Author's response: a list of all relevant changes made in the manuscript and a point-by-point response to the reviews.

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Dear Editor and Referees,

we would like to thank you for both the overall appreciation of our work and the appreciation of our plan to revise it. Considering the referees’ comments, the Editor decided that major revisions are necessary before the review process can be continued. The referees’ comments have been very constructive for the paper improvement and served as the guidelines for the changes we made. We have addressed all the issues raised in the interactive discussion including a reorganization and rewriting of some sections to make the text flow more smoothly and to explain our method in a simpler and more effective way.

The present document is subdivided in two Sections. In the first section we summarize all the major changes applied to the submitted document you have revised. In the second section we report a point-by-point response to the reviews.

In the hope of having met your scientific expectations in the revised manuscript, we kindly ask you to reconsider the publication of our work on the Hydrology and Earth System Sciences Journal.

With king regards,

The Authors

1 List of all relevant changes made in the manuscript.

1.1 Abstract

We have reorganized the abstract to effectively summarize our method. In particular:

- we have highlighted the main assumptions through a bullet-point list.

- we have emphasized at line 33 that the hydrograph separation in our method is 'unconventional' to avoid confusion with the traditional separation into event and pre-event water.
- From line 40 to 45, we have summarized the results, emphasizing that we validated the values of the endmembers obtained from calibration.
- From line 46 to 48, we have underscored that the manuscript outlines the main limitations of the method along with recommendations for its application in catchments different from those investigated in this study.

1.2 Introduction

From line 50 to line 100, some parts have been simply rewritten to make the text more fluent or clearer. Also, Eq. (1) has been further detailed to clarify the method of Gallart et al. (2020) for readers who may not have read the relative paper. From line 89 to line 137, the introduction has been extensively revised, integrating new information requested by the Editor and reviewers:

- From line 89 to line 100, the advantages and limitations of both EC and isotopes are explained, showing that they have complementary characteristics and could be used together for various applications.
- From line 101 to line 114, we have presented several articles from the scientific literature suggesting the use of electrical conductivity as a proxy for water age (thus giving support to our assumption of using EC as a proxy of the water age for a time-source hydrograph separation)
- Accordingly, from line 115 to line 134, we have included many articles (from 1997 to 2023) from the scientific literature employing EC for time-source hydrograph separation and showing good agreement with results obtained using stable water isotopes as requested by the editor and referees.

1.3 Material and methods

1.3.1 Study sites and data set

This section has remained almost unchanged. From line 179 to line 186, we have provided a more detailed explanation of how flow-specific young water fractions can be estimated for readers who may not have read the articles by Kirchner et al. (2016) and von Freyberg et al. (2018). We then changed Figure 2 so that the colors of the three basins are consistent with those shown in the new Figure 3. In Table 2, we added a column which indicates the median electrical conductivity in each flow regime for the three studied catchments.

1.3.2 The *EXPECT* method: two-component *E*lectrical *C*onductivity-based hydrograph separa*T*ion employing an *EXP*onential mixing model

This section has been extensively reorganized and rewritten to explain the method more simply and fluently (as requested by the Editor). Indeed, some paragraphs have been rearranged to help the reader follow the logical thread underlying our method. Moreover, we added an analysis showing how flow-specific young water fractions vary with the median flow-specific EC (reported in Table 2), illustrated in the new Figure 3 of the revised manuscript. This analysis serves both to justify the choice of an exponential mixing model, providing further support (as requested by both reviewers) for our hypotheses, and to provide an approximate estimate of the endmembers ($EC_{ow}^{raw}, EC_{yw}^{raw}$), which will be compared with those obtained from the calibration procedure. This analysis also demonstrates why choosing a linear mixing model would not be suitable for the three basins under study.

By reorganizing the paragraphs, some equations have been moved earlier, and thus, the equation numbers have been updated both in the text and in Fig. 4 of the revised manuscript.

