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.

Review on New water fractions and their relationships to climate and catchment properties across Alpine rivers by Marius G. Floriancic, Michael P. Stockinger, James W. Kirchner, Christine Stumpp

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Overview:

The research in the paper is on the partitioning of new (younger than 1 month old) and young (2-3 months old) water in Alpine rivers in relation to hydroclimatic variables and physical catchment properties. The authors mention that the main importance of the research is to get a better understanding of the partitioning of old and new water so that it can lead to more sustainable water management. The research has been conducted over 32 Alpine catchments. The fraction of new water was determined using ensemble hydrograph separation and the fraction of young water using seasonal isotope cycles. After these fractions have been determined, the authors investigate whether there are explaining hydroclimatic variables or physical catchment properties that show a high correlation with the fraction of new and young water. The obtained results reveal which Alpine catchments transmit recent precipitation more rapidly to runoff. The paper concludes with a conceptualization of the relationship between young and new water fractions with hydroclimatic variables and physical catchment properties.

Recommendation to the Editor:

In the past, studies have mainly focussed on linking new water fraction to hydroclimatic variables and physical catchment properties for small headwater catchments (Gentile et al., 2023; von Freyberg et al., 2018; Ceperley et al., 2020). The main novelty of this research is that the authors have systematically linked new water fractions to hydroclimatic variables and physical catchment properties for both smaller headwater and larger downstream catchments. Furthermore, most previous studies on the partitioning of streamwater have only focussed on the fraction of young water. Together with few earlier studies (Knapp et al., 2019; Kirchner, 2019), this study is pioneering how new and young water fractions together can help improve the understanding of the partitioning of new and old water. These are not major novelties, but still relevant to have an impact on the field of catchment hydrology.

The paper is well written and statistics have been integrated well. The research is being portrayed in a broader perspective as they compare their findings to earlier research. The study addresses some important problems in the analysis of (isotope) data. For example, impact of snow, impact of elevation on precipitation isotopes and spatial resolution of the lithology map. However, there is limited discussion what has been done to validate whether these problems (and other assumptions made) create a significant bias in the results. Finally, there are certain parts that need clarification, especially on methodological and conclusions sections.

To conclude, I think this article could have an impact in the field of catchment hydrology, but it is not major. The paper fits well in the context of the journal. I believe it can be published with minor revisions.

Major comments:

Major issue 1: In the introduction the authors stated the following: "Although most multi-catchment time series have been sampled at low temporal frequency, they can nonetheless be used to assess the mixture of streamflow sources on time scales similar to their sampling intervals." This assumption justifies whether a lower temporal resolution of 1 month can be used for the purpose of this research. I believe this to be a bold statement. The authors back their statement with a paper by Hrachowitz et al. (2009). This paper, however, looked at data with weekly and fortnightly time series instead of a monthly time series. This is a significant difference. Moreover, they did not look into $\delta^{18}O$ and $\delta^{2}H$ isotopes but into Cl^- concentrations as a tracer.

Some processes that determine the partitioning of young and old water in river discharge have an effect at significantly smaller time scales than at a monthly time scale. For example, earlier research suggested that there is significant correlation with distinct storms/precipitation events, meaning that these processes have an effect on a shorter time scale than one month (Knapp et al., 2019). Findings by Knapp et al. (2019) show strong increases in 7-hourly and weekly new water fraction above a precipitation threshold of roughly 5 mm day^{-1}. This entails that water partitioning might behave very differently for two different scenarios with the same rainfall intensity averaged over a month. For example, one single heavy rainstorm in a month or multiple light drizzles might lead to a different partitioning of new and old water. Moreover, the streamflow isotopes were measured at one moment in time in the month. This means that the authors assume that precipitation intensity at the beginning of the month contributes the same to monthly streamflow isotopes as more recent precipitation intensity days prior to the isotope streamflow measurement.

Thus, if processes with a time scale shorter than 1 month have a significant influence on new water fractions in streamflow (which research suggests), there can be a significant bias in the correlations computed for processes similar to or larger than the sampling interval. I believe that this should be made more explicit when making this statement. I would like the authors to go more into depth about the uncertainties, regarding the temporal scale, and the effect it might have on the results.

Major issue 2: Secondly, the authors mention that precipitation isotope data should not be interpolated between individual station measurements to determine precipitation isotopes for the different catchments. This is due to the fact that isotope fractions change with altitude and other factors. This is why they make use of the monthly gridded isotope model framework Piso.AI which makes use of machine learning (Nelson et al., 2021). Furthermore, they averaged the values of these grids within the boundaries of each of the catchments.

Even though this method is probably an improvement over interpolating between measurement stations, I believe it is likely still not accurate enough to precisely estimate precipitation isotopes for the purpose of this research. The resolution of 0.5° is quite course and precipitation isotopes can differ considerably spatially in mountainous areas. Jouzel et al. (2000) argue that higher spatial resolution of models helps significantly to increase the agreement of simulated precipitation isotope patterns with observations. Also, this study looks into some small catchments. Averaging precipitation isotopes on a spatial resolution that is bigger than the catchment size does not seem to give a realistic estimate to me. Moreover, the model framework has only been validated generically and not with a special focus on mountainous areas (Nelson et al., 2021).

