

Interactive comment on “Detecting moisture transport pathways to the subtropical North Atlantic free troposphere using paired H₂O- δ D in situ measurements” by Y. González et al.

Anonymous Referee #1

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In this manuscript, the authors present a new, long-term dataset of water vapour isotopic composition from the Canary Islands and use several diagnostic techniques to interpret the data in terms of water vapour transport. Overall, this is a very good manuscript and dataset from a very interesting and important part of the world. I do have some serious concerns about the standardization protocol used by the authors, and I hope that by simply expanding more on what they did that they can convince me the data are reliable, but they may need to do more than that.

Many thanks to the referee for his/her interest in our work and for sharing his/her concerns. His/her comments are very constructive and we hope that we are able to address them in a satisfactory manner thereby improving our manuscript.

Major Comments:

(1) I have several concerns about the isotopic calibrations. First, the authors use standards that only span a narrow range (-142 per mil and -245 per mil). This is problematic because the data appear to span from >-100 per mil (hard to say because the authors don't report the total range of observations) to apparently as low as -500 per mil. This means that their calibrations are based on extrapolation and it makes me concerned especially about the reliability of the delta values below -245 per mil, which constitute a large fraction of the dataset. The authors need to explain in more detail how they do the corrections - are they generating a 'stretching factor' (which they should be doing)? How do they justify extrapolating over such a large part of their dataset? The reader needs to see in substantial detail how the authors carry out the calibrations.

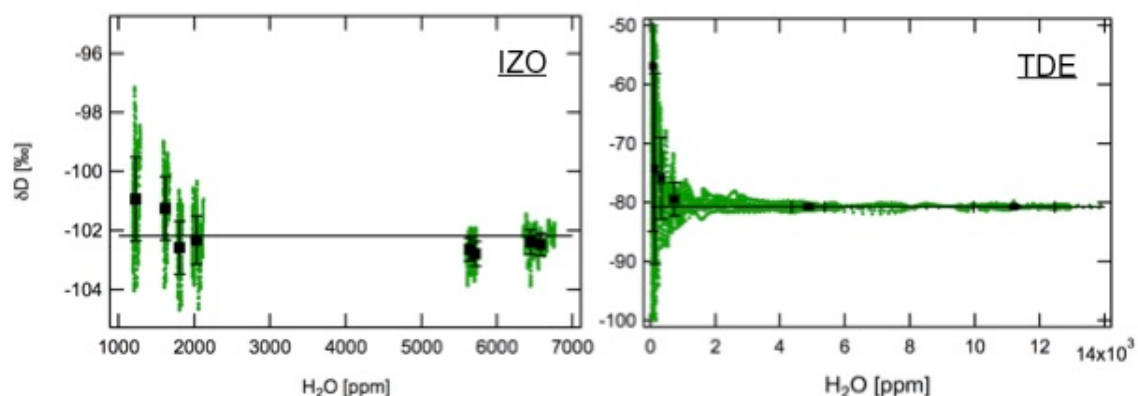
(2) I am also surprised and skeptical at their statement that their bubbler concentration- dependence study showed "no humidity dependences on the Picarro's isotopologues readings". They need to show a figure illustrating that, because I am not sure I believe it. There is almost always some concentration dependence, and it can vary substantially over time and can vary with delta - in other words a heavy standard can have a different concentration dependence than a light standard. This has to be quantified and presented to the reader. Some of their most interesting results are from the drier conditions, so they need to be more rigorous in their evaluation and presentation of concentration dependence.

Answer:

We agree with the referee that calibration of the isotopologue data is a very important point. In the following we will give a more detailed insight in our calibration measurements and justify the correction methods that we apply.

