Reviewer #2

The manuscript entitled "Do streamwater solute cocentrations reflect when connectivity occurs in a small pre-alpine headwater catchment?" by Leonie Kiewiet, Ilja van Meerveld, Manfred Stähli and Jan Seibert, presents an important contribution to the understanding of the hydrological connectivity (or non-connectivity) processes that occur in a pre-alpine catchment, monitored at event scale. The authors presented an exploratory analysis of the hydro-chemical composition of potential water sources and streamflow. They applied widely used, though not so novel, methodologies (simple hydrograph separation and EMMA), but complemented the analysis with hydrological connectivity simulations that make this study interesting. The work is well written, clearly structured and personally enjoyed reading it. Despite the short monitoring period, I find it with potential for publication in HESS after addressing a few suggestions.

We are happy to hear that you enjoyed reading our manuscript.

The concept of baseflow depends on the method used to estimate it and does not always describe active groundwater flow pathways. I suggest the authors describe what they defined in this study as baseflow

We agree that a definition of baseflow can be useful and will include a definition in the introduction. The definition will be along the following lines: “We define baseflow as the streamflow between storms and runoff events and assume that it comes from groundwater”.

The third objective could be modified, it is well known that baseflow and rain mixture (negligible contribution of soil water) does not explain the changes in solutes concentrations in the streamflow.

We agree that the third objective should be modified and we will remove the redundant part of the question. We propose to change the third research questions as follows:

““In how far does conservative mixing of baseflow and rainfall explain the changes in stream solute concentrations and do discrepancies from this mixing indicate when other sources become connected to the stream?”

One of the principles of EMMA is that it relies on conservative tracers (not involved in adsorption or biological processes) and linear mixing process (Hooper, 2001). Did you analyse the conservative behaviour of the tracers? Please include the tests and state what tracers were used. Also, a graph showing the spatial-temporal concentrations of tracers in water sources would help the reader to contextualize their interaction during events.

Following the methodology of Barthold et al. (2011), we considered a tracer conservative when the concentrations are linearly correlated to at least one other tracer. We performed a linear regression on all streamwater, soil water and groundwater samples used in this study (n=549), and tested the correlations of Ca, Mg, Ba, Na, Fe, Mn, Cu, Zn, K, Cl, D_{ex}, δ^2H and $\delta^{18}O$. We set the threshold for a linear trend to $R^2 \geq 0.5$ and a p-value < 0.01 (i.e. the threshold of Barthold et al. (2011)). We found that EC, Ca, Mg, Ba, δ^2H and $\delta^{18}O$ are conservative, and that the other tracers were not. We would like to point out that we list most of these tracers as non-conservative solutes in the introduction (L57-58). If we use only the streamwater samples all tracers exhibit conservative behavior, except Mn and D_{ex}.

We understand the concern of the reviewer with regard to solving a non-linear mixing problem with a linear mixing solution. To avoid this issue we will reduce the tracer set used in the EMMA to EC, Ca, Ba, Mg, δ^2H and $\delta^{18}O$. We included an updated version of the figure and table that summarize the EMMA results using this tracer set (Figure 7 and Table 4 in the original manuscript). The largest changes in the event-average fractions were for Event III, for which the estimated soil water contribution reduced from 0.38 to 0.01, and event II, for which the fraction of groundwater increased from 0.21 to 0.46 and the fraction of rainfall decreased from 0.45 to 0.29. The results for event I and IV changed only slightly.

