Dear Anonymous Referee #1,

We thank you for your appreciation about our effort in developing a multi-tracer method for advancing the knowledge of young water in catchment hydrology. We thank you for your comments, also if, in our opinion, the method has not been fully understood.

We think that many of the criticisms made should be supported by scientific results in the literature to bring substance to the discussion. In this regard we answered point-by-point to your comments by citing published works that support our assumptions and methodology. Moreover, many problems that have been listed have already been addressed by the authors along the manuscript.

Perhaps, we will have to clarify some points better and we will be glad to do so in the revised version of the manuscript if we receive a positive editor's response.

Accordingly, we kindly ask to reconsider the decision of not-recommending the manuscript for publication in light of our answers.

With kind regards,

The Authors

1. Hydrograph components, i.e. the event and pre-event water, do not represent young and old water fractions defined by the young water fraction concept.

Please, note that we are not subdividing the hydrograph into event water and pre-event water. This can be done by applying a time-source separation with the only use of stable water isotopes as tracer (Klaus and McDonnell, 2013). This cannot be done with geochemical tracers like EC_S.

What we actually do is partially described in Kirchner (2016b):

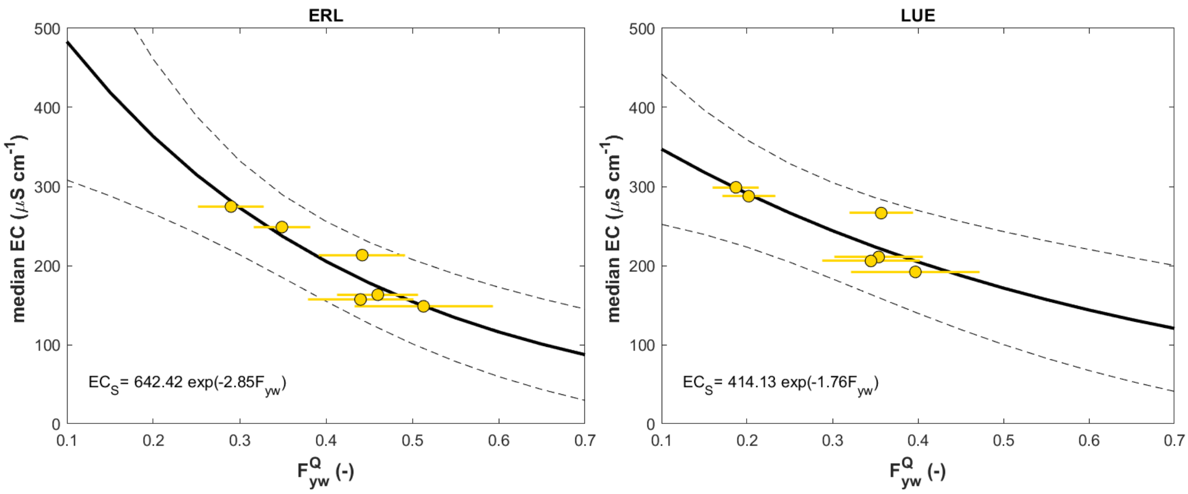
> ***"The young water fraction F_{yw} may also be helpful in inferring chemical processes from streamflow concentrations of reactive chemical species. Many reactive species exhibit clear concentration–discharge relationships. Because one can determine how F_{yw} varies, on average, across different ranges of discharge, one can potentially construct mixing relationships between F_{yw} and the concentrations of reactive species. If the measurable range of F_{yw} is wide enough, one may even be able to estimate the end-member concentrations corresponding to idealized "young water" (F_{yw} = 1) and "old water" (F_{yw} = 0)"***

Accordingly, what we did is to construct a mixing relationship between F_{yw} and the concentrations of reactive species (integrated in the EC_S measure): the exponential decay of EC_S with increasing F_{yw} (see Eq. 5 of the preprint). From this mixing relationship, we can separate the hydrograph in young water and old water by choosing appropriate end-

members. If possible, one could potentially measure the EC of young water (< 2-3 months) and old water (> 2-3 months) in the stream when flow specific young water fractions are equal to 1 or 0, respectively (Kirchner, 2016b). Since the flow conditions in which $F_{yw} = 1$ or $F_{yw} = 0$ are rare scenarios (see line 189-193 of the preprint), we obtain the two EC end-members through calibration because we have additional information deriving from stable water isotopes that we can use to constrain the two end-members: the flow-weighted average young water fraction (F^*_{yw}) and the time-weighted average young water fraction (F_{yw}) (both obtained with the amplitude ratio approach). The calibrated optimal EC_{ow} and EC_{yw} we have obtained are respectively higher and lower than the maximum and minimum EC_S measured in the stream, thus suggesting that they are the idealized old water (F_{yw} =0) and young water (F_{yw} = 1) EC endmembers (see lines 256-263 of the preprint).

