al. 2013). These studies recommend to perform CRDS calibrations for atmospheric observations in natural air backgrounds or to develop transfer functions that translate between the calibration and observation backgrounds (Johnson and Rella 2017).

AUTHOR'S REPLY: Will be done in the revised manuscript. We will also include a reference to some of the cited studies.

15) P.6, l. 24: The use of several drying units in a row, vertical arrangement of drying units to prevent preferential gas flow and careful handling of tubing tightness usually provides the same background humidity as with a gas cylinder.

AUTHOR'S REPLY: We will add this point in the revised manuscript. Kurita et al. 2012 obtained dry air with humidity < 10 ppmv using two drying units in a row.

16) P. 7, l.10: what is the residence time of the sample within the system?

AUTHOR'S REPLY: Referring to the reply to issue 4b) above, the residence time/response time of the system is estimated to be in the order of 1 min (i.e., 35 cm^3 / 35 sccm) within the Picarro analyzer at standard pressure. We will include the

flow rate number in this context.

17) P.7, l.25-30: this sounds like a lot of repetition from the methods section.

AUTHOR'S REPLY: This paragraph will be shortened by removing repetitions.

18) P.11, l.14: as mentioned in the major comments, I don't think -40‰ is a physically sensible value. Even with extremely high ice supersaturation, I would not expect such low dexcess values in vapour to occur. Particularly in the context of the conclusion drawn on p. 20, l. 17 a careful check of the data would be appreciated here.

AUTHOR'S REPLY: We are also aware of these unusually low d-excess values. As mentioned in the reply to major comment 4a) and 4b) above, this may be an artefact caused by the dephasing of d18O and dD profile. It may be possible to alleviate the effect by a longer time averaging. Ultimately, however, this artefact will not affect the conclusion of this study, since we do not attempt to interpret the isotope profile in terms of processes, but rather focus on the impact of the different correction schemes across a range of isotope composition and mixing ratios, especially at the level above 2000 m (where the d-excess profile depicts normal values). To avoid confusing the reader, we consider removing the panel depicting the d-excess measurements from the manuscript.

19) P.13, l. 3: consequently, the measurements after calibration are. . ."

AUTHOR'S REPLY: Will be done in the revised manuscript.

20) P.13, l.19: remove "relatively" (see my minor comment 3 above)

AUTHOR'S REPLY: Will be done in the revised manuscript.

21) P. 14, l. 24: replace "substantially" by "substantial"

AUTHOR'S REPLY: Will be done in the revised manuscript.

22) P. 15, l. 1 (& at other instances): I don't particularly like the "heavy-enriched" and

“heavy-depleted” formulation and have not seen it elsewhere. I actually find it slightly confusing. But this is a matter of taste.

AUTHOR’S REPLY: We will replace these terms by “enriched” and “depleted” respectively.

23) P. 16, l. 17 around the 1H218O and H216O absorption peaks, d18O is a derived Variable.

AUTHOR’S REPLY: Will be done in the revised manuscript.

24) P. 16, l. 28: replace “by” by for

AUTHOR’S REPLY: Will be done in the revised manuscript.

25) P. 17, l. 8: that does not

AUTHOR’S REPLY: Will be done in the revised manuscript.

26) P. 17, l. 27 of the same

AUTHOR’S REPLY: Will be done in the revised manuscript.

27) P. 19, l.13: this is inconsistent with what is described on p. 6, l. 21 (see also my minor comments 14 & 15).

AUTHOR’S REPLY: We will revise the section with respect to dry gas supply and address the discrepancy in the characterisation results between dry air and N2, especially for d18O (Fig. 8a). We will clearly state that our correction scheme is most relevant for ambient air measurements using dry air as carrier gas, but note that there may be laboratory applications where N2 is used as a carrier gas, which will require their own characterisation functions.

28) P. 19, l. 30 replace “humidify” by “humidity”

AUTHOR’S REPLY: Will be done in the revised manuscript.

29) P. 20, l. 4: I find this recommendation a bit random because the number of standards to be used certainly depends on the application and the correction function of each individual instrument.

AUTHOR'S REPLY: We will revise the recommendation (3) in this way: Multiple (e.g., five, such as used in this study) standard waters that span the full range of ambient vapour isotope compositions are recommended to determine the isotope composition–humidity dependency surface.

30) Figures: 30a) Fig. 3: would a log scale for the x-axis help to make this Figure more effective? Furthermore, could the authors add an uncertainty estimate (contours) of the fit. I assume the uncertainty is also much larger at low humidities (due to a combined effect of less data points and lower precision of the measurements).

AUTHOR'S REPLY: The log scale will not make the figure more effective (we have tried it out), since there are only two data points below 1000 ppmv. A plot with normal scale is also more consistent with the previous figures. The uncertainty estimate will be added.

30b) Are the GSM1 ascent fit in Fig. 9b,c really correct? The fit seems not particularly good from eye.

AUTHOR'S REPLY: We will check the fit and correct in the revised manuscript if necessary.

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