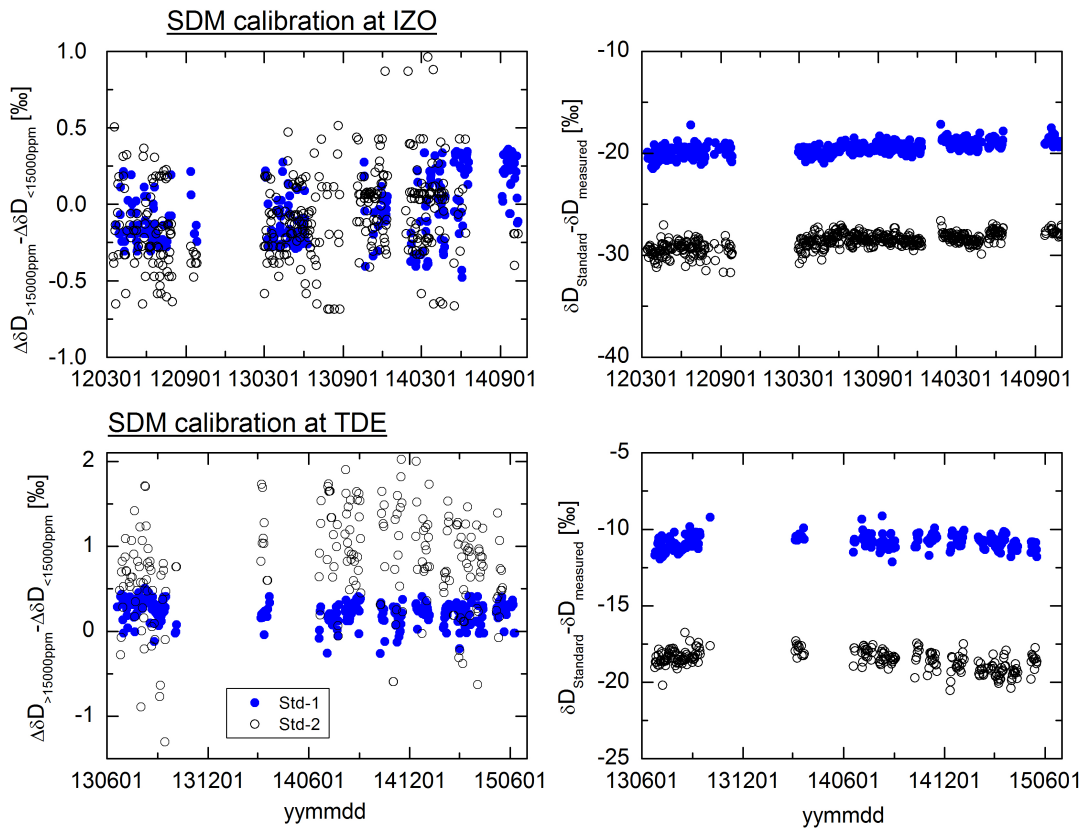
Comment 2:Water vapour humidity dependence:

The Figure below shows an example measurement of humidity dependence of δD at IZO and TDE stations, respectively. An uncalibrated working standard was used in a bubbler to saturate synthetic air with water vapour. This air was then diluted into a variable flow of synthetic air to produce a gas mixture of variable humidity. The data are averaged for 1 min, and the error bars denote the 1-sigma-standard deviation of the δD measurements. For low humidity measurements, where the instrument is most susceptible to a humidity dependence of δD , the dependence remains within the scatter of the data (1-sigma standard deviation). Please also be aware that we use a Picarro L-2120i model. The Picarro models L-21xxi have significantly less dependency on humidity concentrations than the Picarro models L-11xxi (e.g. Aemissegger et al., 2012).



Stability of humidity dependence:

The stability of the humidity dependence for SDM calibrations along the whole study period is shown in the left column of Figure 4 in the Appendix A2. We analyse the differences obtained from the regular calibrations made below and above 15000 ppm. No significant differences are observed along the humidity range covered with the SDM, being the 3σ below 0.8‰ at IZO (1.8‰ at TDE) (instrumental precision < 0.5‰). Each day, the data are calibrated with the resulting combination of the calibration at 3 different humidity points (no humidity dependence was found) and a linear fit between the responses of the 2 standards. The right column of this Figure shows the mean difference with respect the standard for each calibration.

