Authors' response to Reviewer 2 [hess-2024-4169-RC2]

We thank the reviewer for his evaluation of our manuscript and his many helpful comments (hess-2024-4169). Below we address the reviewer's comments (full text) indented by arrows and coloured in blue. We appreciate the efforts by the reviewer, which will help to improve our manuscript.

General comments

One of the major issues is that the authors switch a lot between different timescales, which is confusing for the reader. For example, most of the introduction deals with variations on monthly timescale, but then the record is on sub-daily timescale. Further, Section 3.1 presents the precipitation and meteorological data on monthly scale, but then, in Section 3.2, an event-based model is applied. The authors should restructure the manuscript, including presentation of isotope and model results on different timescales to better guide the reader. They may also decide to stick to only one timescale, if only this is relevant regarding the objective of the manuscript.

→ *Thank you for bringing this to our attention. One of the strengths of the manuscript is the sub-daily isotope dataset, so the most logical decision would be to keep the sub-daily resolution. However, when analysing the influence of the atmospheric circulation types, it is sometimes advantageous to aggregate the data to see the general effect on isotopic signatures. Hence, it might be difficult to restrain ourselves to one timescale only, but we will make an effort to clearly state what timescale we are working with when displaying results, e.g., by including the number of samples that went into calculating statistics. Also, we have decided to not include the generalized model for Europe in the new manuscript, which should alleviate the problem of switching between timescales. The extrapolation of our model calibrated on LIST data on the European scale was one of the major flaws of our approach. Based on your comments and comments received from other reviewers, we decided to remove the generalized model from the manuscript. Instead, we will focus on the effects of atmospheric variability on relations between sub-daily precipitation isotope signatures and meteorologic variables.*

The authors focus on the relationship between temperature and the isotope composition of precipitation, which is definitely an important factor during precipitation and Rayleigh rainout. However, other processes affecting the atmospheric water vapor from which the precipitation is formed, such as changes in climate conditions in the moisture source regions and contribution of continental evapotranspiration are only shortly mentioned, while their effect on the isotope composition of precipitation remains undescribed. It is not until the discussion section that the reader learns about post-precipitation formation processes, such as rainfall re-evaporation, that can modify the isotope composition of precipitation. I suggest restructuring the introduction section, providing an overview of the processes that can affect the isotope composition of precipitation before, during and after precipitation formation and on which timescale they are relevant.

→ *Thank you for this very pertinent remark. We have fully revisited the structure of the manuscript and added two paragraphs in the introduction discussing the processes affecting the atmospheric water vapor from which the precipitation is formed. Some sentences were also taken from the discussion and brought to the introduction, as you mentioned these aspects should be mentioned earlier. The new paragraphs we are referring to are cited below:*

"In Western Europe, the isotopic composition of local precipitation was found to be primarily controlled by large-scale processes, i.e., moist air masses coming primarily from the Atlantic Ocean with different rainout histories (Rozanski et al., 1982). As those air masses travel over continents and orographic obstacles, condensation occurs with a selective transition to the liquid phase of the heavy isotopes – following a Rayleigh distillation scheme. The gradual depletion of precipitation ^{18}O and ^{2}H, leading to increasingly more negative $\delta^{18}O$ and $\delta^{2}H$ values is known as the continental effect (Dansgaard, 1964). The origin of the air moisture also plays a key role in defining $\delta^{18}O$ and $\delta^{2}H$ signals, with several studies documenting the unique isotopic signature of the Mediterranean Sea in contrast to other sources in Europe (Bonne et al., 2020; Casellas et al., 2019; Celle-Jeanton et al., 2001; Krklec et al., 2018). Celle-Jeanton (2001) reported precipitation from the Mediterranean area to be ^{18}O-enriched with higher $\delta^{18}O$ (-5 ‰) compared to Atlantic sources (-8 ‰), and significantly higher d-excess values (22 ‰ against 10 ‰), the d-excess being defined as $\delta^{2}H - 8 \times \delta^{18}O$. The d-excess value is a proxy for evaporation conditions at the moisture source (Merlivat and Jouzel, 1979) and reportedly relates to the remote over-sea relative humidity and the sea surface temperature (Aemisegger et al., 2014; Bonne et al., 2019; Pfahl and Sodemann, 2014). Backward air mass trajectory models, based on Lagrangian techniques, are now implemented to visualize the pathways of incoming airmasses, going back several days before the rain event, to describe the short-term influence of moisture origin on the isotopic signature of precipitation (Aemisegger et al., 2014; Juhlke et al., 2019; Krklec et al., 2018). Integrated vapor transport models can also complement the trajectories to identify air streams that carry most of the moisture (Conticello et al., 2020; Juhlke et al., 2019; Lavers & Villarini, 2013).

