

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 #3

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[We would like to thank the referee for their very helpful review. In the following we will reply to the referee’s comments and discuss their recommendations.](#)

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 nighttime 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 addressed:

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, through flow, 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?

Answer:

At IZO, the sampling inlet is installed 4 m above the roof of a 6-floor building at a height of 30 m above ground (2397 m.a.s.l.). It consists of stainless steel tube of 18m that goes from the terrace of the tower, through the service channel to the Picarro laboratory. A vacuum pump generates an inflow of 2810 lpm (standard conditions) throughout the sampling line, which has an inner diameter of 80 mm. The manifold has an inner diameter of 80 mm and a length of 250 mm. The instrument takes the air sample using stainless steel tube with an inner diameter of 4 mm, which go from the manifold to the inlet of the analyzer (1.6 m). An additional pump with an inflow of 5 lpm is connected

in serie at the inlet of the instrument. The residence time of the air along the sampling is approximately 8 seconds.

At TDE, the inlet is also 4 m above the roof at a height of ~ 6 m above the ground (3556 m.a.s.l.). The sampling line is connected to a manifold with an inner diameter of 60mm and a total length of 5 m, where the air is pumped at 20 lpm. The air then flow to the instrument throughout stainless steel tubes with an inner diameter of 4 mm (3.3 m). At TDE, an additional pump with an inflow of 5 lpm is also connected in serie at the inlet of the instrument. The residence time of the air along the tubing is approximately 44 seconds.

No heated tubing was implemented at any of the stations. The 7.6% and the 4.6% of the data at IZO and TDE station during the study period registered RH values above 90%. In these conditions, the outside temperature at IZO ranges between -6 and 15°C, whereas at TDE varies between 6 and 11°C. Since the tubing in the buildings is kept around 21°C, condensation events in the inlet lines are very unlikely.

This description is now included in section 2.2 after the first paragraph.

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 10000ppmv 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 differentiate 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 opinion the left panels in Fig. A2 should show differences of the δD at different low humidities (e.g. <15'000 ppmv) minus reference δD 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. To me it looks as if there was at least a slight water vapour mixing ratio

dependency below 10000ppmv 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?

Answer:

We agree and significantly improve the characterisation and better justify and explain our calibration method. For more details please see our reply to referee #1.

In particular, we show that the negligible humidity dependence is a stable feature as shown in a new plot (showing the temporal evolution of the differences between the regular calibration below and above 15000ppm).

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

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?

Answer: Yes, uncertainty of humidity calibration in A1 was the result of the high temporal resolution of the data used. It is higher at IZO due to the larger amount of data from this station. When the resolution is fixed to 1 hour the uncertainty is reduced (see now Figure A1). This correction is consistent in all the paper.

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 would be easier to read with less data points.

Answer: The precision of the high-resolution dD data (10 min averages) of Picarro analysers is very high (at 15700 ppm better than 0.2‰, see Aemisegger et al., 2012, Fig. 7a, and for very dry conditions within a few permil. This is more than sufficient for our purpose and means that most of the scatter we see on the short time scales is real (it is no noise!).

Furthermore, it is important to clarify that averaging over longer time periods is not trivial: If we just average all the dD and all the H₂O values the averaged H₂O-dD data point will be below the mixing line or Rayleigh curve described by the individual data points. If we average the dD weighted by H₂O we will lie close to the mixing line but we will not well capture the situation of a Rayleigh process. In order to avoid such artefacts we use high resolution data.

In Figs 4, 5, 6, 8 and 9 we show scatter plots in order to show all data. We summarize these plots by plotting 2D pdfs in Fig. 10, which then gives a good overview.

5. In a few instances in the paper, δ¹⁸O and deuterium excess would be helpful, particularly, when discussing evaporation from the ocean and SAL sources. Why don't you use these data?

Answer:

Additional d-excess data would probably allow studying further details of the different processes. However, this is the first manuscript that interprets our in-situ data from Tenerife Island and we prefer to start with dD. For dD the signals are strong and cover a range of more than 400‰. For this reasons atmospheric processes are easily observable since the signals are clearly larger than the measurement uncertainty. In contrast d-excess signals are rather small (probably within 20‰), meaning that d-excess measurements need to be very accurate, which is in particularly difficult for low humidity concentrations. It is much easier to measure atmospheric dD signals than d-excess signals, especially for low humid concentrations.

Another reason is that in the MUSICA project we focus on dD because this is what can be measured by the remote sensing techniques. Deuterium excess cannot be measured by remote sensing techniques and, although very useful for atmospheric studies, it is not a focus of the project.

Nevertheless we are currently working on the d-excess data quality assurance and plan to work with this data in the future.

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.

Answer:

Yes, we agree that we should better discuss the uncertainty of the parameters that we obtain from the backward trajectories. Please refer to the answer provided to referee #2 in this context (referee #2 has made a similar comment).

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 ΔH_2O_{be} be used in a clustering approach to define the different classes? Along the same lines: Is there a good reason for choosing three categories?

