Authors' response to Reviewer 3 [hess-2024-4169-RC3]

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

The novelty and scientific significance are not well described. Particularly, the application of RSME, which, although highlighted as a novel approach, has been widely used for similar tasks in previous studies or has already been tested (e.g. https://onlinelibrary.wiley.com/doi/abs/10.1002/hyp.14254, https://www.sciencedirect.com/science/article/pii/S016980952300090X).

→ Thank you for bringing this to our attention. It was not our intention to highlight the RMSE as a novel approach. The significance of our work is that while atmospheric circulation patterns are commonly perceived to affect isotope signatures, it is not clear how this affects apparent relations with meteorological variables at local scale. This information is however crucial for δ^{18}O predictions, particularly at the long term (reconstructions into pre-instrumental times spanning over 60 years). That is where we want to contribute with our work. The aims and the novelty of the manuscript have been reformulated as follows:

"In this study, we conjecture that the trajectory of the incoming airmasses affect δ^{18}O and δ^{2}H values in precipitation, and thus potentially change apparent relations with meteorological variables, e.g., the temperature effect. Although atmospheric circulation patterns are generally perceived to affect isotope signatures, it is not clear how this conditions apparent relations with meteorological variables at local scale. 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 δ^{18}O and d-excess signals in precipitation and the relation with meteorological variables at local scale in Luxembourg.

To test our hypotheses, we rely on six years of high-resolution (i.e., sub-daily) precipitation δ^{18}O and δ^{2}H data, and hourly meteorological data recorded in Belvaux (Luxembourg). We use a pre-established Langrangian model to visualize air mass trajectories 36 hours prior to the start of 648 precipitation events. We then analyse how the fact of considering atmospheric trajectories affects a simple modelling approach based on multiple linear regressions (of increasing complexity) and assess potential implications for reconstructions of long chronologies of δ^{18}O in precipitation."

Notably, the authors utilize a sub-daily precipitation approach, which is uncommon in the monitoring of isotopes in atmospheric precipitation, where event-based and composite monthly samples are typically collected. More discussion should be added on the advantages of this method compared to event-based and composite monthly samples. Why are these sub-daily data more beneficial for the construction of isotopes and climate-related data since 1881? How can these data be better compared with ice-core, tree, lake sediment, and other types of isotope data used in climate reconstruction? What is the novelty and scientific importance of the method? The linear method is not the best approach to examine the non-linear relationships that can be highly important in relating isotopes and atmospheric oscillations, which mainly have sinusoidal modes. This method has been compared to the AI ML model of Piso.AI, which is based on determining the principal factors controlling the isotopic composition of precipitation and on the prediction function, which is based on non-linear relationships between isotopes and main determinants. This model also does not account for the outliers derived mainly in the winter months.

→ Regarding the sub-daily isotopic dataset, the main advantage is that for each precipitation event, we can attribute an atmospheric circulation type, which would not be possible working with monthly data. Similar datasets are found in other studies that want to assess the effects of atmospheric circulation on precipitation isotope signals in other regions (e..g., Juhlke et al., 2014; Krklec et al, 2018). The effects of atmospheric circulation on precipitation isotope signals are in turn relevant to consider when reconstructing precipitation $\delta^{18}O$, especially over long timespans, e.g., when comparing them with natural archives, such as ice-core, tree, lake sediment, and other types of isotope data used in climate reconstructions.

That the linear method is not the best approach to examine the non-linear relationships in isotopic signatures is a fair remark, but we want to stress that sinusoidal modes found in the isotopic signals are also found in the input variables, i.e., the temperature. Our modelling approach has also shown that the multiple linear regression models capture the seasonal component of the precipitation isotopic signal well (Fig. 5 in the old version of the manuscript). We also want to stress that the aim of our paper was to explore how simple empiric relations could be used in predicting precipitation $\delta^{18}O$ with few, or generally available variables – also considering the fact that meteorological and isotope data become increasingly scarce when going back in time. We are aware that Piso.AI yields better results by incorporating non-linear relationships between isotopes and main determinants, and partially, the challenges encountered in this study showcase the validity and applicability of AI-based solutions for predicting precipitation $\delta^{18}O$.

Outliers should be given more attention, you are right. We will add a figure in the supplements where we show the data on the dual isotope plot, outliers should obtain more visibility with this representation, as they will often plot below the Global Mean Meteorologic Water Line (GMWL).

The scientific quality should be improved, particularly by considering related works and including appropriate references. For example, the temperature effect is not a stationary effect even in continental stations. This can be a reason for the poor prediction of isotope values in winter precipitation. Here, more climate and possibly orographic parameters should be included in the regression. Non-stationarity of isotope values in winter precipitation can be due to a shift towards the precipitation amount effect, and this should be checked and discussed in relation to similar studies. Another point is whether the temperature effect, as the correlation between isotope and air temperature, is a constant function over time. Maybe this effect can be stronger or weaker depending on larger-scale oscillations such as the Multidecadal Atlantic Oscillation or the shorter-term North Atlantic Oscillation. Additionally, explanations should be added on how to relate isotope values in sub-daily precipitation to daily or monthly climate parameters. The paper is missing a strong discussion based on papers that used a similar approach. More references should be added. Even the references on the physical nature of oxygen and hydrogen (as explained in the Introduction) should be revised, and more classical isotope-related studies should be included.