1.4 Results and Discussion

1.4.1 Physical likelihood of calibrated endmembers and discharge sensitivity of young water fraction

This section has also been extensively reorganized since we have integrated many pieces of information requested by the Editor and reviewers regarding the validation of the obtained endmembers. From line 320 to line 348, we have included several published works supporting the difference of several orders of magnitude between the electrical conductivity of old water (EC_{ow}) and that of young water (EC_{yw}). These studies support our results and our initial hypothesis of considering $EC_{yw} < EC_{ow}$. We have always indicated the types of basins studied in the cited articles, which in most cases are alpine basins. From line 353 to line 357, we have pointed out how the value of the calibrated endmembers is consistent with the value of the endmembers obtained from the analysis illustrated in Figure 3. We have also discussed what discrepancies may be due to, also integrating the observations made by anonymous reviewer #1 (lines 357-359). From line 365 to line 375, we have supported the fact that the calibrated endmembers are higher and lower than the maximum and minimum EC measured in the stream, respectively, is reasonable. Moreover, we added three columns in Table 3 reporting the catchment ID, EC_{yw}^{raw},$\pm SE$, $EC_{ow}^{raw}\pm SE$, where SE indicate the standard error. This allows comparing the endmember values obtained from calibration with those obtained from the analysis shown in Figure 3. The latter have also been reported in Figure 5 along with the measured electrical conductivity values in two wells, one inside ERL and the other nearby.

1.4.2 An immediate application of the EXPECT method: flow duration curves of young/old water and the temporal variability of young water fractions.

This section has remained almost unchanged. We have simply explained the meaning of $Q_{50/50}$ in the label of Figure 6 and some little modification to Figure 7 as requested by the anonymous referee #2.

1.4.3 Limitations of the EXPECT method

This section has been expanded. Firstly, we changed its title from 'Limitations of the EXPECT method' to 'Limitations of the EXPECT and recommendations for future applications.' As requested by reviewer #2, we explained (from line 471 to line 490) how it is possible to apply and/or adapt the methodology presented in this work to different basins, emphasizing the precautions that need to be taken into account. At lines 496-497, we highlighted the importance of estimating the uncertainty of the endmembers and, consequently, of the fractions of young water that will be estimated with these endmembers.

1.5 Summary and Conclusions

This section has been partially rewritten to highlight the main aim and findings of this work.

1.6 Appendix A

This section has remained almost unchanged.

1.7 List of symbols

We have added the list of symbols as recommended by reviewer #2. This list should help the reader not to get lost with the symbols presented in the manuscript and clarify the meaning of the terms used.

2 Response to Referees

2.1 Response to referee #1

Dear authors,

I would like to thank you for the effort put into addressing my comments. The discussion is the best way to clarify the ideas and realize possible misunderstandings or drawbacks. Our discussion can be perhaps useful also to journal readers.

Dear Anonymous referee #1,

We thank you very much for your reply to our comments (AC1, https://doi.org/10.5194/egusphere-2023-1797-AC1) that further stimulates the discussion. We are pleased to note that the discussion has solved some possible misunderstandings and brought constructive comments and feedback to our manuscript. Accordingly, we have incorporated all your constructive feedback in the revised version of the manuscript that have contributed significantly to improving the work.

Please, find below a point-by-point response to your comments.

Sincerely,
The Authors

1. I understood that you did not do hydrograph separation with stable isotopes. It is not necessary to rewrite lines 165-172. The reader can obtain more detailed information from your response to my comments.

Ok, thank you for this.

2. The key assumption of your approach is the exponential relationship between EC and young water fraction. Could you try to justify it also in some other way than just mathematically (l. 176-190)?

Thank you for this comment. We have realized that the exponential relationship between EC and young water fraction could not appear robustly justified as presented in the preprint. In this regard, we have added a new analysis showing how the median flow-specific EC varies along with flow-specific young water fractions (F^{Q}_{yw}). This analysis is reported in Figure 3 of the revised manuscript. From this figure it is possible to visualize the relationship between electrical conductivity and young water fraction. Accordingly, from line 213 to line 216 we have written: "As visible in Fig. 3, the relationship between F^{Q}_{yw} and median flow-specific EC is well described by an exponential mixing model. Indeed, the widely used linear mixing model proves to be poorly suited here since it is pointing to a negative EC endmember of young water (i.e., EC value corresponding to $F^{Q}_{yw} = 1$, Fig. 3). This will be thoroughly discussed in the Appendix A."