Another way to obtain the endmembers, by strictly following Kirchner (2016b), is to look at how flow-specific young water fractions vary with the selected tracer (EC_S in this case) measured in the same flow-regime. We report hereafter flow-specific EC_S (median values) against flow-specific young water fractions for the three study catchments (Fig. 1). First, we observe a non-linear relationship that confirms the mixing relationship presented in the Eq. (5) of our manuscript (i.e., an exponential decrease of EC_S with increasing F_{yw}). Second, by fitting an exponential model on data we can obtain the end-members (EC_{ow} and EC_{yw}) values evaluating the $EC_S(F_{yw})$ equation for F_{yw} =0 and F_{yw} = 1. The main problem is that these end-members would be highly uncertain since the curve is poorly constrained at very low and very high F_{yw} (see Fig. 1).

We did not insert this analysis in the manuscript, but we are glad to add it in the revised version to better clarify our method.



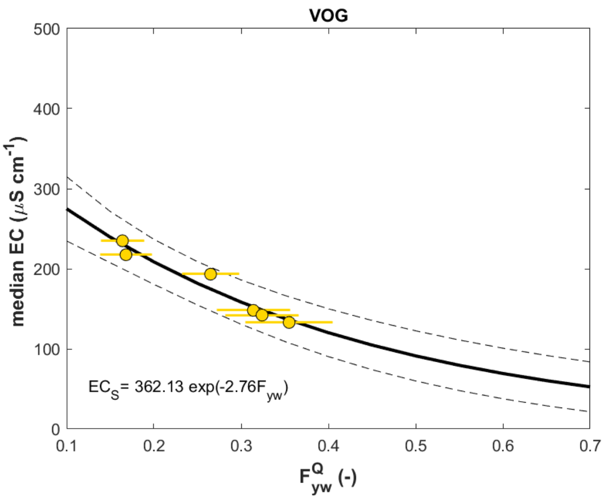


Fig.1 *Median flow-specific EC_S against flow-specific F_{yw}* for the three study catchments. *Horizontal bars indicate the flow-specific F_{yw} standard error. The black curve indicates the exponential fit, while the dashed black lines indicate the 90% prediction bounds.*

In summary, we do not separate the hydrograph by using the stable water isotopes (thus obtaining event water and pre-event water). We separate the hydrograph by using EC_S and by calibrating the EC end-members to reflect the age of the two components (young water and old water). We can rewrite lines from 165 to 172 of the preprint to clarify this point better.

In light of this clarification, we think that your first comment is derived from a misunderstanding of the hydrograph separation we actually did and how we have operated to perform it. Of course, event and pre-event water do not represent young and old water. Event water is a portion of young (< 2-3 months) water while old (> 2-3 months) water is a portion of pre-event water.

2. The conceptual problem in my opinion is that if the young water fraction is defined as a characteristic (metric) calculated from the seasonal variability of a tracer, it is attributed to the seasonal time scale. Thus, it is not meaningful to "improve" the temporal resolution of such a characteristic for finer scales (hydrographs) if the tracer streamflow data is sparse.

There is no conceptual problem in our method. We have obtained a young water fraction timeseries (at daily or sampling resolution) so that its (unweighted) average is equal to F_{yw} and its flow-weighted average is equal to F^*_{yw} and these are the definitions of F_{yw} and F^*_{yw} obtained from seasonal tracer cycles. See the quote from Kirchner (2016b):

> ***"Flow-weighted fits to the seasonal tracer cycles accurately predict the <u>flow-weighted average F_{yw} in streamflow</u>, while unweighted fits to the seasonal tracer cycles accurately predict the <u>unweighted average F_{yw}</u>"***

Of course, the young water fraction is calculated from seasonal tracer cycles as a characteristic at the seasonal time scale. However, "the fraction of runoff with transit

times of less than roughly 2-3 months (Kirchner, 2016a)" is a definition that could be applied also to finer scales. Since the young water fraction calculated from seasonal tracer cycles is an average value (Kirchner 2016a, b) over the period of isotope sampling, it depends on the young water fractions we have in the hydrograph at each (finer) time-step over the period of isotope sampling. Accordingly, it is very useful to improve the temporal resolution of young water fraction estimation: this gives additional information on the hydrological processes and conditions occurring in a catchment that cannot be perceived at the seasonal time scale and that can potentially explain the low or high average young water fraction value.

