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 #2

Received and published: 19 November 2019

This manuscript is a systematic laboratory study of the humidity dependency of water isotopologue measurements by commercial Picarro cavity ring-down spectrometers (CRDS). The authors characterized how water isotopologue ratios and d-excess are biased by water content (‘humidity dependency’), in particular at low water mixing ratios below 1600 ppmv. Furthermore, this humidity dependency varies with isotopic composition, called ‘isotope composition-humidity dependency’ here. The dependency is seen in all three CRDS as an instrument characteristic that is, to first order, constant over 1 to 2 years of measurements.
At higher humidities (>4000 ppmv), Picarro CRDS show negligible bias with water vapor mixing ratio or with the isotopic composition. The authors develop a procedure for correcting the isotope-composition-humidity dependency of Picarro CRDS.

My comments: I recommend that this paper be published only after major changes. My detailed comments are listed below:

1. I do not like the mixed terminology of ‘humidity’ and ‘ppmv’. First of all, ‘ppmv’ or ‘parts per million by volume’ is not defined in the text. The unit ppmv is used only with mixing ratio. Instead, specific humidity is typically in units of mg/kg or ‘parts per million by mass’. These are standard terms but unfortunately the literature uses ‘Humidity dependency’. As a path forward, I suggest that the authors consider the following:

1.1 Define the water mixing ratio measured by the Picarro as units of ‘ppmv’ or ‘parts per million by volume’ where it first appears, page 2, line 2.

1.2 Every time the water mixing ratio is used, change ‘humidity’ to ‘water mixing ratio’, e.g., page 2, line 2, “...within a water mixing ratio range of 19,000~21,000 ppmv (parts per million by volume)”

1.3 Every time you refer to humidity dependency, use ‘humidity dependency’ (because this term is now accepted in the water isotope community).

2. Given that many papers have noted the concentration dependency (Wen et al., 2012, Bailey et al., 2015) or mixing ratio dependency (Aemisegger et al., 2012), then what specifically is new in this paper? The authors should emphasize that characterization of ‘isotope composition-humidity dependency’ is new here (if that is the case?).

3. It seems that the ‘isotope composition-humidity dependency’ is instrument-specific. Can instrument issues like pump speed or plumbing details play a role? These are not discussed.

4. Section 7 aims to explore whether the isotope composition-humidity dependency
is due to mixing with water remaining in the analyzer, or from spectroscopic or other instrument characteristics. The discussion of spectroscopic effects (page 18, lines 3-9) is too short, and I recommend more discussion here to provide basic instrument details.

4.1 What are the wavenumbers of the absorption lines?
4.2 What are typical absorption depths?
4.3 Demonstrate what is the uncertainty in fitting spectra.
4.4 What is the manufacturer’s recommended minimum humidity at which to take measurements?

5. Section 8 speculates, without supporting evidence, that ‘the isotope composition-humidity dependency is to first order a constant instrument characteristics. It probably has a spectroscopic origin, resulting from a larger uncertainty in the fitting of absorption peak at low water molecular concentrations . . .’. Both in Section 8 and Section 7, this same language is used without supporting evidence. I strongly recommend the authors provide more detail on instrument error budget (in general) and the uncertainty in fitting spectra (as I said above).

Editing comments:
1. Page 6, line 25, change ‘we have replaced the gas drying unit to dry gas cylinders’ to ‘we have replaced the gas drying unit with dry gas cylinders’.
2. Page 19, line 14: change ‘revers’ to ‘reverse’.
3. Page 19, line 30: change “humidify” to “humidity”