3. I have downloaded and checked the discharge and EC data for your catchments. Some thoughts are given below (you do not need to respond to them). Although I am still not convinced about the use of EC, the manuscript describes the proposed approach clearly.

We are pleased to note that the discussion led you to reconsider the use of EC, also if you are not fully convinced yet. We are supported in the use of EC by:

- **Kirchner (2016b) statement about the use of not-conservative tracers to create mixing relationship with young water fraction. Please, see 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. 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" ($F_{yw} = 0$)."

  We have reported this from line 201 to line 204 of the revised manuscript.

- **EC provided useful information on water age in past studies and EC-based hydrograph separation results were favorably compared with those obtained with isotope-based hydrograph separation.**
  In this regard, we have included from line 101 to line 134 many published papers supporting the use of EC.

Thanks for pointing out the clarity of our approach description.

4. You may think about using the list of symbols, because there are many symbols from earlier works and some other symbols used in your study. Such a list might be helpful to someone who is not so familiar with all the literature and would like to use your method.

Thank you for this comment. We agree that there are many symbols in our work and a “List of symbols” is very useful for the readers. In this regard, we have added a “List of symbols” in the revised version of our manuscript. Please, see lines from 572 to 664.

5. It is clear that “old water” in your study is related to the young water fraction (the metric calculated from seasonal isotope variability); i.e., “old water” = 1-young water fraction. However, this term is the same as the “old water” from the isotopic hydrograph separation conducted by a mixing formula. To avoid the confusion, it may be useful to explain, e.g., in the List of symbols that your “old water” is different.

Thank you for this. Yes, the term “old” is used with different meanings in the scientific literature and this can bring confusion. We have specified in the text that the term “old” means “with transit times higher than 2-3 months” (e.g., lines 30-31, lines 228-229). Please, see also the definition of “old water” given at line 634 of the List of Symbols reported in the revised version of the manuscript.

6. Despite my comments on the manuscript, if the editor and other reviewer(s) decide that the manuscript can be published, I will not have a problem to accept such a decision.

We appreciate very much that you have reconsidered your initial decision and that you have provided useful comments that improved our manuscript. Considering the major changes applied to the revised version of the manuscript following your comments, we hope to have met the scientific expectations required for publication in HESS.

7. I agree that you acknowledged many uncertainties related to the use of the method. What I mind is this:

A. We (the hydrological community) know for decades that determination of the input (tracer concentration of the water entering the system, e.g., a catchment) is uncertain. The composition of water infiltrating into the soil that eventually appears in the output (e.g., in catchment runoff) is almost always unknown. We acknowledge this uncertainty and use tracer content in precipitation, because that is what we can (more easily) measure and in sometimes adjust it using different approaches.

B. We know that tracer variability in the input varies both temporally and spatially. The range of temporal variability differs in different years. We acknowledge this uncertainty and approximate the input concentration by the sine curve having the same amplitude over different years. Spatial variability in larger catchments is often neglected.

C. Several approaches are used to estimate the sine curve's amplitude (limiting or accepting the outliers) for weighted or unweighted data. Study periods are sometimes shorter than several years. All this brings the uncertainty which we acknowledge and determine the amplitude.

D. From the amplitudes we calculate the metric (an exact number) characterizing studied system. For many years it was the mean residence/transit time. After the inspiring work by Kirchner (2016) we prefer to use the metric called young water fraction.

