Author Responses Reviewer #2

> **We thank the reviewer for his insightful comments that helped significantly to improve the manuscript. Below, we respond to each of the specific comments (orange) and indicate how the comment are addressed in the revised manuscript (*italic grey*).**

Summary:

The authors present one of the first sets of continuous measurements of triple oxygen and hydrogen isotopes in atmospheric water vapor from multiple heights within and above a forest canopy for one year. They seek to identify the processes that change the isotopic values at the diurnal and seasonal time scales, as the title clearly indicates. They conclude that local evapotranspiration during the daytime and water vapor exchange with leaf water at night control the diurnal cycles. They conclude that seasonal variability is consistent with ocean moisture source signals changing environmental conditions, temperature and relative humidity. Also, the paper presents an analysis showing that the isotopic signatures of the potential oceanic moisture sources are not sufficiently different to use the observations to detect source region changes at the event or seasonal scale. However, they do show that vapor 17O-excess mean values are inconsistent with common assumptions made for ocean evaporation isotopic composition and suggest that more 17O-excess sea water observations are needed to resolve this discrepancy.

General comments:

Overall, this study is valuable because 17O-excess measurements in vapor are rare. For that reason, it will be of interest to the research community to quantify the ranges of variability observed. The paper is written clearly and the figures are helpful. However, there are several omissions the authors make in their interpretations and other edits that would improve the quality of the manuscript.

1. The interpretation of the diurnal isotopic variability neglects the influence of vertical mixing within the PBL that has been identified in many previous studies of d18O, dD, and deuterium-excess. See Griffis et al., 2016 and references therein. It is reasonable to believe that this process is also a major influence on 17O-excess.

   We agree that entrainment of the residual layer, a remnant of the convective boundary layer that developed during the previous day, can contribute to increasing ^{17}O-excess and d-excess as suggested in previous studies. However, we note that the high ^{17}O-excess/d-excess in this residual layer is also related to the contribution of ET during the previous day. In the revised version, we add citations of Griffis et al. (2016) and Welp et al. (2012) as suggested. We further specify that entrainment from the residual layer may contribute to increasing ^{17}O-excess and d-excess during boundary layer growth in the early morning. However, we keep that entrainment from the free troposphere is unlikely to have a significant influence due to its low water content. In the conclusions, we highlight the need for investigating vertical gradients of ^{17}O-excess$_V$ in the atmosphere.

“Entrainment of a remnant of the convective boundary layer of the previous day may contribute to the observed increase in ^{17}O-excess$_V$ during boundary layer growth in the morning (Griffis et al.,2016; Welp et al., 2012). This residual layer can contain moisture with high ^{17}O-excess and d-excess due to evapotranspiration. Mixing with the lower free troposphere may also occur. However, its low water vapor mixing ratio ($<$ 4000 ppmv) likely limits its influence on the isotopic composition of atmospheric water vapor. In addition, Rayleigh distillation during adiabatic air ascent and air mass mixing, which drives the isotopic composition of the lower free troposphere may contribute to daily changes in $\delta^{18}O_V$ (e.g., H. He & Smith, 1999; Salmon et al., 2019; Sodemann et al., 2017). However, Rayleigh distillation is not supposed to significantly increase ^{17}O-excess$_V$ (Xia et al., 2023).”

2. Additionally, the influence of nighttime water exchange between the surface and the atmosphere does not have to be confined to leaf waters. Soil water vapor exchange may also play a role as noted by Berkelhammer et al. 2013.