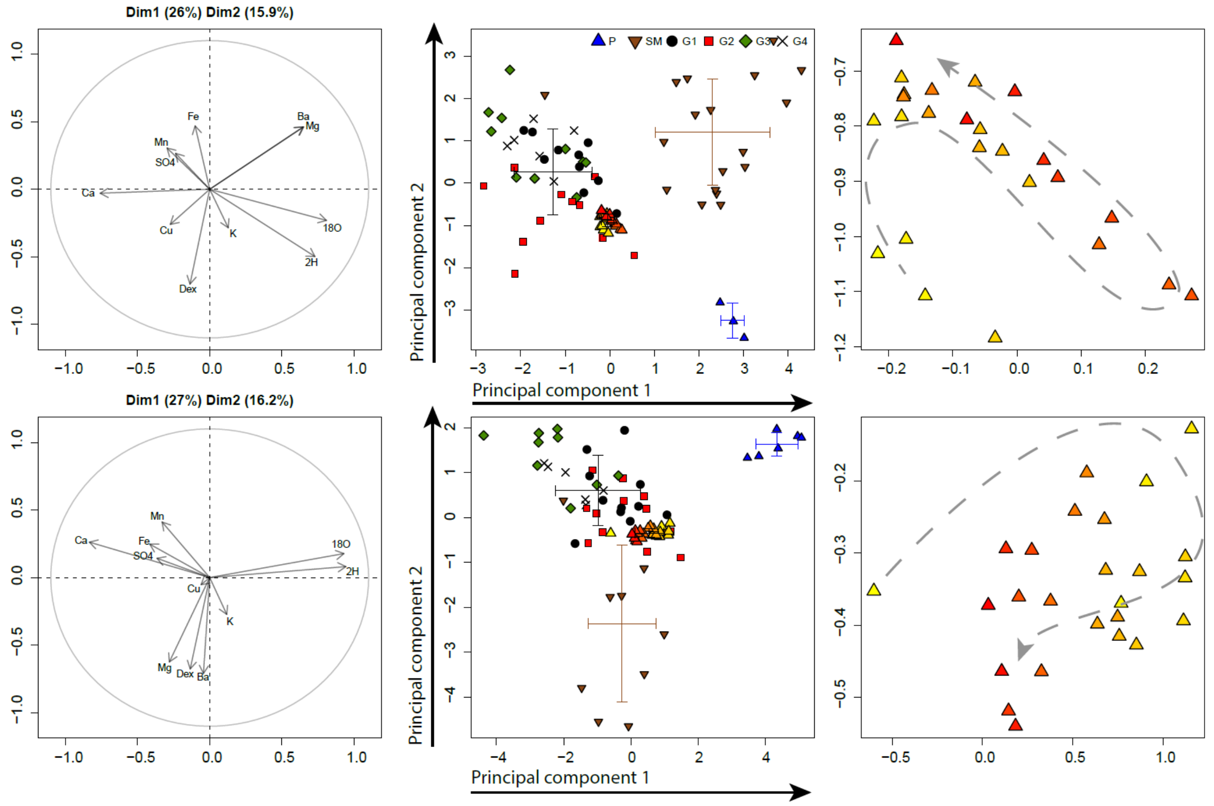

Figure S2: PCA results and mixing diagrams for event I (top row) and event III (bottom row). Event I is representative of a small event, whereas event III is representative of an intermediately sized event. In the biplots (first column), the length of the arrow represents the explanatory power. The mixing diagrams based on the first two principle components (middle column) shows the individual rainfall (blue triangles), soil water (brown reversed triangles), and groundwater samples (black circles, red squares, green diamonds and black crosses, representing groundwater types 1-4 based on Kiewiet et al., 2019). The streamflow samples are shown with yellow (start of the event) to red (end of the event) triangles, and the average and standard deviation for each component is indicated with error bars. The third column shows a zoom in of the streamflow samples and highlights the evolution of the streamwater composition during the event (yellow = start, red = end), and the general direction of change indicated with a grey arrow and dashed lines.

Table S2. Event-average fractions of groundwater (f_{GW}), soil water (f_{SW}), and rain water (f_P) based on the three-component End-Member Mixing Analyses, and the associated uncertainties.

Event	Three-component End-Member Mixing Analyses			
	f_{GW}	f_{SW}	f_P	uncertainty
I	0.81	~0	0.19	0.92
II	0.46	0.24	0.29	0.50
III	0.72	0.01	0.27	1.34
IV	0.73	0.02	0.25	0.91

Additionally, we will follow the suggestion of the reviewer to include a figure showing the spatial-temporal variability of tracer concentrations in each water source. We are testing different figure types but most likely it will be a figure that has a panel for each tracer and shows one boxplot per source in each panel (Figure S1). We prefer to add this figure to the supplementary information but of course will mention it in the text.

Regarding EMMA's analysis, I suggest examining the evolution of events in the PCA space (Inamdar et al. (2013); Barthold et al. (2017); Correa et al. (2018)). Their dynamics and hysteresis can show the proximity of the streamflow to a certain source in the different stages of the event. Although as "soft data" it can bring insights into what groundwater or soil water contributes at a certain time.