E. Young water fraction (an exact number) is defined as "the fraction of runoff with transit times of less than roughly 0.2 years" (Kirchner, 2016). It represents an average over the study period. It seems obvious that when the discharge in a study catchment increases, the young water fraction should likely be greater than in the low flow periods when the streamflow is supplied by water that probably stayed in the catchment longer (we do not know how much longer than 2-3 months, but part of that water may be in the catchment not much longer 2-3 months, i.e. 4, 5, 6?).

F. We introduce a new metric called discharge sensitivity of the young water fraction and assume the exponential relationship between the young water fraction and a virtual young water fraction for discharge equal to zero.

G. It is fascinating and potentially very useful to know how big is the young water fraction on every day, hour, etc. We continue with the development of methodology and calculate daily young water fractions using another, non-conservative tracer (EC) and two-component hydrograph separation. We estimate the unknown tracer concentrations for the two end members though calibration. We assume that there is exponential relationship between the tracer and young water fraction and optimize the daily values so that their average is the same as the young water fraction obtained from seasonal variations of stable isotopes. We acknowledge possible uncertainties.

H. Having the daily young water fractions, we can investigate their relationships with meteorological drivers, and so on and so forth. …..

I. A to H indicate that we are adding uncertainties with every step in the development of our methodology. Please note I am saying “adding” not “accumulating”, because I do not know if the uncertainty increases in the described chain of methodology development.

J. We are acknowledging the uncertainty, but continuing to develop the methodology and adding other uncertainties. The result is that since the 1970’/1980’ we moved from a simple method providing a rough, but useful characteristic (especially in groundwater hydrology, because it matters if possible pollutant enters an aquifer with mean transit time 6 or 26 months for example) to a complex methodology involving many acknowledged uncertainties providing “exact” numbers for the short time steps.

K. I am not sure how much can the obtained numbers be trusted and whether we are obtaining a substantially new knowledge about the subject of our study, e.g., catchment hydrological cycle (in addition to the information on tracer dynamics). Benetin et al (2022) noted: “In the light of the complexity of the theoretical apparatus underlying time-variant TTDs …, one might wonder if this effort is actually worthwhile and all this complexity is really needed for practical purposes. Our claim is that, while time-variance might not be needed a priori to characterize transport processes in a catchment, it directly affects tracers and solute signals in stream water and plant water. Therefore, acknowledging and incorporating this time variance may be necessary to capture and explain both high-frequency and long-term tracer dynamics.”

We have understood what you mind. We would like to make some clarification about some points:

We recognize the challenges in determining the input tracer concentration and the temporal and spatial variability (Point A and B) of tracer content in the input, which is often neglected (Point B). However, the data uncertainty remains regardless of the method we use to process them. Accordingly, we have to choose the elaboration method that preserves as much as possible the information provided by data. Kirchner (2016a) demonstrated that if we use the isotope data measured in precipitation and streamflow, the convolution approach is not suitable to infer the Mean Transit Time (MTT) as reliable info (Point J), since it is subject to the aggregation error. Thus, Kirchner (2016a) proposed a new metric, the young water fraction, that is not affected by this error. Following Kirchner (2016a), the

young water fraction, and not MTT, is the information we can reliably extract from seasonal tracer cycles. Indeed, also 6 or 26 months to which you are referring are exact numbers with an uncertainty that, according to Kirchner (2016a), is much higher than those we can obtain from estimating the young water fraction from the amplitude ratio approach. Nevertheless, we agree that by neglecting the temporal variability of tracer input, e.g., assuming that input concentration can be represented as a sine curve having the same amplitude over different years, is a simplifying assumption, but it is a starting point to estimate quantities more reliable than MTT.

Following the key works of Kirchner (2016a, 2016b), the young water fraction has become a cornerstone, and the methodological chain has continued from this point. Accordingly, following the paper of Kirchner (2016b), the concept of discharge sensitivity of young water fraction has been developed by von Freyberg et al. (2018) and improved by Gallart et al. (2020b). Similarly, starting from Kirchner's paper (2016b), we have developed our own methodology that also allows for the estimation of discharge sensitivity. These are two distinct methods with two different uncertainties that can, at the latest, be compared.

