

Earth Syst. Sci. Data Discuss., referee comment RC3
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Comment on **essd-2021-238**

Anonymous Referee #2

Referee comment on "Aircraft measurements of water vapor heavy isotope ratios in the marine boundary layer and lower troposphere during ORACLES" by Dean Henze et al., Earth Syst. Sci. Data Discuss., <https://doi.org/10.5194/essd-2021-238-RC3>, 2021

Review of "Aircraft measurements of water vapor heavy isotope ratios in the marine boundary layer and lower troposphere during ORACLES" by Henze, Noone and Toohey, ESSD paper number **essd-2021-238**.

Note: I have seen in my email that the other referee has posted at least one comment and there have been responses from the authors. In an effort to develop an independent assessment of the manuscript, I have not read those comments/responses before writing this comment.

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Summary:

The authors present measurements of water and its isotopic composition in the lower troposphere obtained during the ORACLES field campaign. In the first half of the paper, a brief description of the campaign and the place of isotopes within ORACLES is followed by extended descriptions of (1) the measurement system used to feed samples of water to commercially-produced instruments that measure isotopes and (2) the calibration of a reference instrument against standards of known composition and of a second instrument against the first. Last, some of the data itself is presented.

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Assessment: Major revisions

As the authors note, this dataset is new and exciting, as it shows the vertical structure of isotopic composition in the lower troposphere over the southeast Atlantic and its variation with latitude. This dataset should be published, but I have several suggestions below that

I believe could help the reader better understand the dataset and its properties. The main suggestion is to either add cloud water isotopic data to section 6 or to remove the extended discussion of the CVI inlet and its plumbing since it is only relevant to the cloud water measurements. In addition, I have several suggestions that I would ask the authors to consider in their revisions. At the bottom, optional stylistic suggestions are also made.

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Major comment:

1. The measurements in the dataset are of total water (vapor + condensate) and cloud water, yet no observations of cloud water are shown in section 6. As far as I could tell, section 6 also makes no mention of whether the measurements presented in figures 7-12 are of water vapor or total water. If someone wanted to use the cloud water data included in the dataset, this paper does not seem to present the data itself, so I would encourage the authors to choose one of the following two options:

- shorten the paper substantially by removing the discussion of the CVI (and possibly also the cross-calibration of the two analyzers), since they are not relevant unless the cloud liquid measurements are presented here, or

- add at least one figure showing coincident measurements of cloud liquid and total water mass and isotopic composition, as well as how far the cloud water isotopic composition is from isotopic equilibrium with the surrounding vapor. Note that this can be done using the total water isotopic composition and the ratio of cloud liquid mass to vapor mass.

2. It would be helpful if there was a standard reference about the calibration of water vapor isotope analyzers, so that the authors could refer to that and only highlight the details where their approach differs from that reference. I suppose each scientist or group has their own techniques, so that they prefer their own approach. This isn't a complaint about this paper but a general lament.

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Things that should be considered and responded to before publication:

section 3: I understand the structure of this section, dividing the presentation into 1) inlets, 2) flow configuration, 3) transfer lines, 4) heating of transfer lines/inlets, and 5) analyzer details. However, the section is really dominated by the extended discussion of the CVI inlet, so I would suggest presenting the full description of the SDI inlet (and its transfer line and heating system) before doing the same for the CVI inlet. This would have the benefit of emphasizing that the SDI inlet brings both droplets and vapor together and allows the droplets to evaporate before the resulting vapor (which reflects total water) is

ingested into the isotope analyzer. When the treatment of the CVI piping/heating is similar to that of the SDI, this could be noted, making the CVI description shorter.

l111: Please do not use an abbreviation that comes from a brand name of a commercial product (here, Pic is short for Picarro, I assume). I would suggest something more generic: WVIA1 and WVIA2.

l101-102, 129-131 and 176: Please string a few sentences together here to tell the reader how the CVI system generates a measurement of cloud liquid mass and isotopic composition. Include in this an explanation of the CVI enhancement factor. Only a few sentences are needed, but please carry the reader from inflow to the separation of cloud droplets and the surrounding vapor, to the evaporation of those droplets in the dry counterflow air, and from there to the isotope analyzer. Make the reader understand why this procedure leads to a robust measurement of cloud liquid isotopic composition.

