#### Review of

# "Moisture pathways and $H_2O-\delta D$ pairs in the subtropical North Atlantic free troposphere"

# by Y. González et al. Paper published in ACPD on 8 October 2015

## 1 General Comments

This paper presents and discusses valuable high temporal resolution water vapour isotope measurements from two sites on Tenerife Island in the subtropical Atlantic. The authors convincingly show that the night time data can be used for analysing possible transport pathways of free tropospheric subtropical moisture. They provide a trajectory-based analysis and categorisation of their water isotope and total mixing ratio data using the temperature at the last condensation point. Important and very relevant aspects of the moisture transport and moisture budget in the subtropical Atlantic are discussed in this paper. I recommend publication of this overall very interesting and well-written manuscript after the following points from my two main concerns have been adressed:

- A **Isotope measurements setup and calibration:** The isotope measurements set up, calibration and standardisation is described only very shortly and important information relevant for ensuring the data quality is missing.
  - 1. A description of the measurement set up is missing and should be given for example in Section 2.2. The inlet type, tubing length, throughflow, pumping rates, response times, tubing material, etc. are important characteristics of the measurement system that have to be mentioned. Do you use heated tubings, how did you avoid condensation problems?
  - 2. In the literature on water vapour isotope measurements using laser spectrometric techniques the water vapour mixing ratio dependency of these measurements is discussed as a very prominent measurement bias that has to be taken into account (e.g. Sturm and Knohl, 2010; Johnson et al., 2011; Aemisegger et al., 2012; Bailey et al., 2015, and many others referenced in these papers). Since this would be (to my knowledge) the first study showing water vapour isotope measurements using a Picarro cavity ring-down instrument without water vapour mixing ratio bias this aspect has to be discussed in a more convincing way and more information has to be provided on the laboratory tests. For instance in Fig. A2: are these averaged data? over what time window? To me it looks as if there was at least a slight water vapour mixing ratio dependency below 10000 ppmv at TDE. Can you quantify this and use a statistical test to reject the necessity of a correction? Are the data from Fig. A2 all from routine calibration runs or do they include some laboratory tests? Overall the data in Fig. A2 looks very noisy to me. At first sight the instrument precision seems to be dominating the uncertainty and this is probably why the authors say there is no apparent water vapour mixing ratio dependency. But I think one should differenciate between different uncertainty sources here and try to correct for the know biases. Since the data in Fig. A2 has been collected over more than 2 years the instrument's absolute calibration characteristics vary strongly. Thus, each calibration run made at low water vapour mixing ratio (say < 15'000 ppmv) should be related to a temporally very close calibration run made (in the same few hours) at higher water vapour mixing ratio. In my opininon the left panels in Fig. A2 should show differences of the  $\delta D$  at different low humidities (e.g. <15'000 ppmv) minus reference  $\delta D$  at high water vapour mixing ratio (e.g. at >15'000 ppmv). Also the data from the laboratory experiment at water vapour mixing ratios between 5000 ppmv and 500 ppmv should be shown in the paper.
  - 3. Concerning the water vapour mixing ratio calibration with other collocated instruments at the two sites, I find the spread in the scatter plot in Fig. A1 huge especially for IZO (why?). The uncertainty resulting from this calibration is very large and should be discussed somewhere. Does this large spread result from the relatively high temporal resolution of the data used? Does the comparison improve when using hourly averaged data?

- 4. Why do you use such high temporal resolution (10 min) of the data. Wouldn't hourly or even 3-6 hourly data be sufficient for your analysis? It would also probably lower the uncertainty of the data through increased instrument precision due to averaging. Furthermore the Figures whould be easier to read with less data points.
- 5. In a few instances in the paper,  $\delta^{18}$ O and deuterium excess would be helpful, particularly, when discussing evaporation from the ocean and SAL sources. Why don't you use these data?

#### **B** Last condensation temperature analysis:

- 1. The starting height of the trajectories is probably a very sensitive parameter in this analysis, amongst others due to the steep topography. More trajectories at somewhat higher as well as somewhat lower elevations should be computed to take this uncertainty into account and provide a sensitivity assessment of this aspect.
- 2. To me the categorisation into different temperature at last condensation classes is somewhat arbitrary and the authors should explicitly motivate their choice. Is there a more objective way to choose the thresholds of the three groups of data? Or could all the relevant parameters like latitude, longitude, temperature, pressure at the LC point and  $\Delta H_2$ Obe used in a clustering approach to define the different classes? Along the same lines: Is there a good reason for choosing three categories?