We agree that water exchange between the atmosphere and highly evaporated surface soil layers can also contribute to lowering of ^{17}O-excess$_V$ and d-excess$_V$ during night. We note that late afternoon leaf waters are usually more depleted than soil waters at our study site so that even low exchange rates can have a significant impact. In the revised version, we will modify this paragraph as follows:

“[…] On the daily scale, higher q below the canopy, lower $d^{18}O_V$ and higher d-excess$_V$ and ^{17}O-excess$_V$ during the day (with a peak in the afternoon) are observed. The fact that this day-night isotopic profile is more pronounced during spring and summer than in winter (Fig. 3) can be explained by several processes. Day-night variations in d-excess$_V$ have been reported across diverse environments, including forests, grasslands, wetlands, agricultural areas and urban regions (Berkelhammer et al., 2013; Delattre et al., 2015; Welp et al., 2012). Continental evaporation to the atmosphere decreases $d^{18}O_V$ and increases d-excess$_V$ and ^{17}O-excess, assuming the continental surface water has an isotopic composition close to that of precipitation (Huang & Wen, 2014; Rothfuss et al., 2021; Simonin et al., 2014; Welp et al., 2012; Zhao et al., 2014) (Fig. 6). Plant transpiration, which is assumed to be non-fractionating relative to soil water (Galewsky et al., 2016 and references therein) should increases $d^{18}O_V$ but have little impact on d-excess$_V$ and ^{17}O-excess$_V$. In total, net evapotranspiration will affect $d^{18}O_V$, with the direction and magnitude depending on the relative contributions of evaporation and transpiration. It will affect d-excess$_V$ and ^{17}O-excess$_V$ only when evaporation is substantial (Fig. 6). In addition to local evaporation fluxes that lead to high d-excess$_V$ during the day (Huang & Wen, 2014; Simonin et al., 2014; Welp et al., 2012; Zhao et al., 2014), low nocturnal d-excess$_V$ values have been linked to exchange between plant water, soil water and atmospheric water vapor when RH is high (Bastrikov et al., 2014; Berkelhammer et al., 2013; Lai & Ehleringer, 2011; Simonin et al., 2014; Welp et al., 2012). Although plant transpiration decreases during night, incomplete stomata closure allows continued equilibrium isotope exchange between evaporated leaf water and the atmosphere under high relative humidity (Berkelhammer et al., 2013), leading to higher $d^{18}O_V$ and lower d-excess$_V$ and ^{17}O-excess$_V$. Evaporation from surface soil layer and exchange between the

atmosphere should impact the atmospheric water vapor's isotopic composition in the same direction (Berkelhammer et al., 2013; Welp et al., 2012). […]"

3. In the conclusions, it's stated that 17O-excess can separate evaporation and transpiration signals. D-excess has this potential too, but neither is shown in this dataset. Please provide support or remove that conclusion.

   Indeed, our results do not directly show that ^{17}O-excess can separate evaporation and transpiration signals. Instead, we show that it is helpful to identify the contribution of evapotranspiration to the atmosphere on local scale. The magnitude of change in ^{17}O-excess together with changes in the atmospheric water mixing ratio potentially allows quantification of its impact. The conclusion and the abstract will be reworked to account for the changes in the discussion section on terrestrial moisture recycling.

4. Please provide more description of how uncertainty in 17O-excess and deuterium-excess are quantified. See specific comments below.

   A similar question was raised by reviewer #1. The uncertainty in raw isotopic measurements of atmospheric water vapor was estimated from Allan deviation of atmospheric water vapor measurements at our study site for 60 min average. To determine the precision of the calibrated water vapor isotope data, a Monte Carlo simulation was performed. This simulation accounted for the uncertainty in the raw isotope data, and additional uncertainty introduced by the mixing ratio dependency correction and the VSMOW-SLAP normalization. See reply to reviewer #1 for details and how this will be implemented in the revised manuscript.

5. As reviewer #1 mentions, the moisture source region discussion is rather qualitative, and I agree with many of their points.

   We now applied the concentration weighted trajectory model after Salamalikis et al. (2015) to identify moisture source regions that contribute to high/low isotope values at our study site. We also quantify moisture source uptake zones after Sodemann et al. (2008). Both was suggested by reviewer #1. See reply to reviewer #1 for details and how this will be implemented in the revised manuscript.

Specific comments:

Section 2.1: Include canopy LAI, tree stem density, or other metric of closed vs. open canopy so that vertical mixing with the boundary layer can be put into context.

In the revised version, we will specify the leaf area index (LAI), tree density, basal area of the stand and gap fraction so that the reader can get a better idea of the proportion between closed and open tree canopy.