In the revised version, we have validated our results about the optimized endmembers and the daily/sampling young water fraction of which we compute the uncertainty. Please see section 3.1 and Fig. 5. As reported at the point 2, in the revised version we have added a new analysis showing how the median flow-specific EC varies along with flow-specific young water fractions. This analysis allows us to have a first-order estimate of the endmembers (see lines from 216 to 221 of the revised version) that have been used as a benchmark compared to those calibrated. Moreover, we have validated the daily/sampling young water fractions (white-brown points in Fig. 5) with both flow-specific young water factions and the exponential fit with parameters previously obtained by Gallart et al. (2020b) (see black solid line in Fig. 5) that we use as benchmark. Our results favourably compared with the considered benchmarks. Accordingly, we retain that our results are reliable, and you can trust in the obtained quantities.

I have downloaded the discharge and EC data from your catchments and period October 1st, 2010-November 30th, 2015 which is approximately your study period according to Table 1.

1. I agree with you that discharge increase almost always corresponds to EC decrease and vice versa.

2. A few thoughts on the optimized EC values of the endmembers: The low flow periods in the study catchments are never very long (even in winter). Yet, the difference between the optimized EC of the old water fraction in ERL (501 μS.cm-1) and the **<u>minimum</u> (do you mean maximum?)** EC values measured in the stream in period October 2010-November 2015 (334.3 μS.cm-1) is quite high. Even the absolute EC **<u>minimum</u> (do you mean maximum?)** in ERL (439.5 μS.cm-1) between January 1978 and February 2023 (daily data) that was measured on 23rd January 1990, i.e. outside of your study period, was quite different from the optimized value. I am therefore not sure if the optimized EC values are correct. The young water

fraction was maybe not very big in January 1990 at catchment discharge of about 0.3 l.s-1. I would assume that streamflow EC would be closer to that of the groundwater, i.e. the measurements over long periods could identify this end member. Similarly, the optimized EC values of the young water fractions seem to be a little higher than data on Central European precipitation suggest (Monteith et al., 2023), but it can be argued that the young water fraction contains some soil water with higher EC.

Thank you for this comment since this is a key point of our results. You can potentially find the EC of the old water equal to the maximum EC measured in the stream during low-flow periods only if the young water fraction is equal to 0 in such flow conditions (i.e., <u>all the streamwater is old water and you can directly measure in the stream the old water endmember</u>). This is not the case of our three study catchments. We report here what we have written from lines to 365 to 375 of the revised manuscript:

"Our method estimates the EC endmember values for the cases $F_{yw}(t_i) = 1$ and $F_{yw}(t_i) = 0$ that are generally difficult to determine experimentally, thus providing additional information about young and old water in the systems under study. In this regard, in each one of the three study sites, the theoretical endmembers EC_{yw}^{opt} are lower than the minimum EC value measured in the streams; analogously, the calibrated EC_{ow}^{opt} values are higher than the maximum measured EC value (boxplots *versus* horizontal dashed lines in Fig. 5). This is expected for a natural, heterogeneous system where incoming precipitation mixes with stored water, and thus streamwater never contains 100% young or old water, respectively. Instead, streamwater is a mixture of these two components. This is supported by the fact that $F^{Q}{}_{yw}$ cover only a limited range of young water fractions (roughly from 0.1 to 0.5). This result demonstrates that the choice of the old water endmember based on tracer values sampled during baseflow conditions can result in an underestimation of the theoretical old water endmember. Although these stream conditions suggest the prevalence of old water, if the percentage of old water is less than 100%, then the measured tracers still reflect some mixing (albeit limited) with young water."

In the revised manuscript we have included your comments about the fact that the optimized EC values of the young water are a little higher than data on Central European precipitation (Monteith et al., 2023), and that this can be explained by considering the presence of soil water with higher EC. Please see lines 357-359 of the revised manuscript. Thank you for this.

3. According to the coefficient of determination, Q explains about 50% of daily EC variability in your catchments. It would be great if part of the variability could be explained by young water fraction. However, how can it be confirmed or rejected if daily young water fractions were estimated on the basis of EC?