We appreciate the suggestion of examining the evolution of events in the PCA space. We performed a similar analysis in an earlier stage of the data analysis but did not include the results in the final work. However, we re-examined the data and will add one figure per event to the supplementary materials. We plan include to a figure that shows the evolution of events in the PCA space by adding a panel to the figure showing the EMMA results (Figure 7 in the initial manuscript). We show this for event I and III in Figure S2, and for event II and IV in Figure S3.

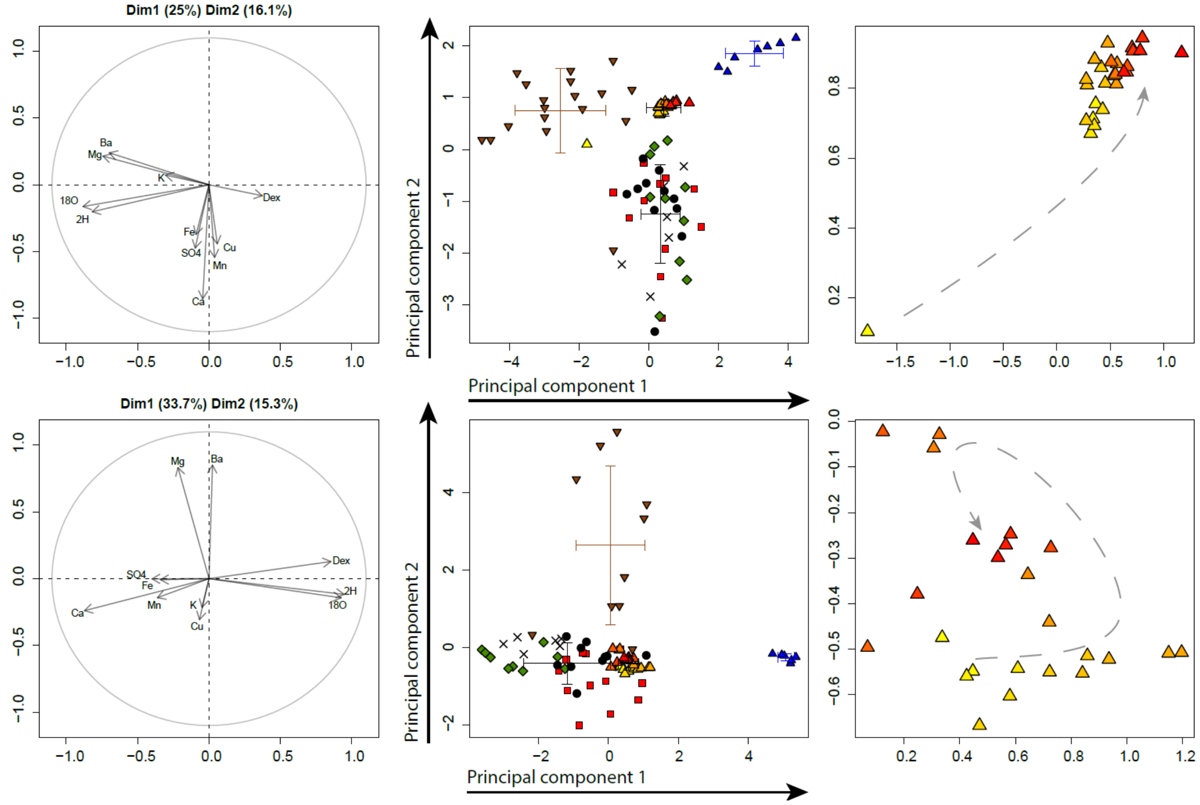

Figure S3: PCA results and mixing diagrams for event II (top row) and event IV (bottom row). Event I is representative of a small event, whereas event III is representative of an intermediately sized event. In the biplots (first column), the length of the arrow represents the explanatory power. The mixing diagrams based on the first two principle components (middle column) shows the individual rainfall (blue triangles), soil water (brown reversed triangles), and groundwater samples (black circles, red squares, green diamonds and black crosses, representing groundwater types 1-4 based on Kiewiet et al., 2019). The streamflow samples are shown with yellow (start of the event) to red (end of the event) triangles, and the average and standard deviation for each component is indicated with error bars. The third column shows a zoom in of the streamflow samples and highlights the evolution of the streamwater composition during the event (yellow = start, red = end), and the general direction of change indicated with a grey arrow and dashed lines.