"The stand density was about 3550 trees per hectare with a stand basal area 18.8 $m^2\ ha^{-1}$ and an average leaf area index (LAI) of about 2 $m^2\ m^{-2}$, ranging between 1 and 3, with a canopy gap fraction of about 25%."

Line 37: unclear meaning: 'recharge conditions during lake evaporation (Surma et al., 2015, 2018)'

> **We refer here to the fact if the lake receives inflow by river or groundwater continuously or not. In the revised version, we will rephrase this sentence as follows:**
>
> *"Moreover, the ^{17}O-excess of surface waters can be used for identifying if the lake receives continuous surface or subsurface inflow (Surma et al., 2015, 2018) and mixing processes between evaporated and unevaporated waters (Voigt et al., 2021), lake hydrological balancing (Pierchala et al., 2021; Voigt et al., 2024) and water exchange at the soil-plant-atmosphere interface (Landais et al., 2006; Li et al., 2017; Voigt et al., 2023)."*

Line 66: Do these site acronyms mean anything? 'AnaEE in natural experimental platform O3HP'

> **Yes. AnaEE refers to the European Research Infrastructure 'Analyses and Experimentation on Ecosystems' and O$_3$HP is the acronym for 'Oak Observatory of the Observatory of the Upper-Provence'. We will add this information in the revised manuscript.**
>
> *"The AnaEE (European Research Infrastructure 'Analyses and Experimentation on Ecosystems') in natura facility O$_3$HP (Oak Observatory of the Observatory of the Upper-Provence) is situated in a Mediterranean forest about 70 km north of Marseille (France) at an altitude of 680 m above sea level (43.935° N, 5.711° E)."*

Section 2.2: 5 L/min continuous flushing of inlet lines with 70 min switching is likely sufficient for d18O and dD, but I'm not familiar with typical memory timescales for 17O-excess. While I don't expect d17O memory to be longer than d18O, a demonstration of step-change response curves or discussion of equilibration time for this system would be appreciated.

> **As memory effects for oxygen are generally lower than for δ^2H and as similar memory effects have been found for δ^{17}O and δ^{18}O in liquid measurements so that ^{7}O-excess is not affected (Vallet-Coulomb et al., 2021), we believe that impact of the memory effect on our measurements is minimal. We assessed the memory effect for a 1/4'' 30m long PFA tube, flushed at 5 L min^{-1} by switching from vapor generated using a vapor generator to ambient laboratory air. The raw data of this experiment are illustrated in the figure below. The raw water mixing ratio of the vapor generated with the vapor generator was about 12700 ppmv and similar to ambient air. The horizontal line shows the average value of the last 30 seconds of ambient air measurement and serves as a guide for the eye. As shown in previous studies, memory effect lasts longer for δ^2H compared to δ^{18}O, even more than the 10 min that we discarded for this tubing length (close to the longest tubing we used in the field (32m)). However, as we later integrate 60 min measurement intervals, the impact of the little remaining memory effect on δ^2H should be insignificant compared to the isotopic variability of the atmosphere. The memory effect of ^{17}O-excess is difficult to assess as 10-15 min need to be integrated to obtain meaningful data.**