Also emphasize that the WVIA1 is almost always pulling from the same air stream that WVIA2 is measuring and that only inside cloud is WVIA1 switched to the CVI line. This was my understanding from later in the paper. Is this true?

l131-139: The comparisons with the NCAR GV CVI system sound strange here unless there is an existing reference on the GV CVI system that you can reference here. I would suggest starting by saying that the CVI system design was based on that of the NCAR GV and then just describing how it works before mentioning the appendix. The comparisons make sense in the appendix but not here.

l140-147: Introduce the three water vapor isotope analyzers first, then talk about their positions in WISPER (i.e., WVIA1 and WVIA2). Also, I would suggest always going in chronological order from 2016 to 2017-18, unless there's a really good reason not to.

l243-252: The fudge factor, f , in the calibration of $\delta^{18}\text{O}$ does not inspire great confidence in the data, even if it is necessary. The accumulation of aerosol on the mirrors within the cavity is a plausible explanation, but could the authors suggest why this affects only $\delta^{18}\text{O}$ and not δD and water vapor? As the Benetti data came from the surface layer, it may not exactly apply to the aircraft data at higher altitudes, though I do imagine that vertical gradients in deuterium excess would not be strong.

l268, eqn 4, fig 5-6: This calibration polynomial fit (fifth order in each of $\log(q)$, δ and $\log(q)*\delta$) seems very complicated, and its presentation in figure 5-6 makes it hard for the reader to understand the motivation for the form suggested in equation 4 and the quality of the calibration. My first suggestion would be to calibrate WVIA2 against WVIA1 in the same way that WVIA1 was calibrated against the standard. This would require little text to explain, and the coefficients of the fits could be presented compactly, perhaps by

adding them to the tables with the coefficients for WVIA1.

As the authors have already produced a data set based on equation 4, I expect that they are reluctant to re-do the cross-calibration of WVIA1 and WVIA2. I have a couple of suggestions to make equation 4 and figures 5-6 more clear for the reader. First, equation 4 should have Δ_{2_calib} on the left hand side and not Δ_1 . If the authors want to keep Δ_1 on the left hand side, an error term E_{calib} should be added to the right hand side because the polynomial fit will not in general match the value of Δ_1 . Second, the quality of the calibration will be shown better in figures 5-6 by plotting this error ($E_{calib} = \Delta_1 - \Delta_{2_calib}$), rather than the calibration curves. I would suggest putting $\log(q_1)$ and Δ_1 on the x- and y-axes since they are the reference and binning the data into $\Delta_1 - \log(q_1)$ bins with about 10-15 bins in each direction. The RMS error of $\Delta_1 - \Delta_{2_calib}$ in each bin could be shown with the colorscale. Bins with no data could be left blank (by filling them with NaNs in MATLAB or whatever is the equivalent in python).

l296-311: This is more of a list than a paragraph. Perhaps it could be shifted to a bulleted list in an appendix.

l334-350, eqn 5 and table 5: A reader will want to look at table 5 and be able to read off the uncertainty in at least one value of q/Δ and see how the uncertainty varies around that value. The formulation of equation 5 makes this difficult at best. I would suggest finding the most common combination of q and Δ in the dataset, calling them q_{ref} and Δ_{ref} and then replacing q and Δ in equation 5 with q/q_{ref} and Δ/Δ_{ref} . Then, α_0 will give the value of the uncertainty for $q/\Delta = q_{ref}/\Delta_{ref}$ and α_1/α_5 will show how they vary linearly with $\log(q)$ and Δ around that point.

section 6: Three thoughts:

- If the authors are encouraging users to average the 1 Hz data to 10s intervals, perhaps they should consider providing a 0.1 Hz dataset. If nothing else, it would reduce the dataset size by a factor of ten for users who were not interested in the 1Hz data.

