Reply to

RC1: 'Comment on egusphere-2024-3394', Anonymous Referee #2, 28 Jan 2025

In the following text the Referee's (#2) comments are reported as normal lead text and the authors answers are reported in grey shaded box like this one *with italic font*. The edited text in the manuscript is in *red color*.

General thoughts

Zannoni et al. presents a new dataset of atmospheric water-vapor isotopes and dexcess above southern France. They achieve this by integrating a Picarro instrument into an ultralight aircraft (ULA) and performing a series of flights of differing flight patterns, both horizontally and vertically. They pair these observations with model realizations of water-vapor isotope composition via COSMOiso to evaluate claims they make. The authors describe several key conclusions which are supported by both their observations and their model results. They find that (i) vertical mixing is a key determinant of atmospheric isotope composition, (ii) the bottom mixing endmember is likely evapotranspiration and (iii) fine-scale structure exists that aren't captured by models. This study works towards understanding the representation of water-isotope composition in the atmosphere with the framing of both understanding basic science but only serving alternative measurement techniques such as remote sensing and groundbased observation systems.

This study is pioneering in several ways. For observations, the approach is a logistically-light implementation of in-situ vapor measurement including a rigorous calibration scheme. With those observations, they apply two different frameworks to explain vertical isotope distribution, a Rayliegh framework, and a vertical mixing framework. Within error bars, they are unable to distinguish between which framework might be the best fit, but with additional context clues, such as the consideration of the bottom endmember, they ascribe the atmospheric column to be best described by mixing.

We are grateful to Referee #2 for her/his valuable comments and insightful suggestions, which have helped improve our manuscript. We believe we have addressed all the Referee's comments. Below, our detailed step-by-step responses.

Please note that we have slightly trimmed the methodological section. The text was edited specifically at the following locations (line numbers refer to the original preprint):

***Lines 122-126**: moved to Supplementary Material SM0. Main text in the manuscript edited as follows:*

The reader is referred to Supplementary Material SM0 for details on frequency of usage, values of isotope standards and calibration performances of the CRDS analyzer.

***Lines 197-205**: Rephrased in a more synthetic way*

In the horizontal domain, with the aid of the isotope-enabled model $COSMO_{iso}$, the authors find the distance before air parcels can be considered statistically unrelated.

The authors don't report this as a major conclusion, but I disagree with that approach. It most certainly informs the design of a measurement campaign that would work from another conclusion of theirs, that a surface vapor measurement may inform the total column composition in a log relationship.

Thank you for highlight this point. We have modified the key findings in the abstract to put more emphasis on this aspect. We have also slightly edited the first and second key finding in the abstract and conclusion to put more emphaisis on the altitude we are referring to (lowermost boundary layers vs lower troposphere). Here is the edited sentense in the abstract:

The key findings of this study are that (i) at hourly and sub-daily scales, vertical mixing is the primary driver of isotopic variability in the lowermost troposphere above the study site, and (ii) evapotranspiration significantly impacts the water vapor isotopic signature, specifically in the boundary layer, as revealed by the δ^{18}O-δD relationship; (iii) while water vapor isotopes generally follow large-scale humidity patterns with separation distances that might range up to 100–300 km, they also reveal distinct small-scale structures (~100 m) that are not fully explained by humidity variations alone, highlighting sensitivity to additional fine-scale processes.

The authors also find fine-scale microstructures on the order of 100s of meters. Observational evidence of these microstructures is new and a relevant contribution to the broader body of work on watervapor isotopes. They attribute this to potentially being from the surface terrain's aspect, producing thermals that affect isotope composition aloft. This may or may not be true, but the observation of microstructures at this scale provides a landscape for similar testable hypothesis that are a benefit to the community.

Regarding the discussion on such fine-scale structure, following also more clarifications requested by Referee #1, we have expanded section 4.2 by estimating the characteristic size and lifetime of such structures (with references to previous studies), and their significance (along with their limitations with CRDS technology) for studying boundary layer development and turbulent mixing processes.

The paper is mostly clear and well-written. With its expanded and detailed approach to observational methods, this paper should encourage more measurement of its kind. I have several comments for the text which do not disagree with their main conclusions but work to better represent them. I additionally have several technical edits to text. I hope this type of research continues and I support the statement that Zannoni et al. contributes a valuable study to the water-vapor isotope field in the scope of this journal.

We are grateful to Referee #2 for the constructive approach in this review. We have addressed all the technical edits, as reported hereafter.