Moreover, we would not say that "is meaningful to improve the temporal resolution of such a characteristic for finer scales" since previous papers in the scientific literature have addressed the problem of understanding how the young water fraction varies with different flow regimes, and thus over time (e.g. by using automatic water samples triggered by time and by flow, see Gallart et al. 2020a, 2020b). In this regard, von Freyberg et al. (2018) and, subsequently, Gallart et al. (2020b) worked on the sensitivity of young water fraction to discharge (*Q*), the latter considered as a proxy of the catchment wetness. By studying how the young water fraction changes with *Q* is implicitly an investigation of how the young water fraction varies over time since *Q* varies over time. In this regard, we report here a quote of von Freyberg et al. (2018) paper: "*In individual catchments, one would also expect young water fractions (and thus seasonal isotope cycles) to be variable in time, i.e. to be larger during periods of stronger precipitation forcing and wetter antecedent conditions, as shallower, faster flow paths become more dominant, and as the stream network extends farther into the landscape, shortening the average path length of subsurface flow (Godsey and Kirchner, 2014).*"

Please, note that the method used to estimate the so-called discharge sensitivity of young water fraction has been designed to be applied in catchments in which tracer streamflow data is sparse. In this regard, again, we report here a quote of von Freyberg et al. (2018) paper: "*…we calculated the linear slope of the relationship between Q and F_{yw}, using a method that does not require breaking the streamwater isotope time series into separate flow regimes (and thus has more modest data requirements*…)"

3. ***EC is not a conservative tracer** although it is generally true that the longer the water stays in the catchment, the more ions it contains. However, EC varies also with air (water) temperature despite temperature compensation employed in the sensors and if an event water meets very soluble minerals, it can have high EC as well.

About the combined use of not conservative tracers and the young water fraction, please see, again, the quote from Kirchner (2016b):

> ***"The young water fraction F_{yw} may also be helpful in inferring chemical processes from streamflow concentrations of reactive chemical species. Many reactive species exhibit clear concentration–discharge relationships. Because one can determine how***

F_{yw} varies, on average, across different ranges of discharge, one can potentially construct mixing relationships between F_{yw} and the concentrations of reactive species. If the measurable range of F_{yw} is wide enough, one may even be able to estimate the end-member concentrations corresponding to idealized "young water" ($F_{yw} = 1$) and "old water" ($F_{yw} = 0$)".

***According to Kirchner (2016b), we do not need a conservative tracer to construct a mixing relationship with F_{yw}. Thus, we do not understand why you think it is incorrect to use EC_S.**

Of course, the use of EC_S has some limitations, but we have been extremely transparent about this: we have dedicated the whole section 3.3 of the manuscript regarding the limitations of the *EXPECT* method (including the limitations of EC_S as a tracer). Accordingly, the application of the *EXPECT* method, as it is, could be critical in some catchments with very soluble minerals (please, note that we have underlined this limitation in the paper, see lines 353-357 of the preprint), but could be successful in many other catchments (like the three alpine catchments investigated in this work).

In conclusion, we think that is crucial to underline the limitations of EC_S as a tracer (as we did in the section 3.3 of the preprint) to separate the young water from the old water, but that it is wrong to say that it cannot be used since it is not a conservative tracer.

We can integrate in section 3.3 of the manuscript the influence of air (water) temperature on EC_S despite temperature compensation employed in the sensors, as you have suggested. Thank you for this.

4. **Exponential relationship*** between EC and discharge (increasing **event water**** contribution) appears when the long-term data (combining many events) is analysed. However, **measurements I have seen***** did not document such a relationship for individual runoff events (hydrographs). While generally the EC does decrease with increasing discharge for many events, it does not happen so for each event. In fact, **in my experience a decrease in EC with increase in discharge was evident only during larger events******. Thus, it is in my opinion incorrect to apply the general relationship emerging from the long-term data for all individual events.