## 2 Specific comments

- 1. p. 27220, L.1: The authors should shortly mention that these are point measurements from a ground-based measurement station.
- 2. p. 27221, L.8: The introduction in general is kept very short and in my opinion the literature review is a bit too sparse. Noone, et al. (2011) and Bailey, et al. (2013) show some free tropospheric measurements from Hawaii, Tremoy, et al. (2012) discusses measurements from continental Africa. The sentence on line 8-9 should be refined a bit. The same is true for the Results part, where a comparison to existing measurements from the subtropics should be made.
- 3. p. 27221, L. 13: Replace "stable isotopic composition" by "stable isotope ratio".
- 4. p. 27221, L. 15: For the isotope ratio standardisation Coplen (2011) should be referenced.
- 5. p. 27222, L. 15: Two times "from", remove one.
- 6. p. 27222, L. 23: Add "it" in "while  $\mathbf{it}$  is normally".
- 7. p. 27222, L. 25: Change "regimen" to "regime".
- 8. p. 27223, L. 5-11: Here the authors should shortly explain how they "calibrate" their measurements. If they normalised the data to the VSMOW2-SLAP2 scale as recommended by the IAEA, the reference sheet for isotope measurement normalisation from the IAEA (2009) should be mentioned.
- 9. p. 27223, L. 5-11: How do you come up with these uncertainty estimates? Are the total error estimates additive or the result of error propagation?
- 10. p. 27223, L. 7: It would be very helpfull if water vapour mixing ratio units were used consistently throughout the manuscript (either ppmv or mmol·mol<sup>-1</sup> or  $g \cdot kg^{-1}$ ).
- 11. p. 27224, L. 15: "The upslope flow prompts the climb of gases...". This is a strange formulation, maybe "transport" would be more adequate?
- 12. p. 27224, L. 22: Plot the annual cycle as well in the Figures, it would help the reader follow your argumentation.
- 13. p. 27225, L. 10: The parenthesis with "(2015,...)" after the reference to Dyroff is a bit confusing. Maybe you could use 2 different parenthesis for the reference and the  $\delta$  D indication?
- 14. p. 27225, L. 13: Couldn't there be also some influence of local evaporation from the land surface (Tenerife Island)?
- 15. p. 27225, L. 14: Replace "those" by "the one" or similar. The current formulation is a bit awkward.

- 16. p. 27226, L. 25: "Rayleigh distillation" as a process has not been properly introduced, defined and referenced.
- 17. p. 27227, L. 3: A short note here could indicate that the super-Rayleigh observations below the Rayleigh curve are discussed later.
- 18. p. 27228, L. 18-22: Evaporation from the North African continent (particularly Morocco and Western Sahara) could also at least partly contribute to the moisture in dust-laden Saharan airmasses, particularly for the moisture with high  $\delta D$ .
- 19. p. 27228, L. 19: "...has its origin on the evaporation...", rephrase, "on evaporation" sounds awkward.
- 20. p. 27228, L. 23: The title of this section is a bit too general. It is more or less a reformulation of the title of the paper. I would suggest a more specific subtitle here, mentioning the LC temperature classification of the data.
- 21. p. 27230, L. 6: Remove "a" in "and a generally".
- 22. p. 27230, L. 6: To me the blue distribution in Figure 7 at TDE is not indicating a "reasonable conservation" for TLC<250 K but a relatively clear moistening.
- 23. p. 27230, L.9: Remove parentheses for " $T_{LC}(>250 \text{ K})$ ".
- 24. p. 27230, L.23: Change "orange" to "black", here and in other instances, when Fig. 8 and 9 are discussed.
- 25. p. 27231, L.23: Here I think the authors could expand a bit their discussion, compare their measurements with others from the subtropics (as mentioned above) and shortly write on what the implications of their findings are.
- 26. p. 27235, L.25: Change "Liquid standard bias" to "Liquid standard uncertainty" as you write it in the main text. If it was a bias you would be able to correct for it.
- 27. Figures: in general I think it would be easier for the reader if the panels were referenced using Fig. Xa,b,c,... instead of bottom left, etc.

### References

- Aemisegger, F., Sturm, P., Graf, P., Sodemann, H., Pfahl, S., Knohl, A., and Wernli, H.: Measuring variations of  $\delta^{18}$ O and  $\delta^{2}$ H in atmospheric water vapor using two commercial laser-based spectrometers: an instrument characterisation study, *Atmos. Meas. Tech.*, **5**, 1491-1511, doi:10.5194/amt-5-1491-2012, 2012.
- Bailey, A., Toohey, D., and Noone, D.: Characterizing moisture exchange between the Hawaiian convective boundary layer and free troposphere using stable isotopes in water, J. Geophys. Res., 118, 8208–8221, doi: 10.1002/jgrd.50639, 2013.
- Bailey, A., Noone, D., Berkelhammer, M., Steen-Larsen, H. C., and Sato, P.: The stability and calibration of water vapor isotope ratio measurements during long-term deployments, *Atmos. Meas. Tech.*, 8, 4521-4538, doi:10.5194/amt-8-4521-2015, 2015.
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- IAEA: Reference Sheet for VSMOW2 and SLAP2 international measurement standards, International Atomic Energy Agency (IAEA), 2009.
- Johnson, L. R., Sharp, Z. D., Galewsky, J., Strong, M., Van Pelt, A. D., Dong, F., and Noone, D.: Hydrogen isotope correction for laser instrument measurement bias at low water vapor concentration using conventional isotope analyses: application to measurements from Mauna Loa Observatory, Hawaii, *Rapid Commun. Mass Sp.*, 25, 608–616, 2011.

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- Sturm, P. and Knohl, A.: Water vapor  $\delta^2 H$  and  $\delta^{18}O$  measurements using off axis integrated cavity output spectroscopy, Atmos. Meas. Tech., 3, 67–77, doi: 10.5194/amt-3-67-2010, 2010.
- Tremoy, G., Vimeux, F., Mayaki, S., Souley, I., Cattani, O., Risi, C., Favreau, G., and Oi, M.: A 1 year long 18O record of wa- ter vapor in Niamey (Niger) reveals insightful atmospheric processes at different timescales, Geophys. Res. Lett., 39, L08805, doi: 10.1029/2012GL051298, 2012