Line 149: The author's note after vehicle vibration calibration:
"Note that shocks and vibrations are expected to be less pronounced when the ULA is airborne, thus we provide here a conservative estimate of the vibrational impacts." This is factually inaccurate. Running the engine on the ground does not adequately probe all vibrational modes, some of which will be shared by the Picarro's cavity. From my experience in aviation, I understand that official advice on the topic of aircraft vibrations

for airworthiness is to test the aircraft in all operating conditions. I have attached the American Federal Aviation Administration's Advisory Circular on the topic still in use in aircraft manufacturing. See Chapter 1: Section 2: General Considerations: a (1.2.a). Still, calibration for vibration at all is an improvement on previous work in Chazette et al 2021 and I believe constitutes current due diligence on the subject. My recommendation is to remove the sentence claiming conservative estimates in favor of an acknowledgement that not all vibrational modes can be reasonably tested in the scope of the study.

Thank you for pointing out this weakness on the evaluation of the uncertainty and thank you for the useful reference. We have specified that our attempt may be representative of vibrations only during the stand-by phase of the aricraft on the ground. We edited the text accordingly:

These ADEV values can therefore be assumed representative of the instrumental precision at 1 second averaging time and at q = 8.2 g kg^{-1} in the Taxi to Runaway phase. On this latter point, it is worth to be noted that our approach does not adequately probe all vibrational modes, hence instrumental precision might be worse. Indeed, instrument performances should be evaluated under all normal operating conditions to obtain the full spectrum of vibrational noise (AC No. 20-66, 1970).

Line 255: The author's would benefit from describing the time step of COSMOiso. Using ECHAM6-wiso as a boundary condition at 6-hour resolution, it appears that COSMOiso might be the same which would affect the interpretability of comparisons to observations. It seems that the time step might be 1 hour based on a careful reading of Villiger el al. 2023 but either way, this should be clear in this text.

We have now provided the information about the model time step (30s and 20s for the 10km and 2km simulations, respectively) and the temporal resolution of COSMO$_{iso}$ (1 hour).

..., and with a model time step of 30s for the 10km and 20s for 2km simulation. The COSMOiso fields are output at a 1-hourly resolution.

Figure 5: The days selected to plot does not follow a pattern I can recognize and all days are discussed in the text. In fact, if looking to plot days with the most flights, the plotted days are ill-suited to represent measurements. Consider days with high number of flights, or including a figure in supplementary materials with all flight days.

Figure 5 serves as an indication on the general weather situation during the campaign. Specifically, for the development of sparse rain on 18-19 and 20-21 Sep which interested the study area, but not directly the flight operational conditions.

Line 323: The author's make a statement on observations of d-excess:
"Among the flights which reached altitudes > 3000 m (flights 3, 7, 11-16), only flight 7 exhibits a consistent positive deviation of d-excess from the mean value observed at lower altitudes, ranging from 12 ± 2 ‰ at 2000 m to 19 ± 3‰ at 3000m."

And then follow with the statement:
"The d-excess increase as a function of the altitude is a well-known feature of atmospheric water vapor and typical of clear sky conditions".

From my understanding of the text, the authors note lack of an increase of d-excess with altitude for many flight yet immediately state that the opposite is typical. If my understanding on their intent is correct, I would expect that the claim is cited and some justification given for why the result deviates from the norm.
We expected an increase in d-excess with altitude, as commonly reported in airborne measurements. However, this trend was not observed in our data, except for flight 7, which also showed a marked humidity decrease near 3000 m. In our case, the absence of a significant d-excess increase may be explained by a well-mixed boundary layer and relatively uniform RH profiles. We have clarified the statement noted by the Referee, emphasizing the role of low humidity at high altitudes in enhancing d-excess through non-equilibrium fractionation between water vapor, liquid water, and ice. To support this interpretation, we reference other high-altitude studies, including modeling approaches. *....We speculate that the absence of a similar trend in the other flights may be due to a well-mixed boundary layer and relatively homogeneous RH profiles. Notably, the d-excess increase during flight 7 begins after passing a relative humidity maximum around 1800–2000 m, which may correspond to the cloud base and suggest the impact of cloud droplets evaporation. The d-excess increase as a function of the altitude is a well-known feature of atmospheric water vapor, typically resulting from non-equilibrium fractionation processes under low humidity at higher elevations, as shown by both in situ observations and model studies (e.g. Bony et al., 2008; Samuels-Crow et al., 2014).* *Bony, S., C. Risi, and F. Vimeux. Influence of convective processes on isotopic composition of precipitation (δ^{18}Oand δD) of precipitation and watervapor in the tropics: 1. Radiative-convective equilibrium and Tropical Ocean-Global Atmosphere-Coupled Ocean-Atmosphere Response Experiment (TOGA-COARE) simulations, J. Geophys. Res., 113, D19305, https://doi.org/10.1029/2008JD009942, 2008.* *Samuels-Crow, K. E., J. Galewsky, Z. D. Sharp, and K. J. Dennis: Deuterium excess in subtropical free troposphere water vapor: Continuous measurements from the Chajnantor Plateau, northern Chile, Geophys. Res. Lett., 41, 8652–8659, https://doi.org/10.1002/2014GL062302, 2014.*

Line 349: The author's state "Discrepancies between observed and modelled d-excess can be attributed to differences in simulated and observed δ^{18}O and δD at high altitude,…". This statement is definitional of dxs and can be removed in favor of focusing on the rest of the sentence.
Done.