Note that other effects also need to be considered, such as complex local processes during cloud formation at the boundary layer (frontal and convective activity, re-evaporation of rain drops) (Aemisegger et al., 2014; Coplen et al., 2015; Moore et al., 2014), or continental moisture recycling, as landmasses can be large contributors of recycled moisture (Insua-Costa et al., 2022; Krklec et al., 2018). Plant transpiration complicates the identification of continental inputs further, making them more difficult to distinguish from oceanic sources, and it can change the apparent relation between isotopic signatures and local meteorological variables (Aemisegger et al., 2014, Krklec et al., 2018). A decrease of secondary evaporation with higher convection strength can also mistakenly be interpretated as the amount effect because of the apparent depletion (or lack of enrichment) of the isotopic signal with higher precipitation amounts (Moore et al., 2014)."

The authors observe variations in the isotope composition of precipitation with atmospheric circulation patterns. However, the processes behind these isotope variations as well as their relevance on different timescales are not discussed. There is a need for a climate characterization of the different CPs. Also, the authors focus mainly on temperature, but other factors such as rainfall amount and RH during the precipitation event may provide information on local processes such as rain re-evaporation. Also, changes in moisture sources should be discussed in relation to CPs. There is a debate on isotope differences between precipitation derived from Atlantic and Mediterranean air masses, the latter being characterize by a higher $\delta^{18}O$ and d-excess values. Do the authors observe similar isotope differences between air mass sources? Which sources can be attributed to different CPs?

→ Thank you for the suggestion, we will also consider the precipitation amount, the relative humidity and the surface pressure as additional meteorologic variables. We will gradually include them in the multiple linear regression models to assess their performance under increasing complexity. We account for these aspects in the manuscript with the following new paragraphs:

"To test if including air mass trajectories in our modelling approach improves results for precipitation $\delta^{18}O$ predictions, we rely on multiple linear regression models (MLRMs) fed with meteorologic variables at event scale. We compare models sub-setting the $\delta^{18}O$ data for each trajectory in one scenario (hereafter referred to as "separated" model) and keeping the data together in the other (hereafter referred to as "traditional" model). The results indicated for the separated model are the weighted mean of all five trajectory-specific models, considering the number of observations in each group with the weighting. More variables are gradually fed to the model augmenting the degrees of

freedom to also test under which conditions the models perform better. Hence, four MLRMs will be tested under two scenarios, one regular and the other separated according to the air mass trajectory types."

Regarding atmospheric circulation patterns and moisture origins, we have simulated the air mass trajectories using the backward trajectory HYSPLIT model and found that the trajectories do not always correspond to the broader synoptic atmospheric circulation types. This has led us to prefer the HYSPLIT simulations for the characterization of the precipitation events over the Hess Brezowsky (HB) catalogue. We will thus replace HB categories by new categories derived from HYSPLIT simulations, which shall be more informative about moisture origins. Below is an extract from the new manuscript where isotope differences between precipitation derived from Atlantic and Mediterranean air masses are discussed:

"In response to our research question on synoptic influences on precipitation isotopic signatures, there is a difference in d-excess (and, to a lesser degree, in $\delta^{18}O$) signatures coming from Mediterranean or continental trajectories, and trajectories influenced by sometimes remote centres of activity over the Atlantic Ocean. […] With slopes over 0.55 ‰/°C, the Mediterranean and the continental, but also South Atlantic, trajectories are striking examples. A possible explanation for this similarity lies in the long travel distances of these airmasses over continents and mountain ranges (e.g., the Alps for Mediterranean trajectories and Pyrenees for South Atlantic ones) or other sorts of orographic obstacles. High antecedent rainouts or strong convection causing depletions of heavy ^{18}O isotopes (Aemisegger et al., 2015; Moore et al., 2014), could lead to steeper $\delta^{18}O$-T regressions comparable to landlocked/alpine sites. Broader $\delta^{18}O$ ranges for Mediterranean and the continental trajectories, characteristic of inland locations far from the coast (McGuire and McDonnell, 2007), also support this explanation."