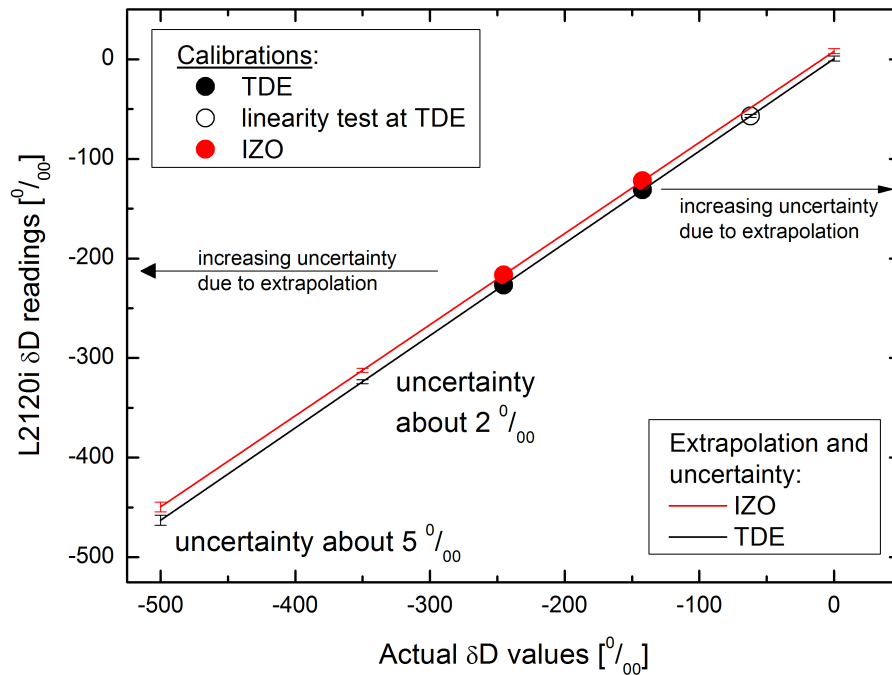


Comment 1: Isotopic calibrations / Delta scale linearity

For routine measurements we need a significant amount of liquid standards (1 l/year and instrument) and we produce our standard from ice we got from colleagues of the Arrival Heights station in Antarctica. This standard has -245.3‰. The second standard (-142.2 ‰) is produced by mixing this Antarctic standard with middle European tap water. This limits the delta range covered by our standards but assures that we have standards available for continuous calibrations during long measurement periods.

For the data evaluation we determine a linear regression function of the two working standards S1 and S2 measured during calibration (see Figure shown below). This function is of the form $dD_{VSMOW} = a + b \cdot dD_{measured}$. We apply this function to the ambient measurements in order to transfer these measurements onto the VSMOW2/SLAP2 scale. The uncertainty in this linearity is about +/-2‰ (determined with standards between +15‰ and -428‰, see Fig. 2 of Aemissegger et al., 2012). Since our working standards cover 100‰, the uncertainty in of slope "a" of the aforementioned calibration function is 2‰/100‰.

This uncertainty is important for data outside the range of our two isotope standards, because we calibrate them by extrapolating the calibration function.- The uncertainty due to extrapolation is about 2‰ for each 100‰ away from the range of our standards. For instance, it is about 2‰ at -350‰ and 5‰ at -500‰ (see the Figure below).



For the total uncertainty estimation we consider the instrumental precision as well as uncertainty components: a) uncertainty of the standards (0.7‰ for both dry and humid air), b) humidity dependence (from 0.3‰ for 10000 ppm, up to 8.0‰ at 200 ppm), c) extrapolation of VSMOW2-SLAP2 scale outside the range of calibration (for humid air: <2.0‰; up to 5‰ for strong depleted air), d) calibration (1‰ for the whole humidity range). The absolute uncertainties in dD are then <14.7‰ for strong depleted air at 500 ppm and <4‰ at 4500 ppm.

We would also like to mention that for our measurements at IZO (and TDE), our two calibration working standards bracket around 41.9% (52.4%) of all measurements. 38.2% (17.4%) of the measurements have $dD > -142.2‰$ (S1), and 17.8% (28.5%) of the measurements have $dD < -245.3‰$ (S2). A small fraction of 0.1% (0.6%) of all data were measured to have $dD < -400‰$.

This information is now better described in Appendix A, section A2.