***If possible, please indicate the equation number of the relationship you are referring to since it is unclear. If you are referring to Eq. (5), please note that $EC_S(t_i)$ decreases exponentially with increasing $F_{yw}(t_i)$ (since we construct a mixing relationship between $F_{yw}(t_i)$ and $EC_S(t_i)$, Kirchner, 2016b), but we do not have discharge in the equation. Accordingly, we are not assuming that $EC_S(t_i)$ decreases with increasing $Q(t_i)$. The fact that $F_{yw}(t_i)$ increases with $Q(t_i)$ is a result of the paper (not an assumption) as visible in Fig. 4 of the preprint (and consistent with results of Gallart et al. 2020b).**

**** We are not referring to event water; we are referring to young water.**

*****Also, we do not understand what are the measurements you have seen: are you referring to the measurements of the three catchments reported in this manuscript? Are you referring to measurements of your study catchments? Are you referring to specific works published in literature? If so, it would be nice to know the temporal resolution of measurements you are referring to (is it the same as our data?) and to see what the boundary conditions of such measurements are (e.g., latitude, longitude, hydro-climatic regime, mean annual precipitation, geology, catchment area, mean catchment elevation, influence of human activities, presence of karst systems...) in order to have some concrete material for discussion.**

Looking at daily Q and EC data of our three catchments it is clear that the dominant functioning is a decrease in $EC_S(t_i)$ if $Q(t_i)$ increases and viceversa. This is visible from Fig. 2 of the preprint, but also from an in-depth analysis we did and that we report hereafter. Looking at what happens day-by-day in our data, we calculate the number of days in which to an increase in stream discharge corresponds a decrease in EC_S (i.e., $Q(t_{i+1}) - Q(t_i) > 0$ AND $EC_S(t_{i+1}) - EC_S(t_i) < 0$) OR in which to a decrease in stream discharge corresponds an increase in EC_S (i.e., $Q(t_{i+1}) - Q(t_i) < 0$ AND $EC_S(t_{i+1}) - EC_S(t_i) > 0$). Our results show that in 88%, 82% and 84% of the days at ERL, LUE and VOG catchments, respectively, we observe this functioning. When this is not true, we calculate the absolute difference in EC_S in the two adjacent days (i.e., $EC_S(t_{i+1}) - EC_S(t_i)$). The frequency distributions of these differences reveal a third quartile of 10.9, 6.8 and 4.8 µS/cm for ERL, LUE and VOG, respectively. These are little differences if compared with the range of variation of EC_S in these catchments, ranging from about 80 µS/cm to 400 µS/cm.

According to these results, we overall agree that EC_S does not decrease with increasing discharge at each time-step, but in our study catchments this happens only in a very limited number of days over a study period of about 5 years. Nevertheless, this fact does not affect the validity of Eq. (5) since we assume that $EC_S(t_i)$ decreases exponentially with increasing $F_{yw}(t_i)$, not with increasing $Q(t_i)$.

******Hydrograph separation by using EC_S has been applied in a previous study where EC_S decreases with increasing Q during both larger and smaller events (Cano-Paoli et al. 2019), and not only during larger events.**

In conclusion, we think that it is limiting to evaluate the goodness of our method by only considering its application in catchments studied during its own experience (of which we do not have any information). Indeed, the behavior of such catchments turned out to be different from other catchments studied in literature (e.g., Cano-Paoli et al. 2019) in which the method, as it is, could potentially work well (as in the three alpine catchments of our study).

The applicability of the method in catchments with different characteristics (e.g.,in karst systems with very soluble minerals or in catchments where EC_S increases with Q) is a

possible future development of this work: at present, we have detailed the limitations of the *EXPECT* method by explaining the conditions in which it can work fine or badly.

5. I agree that catchments with a greater number of runoff events (i. e. more frequent higher discharge) likely have higher young water fraction. Therefore, I appreciate the idea of calibrating separated **event/pre-event water components*** for all the events of period used to determine the young water fractions to estimate the proportion of “young water fractions” (see comment 2) in **individual events****. However, as I argue above, the EC does not provide the reliable information. Furthermore, I think that isotopes (atoms of elements forming water) and EC (ions of compounds saluted in water) may not provide the same (compatible) information about the streamwater sources. Last but not least, catchment runoff response is nonlinear. It is therefore questionable to assume that the young water fractions of **individual events**** are proportional to distribution of the event water fractions.