The new categories based on the HYSPLIT air mass trajectory simulations were also clearly defined:

"We plotted the trajectories on a map of Europe (25°N – 75°N, -45°E – 45°E) using the sf package in R (Pebesma, 2018; Pebesma and Bivand, 2023) and assigned five categories (Atlantic, North Atlantic, South Atlanic, Mediterranean, and continental) to the precipitation events based on the location of the mean latitude and longitude of the point-location of the hourly trajectories. Since the trajectories converge on the last part of the track, we only retained the duration 18 to 36 hours prior to the event to calculate the means. We then drew boxes to determine the origin and overall direction of the trajectories, definig the categories attributed to the indual events. The Atlantic Ocean in the Northern Hemisphere was split into three parts, South (30°N – 45°N), West of the Bay of Biskay (45°N – 55°N), and North (55°N – 70°N), as these parts have been reported to carry different isotopic signatures (e.g., Bonne et al., 2019; Pfahl and Sodemann, 2014). The Mediterranean trajectories were defined as traversing the box encopassing the Mediterranean basin, notorious for isotope contributions contrasting from Atlanic sources (Celle-Jeanton et al., 2001), between the latitudes 30°N and 45°N and the longitudes 0°E and 40°E. Continental trajectories were defined as all remaining events only traversing the European continent between the latitudes 45°N and 55°N."

Specific comments

Line 29: In which sense stable isotopes of water are "near-conservative" if isotope fractionation occurs during phase transitions?

→ Stable isotopes of O and H are near-conservative in the chemical sense as they are part of the water molecule, so they are not absorbed or do not react with other substances in chemical reactions, unlike other tracers that are dissolved in the water, e.g., Cl^-. We will clarify this aspect in the manuscript.

Line 47-48: What is the timescale of hydrological processes that is interesting for the community/in this study? Daily/Monthly/Seasonal/Yearly?

→ In hydrology, the timescale of hydrological processes that is typically interesting for the community goes from hourly to weekly when analysing flood events and saturation processes, but for droughts and groundwater recharge, longer timescales going from weeks to years can be considered. In any case, this sentence will be removed as it leads to confusion and is not crucial to the manuscript.

Line 55: Why ~20 years if GNIP data exists for 50 years? Give a range?

→ 20 years referred to the bulk of GNIP stations, but that statement does not add much to the discussion on top of being contestable. We will remove it.

Line 65: Why are isotope-enabled climate models difficult to constrain? Is it due to the difference in timescale between observations and models or because processes driving isotope variations in precipitation are not well understood? Not clear.

→ Both, and because GNIP stations are unevenly distributed and observations are lacking in some regions of the world, e.g., boreal regions.

Line 77ff: Your study is based on daily to sub-daily data. Which processes are relevant at this timescale?

→ This relates to the second general comment you made, please refer to our previous answer.

Line 77ff: It is not clear how atmospheric circulation patterns influence δ18OP. Changes in moisture source, condensation conditions, post-formation processes? Specify this.

→ Below is the section in the corrected manuscript where we address this.

"In this study, we conjecture that the trajectory of the incoming airmasses affect $\delta^{18}O$ and $\delta^{2}H$ values in precipitation, and thus potentially change apparent relations with meteorological variables, e.g., the temperature effect. More specifically, we hypothesize that contrasted moisture origins over Western Europe (Atlantic, Mediterranean or continental) and rainout strengths with different air mass trajectories affect sub-daily $\delta^{18}O$ and d-excess signals in precipitation and the relation with meteorological variables at local scale in Luxembourg."

Line 81: Why you choose a subjective classification scheme and not an objective criterion.

→ As mentioned previously, we have simulated the trajectories using the backward trajectory HYSPLIT model and found that the trajectories do not always correspond to the broader synoptic atmospheric circulation types. This has led us to prefer the HYSPLIT simulations for the characterization of the precipitation events rather than the Hess & Brezowsky (HB) catalogue. We will thus replace HB by categories derived from HYSPLIT simulations.

Line 89: What do you refer to with "precipitation data"? Is it isotope data, samples or meteorological data? Temperature, relative humidity, precipitation amount? Did you use other parameters?