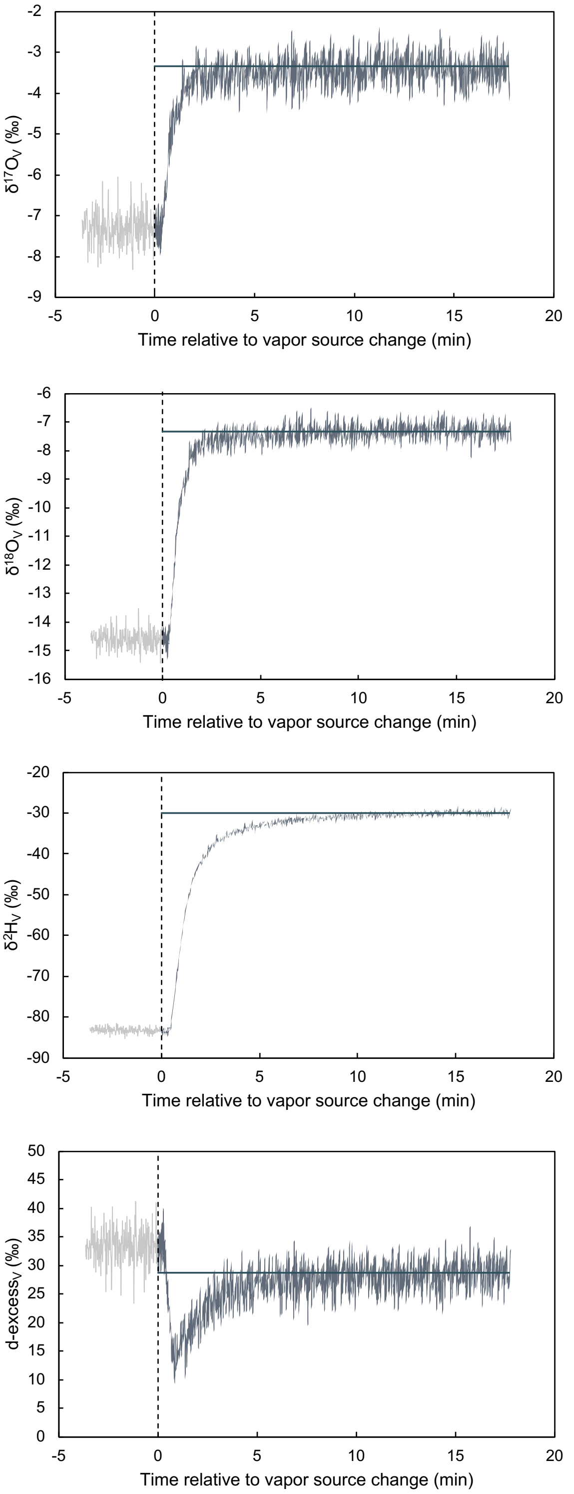

Figure AC1: Illustration of the memory effect for raw $\delta^{17}O_V$, $\delta^{18}O_V$, δ^2H_V and d-excess$_V$ for a 30m 1/4'' PFA tubing. We switched from a water vapor generated by a custom-built vapor generator (light grey curves) to ambient laboratory air (dark grey curves). The raw water mixing ratio was about 12700 ppmv for both vapor sources. The vertical dashed line indicates the moment of vapor source change and the horizontal solid line indicates the average over the last 30s of isotope measurement of ambient air.

Line 115: ‘Precision was better than 0.1 ‰, 0.2 ‰, 1.8 ‰ and 14 per meg, and 0.9 ‰ for δ17O, δ18O, δ2H, 17O-excess, and d-excess, respectively.’ How was precision quantified? Averaging over a defined time period? Propagation of error of d18O and dD would result in a d-excess uncertainty of 3.4 permil, much greater than the authors’ estimate of 0.9 permil.

> **As described above in the general comments, a Monte Carlo simulation was applied accounting for the uncertainty in the raw isotopic composition derived from Allan deviation, and additional uncertainty introduced by the mixing ratio dependency correction and VSMOW-SLAP normalization. This will be specified in the revised version as described in the reply to reviewer #1.**

Line 191: ‘The average wind speed at 10 m height was 0.3 m s-1’ How is the stdev determined?

> **0.3 m s^{-1} is the standard deviation of the monthly mean values. We find this value might be a bit misleading and provide now the standard deviation over the daily average wind speed, which is 1.1 m s^{-1}.**

> *“The average wind speed at 10 m height over daily mean values was 2.6 ± 1.1 m s^{-1} in 2021.”*

Line 195: ‘The largest day-night differences occurred near the ground and in summer (Fig. A1-A3). During the day, q and Tair were highest near the ground, whereas RH was vertically homogenous (Fig. A1-A3). At night, the Tair vertical gradient was inverted, with the lowest values occurring near the ground, while q showed no vertical variation, resulting in decreasing RH from the surface to 10 m agl (Fig. A1-A3).’ Assuming this refers to summer conditions, wouldn’t it be unusual for air temp to be cooler near the surface than above when the surface usually radiates heat at night?