*Included reference: Aemisegger et al., 2012

Aemisegger, F., Sturm, P., Graf, P., Sodemann, H., Pfahl, S., Knohl, A., and Wernli, H., Measuring variations of $\delta^{18}O$ and δ^2H in atmospheric water vapour using two commercial laser-based spectrometers: an instrument characterisation study, *Atmos. Meas. Tech.*, 5, 1491–1511, 2012 www.atmos-meas-tech.net/5/1491/2012/ doi:10.5194/amt-5-1491-2012

(3) The paper would benefit from an expanded discussion in which the authors relate their results to other studies from subtropical sites. This dataset fits nicely into an existing suite of studies from Mauna Loa, Hawaii, and from the

Chajnantor Plateau, Chile, and I would like to see the authors attempt to place their results into the growing context of subtropical humidity and isotopes. In particular, they need to expand upon their discussion of Noone et al 2011, Samuels-Crow et al 2014, and add other relevant studies by Hurley et al 2012, also on Mauna Loa, and the Chilean studies of Galewsky, 2015 and Galewsky and Samuels-Crow 2014. What are we learning from the use of water vapor isotopic measurements in subtropical sites? What are they telling us about the humidity of the global subtropics?

Answer: The introduction has been improved by placing the work under the context of the latest studies carried out in the subtropics (see paragraphs 2-4 in section 1).

Apart from those works recommended by the referee, the study of Risi et al. (2010) has been included in order to compare our results under Saharan dust conditions with previous results.

Comparison with existing measurements in the subtropics has been included on the results (see third paragraph in section 3.1, last paragraph in section 3.2 as well as paragraphs 7 and 8 in section 3.3).

(4) I find many of the figures hard to follow because there are so many (too many) data points. Instead of plotting a giant blob of data, can the authors use contours of the 2D histogram (or equivalently the PDF)?

Answer: In these plots we would like to show all data in order to give the user an idea of the large amount of observations. Then in the last figure of the paper we summarize the results in a contour plot.

(5) Along the same lines, I find the units of mmol/mol to be hard to follow and prefer either ppmv or g/kg. Can the authors at least translate mmol/mol into these other units in a few places in the paper? This is especially relevant because the standardization section uses ppmv and it's hard to relate that to the measurements presented in the paper.

Answer: all the units are now presented in ppm.

(6) In general, the authors refer to moistening from the marine boundary layer via evaporation from the ocean surface. Can the isotopic measurements be used to distinguish between this direct moistening mechanism and moistening from the outflow of shallow convection? I suspect the latter is a more frequent moistening mechanism, but it would be interesting to see if the isotopes can help constraint that.

Answer:

The isotopologue composition of the outflow of shallow convection depends strongly on the precipitation efficiency (Bailey et al., 2015). The higher the precipitation efficiency the closer the dD values get to the Rayleigh line. The lower precipitation efficiency the closer the dD values get to the mixing line.

In this context category (3) as shown in Fig. 10 can be interpreted as outflow from shallow convection and high precipitation efficiency (or even reevaporation of falling rain below the clouds of higher convection events). Category (4) as

shown in Fig. 10 can be interpreted as mixing between dry air with humid air that experienced no condensation or with outflow from convection where precipitation efficiency was rather low. This is in agreement with the discussion made in Bailey et al. (2015) for in-situ measurements at Mauna Loa. Additional $d^{18}\text{O}$ measurements could help to better identify the reevaporation of falling rain (e.g. Risi et al., 2010).

Bailey, A., Nusbaumer, J., and Noone, D., Precipitation efficiency derived from isotope ratios in water vapour distinguishes dynamical and microphysical influences on subtropical atmospheric constituents, *J. Geophys. Res.: Atmos.*, 120, doi: 10.1002/2015JD023403.

Risi, C., Bony, S., Vimeux, F., Frankenberg, C., Noone, D. and Worden, J., Understanding the Sahelian water budget through the isotopic composition of water vapor and precipitation, *J. Geophys. Res.*, vol. 115, D24110, doi:10.1029/2010JD014690, 2010

Minor Comments:

(1) The citation to 'Kimberly et al, 2014' is incorrect - the author is Kimberly Samuels-Crow, so the citation should be 'Samuels-Crow et al, 2014'.

[Answer:](#) The citation has been corrected.

(2) Rather than referring to 'depleted dD values', it's much better to say 'lower dD values'. A value can't be depleted or enriched. Please edit the use of 'depleted' or 'enriched' as those words are used incorrectly throughout the manuscript.

[Answer:](#) done.