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Atmospheric Measurement Techniques Discussions
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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 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

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Discussion paper

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.

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

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 19,000âĹij21,000 ppmv (parts per million by volume)"

AUTHOR'S REPLY: Mixtures of water vapour and dry air can be quantified by various measures of absolute humidity, such as specific humidity in units of g/kg or water vapour mixing ratio in units of parts per million by volume or by mass, or as g/kg. Conversion from one definition to the other is straightforward. Importantly, the choice of the unit does not change the isotope-humidity dependency. In the revised manuscript, we will clearly state our choice of the unit to be ppmv for the absolute humidity in this manuscript.

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

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

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?).

AUTHOR'S REPLY: The new aspect of this study is indeed that the humidity dependency is found to be systematically dependent on the isotope composition, which opens up the opportunity to correct for this influence. We will further emphasize this point in the revised manuscript (see reply to Referee #1).

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.

AUTHOR'S REPLY: We do not think pump speed is likely to play a role here. The measurement system includes up to three pumps: an SDM air pump, and external vacuum pumps supplied by Picarro Inc (S2003). The flow through the Picarro analyzer depends on the measurement mode and analyzer type, and is regulated by the analyzer through different measures (critical orifice/flow regulator). The adjustment of the pump speed of the SDM air pump would affect the amount of dry gas and thus the mixing ratio of the humid air supplied to the analyzer. In liquid injection mode, a stronger vacuum pump connected to the vapourizer could potentially increase the efficiency of removing the remaining vapour in the vaporizer between injections, reducing the so-called memory effect from the previous measurement. However, as we have discussed in Sect. 7, due to the non-monotonous behaviour of the isotope-humidity dependency, we consider it unlikely to be a result from mixing with remnant water in the system. Therefore, we do not think the adjustment of pump speed of the external vacuum pump would affect the behaviour of humidity dependency that we have observed. A brief statement to that effect will be made in the revised manuscript. Plumbing details are unlikely to play a

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role either, since different methods to generate the vapour provide very similar results. The exception may potentially be parts that are inside the analyzer and beyond the user's control.

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?

AUTHOR'S REPLY: Based on the input from all three Referees, the discussion will be extended, also addressing the questions 4.1-4.4. 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.

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).

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, to a large part because we would not expect

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mixing to produce a non-monotonic isotope-composition humidity dependency. This therefore points to a spectroscopic origin, supported with previous studies including Rella et al., 2015. In the revised manuscript, we will attempt to provide a more general instrument error budget, and discuss the uncertainty from fitting spectra according to the available information, as now discussed in section 8 and as suggested by all 3 referees.

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”

AUTHOR’S REPLY: Editing comments 1-3 will be implemented in the revised manuscript.

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