> **From Fig. A1-A3 it becomes clear that nighttime gradients in T and q are rather weakened. Overall cooling leads to higher RH compared to daytime that decrease from ground to 10 m agl. The section will be rephrased in the revised version to clarify this.**

> *“During the day, q and T_{air} were highest near the ground, whereas RH was vertically homogenous (Fig. A1-A3). At night, the vertical gradient in T_{air} and q weakened. Nighttime cooling resulted in higher RH that decreased from the surface to 10 m agl (Fig. A1-A3).”*

Section 3.6: what frequency of observations was this analysis based on? Monthly means or hourly resolution?

> **This analysis is based on the moisture source identification using the hourly air-mass back trajectory analysis.**

Fig 6: 17O-excessv is different for summer and winter. Driven by RHsst differences. The process label ‘E’ is not described in the text.

> **E refers to evaporation from open-surface waters or soil, while T is plant transpiration. We specify this now in the revised version. Both together form**

> **evapotranspiration (ET), which we here simply term moisture recycling as it is the process of bringing back meteoric water to the atmosphere.**
>
> *"Figure 6: Synthesis of the effect of ocean evaporation, rainout, air mass mixing, continental moisture recycling (ET) resulting from evaporation (E) and plant transpiration (T), and post formation precipitation processes in winter (blue) and summer (yellow) on the triple oxygen isotope composition of (a) atmospheric water vapor and (b) precipitation (see Sect. 4 for further details)."*

Section 4.1: These patterns are consistent with many other continuous water vapor isotope studies including d-excess and citations should be included. The novelty here is adding on 17O-excess and comparing how it's similar/different from d-excess as it's sensitive to many of the same influences.

> **Previous studies found also that not only d-excess but also ^{17}O-excess reflects climate conditions in the moisture source regions. We add corresponding references in the revised version.**
>
> *"This is in agreement with previous interpretations of the triple oxygen isotope composition of water vapor and precipitation (Affolter et al., 2015; Landais et al., 2012; Liotta et al., 2008; Merlivat & Jouzel, 1979; Pfahl & Sodemann, 2014; Tian et al., 2018; Uechi & Uemura, 2019)."*

Line 371: 'thus the isotope compositions of water vapor evaporated from these sources are ***predicted to be*** similar.' I suggest qualifying this statement because later the authors mention uncertainty in the inputs for calculating these estimates.

> **Thanks for pointing this out. We will change this phrase in the revised version as suggested.**

Line 420-430: could use improved citations and is misleading in present form. Berkelhammer et al., 2013 and references therein attribute diurnal variability to increased vertical mixing or PBL entrainment during the daytime as well as vapor exchange with the surface (leaf water and soil water) at night. The authors minimize this process because PBL air is drier, but nevertheless, it has been previously shown to be important and is likely contributing here also. Some well-documented entrainment influence citations like Griffis et al., 2016 and Welp et al., 2012 should be included.

> **This was major point #1 of the reviewer. See author response above.**

Line 430: The authors argue that Rayleigh distillation is not expected to lead to 17O-excess enrichment in the lower free troposphere. Xia et al., 2023 shows theoretical deuterium-excess and 17O-excess signals increase as Rayleigh distillation intensifies.

> **According to Fig. 3 in Xia et al. (2023) the ^{17}O-excess of atmospheric water vapor is increasing not more than 5 per meg considering only liquid condensation (Fig. 3b) and can even decrease by more than 30 per meg when condensation has ice (Fig. 3d). Thus, a ^{17}O-excess$_V$ in the lower troposphere is expected to be similar or even lower than near ground. We will add the citation of Xia et al. (2023) in the revised version.**

Line 440-443: Ice/snow formation in cloud is likely not in isotopic equilibrium with cloud vapor due to super saturation effects Dutsch et al., 2019 and Xia et al., 2023.

