This review was prepared as part of graduate program course work at Wageningen University, and has been produced under supervision of Ryan Teuling. The review has been posted because of its good quality, and likely usefulness to the authors and editor. This review was not solicited by the journal.

Peer review "New water fractions and their relationships to climate and catchment properties across Alpine rivers" by Floriancic et al., 2023.

The paper by Floriancic et al. (2023) aims to quantify the new and young water fractions in Alpine rivers and to link them to hydroclimatic drivers and physical catchment properties. Stable water isotope time series in precipitation and streamflow are used to determine the relative proportions of young (younger than 2-3 months) and new (younger than one month) water. Young water fractions (F_{young}) are determined based on seasonal precipitation isotope cycles, as summer precipitation is isotopically heavier than winter precipitation. New water fractions (F_{new}) have been determined based on hydrograph separation.

Overall, the paper is written well and the conclusion provides a clear overview of the research by answering the research questions as stated in the introduction. Besides, the introduction clearly explains the importance of knowing young and new water fractions in Alpine rivers. However, the novelty of the paper, other than using a range of catchment sizes, remains unclear to me, considering that there are multiple papers on the same topic (Knapp et al., 2019; Kirchner, 2019; Ceperly et al. 2020) some of which with partly overlapping study areas (von Freyberg et al., 2018; Gentile et al., 2023). Therefore, I would like to encourage the authors to expand the introduction by highlighting the novelty and scientific contribution of their research. The research fits the scope of the journal and is in my opinion suitable for publication after addressing the issues mentioned below.

Major comments

Covariances influencing correlations

In section 2.6 it is explained how the authors will draw conclusions based on statistical measures such as Spearman rank correlations and Wilcoxon Signed-Rank tests. One of the findings is a positive relationship between Potential Evapotranspiration (PET) and F_{new}, which is described as counterintuitive in the discussion section (Line 505) as one would expect the fraction of new water to decrease with increasing evapotranspiration. However, the authors do not go into this any further nor do they refer to other researches with similar or contradicting results. In section 4.2 Figure 9 shows the Spearman rank correlations between the selected hydroclimatic variables and physical catchment characteristics across the study area. In this figure a positive relationship can be seen between the fraction forest and PET. The authors found a (weak) positive correlation between F_{new} and forest cover, which was also found by Freyberg et al. (2018). In the paper the authors suggest that forest might have a role in shaping flow paths and therefore influence water ages. This makes me wonder whether PET is actually influencing the amount of F_{new} in the streamflow or whether it is the other way around; due to more forest F_{new} is higher, but the forest will also lead to an increase in PET.

This leads to issue (1): the authors seem to overlook the fact that many things co-vary, other than stating, based on Figure 9, that it remains unclear which of the variables is a first-order control on new water fractions. Section 2.6 does not give a proposed mechanism to find out which variables have the largest impact on new water fractions. Without researching covariances, the question remains how useful this type of conclusions is, and to what extent it fulfills the aim of the paper to understand the origins of streamflow and to determine the influence of hydroclimatic variables and physical catchment properties. This issue could be addressed by extending the discussion section by reflecting more on the implications of the results. As an alternative, the authors could extend the methodology by proposing a mechanism to investigate the control of variables on new water fractions ruling out covariances between the variables. Besides, correlations are more convincing when a plausible mechanistic explanation can be identified. Identifying the first-order control on new water fractions leads to more robust conclusions when mechanistic explanations can be provided as evidence for the found correlations.

Robustness of results

New water fractions are calculated using ensemble hydrograph separation, clearly explaining how this method is insensitive to unknown or unmeasured endmembers. Next, the authors explain the use of volume weighted new water fractions, which reduces the effect of catchment wetness. This is in agreement with von Freyberg et al. (2018), who use the same approach. Also, the dataset that is used is split up based on the monthly precipitation values to assess the differences in F_{new} for the wettest and driest half of the year. This type of analysis will provide insight into the effect of climate and antecedent conditions on the fraction of new water. The issue (2) that rises is that, surprisingly, the authors did not take into account the effects of hydrograph shape, which is determined by catchment characteristics such as shape and slope, on the calculation of new water fractions. This might indirectly influence the reliable of the results through the calculations of F_{new} across catchments and the therewith calculated correlations. Therefore, the robustness of the results drawn based on hydrograph separation is questionable.

Expanding the analysis by reducing the effect of hydrograph shape would improve the robustness of the results. Otherwise, the studied catchments could be selected such that they consist of similar catchment characteristics, but one characteristic. The influence of that certain characteristic on new water fractions can be researched, also addressing the issue of covariances. This however, would limit the research, as it aims to study the water fractions to hydroclimatic variables and catchment properties across small to very large basins. Besides, the correlations that are found might still not be causal, as variables could be overlooked.

Spatial and temporal resolution of precipitation isotope data

In section 2 the data collection is described. Precipitation isotope measurements of most catchments are available only at single sampling locations and the authors chose not to interpolate individual station measurements. Instead, issue (3), the precipitation isotope data is based on monthly gridded precipitation isotope reanalysis database by Piso.AI, averaged within the boundaries of the study catchments. The authors lack to mention the spatial resolution of the gridded precipitation isotope data, which undermines the decision to use the reanalysis database. Besides, the correctness of the precipitation isotope reanalysis should be evaluated, before a substantiated decision can be made to use the Piso.AI database.

Next, the use of monthly data, which is equal to the time scale over which water is new, might be too coarse to be able to say something about the fluctuations in F_{new} following precipitation events. Knapp et al. (2019), who used 7 hourly and weekly timescales, observed stronger increases in F_{new} as a result of precipitation, which leads to the question whether using monthly precipitation isotope data gives reliable F_{new} values. The paper needs more in depth discussion on the consequences of using monthly precipitation isotope data on the outcome on the research, clarifying the choice to use this temporal resolution.

Minor comments

The fourth research question (Line 115 & 116) "*How do new water fractions propagate downstream from headwater catchments to the large basins of the Danube and Rhine catchments?"* This research question is not introduced in the introduction nor is it mentioned in the abstract. Subchapter "*Downstream propagation of F_{new} in Danube and Rhine"* is not related to any other research chapters in the paper. Therefore, the question is secluded from the rest of the research. Please add the results from this chapter to the abstract and make sure to introduce the research question and mention its use in this paper. Otherwise, it might be better to remove the question and its results from the manuscript.

The title of the paper falls short on its content as it only new water fractions are mentioned. The calculation of young water fractions cannot be inferred from the title, even though it is part of the research. Consider changing the title to *"Quantifying young and new water fractions and their relationship to climate and catchment properties across Alpine rivers".*

The conclusion ends with the statement that the analysis highlights the importance of further research on the effect of snow processes on partitioning of new (or young) and old waters. However, the authors do not elaborate on how this would improve the research and what they would expect to find. I would like to encourage the authors to go into depth on this a bit more, especially since Gentile et al. (2023) discusses the impact of snow on the seasonal cycle of young water fractions and Ceperley et al. (2020) provides insight into the effect of snow cover on young water fractions. How would the further research that is needed according to the paper complement this research?

Technical comments

Line 50: Reference IAEA, 2019a missing in reference list.

Line 51: Reference IAEA, 2019b missing in reference list.

Line 61: Reference Kirchner et al., 2023 missing in reference list.

Reference list not in correct alphabetical order.

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