→ Samples is the correct term. We also obtained, temperature, relative humidity, surface pressure and the precipitation amount from nearby stations.

Line 100-104: Can you give more details on the analyses? How many injections per sample? Did you account for the memory effect? What is the frequency of standard analysis?

→ Below is the section in the corrected manuscript:

"Standards provided by the instrument manufacturer were used for the calibration, as well as an internal standard (δ^2H: -52.6 ‰, $\delta^{18}O$: -8.1 ‰) consisting of local tap water calibrated on IAEA standards. For each sample, eight injections were made, discarding the first four to avoid memory effects. The standards were tested every three samples to check for deviations and later correction."

Line 104: the secondary d-excess parameter is not introduced. Add the formula and explain how it complements the δ18O and δ2H data.

→ We will add the formula. Below is the statement on how it complements the $\delta^{18}O$ and δ^2H in the new manuscript.

"The d-excess value is a proxy for evaporation conditions at the moisture source (Merlivat and Jouzel, 1979) and reportedly relates to the remote over-sea relative humidity and the sea surface temperature (Aemisegger et al., 2014; Bonne et al., 2019; Pfahl and Sodemann, 2014)."

Line 105: Reference Kirchner (2016) missing in the reference list. Why the amplitude of monthly amount-weighted δ18OP is of interest?

→ Reading the reviewers' comments, we realized that it added unnecessary complexity and led to reader confusion. We decided to remove the sine wave fits from the manuscript and instead work with more common metrics such as mean, median, interquartile range, etc.

Section 2.2: The classification is obtained from a database or have you done it on your own? In the former case, cite the database. In the latter case, specify which criteria were used. Give the period and temporal resolution of this classification. Did you distinguish only the three major patterns or also the sub-types? Meteorological characterization of the CPs would help to better understand the differences. Consider adding a map.

→ Please refer to our previous response where we explain how we decided to use HYSPLIT simulations instead of the subjective Hess & Brezowsky catalogue. We will add maps showing the trajectories of incoming air masses for precipitation events.

Section 2.3: Why "reanalysis data" in the section title? There is no reanalysis data described in this section.

→ That was a mistake, we apologize for that.

Line 139: Which GNIP stations did you include and how many? Was there a criterion to include or exclude stations?

→ The GNIP stations had to be located in continental Europe and have at least 12 observations. This section was removed from the manuscript because we have decided to not include the generalized model for Europe in the new manuscript.

Line 168: Give minimum and maximum values instead of the range of δ18O and d-excess as it might be unevenly distributed around the amount-weighted average value.

→ Thank you, we will do that.

Line 170: Not clear which one is high in which season as δ18O and d-excess show inverse patterns.

→ We split the sentence in two parts to make it clearer.

"The mean weighted summer high for precipitation $\delta^{18}O$ was -5.6 ‰ with an IQR of 3.6 ‰ and the mean weighted winter low for $\delta^{18}O$ was -8.9 ‰ with an IQR of 5.4 ‰ (N = 613). For the d-excess, the mean weighted summer low was 7.2 ‰ with an IQR of 5.2 ‰, and the mean weighted winter high was 11.8 ‰ with an IQR of 5.9 ‰, and even higher values in autumn (weighted mean 12.2 ‰, IQR 5.1 ‰)."

Line 172-174: How the LMWL was determined? Based on sub-daily, daily or monthly data or interannual monthly data?

→ We will add a figure in the supplements where we show the data on the dual isotope plot. It should be clear then that it is sub-daily data.

Line 175-181: Is there seasonal variability in the precipitation amount?

→ Yes, we have added a sentence on that.

"Mean annual precipitation was 876 mm, with seasonal fluctuations comprised between 167 mm (MAM/JJA) and 310 mm (DJF), and 230 mm in autumn."

Line 189: To which CP refer HCE and LCE? Zonal/Meridional/Mixed? They haven't been introduced in Section 2.2, aren't they?

→ This comment does not apply anymore with the new trajectory classification. We will make sure the new categories are well-defined.

Line 205: Why these values are relevant? Do they reflect the annual average isotope composition of precipitation? Why they deviate from this value?

→ Please refer to our previous response, we decided to remove the sine wave fits from the manuscript.

Line 208: Does the seasonality of CPs influence the sine wave curve calculation?