> **We thank the reviewer for noting this. We now specify the difference in isotope fractionation for liquid and solid precipitation as follows:**
>
> *"Liquid precipitation forms in isotope equilibrium with atmospheric water vapor at cloud height, while ice formation may be accompanied by an additional kinetic effect due to supersaturation of water vapor (Dütsch et al., 2017, Xia et al., 2023). Vapor at cloud height is typically depleted in heavy isotopes compared to near-surface atmospheric water vapor due to Rayleigh fractionation processes (Giménez et al., 2021 and references therein; Salmon et al., 2019; Sodemann et al., 2017)."*

Line 467: main conclusions are mostly asserted by theory rather than using observations as an independent test.

> **The conclusion and abstract will be reworked to account for the changes in discussion section and the implementation of the quantitative moisture source uptake analysis.**

Line 473: The findings in this paper contrast previous findings that mediterranean moisture source has a high deuterium-excess compared to North Atlantic, both in theoretical predictions and observations of downwind vapor and precipitation. What makes this study different? Different assumptions about conditions in the source regions? Perhaps ERA5 doesn't accurately capture near-surface RH differences? Does monthly resolution mute signal? Etc.

> **High d-excess values in atmospheric water vapor and precipitation (> 20‰) are mainly observed in the Eastern Mediterranean (Casellas et al., 2019; Celle-Jeanton et al., 2001; Cruz-San Julian et al., 1992; Delattre et al., 2015; Natali et al., 2021). However, the Eastern Mediterranean contributes insignificant moisture to our study site. As we state in the manuscript, often multiple moisture sources contribute to specific humidity at our study so that the isotopic composition of atmospheric water vapor likely represents a mixed signal.**

Fig 2: d-excess deserves error bars also

> **The error bars of d-excess are smaller than symbol size. This is now specified in the figure caption.**

Fig 3: What frequency of data was used for the monthly means? 15-min or hourly, etc. Is the plot a smoothed spine fit through discrete values?

> **We used hourly data to calculate monthly means. The curves show the discrete monthly mean values per hour of the day.**

Fig A8: please include d-excess vs 17O-excess correlation here or somewhere in the paper

> **In the revised version, we also show the correlation between δ18O, d-excess and ^{17}O-excess in Fig A8 and Fig A9.**