I am concerned about the very high uncertainties (Table 4), 160% in event III and 143% in event IV. Could it be due to the limited streamflow data, input-data uncertainty or time-dependent endmember variability (Chaves et al., 2008; Christophersen and Hooper, 1992). Unluckily end-member solutions do not exhibit low variability compared to the stream chemistry and not exhibit distinctive concentrations between end-members. I encourage the authors to analyse this limitation in more detail.

We agree that the uncertainties are extremely high and attribute this mostly to the high spatial variability in the tracer concentrations (i.e., input-data uncertainty). To be more explicit about this limitation, we will mention and quantify the other potential sources of uncertainty as well.

As an alternative the authors could refer to: Phillips, D. L. and Gregg, J. W.: Uncertainty in source partitioning using stable isotopes, Oecologia, 127(2), 171–179, doi:10.1007/s004420000578, 2001, to compute individual uncertainties in the calculation of source contributions to streamflow, this methodology considers the number of samples. The author could identify whether the uncertainties remain very high.

We appreciate the suggestion to investigate which of the water sources induces the largest uncertainty. The uncertainty analysis by Phillips et al. (2001) is very similar to the method that we used (Genereux, 1998). Both Genereux (1998) and Phillips et al. (2001) show that the uncertainty depends on the variability within each water source and in the mixture, and the differences in the composition of the water sources and the mixture. We will double check that these different methods give a similar uncertainty using the IsoSource mixing model (Phillips et al., 2005).

We agree that it is important that the reader is comfortable with the high uncertainties that we present, and thus that we need to elaborate the discussion of the high uncertainties. We plan to add such a description to discussion section 5.2 ("Which areas contribute to stormflow?").

The uncertainties that we present might be higher than for most other published mixing analyses because we use more groundwater and soil water samples than is typical. We have written a manuscript that exclusively deals with these high uncertainties. This manuscript is currently under review for WRR (soon to be resubmitted after minor revisions). If the WRR manuscript is accepted before the final publication of this paper, we will include a reference in the discussion, in addition to the revised discussion described above.

The introduction, methods and results sections are complete and clear to follow, despite some very long sentences that make a little difficult to follow the ideas.

We will carefully read through the text and split long sentences.

However, I find the manuscript poorly discussed. The authors support their findings in an extremely local context. The study would benefit from a broader perspective, comparing it with other similar ecosystems and/or with studies of the dynamics of water source contribution streamflow during events for example.

Upon re-reading the manuscript, we also recognize the weaknesses highlighted by the reviewer and the lack of a broader discussion and clear take-home messages. To overcome this, we plan to rewrite the discussion so that it also includes:

- A comparison of the results to literature from other study sites, as we did in the introduction. We think that, for instance, linkages to the studies of Ladouche et al. (2001) and Soulsby et al. (2007) would be useful here.

- A section that shows the broader impact of the study. We think that such a section should include how our results fit with current concepts of hydrologic connectivity (e.g., Blume and van Meerveld, 2015). It should also address the assumptions made with calculations of connectivity as mentioned above (e.g., Jackson et al., 2014).

In addition, we will rewrite parts of the existing discussion and emphasize the take-home message. We can achieve this with a section on the broader impact of our study as the final paragraph, and finish with a take-home statement. This could be something along the following lines: "The combination of hydrometric and hydrochemical data can be useful to identify hydrological connectivity and aid the interpretation catchment-scale runoff generation. However, we have to take the variability of the tracer concentrations in different water sources into account, as they can be large compared to the change in streamwater concentrations. The observed gradual deviations in the concentrations that are expected based on mixing of baseflow and precipitation are likely the result of increases in the contributions from many (small) landscape elements in the catchment and thus reflect the gradual increase in connectivity during events."

I assume the figures will be uploaded in a high-quality prior publication. In S1 please include rain and streamflow samples to visualize their distribution (potential streamflow at different colour scale for low, medium and high flows) and check the paper for a few typos.

Indeed, the quality of the figures deteriorated significantly when the file was converted into a .pdf. All figures, except figure 2, are vector images. Therefore, it should not be an issue to provide figures at the required DPI standards.

Including the rain and streamflow samples in S1 will make the figure too busy. However, we can add a second panel that shows the streamflow and the rainfall samples using the same axes as for the groundwater and soil water panel (Figure S3). By doing so, the figure will still be readable, and the rainfall and streamflow data are included.

We will certainly proof-read the manuscript carefully after making all the edits.