***We are calibrating the young/old water EC endmembers**

****We are not looking at specific individual events: we are estimating daily (or sampling) young water fractions. In both cases we use daily *Q* and EC_S data. To work at the event-scale, a finer (e.g., hourly) resolution data should be used.**

Thank you for appreciating the idea of calibrating young/old water EC endmembers to estimate the young water fractions at each time step. However, we do not agree about the fact that EC_S cannot provide reliable information. Of course, the use of EC_S has some limitations, and it should be used with care (see section 3.3 of the preprint), but our results show the opposite of what you are saying. We have found consistency between the $F_{yw}(Q)$ relationship found by Gallart et al. 2020b (using only stable water isotopes measurements) and our $F_{yw}(Q)$ relationship found by using both daily EC_S measurements and average young water fractions (estimated with the amplitude ratio approach) to constrain the endmembers. Our results reveal a good compatibility of information.

Moreover, there are previous papers that conveniently used EC_S and stable water isotopes obtaining coherent results (e.g., Cano-Paoli et al. 2019, Mosquera et al. 2018). Also, in a recent paper Riazi et al. (2022) said that water from different sources within the catchment is likely to have different ages. Hence, EC can potentially provide useful information on water age (lines 169-170 of the preprint).

Concluding, we report again the quote from Kirchner (2016b) about the synergic use of young water fraction and reactive chemical species:

> ***“The young water fraction F_{yw} may also be helpful in inferring chemical processes from streamflow concentrations of reactive chemical species.* *Many reactive species exhibit clear concentration–discharge relationships. Because one can determine how F_{yw} varies, on average, across different ranges of discharge, one can potentially construct mixing relationships between F_{yw} and the concentrations of reactive***

species. If the measurable range of F_{yw} is wide enough, one may even be able to estimate the end-member concentrations corresponding to idealized "young water" (F_{yw} = 1) and "old water" (F_{yw} = 0)".

Please be clearer (e.g., indicate the lines of the manuscript) about the fact that we assume that "young water fractions of individual events are proportional to distribution of the event water fractions". We did not make this assumption (or we do not understand what you are referring to).

References

Cano-Paoli, K., Chiogna, G., and Bellin, A.: Convenient use of electrical conductivity measurements to investigate hydrological processes in Alpine headwaters, Science of The Total Environment, 685, 37–49, https://doi.org/10.1016/j.scitotenv.2019.05.166, 2019.

Gallart, F., Valiente, M., Llorens, P., Cayuela, C., Sprenger, M., and Latron, J.: Investigating young water fractions in a small Mediterranean mountain catchment: Both precipitation forcing and sampling frequency matter, Hydrological Processes, 34, 3618–3634, https://doi.org/10.1002/hyp.13806, 2020a.

Gallart, F., von Freyberg, J., Valiente, M., Kirchner, J. W., Llorens, P., and Latron, J.: Technical note: An improved discharge sensitivity metric for young water fractions, Hydrology and Earth System Sciences, 24, 1101–1107, https://doi.org/10.5194/hess-24-1101-2020, 2020b.

Kirchner, J. W.: Aggregation in environmental systems-Part 2: Catchment mean transit times and young water fractions under hydrologic nonstationarity, Hydrology and Earth System Sciences, 20, 299–328, https://doi.org/10.5194/hess-20-299-2016, 2016.

Klaus, J. and McDonnell, J. J.: Hydrograph separation using stable isotopes: Review and evaluation, Journal of Hydrology, 505, 47–64, https://doi.org/10.1016/j.jhydrol.2013.09.006, 2013.

Mosquera, G. M., Segura, C., and Crespo, P.: Flow Partitioning Modelling Using High-Resolution Isotopic and Electrical Conductivity Data, Water, 10, 904, https://doi.org/10.3390/w10070904, 2018.

Riazi, Z., Western, A. W., and Bende-Michl, U.: Modelling electrical conductivity variation using a travel time distribution approach in the Duck River catchment, Australia, Hydrological Processes, 36, e14721, https://doi.org/10.1002/hyp.14721, 2022.

von Freyberg, J., Allen, S. T., Seeger, S., Weiler, M., and Kirchner, J. W.: Sensitivity of young water fractions to hydro-climatic forcing and landscape properties across 22 Swiss catchments, Hydrology and Earth System Sciences, 22, 3841–3861, https://doi.org/10.5194/hess-22-3841-2018, 2018.