→ Most likely they do, but again, we decided to remove this section from the manuscript.

Line 210-211: Is there a table or figure showing these data for all CPs?

→ There was not. We will add those in the supplements.

Line 216-220: Is this also reflected in the amount-weighted average for each CP?

→ Yes. The all the trajectory-specific medians, IQR, minima, maxima and ranges are now given in Fig. 4 and Table 1. They are also discussed in the new manuscript:

"This was reflected by a higher $\delta^{18}O$ median (-5.8 ‰) for Mediterranean trajectories than the overall median (-6.9 ‰), with a minimum median of -7.5 ‰ (South Atlantic). For the d-excess, IQRs were comprised between 5.3 ‰ (South Atlantic) and 7.4 ‰ (Mediterranean), but showed greater spreads of the medians with values ranging from 8.8 ‰ (Mediterranean) to 14.4 ‰ (North Atlantic)."

Line 224: Does calculating a sine wave curve make sense for HCE of there is little data in winter (or summer?)?

→ You are right to ask this; it does not. We removed it from the manuscript.

Line 234: Is this expected?

→ Yes, it is. But since it added little to the discussion, we will remove it.

Section 3.2: Here, you evaluated data on weekly scale, while before you presented data on monthly scale, but it is an event-based model... Please restructure to guide the author with the different timescales!

→ That was indeed confusing. Please note that this section will also be removed.

Line 280: Explain this normalization. Is it commonly used? How to interpret this normalized value?

→ The underlying idea was that the RMSE should never be higher than the standard deviation of the data, elsewise the model results could not be considered better than random value attributions. It was also meant to prevent coastal stations with low isotopic signal amplitudes to artificially drive the RMSE down to lower values. This normalization of the RMSE becomes obsolete with the new version of the manuscript, however.

Line 327: This is the first time you mention these post-precipitation formation processes. They should already be introduced in the introduction.

→ Thank you for bringing this up, they are now mentioned in the introduction:

"Note that other effects also need to be considered, such as complex local processes during cloud formation at the boundary layer (frontal and convective activity, re-evaporation of rain drops) (Aemisegger et al., 2014; Coplen et al., 2015; Moore et al., 2014), or continental moisture recycling, as landmasses can be large contributors of recycled moisture (Insua-Costa et al., 2022; Krklec et al., 2018)."

Line 330-331: Do you observe lower slopes in the dry season? Show these results in the Result Section. Why would you expect lower slopes during the dry season, i.e. why rain re-evaporation should be pronounced in the dry season? Is it a temperature or an amount effect?

→ We will add those in the supplements. The dry season often corresponds with the summer season, which is a period with high energy at the boundary layer, which enhances effects such as re-evaporation.

Line 333-336: Does this exclude the rain re-evaporation process being the key driver of the precipitation isotope composition or do both, moisture source and re-evaporation overlap?

→ This is probably impossible to say with the data we have. Our assumption is that both overlap.

Line 337: What do you mean with "memory effect" here?

→ We meant that precipitation isotopic signals have an integrative nature due to long residence times in the atmosphere. But since it leads to confusion, we will remove it.

Line 346-349: I found the observed d-excess not exceptionally high. It is rather close to the global average. So, there is no contribution of Mediterranean air masses or moisture recycling or are there certain CPs that show higher values?

→ We were referring to d-excess values that were occasionally high. There were some trajectories that showed higher values:

"In response to our research question on synoptic influences on precipitation isotopic signatures, there is a difference in d-excess (and, to a lesser degree, in $\delta^{18}O$) signatures coming from Mediterranean or continental trajectories (d-excess ~ 8.0 ‰), and trajectories influenced by sometimes remote centres of activity over the Atlantic Ocean (d-excess ~ 10.0 ‰)."

Line 349-351: Do you observe seasonal variations in d-excess that could be linked to seasonality in continental ET?

→ For this, I would refer to Table 2, where we have included seasonal $\delta^{18}O$ relations with meteorologic variables. We saw that the $\delta^{18}O$-temperature relation is weaker in summer (0.34 ‰/°C) than, e.g., in winter (0.55 ‰/°C).

Github: It would be great if you could provide a metadata sheet that explains shortly the different files and R scripts.

→ We will add a metadata sheet for the files and R scripts as suggested.