Figure 11: The author's reference that terrain aspect might be the cause for microstructure in water vapor isotopes aloft. However, figure 11 poorly shows this. I suggest rearranging such that this claim seems more plausible and include a color bar for the grey elevation at the bottom
Following Referee #2 suggestion we have included a second gray-scale bar, which reports

the altitude scale, hence highlighting where the Rhône Valley and the nearby slopes are located. We believe that this information, together with contour lines of terrain elevation, helps the reader identifiyng where the slopes are more steep, and where thermals are more likely to develop.

Please also note that following the Referee #1 suggestion for Figure 10 and 11, we centered the horizontal coordinate sytem on the flown-over area. The axis values are in meters, based on the WGS84 UTM Zone 31 projection, but distances can now be more easily evaluated visually. We now also report in the Figures' caption the vertical exhageration values (to enhance visualization of vertical features).

Line 588: The authors note that near surface vapor is similar the recent GNIP precipitation data. I believe this isn't the comparison to make for evapotranspiration. The better one would be to compare vapor data to water vapor in equilibrium with GNIP precipitation. Of course, there is an open variable here in surface humidity but even a blind choice of being at saturation would be a better comparison target for comparing the surface end member in a mixing model.

Thank you for highlighting this important aspect of our analysis. We agree that the precipitation signal alone may not fully represent the isotopic composition of the evapotranspiration flux, since evapotranspiration includes both soil evaporation (which introduces isotopic fractionation) and transpiration (which does not). Following Referee #2's suggestion and Referee #1's remarks on the role of transpiration, we further investigated this issue.

***First**, we estimated the isotopic composition of water vapor in equilibrium with precipitation using GNIP data from the Avignon station (~100 km south of the study area) and monthly mean air temperature data from Avignon (ECA&D) for the period 1997–2021. The GNIP values were corrected for the altitude difference (Δz = 255 m) using lapse rates of 0.2‰ for $\delta^{18}O$ and 1‰ for δD (Masiol et al., 2021).*

***Table**: Isotopic composition of water vapor in equilibrium with precipitation at Avignon between 1997 and 2021, corrected for altitude effect. The *starred values are for the temporal interval of the field campagin.*

Date	T (K)	$\delta^{18}O$ Eq.Vap	δD Eq. Vap
Sep-97	293,4	-13,38	-105,4
Sep-98	292,0	-13,92	-109,9
Sep-99	294,2	-15,07	-116,9
Sep-00	293,2	-15,64	-122,1
Sep-01	290,8	-15,94	-125,6
Sep-02	291,1	-16,41	-124,4
Sep-03	292,2	-13,89	-107,6
Sep-04	293,2	-17,17	-134,0
Sep-05	292,5	-16,78	-130,0
Sep-06	294,1	-14,11	-107,0
Sep-07	292,0	-18,04	-135,9
Sep-08	291,3	-14,51	-110,8

Sep-09	293,2	-21,38	-163,9
Sep-10	291,7	-15,18	-115,5
Sep-11	293,9	-14,78	-112,9
Sep-12	293,0	-15,49	-119,4
Sep-13	292,8	-14,70	-112,3
Sep-14	293,7	-15,32	-118,1
Sep-15	292,0	-12,34	-97,6
Sep-16	294,8	-14,25	-108,1
Sep-17	291,1	-11,97	-103,4
Sep-18	294,3	-11,89	-95,0
Sep-19	294,1	-14,65	-117,0
Sep-20	293,6	-17,04	-131,0
Sep-21*	293,9*	-13,38*	-107,5*
	Average	-15,09	-117,3
	Std. Dev.	2,05	14,5

The analysis of water vapor in equilibrium with precipitation suggests that $\delta^{18}O_F$ aligns more closely with water vapor in equilibrium with precipitation, which is at first order comparable to evapotranspiration signal over the study area (and also consistent wth our $\delta^{18}O$ vs δD analysis in section 3.3). As the referee correctly pointed out, this approach is not entirely precise due to the assumption of saturation, but it provides a more reliable comparison than directly linking water vapor and precipitation. Please note that we have now computed the $\delta^{18}O$ flux composition (<u>estimated as the keeling-plot intercept</u>) using the 150m vertically binned flight observation data. The results do not change significantly but we have specified how we have calculated the flux for completeness.