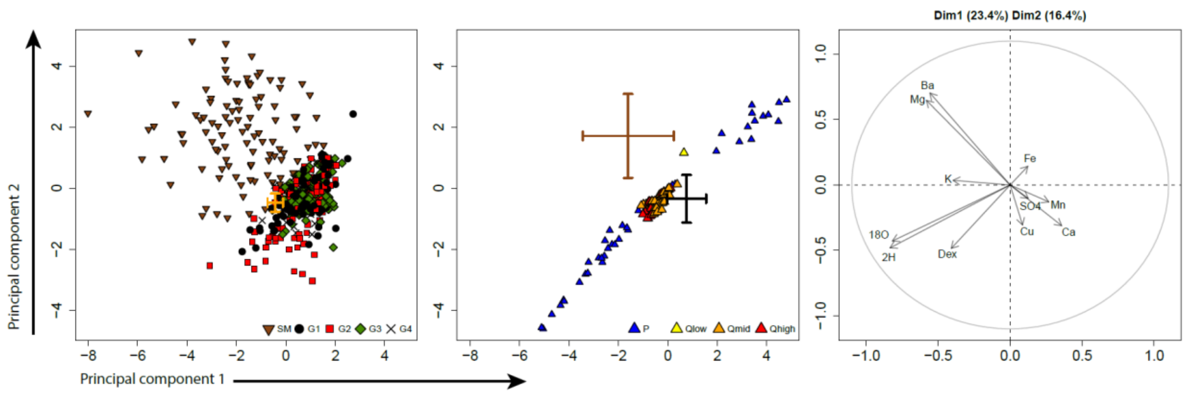

Figure S4: PCA results for all groundwater (n=335) and soil water samples (n=116) taken during the nine baseflow snapshot campaigns (Kiewiet et al., 2019), and all streamwater (n=100) and rainfall (n=47) samples taken during the four events used in this study. The mixing diagrams (left and middle panel) show the individual soil water samples (left-hand panel, brown reversed triangles) and groundwater samples (left-hand panel, black circles, red squares, green diamonds and black crosses, representing groundwater types 1-4 based on Kiewiet et al., 2019) for the first two principal components. The middle panel shows the rainfall samples (blue triangles) and streamwater samples taken during low flow (Q low, one baseflow sample) in yellow, during high flow (Q high) in red and during all other flow conditions in orange (Q mid). The error bars in both mixing diagrams indicate the average and standard deviation for each component (orange, brown and black error bars for streamwater, soil water and groundwater, respectively). In the biplot (right-hand panel) the length of the arrow represents the explanatory power for the solutes. The explanatory power of the first two principal components (PC1 and PC2) was 23.4 and 16.4%, respectively.

References:

Barthold, F. K., Tyralla, C., Schneider, K., Vaché, K. B., Frede, H.-G., and Breuer, L. (2011), How many tracers do we need for end member mixing analysis (EMMA)? A sensitivity analysis, *Water Resour. Res.*, 47, W08519, doi:10.1029/2011WR010604.

Blume T, van Meerveld HJI. 2015. From hillslope to stream: methods to investigate subsurface connectivity. Wiley Interdisciplinary Reviews: Water 2 (3): 177–198 DOI: 10.1002/wat2.1071

Genereux, D. (1998), Quantifying uncertainty in tracer-based hydrograph separations, *Water Resour. Res.*, 34(4), 915– 919, doi:10.1029/98WR00010.

Jackson, C. R., Bitew, M., & Du, E. (2014). When interflow also percolates: Downslope travel distances and hillslope process zones. Hydrological Processes, 28(7), 3195–3200. https://doi.org/10.1002/hyp.10158

Ladouche B, Probst A, Viville D, Idir S, Baqué D, Loubet M, Probst J-L, Bariac T. 2001. Hydrograph separation using isotopic, chemical and hydrological approaches (Strengbach catchment, France). Journal of Hydrology 242 (3–4): 255–274 DOI: 10.1016/S0022-1694(00)00391-7

Soulsby, C., Tetzlaff, D., Van Den Bedem, D., Malcolm, I. A., Bacon, P. J., & Youngson, A. F. (2007). Inferring groundwater influences on surface water in montane catchments from hydrochemical surveys of springs and streamwaters. Journal of Hydrology, 333(2-4), 199-213. https://doi.org/10.1016/J.JHYDROL.2006.08.016