- Does q in the figures, text and tables correspond to total water or water vapor? This should be specified somewhere.

- If the discussion of the CVI is maintained in the revised manuscript, some cloud water data should be presented here. A couple of suggestions are made above.

l388-394: Some of the differences between measurements in 2016 and those in 2017-18 could be related to the different regions that were observed then.

sec 6.2.1: Since the composite curtains are based on water-mass-weighted values, the isotopic composition will be skewed towards its value in samples with high q . This probably matters most in regions where the variability of q is largest. In particular, variations in the height of the trade inversion probably leads to the largest amount of variability in q . I would speculate that this could contribute to the unexpectedly low correlation between q and dD in the composites for 2017 and 2018.

l411: Could a brief explanation (only a half or full sentence) be added to make clear why "it's clear" that the moisture and dD come from the the continental PBL? This might not be obvious to the uninitiated reader.

Figures 7-9: Is there some way to specify what inside/outside the plume? This is less obvious in figures 8 and 9. My suggestion would be to close the contour with a thick line on the right edge of the panels in figure 7, with similar thick lines bounding the edges of the plume in figures 8-9.

Figures 10-12: A couple of suggestions:

- It would be useful to add a thin line (perhaps dashed or dotted) to show the y -axis for q . Otherwise, it is difficult to gauge how small q becomes at higher levels.

- Give the latitude, longitude and time of day (or range of those values) when the profile was sampled. The interested reader might wish to look at satellite images or reanalysis to learn about the meteorological situation when they were sampled.

l484-486: Is it possible that the ingestion of cloud liquid has a lasting effect after passing through a cloud, or that the differing timescales of dD and $d18O$ might lead to such excursions of deuterium excess (Aemisegger et al, 2012, ACP, <https://doi.org/10.5194/amt-5-1491-2012>, sec. 7)? On this point, I found myself wondering whether there were any systematic differences between isotopic measurements during upward and downward profiles.

In addition, the large δD excursion just above the PBL in figure 12b surprised me because the air was only slightly drier than the subcloud layer, so I didn't understand how it could be so depleted. Perhaps, I am missing the key physical process going on there.

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Wording/stylistic suggestions that are not essential:

l55: Since ORACLES is defined in the abstract, the abbreviation could be used here without writing out the full name.

l80: "... in the strong inversion _atop_ MBLs _in this_ region." Also remove "then" before "transition".

l91-92: "... every 2-3 days, lasted 7-9 hours and occurred during daytime hours (from 7am to 5:30pm local time)."

l175/table 1: If the transit flights are not included in the dataset, maybe they don't need to be in table 1.

l176: Explain CVI enhancement factor if it wasn't already done above.

l177: Define deuterium excess here if not done elsewhere.

l185-190: The chunk of long instrument names upsets the flow of this paragraph. I would suggest moving the explanation of the coincident spikes ahead of the instrument names, as in "Time synchronization to the cloud probes was achieved indirectly by aligning coincident spikes in biomass burning aerosol, carbon monoxide and water vapor specific humidity, as measured by the ... (PCASP), COMA instrument (...) and the two water vapor isotope analyzers, respectively."

l201: There must be a good reference for the way the Picarro measures water vapor. Please add a citation to it.

figure 3: Maybe add an arrow and text to indicate that the curved black line is the P3 fuselage.

l217-221: Move the "Table 2 ..." sentence ahead of "The calibration parameters do not change ...". I think it's important for the reference to the table and figures to be close to the equation.

I388: "... over the African _continent_ contains ..."

I406: Figure 7 is being discussed here, not the present figure 8. Also, figure 10 should be moved forward, so that the figures are ordered corresponding to when they appear in the text. This keeps the reader from having to flip back and forth a lot.

I409-419: The MBL is part of the lower troposphere. When referring to the region above the MBL, I would suggest using "lower free troposphere" or LFT.

I474: "colder, drier air" rather than "cold, dry"

I516-517: "... several instances of layers just above the MBL whose dD values are more depleted than the air above and below."

I559: "of the feedback loop" is unnecessary.