→ Thank you for the suggestions. We have added two paragraphs in the introduction discussing the processes affecting the atmospheric water vapor from which the precipitation is formed.

"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 $\delta^2H - 8 \times \delta^{18}O$. 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)."
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. In the new manuscript:

"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."
We checked for the amount effect and found that it did not influence our data significantly. The amount effect is usually reported to more important in (sub-) tropical regions, which is why we did not explore it explicitly.

"We did not find a significant precipitation-amount effect, except weak negative correlations in autumn (ρ = -0.29, $p < 0.001$), and with Atlantic (ρ = -0.22, $p < 0.001$) and South Atlantic (ρ = -0.20, $p = 0.034$) trajectories."
The correlation between the isotopic signature and air temperature is not a constant function over time. We explore this in Fig. 5, and Table 2 and 3 in the new manuscript (Fig. 4 and Table 3 in the old version).
The Multidecadal Atlantic Oscillation (AO) and the shorter-term North Atlantic Oscillation (NAO) are interesting leads. We did find a certain correlation between the GNIP $\delta^{18}O$ data in Trier and the NAO index, but given the new structure of the manuscript, it does not fit the scope of the paper.

The introduction doesn't reflect the title of the paper, results, and discussion. A significant part of the introduction is focused on isotopes in streams, but this is not well documented in the results and discussion. The introduction should cover the state of the art related to isotopes and atmospheric circulation, reconstruction of the climate and isotope values, and more clarification on daily circulations should be added. The figures should be improved, for example, by reducing the abbreviations in the legends.

→ *Again, thank you for bringing this to our attention. We have fully revisited the structure of the manuscript and added more state-of-the-art studies related to isotopes and atmospheric circulation, and reconstructions of the climate and isotope values in the introduction.*

"For large scale and long-term studies, isotopic signals in precipitation are typically retrieved from platforms such as the Global Network of Isotopes in Precipitation (GNIP), the Online Isotopes in Precipitation Calculator (OIPC) (Bowen and Revenaugh, 2003; Bowen et al., 2005), or similar isoscapes modelling the spatial distribution of isotopic signals (Terzer et al., 2013; Allen et al., 2019). The GNIP network was established in 1960 and holds monthly $\delta^{18}O$ and $\delta^{2}H$ data to the present day, yet complete records from the start exist only for a few locations. While approaches based on these datasets led to great advances in watershed hydrology (Klaus and McDonnell, 2013), recent progress in paleohydrology opened new avenues to venture beyond rather short (in terms of climate change) historic observation intervals. To overcome the limitation of rather short and truncated time series, pre-instrumental $\delta^{18}O$ data can be obtained from environmental archives, such as sediments, ice-cores (Konecky et al., 2020), tree-rings (Álvarez et al., 2024; Rodriguez-Caton et al., 2024) or mollusc shells (Pfister et al., 2018; Schöne et al., 2020). Thus, isotope-enabled global circulation models or, more recently, AI models (Nelson et al., 2021; Erdélyi, 2023), are promising tools that are complementary to proxy-based approaches (Sturm et al., 2010). A direct comparison of open-access, ready-to-use $\delta^{18}O$ products from different modelling approaches is also available in Nelson et al. (2021) - amongst which Piso.AI (Nelson et al., 2019), the sine wave fitting approach (Allen et al., 2019), IsoGSM (Yoshimura et al., 2008), OPIC (Bowen and Revenaugh, 2003; Bowen et al., 2005), and the Regionalized Cluster-based Water Isotope Prediction model (RCWIP) (Terzer et al., 2013). This product portfolio highlights the potential of modern AI-enabled technologies, with an unprecedented $\delta^{18}O$ RMSE of solely 1.68 ‰ (Piso.AI), and even 1.345 ‰ (RFSP, Erdélyi, 2023) for Europe, fitted and calibrated on GNIP data.
However, the prediction accuracy of many of these models significantly decreases for earlier decades as meteorological and location data become increasingly sparse and fragmented. Reanalysis datasets, such as ERA5 serve for reconstructing precipitation $\delta^{18}O$ chronologies with high accuracy over large geographical extents until the 1950s. For reconstructions prior to that date, modelling tools with very limited data requirements are needed. Systematic instrumental air temperature measurements having been conducted in many parts of the worlds since the middle of the 19th century, the relation between $\delta^{18}O$ and surface temperature, or the so-called temperature effect (Dansgaard, 1967), appears as a tool of choice in this respect. Still, a simple empiric approach also requires caution, as Sturm et al. (2010) point out non-stationarities in the relation between $\delta^{18}O$ and meteorologic variables, inherent to changing atmospheric circulation patterns (Noone and Simmonds, 2002; Lee et al., 2008). The temporal $\delta^{18}O$ -T gradient may have been substantially lower for the LGM – Pre-Industrial (LGM-PI) era than under the present climate for most mid to high-latitude regions (Werner et al., 2016), and changing $\delta^{18}O$ and temperature relations have existed in past climates (Jouzel, 1999; Buizert et al., 2014). Colder climates (e.g., Last Glacial Maximum, LGM) are typically associated with lower $\delta^{18}O$ values in precipitation (Lee et al., 2008; Risi et al., 2010; Werner et al., 2016)."
We will also remove all abbreviations from the legends.