Second*, as suggested by Referee #1 we delved more into the model data to verify if it is possible to separate the transpiration to evapotranspiration signal. Unfortunately, only the total surface moisture flux, and its isotopic composition, was stored in the COSMOiso output data, without partitioning between bare soil evaporation, transpiration etc. Hence, we analysed the variability of surface moisture flux throughout the day in COSMOiso data.* On 18 September, $\delta^{18}O_{F\text{-}COSMOiso}$ interpolated along flight tracks f04 to f07 changed from –3.13 to –5.15‰, indicating a shift in the flux composition also in the model. *A clear diurnal cycle in $\delta^{18}O_{F\text{-}COSMOiso}$ can be observed on 21 and 22 September at the model grid point corresponding to the study site, as shown in the following figure:*

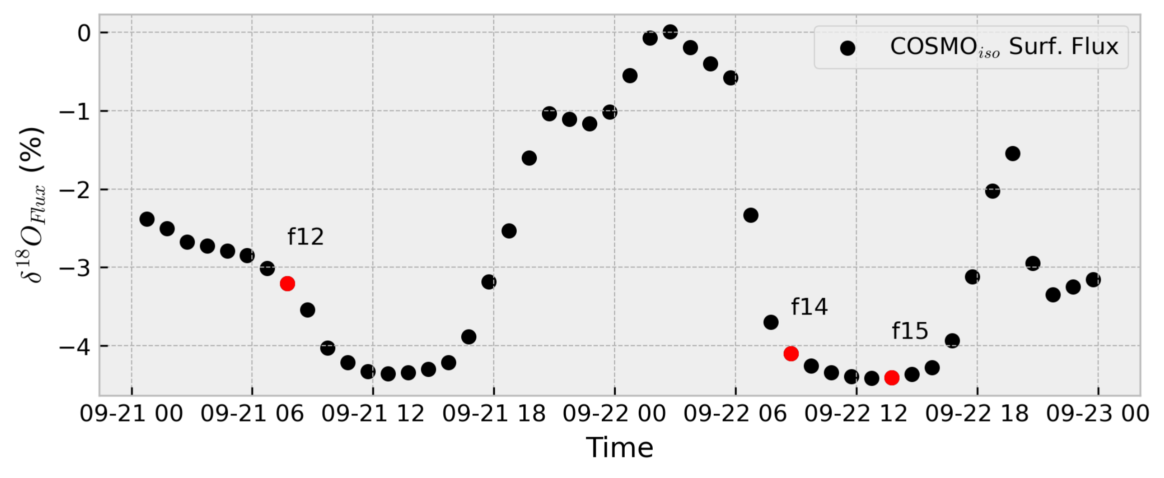

***Figure**: Isotopic composition of the total surface moisture flux ($\delta^{18}O_{F\text{–}COSMOiso}$) at the Lanas Airfield model grid point for 21 and 22 September 2021. Red-highlighted dots indicate the times of the flights on these specific days.*

Thus, both observations (Keeling plot intercepts representative of $\delta^{18}O_F$) and model simulations ($\delta^{18}O_{F\text{-}COSMOiso}$) show a daytime shift in the isotopic composition of the flux. We therefore maintain our conclusion that $\delta^{18}O_F$ varies throughout the day. While we do not claim whether evaporation or transpiration dominates this shift, we emphasize that assuming turbulent mixing either one endmember is changing its isotopic signature or multiple endmembers contribute to the boundary layer moisture composition.

We edited the text as follows:

For example, we estimated a change from $\delta^{18}O_F$ = -6.12‰ at 5 UTC to $\delta^{18}O_F$ =-13.38‰ at 15 UTC on 18 Sep (flights 4 to 7) with keeling-plot method applied on 150 m binned vertical profiles. Intriguing, the average $\delta^{18}O$ of water vapor in isotopic equilibrium with precipitation for September 2021, estimated from altitude-corrected GNIP (IAEA) data and air temperature records from Avignon (~100 km south, ECA&D) is –13.38‰. Although this estimate assumes saturation and equilibrium, making it approximate, it supports the hypothesis that evapotranspiration influences boundary layer moisture during the day. However, the observed shift in the $\delta^{18}O_F$ end-member composition from morning to afternoon also indicates that assigning a constant isotopic signature based on nearby precipitation is not reliable.

Technical corrections Line 366: Boundary layer height, referred as “blh” should be capitalized as an acronym
Corrected here and elsewhere in the manuscript.

Line 666: “spati 6al anisotropy” is a typo
Corrected.