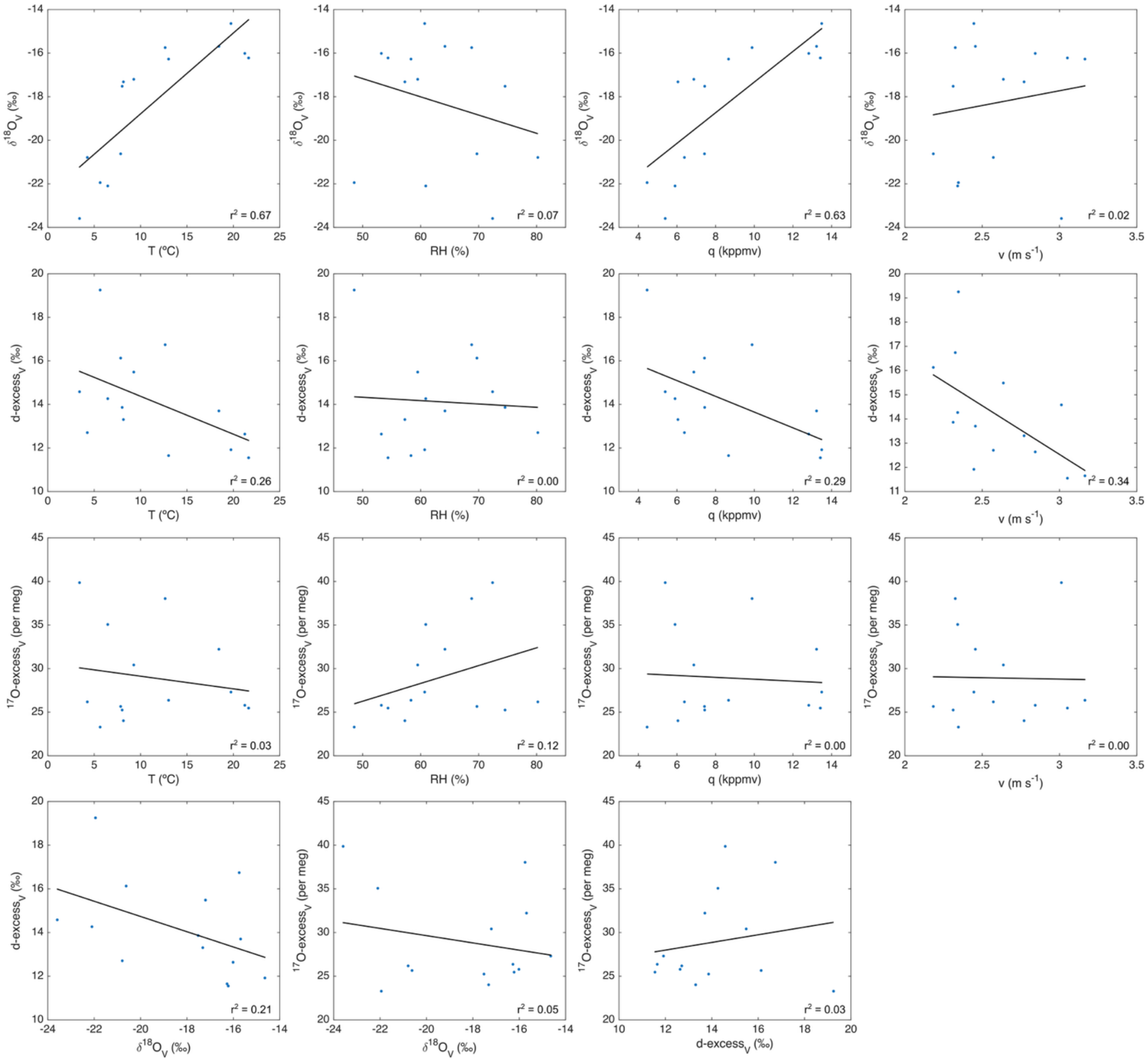

Fig. AC2: New Fig A1.8

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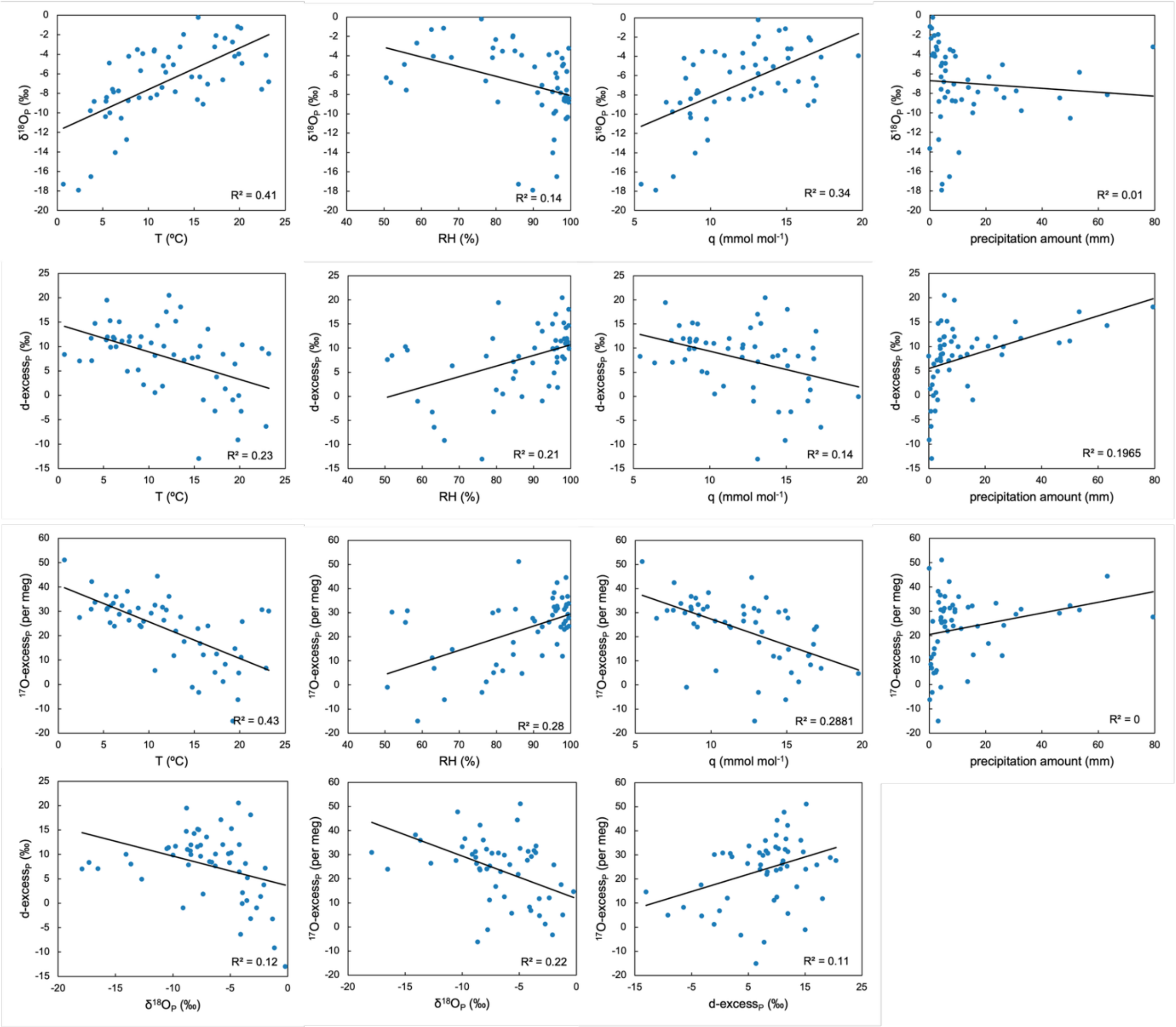

Fig AC3: New Fig A09.

Fig A10: There are more statistics that could be helpful for the reader. The spread of back trajectories and/or the frequency of each cluster over the year.

In the revised version, we will add the results of the quantitative moisture source analysis and the relative contribution of the moisture sources per month (Fig. 2-5 in author response to reviewer 1).

Table B2: How is the SD of veq determined. The precip is collected monthly and event scale during some months, so are different methods used?

Table B2 summarizes only precipitation data from 2021 when precipitation was collected on quasi-event scale as specified in the Methods Section. The standard deviation is the amount-weighted standard deviation of the precipitation data per month.

References:

Berkelhammer, M, J Hu, A Bailey, et al. “The Nocturnal Water Cycle in an Open-Canopy Forest.” *Journal of Geophysical Research-Atmospheres* 118, no. 17 (2013): 10,225-10,242. https://doi.org/10.1002/jgrd.50701.

Dütsch, Marina, Peter N. Blossey, Eric J. Steig, and Jesse M. Nusbaumer. “Nonequilibrium Fractionation During Ice Cloud Formation in iCAM5: Evaluating the Common Parameterization of Supersaturation as a Linear Function of Temperature.” *Journal of Advances in Modeling Earth Systems* 11, no. 11 (2019): 3777–93. https://doi.org/10.1029/2019MS001764.

Griffis, Timothy J, Jeffrey D Wood, John M Baker, et al. “Investigating the Source, Transport, and Isotope Composition of Water Vapor in the Planetary Boundary Layer.” *Atmospheric Chemistry and Physics* 16, no. 8 (2016): 5139–57. https://doi.org/10.5194/acp-16-5139-2016-supplement.

Xia, Zhengyu, Jakub Surma, and Matthew J. Winnick. “The Response and Sensitivity of Deuterium and ^{17}O Excess Parameters in Precipitation to Hydroclimate Processes.” *Earth-Science Reviews* 242 (July 2023): 104432. https://doi.org/10.1016/j.earscirev.2023.104432.