

# ***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 #3**

Received and published: 21 November 2019

Review of “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.

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

Printer-friendly version

Discussion paper



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 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).

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.

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.

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).

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).

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).

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 lose 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.

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?)?

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 d2H in a downward profile with the d2H lagging behind the d18O signal. Before publishing

such very low values of d<sub>excess</sub> (-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.

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‰ (d<sub>2</sub>H), 1-2 permil (d<sub>18</sub>O) and 10-15‰ (d<sub>excess</sub>).

Minor comments and typos:

- 1) Title: “Impact of the isotope composition. . .”
- 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?
- 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.
- 4) P.1, l. 7: of the measured water vapour
- 5) P.1, l. 8: humidity correction 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.
- 7) P. 2, l. 19: likely an artefact
- 8) P.2, l. 29: the masking came mainly from the lower precision of the older versions of the CRDS instruments
- 9) P. 3, l. 19: Eq. 1: missing factor 2 for the H<sub>2</sub>16O concentration in the denominator.

Or alternatively write the equation for the atomic ratio.

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?

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

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

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.

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).

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.

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

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

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 de excess 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.

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

[Printer-friendly version](#)[Discussion paper](#)

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

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

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.

23) P. 16, l. 17 around the  $1\text{H}218\text{O}$  and  $\text{H}216\text{O}$  absorption peaks,  $\text{d}18\text{O}$  is a derived variable.

24) P. 16, l. 28: replace “by” by for

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

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

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

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

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.

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).

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

References:

[Printer-friendly version](#)[Discussion paper](#)

Chen, H., Winderlich, J., Gerbig, C., Hoefer, A., Rella, C. W., Crosson, E. R., Van Pelt, A. D., Steinbach, J., Kolle, O., Beck, V., Daube, B. C., Gottlieb, E. W., Chow, V. Y., Santoni, G. W., and Wofsy, S. C.: High-accuracy continuous airborne measurements of greenhouse gases (CO<sub>2</sub> and CH<sub>4</sub>) using the cavity ring-down spectroscopy (CRDS) technique, *Atmos. Meas. Tech.*, 3, 375–386, doi:10.5194/amt-3-375-2010, 2010.

Johnson, J. E. and Rella, C. W.: Effects of variation in background mixing ratios of N<sub>2</sub>, O<sub>2</sub>, and Ar on the measurement of  $\delta^{18}\text{O}$ –H<sub>2</sub>O and  $\delta^2\text{H}$ –H<sub>2</sub>O values by cavity ring-down spectroscopy, *Atmos. Meas. Tech.*, 10, 3073–3091, <https://doi.org/10.5194/amt-10-3073-2017>, 2017.

Kurita, N., Newman, B. D., Araguas-Araguas, L. J., and Aggarwal, P.: Evaluation of continuous water vapor  $\delta\text{D}$  and  $\delta^{18}\text{O}$  measurements by off-axis integrated cavity output spectroscopy, *Atmos. Meas. Tech.*, 5, 2069–2080, <https://doi.org/10.5194/amt-5-2069-2012>, 2012.

Long, D. A., Gameson, L., Truong, G. W., Bielska, K., Cygan, A., Hodges, J. T., Whetstone, J. R., and van Zee, R. D.: The Effects of Variations in Buffer Gas Mixing Ratios on Commercial Carbon Dioxide Cavity Ring-Down Spectroscopy Sensors, *J. Atmos. Ocean. Tech.*, 30, 2604–2609, <https://doi.org/10.1175/JTECH-D-13-00039.1>, 2013.

Nara, H., Tanimoto, H., Tohjima, Y., Mukai, H., Nojiri, Y., Katsumata, K., and Rella, C. W.: Effect of air composition (N<sub>2</sub>, O<sub>2</sub>, Ar, and H<sub>2</sub>O) on CO<sub>2</sub> and CH<sub>4</sub> measurement by wavelength-scanned cavity ring-down spectroscopy: calibration and measurement strategy, *Atmos. Meas. Tech.*, 5, 2689–2701, <https://doi.org/10.5194/amt-5-2689-2012>, 2012.

---

[Interactive comment on Atmos. Meas. Tech. Discuss.](#), doi:10.5194/amt-2019-316, 2019.

[Printer-friendly version](#)[Discussion paper](#)