Answer:

The exact values of the temperatures that define the three temperature groups are more or less arbitrary. Important is here not the absolute value. What is important is that we distinguish airmasses according to their temperatures at the last condensation point. We group all airmasses for low T_{LC} (last condensation at low temperatures, i.e. dry at the last condensation point). And we group all airmasses for high T_{LC} , i.e. last condensation at high

temperatures and accordingly humid airmasses. Furthermore, we create a group that lies in between.

This classification groups that data automatically with respect to the altitude and location of the last condensation point (see Figure 7) and with respect to the humidity at last condensation. This clarification will be considered in the revised manuscript (section 3.3).

Specific comments

SC1: p.27220, L.1: The authors should shortly mention that these are point measurements from a ground-based measurement station.

[Answer to SC1: Done.](#)

SC2: 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.

[Answer to SC2: We agree and will improve the introduction and the result section accordingly to the latest studies carried out in the subtropics.](#)

SC3: p. 27221, L. 13: Replace “stable isotopic composition” by “stable isotope ratio”.

[Answer to SC3: done.](#)

SC4:p. 27221, L. 15: For the isotope ratio standardisation Coplen (2011) should be referenced.

[Answer to SC4: done.](#)

SC5:p. 27222, L. 15: Two times “from”, remove one.

[Answer to SC5: done.](#)

SC6:p. 27222, L. 23: Add “it” in “while it is normally”.

[Answer to SC6: done.](#)

SC7: p. 27222, L. 25: Change “regimen” to “regime”.

[Answer to SC7: done.](#)

SC8: 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.

[Answer to SC8: The measurements were calibrated continuously against two standards \(-142.2 and -245.3‰\). The isotopologue standards have been prepared from Antarctic snow water probes \(snow taken close to the Arrival](#)

Heights station, $\delta D = -245\text{‰}$). The isotopologue composition of the probes was certified in Le Laboratoire des Sciences du Climat et de l'Environnement (LSCE-CEA, France). The data was normalized to the VSMOW2/SLAP2 scale. This information is now included in Appendix A2, paragraph 1.

SC9: 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?

Answer to SC9: the total error estimation is based on additive.

For the total uncertainty estimation we consider the instrumental precision (within a few permil for dry and below 0.2‰ for humid conditions) as well as the following 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 δD are then <14.7‰ for strong depleted air at 500 ppm and <4‰ at 4500 ppm. Please refer to reply to Referee#1 for more details. This information is included in the Appendix A (section A2).

SC10: p.27223, L.7: It would be very helpful if water vapour mixing ratio units were used consistently throughout the manuscript (either ppmv or $\text{mmol}\cdot\text{mol}^{-1}$ or $\text{g}\cdot\text{kg}^{-1}$).

Answer to SC10: done.

SC11: p.27224, L.15: "The upslope flow prompts the climb of gases...". This is a strange formulation, maybe "transport" would be more adequate?

Answer to SC11: done.

SC12: p. 27224, L. 22: Plot the annual cycle as well in the Figures, it would help the reader follow your argumentation.

Answer to SC12: The annual cycle s now included.

SC13: 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 δD indication?

Answer to SC13: done.

SC14: p.27225, L.13: Couldn't there be also some influence of local evaporation from the land surface (Tenerife Island)?

Answer to SC14: Along the paper, the analysis is done with nighttime data. During this time of the day, the stations are not significantly affected from local upslope winds on the islands surface. Furthermore, the land surface around the stations is lava terrain. So in general we think that evaporation from the Island's land surface is not a decisive contribution to the water mass as detected at the stations.

SC15: p. 27225, L. 14: Replace "those" by "the one" or similar. The current formulation is a bit awkward.

[Answer to SC15: done.](#)

SC16: p. 27226, L. 25: “Rayleigh distillation” as a process has not been properly introduced, defined and referenced.

[Answer to SC16:](#)

Rayleigh distillation/processes mean that as soon as condensate forms it is completely removed. For more details about the Rayleigh curves please also refer to the reply to Referee #2.

SC17: p.27227, L.3: A short note here could indicate that the super-Rayleigh observations below the Rayleigh curve are discussed later.

[Answer to SC17: done.](#)

SC18: 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 δD .

[Answer to SC18: This is true. Text has been re-written.](#)

SC19: p. 27228, L. 19: “...has its origin on the evaporation...”, rephrase, “on evaporation” sounds awkward.

[Answer to SC19: done.](#)

SC20: 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.

[Answer to SC20: done.](#)

SC21: p. 27230, L. 6: Remove “a” in “and a generally”.

[Answer to SC21: done.](#)

SC22: p.27230, L.6: To me the blue distribution in Figure 7 at TDE is not indicating a “reasonable conservation” for $T_{LC} < 250$ K but a relatively clear moistening.

[Answer to SC22: This has been corrected.](#)

SC23: p. 27230, L. 9: Remove parentheses for “ $T_{LC} (>250$ K)”.

[Answer to SC23: done.](#)

SC24: p. 27230, L. 23: Change “orange” to “black”, here and in other instances, when Fig. 8 and 9 are discussed.

[Answer to SC24: done.](#)

SC25: 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.

[Answer to SC25: yes we agree. Will be improved for the revised manuscript.](#)

SC26: 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.

[Answer to SC26:](#) done.

SC27: 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.

[Answer to SC27:](#) We would prefer leaving it like is.