I would recommend validating the Piso.AI data with the available data. As the precipitation isotope data gets averaged over the catchment area, I would suggest investigating the distribution of the measuring location used in Piso.AI. If these locations happen to be located near the mean elevation of the larger grid, there is a good reason to believe the precipitation isotope data is representative for the average precipitation isotope fraction over the area. If the authors cannot validate the data, I would like the authors to stress the effect the uncertainty in precipitation isotopes has on the results. If one uses precipitation isotope data with a significant error, fractions of new and young water in streamflow are calculated with a bias. This will show in the eventual correlations between new and young water fraction and hydroclimatic variables and catchment properties.

Major issue 3: Furthermore, I think some of the claims made in the conclusion are not supported well enough with evidence. For instance, I do not believe that the correlation between the fraction of young water can be described by the amount of forested area in the catchment. I believe that this is probably an example of cross-correlation. Forest might just happen to thrive better at certain areas that favour quick run-off (e.g., certain slope, elevation). At higher altitudes there is limited to no forest cover in the Alps. As the new water fraction is lower at higher altitudes (probably due to other factors), it is likely to find a positive relationship with forest cover. *Figure 9* supports my suspicion as there seems to be a significant correlation with elevation. The authors do shortly touch upon this in the discussion, but seem to discard this in the conclusion. Moreover, the authors mention that Hrachowitz et al. (2021) found the opposite relationship for a forest removal experiment. The authors give no explanation why these two different studies could contradict each other. If there seems to be contradicting results between studies, I suggest being more hesitant to draw conclusions. I would recommend removing this claim from the conclusions.

Minor comments:

Minor issue 1: I believe the title of the paper can be polished a bit. The title at the moment is: "New water fractions and their relationships to climate and catchment properties across Alpine rivers." The title could also be interpreted in a different way. One could also think this paper is about changing discharge patterns due to changing climate and catchment properties. I can understand why the authors chose the word 'new', as it is one of the first studies to look into the water fraction younger than one month old, as previous research looked into young water that was younger than 2-3 months. Also, previous studies (Knapp et al., 2019) used a similar title. My suggestion would be to change the title to "New and young water fractions…", as the paper looks into both new and young water fractions.

Minor issue 2: The authors mention the knowledge gap, but it would be clearer if they would also explicitly mention what the aim of the research is. The aim could be along the following lines: *To get a better understanding of how much streamflow is derived from old water stored in the subsurface, versus more recent precipitation that reaches the stream via near-surface quick flow processes and also how this partitioning varies across different Alpine catchments in response to hydroclimatic forcing and catchment characteristics.*

Minor issue 3: Ensemble hydrograph separation has been used to calculate new water fractions in streamflow. However, the authors do not discuss potential biases in the result that this method might produce. I would suggest the authors to discuss in the methods section.

Minor issue 4: The authors try to correlate catchment slope to the fraction of new water in streamflow, as earlier research by Jasechko et al. (2016) suggested that there seems to be a strong negative correlation. The authors did not seem to find such a strong correlation between slope and new water fractions in streamflow in this research. I believe this is why they decided to look at slopes below 10° and above 40°. The reasoning why the authors picked these specific slopes is not mentioned. I understand that the authors look at areas with milder and very steep slopes, but the number seems a bit arbitrary to me. Maybe the authors can explain how they got to these specific slopes.

Minor issue 5: The conclusions made in the conclusion do not match the conclusions made in the abstract. In the abstract they mention the differences in new water fractions between rainfall-dominated and snowfall dominated catchments. However, there is no mention of this in the conclusion. Also, the authors mention in the conclusion that that new water fractions decrease from headwater streams to large downstream basins of the Danube and Rhine, but this is not explicitly mentioned in the abstract. There are more examples of these which I will not mention. I would strongly suggest to align the conclusion stated in the abstract and conclusion.

Minor issue 6: The authors switch between 'new water fraction' and 'F_{new}' through the course of the paper. I would settle on using one of the two. This also applies to the fraction of young water.

Minor issue 7: Most figures do not have a title/heading. I would suggest putting up headings for most figures (and sub-figures) as it makes it easier to interpretate the figures.

Specific comments:

P1-2, lines 29-32: this sentence is very long. It might be easier to comprehend when it is split up in two different sentences.

P3, lines 73-74: "… found although…'' this part of the sentence does not read well. Either put a comma after "found" or change the order of the sentence by rewriting it to: "In global-scale syntheses, Jasechko *et al.* (2016, 2017) found that 25% of global streamflow is younger than 1.5 - 3 months, despite most groundwaters are dominated by fossil waters" I would suggest the latter option.

P4, lines 109-118: I think the list of research questions could be better formatted. I do not see the need for the blank line in between the research questions.

P5, figure 1: please make a larger northern arrow. It would look better if the northern arrow scale bar and legend are properly aligned. Also, the city names are difficult to read. Please enlarge these.

P16, figure 5: the graph is messy which makes it difficult to read. The graph might become easier to read if the y-axis is set to a logarithmic scale.

P18, figure 6a: please add a legend to this map. I believe the legend might be the same as in figure 6b, but that is not clear. One could also combine the two figures in such a way that this is clearer. Also, the city names are difficult to read. Please enlarge these.

P18, figure 6b: please align the scale bar and northern arrow.

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