You can look at median electrical conductivity in specific flow regimes versus flow specific young water fractions (F^{Q}_{yw}) or median discharge in each flow regime. Accordingly, electrical conductivity in specific flow regimes and F^{Q}_{yw} have been obtained independently. For example, in the ERL catchment the adjusted R^2 obtained by fitting a linear model on electrical conductivity in specific flow regimes vs F^{Q}_{yw} is 0.83, while that obtained by fitting a linear model on electrical conductivity in specific flow regimes vs median discharge in each flow regime is 0.59. This result suggests that the young water fraction explains a larger portion of EC variance than discharges in the ERL catchment.

2.2 Response to referee #2

Dear Anonymous referee #2,

Thank you for your care during your reading of the manuscript, your positive remarks and your comments that helped to improve the work a lot. We have implemented all your constructive feedback in the revised version of the manuscript. Please, find here below the responses to all your comments.

With kind regards,

The Authors

This article presents an interesting method for estimating the young water fraction based on high-resolution EC measurements.

Thanks for the positive overall assessment.

My only two major concerns are:

1) the authors may consider providing more evidence or referencing literature to support their three main assumptions for the method.

Thank you for this comment. In the revised version we have provided more evidence of our assumptions.

- **The assumption of considering an exponential mixing model for hydrograph separation has been robustly justified in the revised manuscript. Please, see the analysis reported in Fig. 3 of Section 2.2 and the Appendix A of the revised manuscript. We report here what we have written in lines from 213 to 216: "As visible in Fig. 3, the relationship between F^{Q}_{yw} and median flow-specific EC is well described by an exponential mixing model. Indeed, the widely used linear mixing model proves to be poorly suited here since it is pointing to a**

negative EC endmember of young water (i.e., EC value corresponding to F^{Q}_{yw}= 1, Fig. 3). This will be thoroughly discussed in the Appendix A."

- **The assumption of considering EC as a proxy of water age for a time-source hydrograph separation has been widely supported by past papers we have included in the revised version of the manuscript. Please, see lines from 101 to 134 that I report hereafter:**
"A time-source separation is generally performed using isotope hydrograph separation, IHS (Klaus and McDonnell, 2013), while major ions (approximated by EC) have been previously used for geographic-source separation in endmember mixing analysis (Hooper, 2003; Penna et al., 2017). Major ions concentration in streamwater derives from mineral weathering. Weathering processes can be viewed as a series of geochemical reactions influenced by characteristics of fluid movement, such as the contact time between the flowing water and mineral surfaces (Benettin et al., 2015, 2017). Thus, the longer a water particle remains within the subsurface, the higher its solute concentration (and thus EC) will be once it will be released as streamflow (Benettin et al., 2017). Indeed, Mosquera et al. (2016), investigating the mean transit time (MTT) of water and its spatial variability in the wet Andean páramo, found that the mean electrical conductivity is an efficient predictor of mean transit time in this high-elevation tropical ecosystem. More recently, Riazi et al. (2022), modelling the EC variation using a travel time distribution approach, assumed that the salinity of water in catchment storages is a function of water age. Ognjen Bonacci and Tanja Roje-Bonacci (2023) used EC measurements of a karst spring to estimate the time that water spent in the karst aquifer. In addition, Kirchner (2016b) stated that the concentration of reactive chemical species, such as EC, can be used to construct mixing relationship with young water fraction, which provides information about the water age. Overall, these studies suggest that EC may provide useful information on water age (Riazi et al., 2022). Indeed, past studies used EC for time-source hydrograph separation (HS) in event and pre-event water with promising results that favourably compared with those obtained from conservative tracers (Riazi et al., 2022). For instance, Laudon and Slaymaker (1997), applied HS in two small nested alpine /subalpine catchments by using different tracers (δ^{18}O, δ^{2}H, EC and silica) overall returning comparable results. Cey et al. (1998), with the aim of quantifying groundwater discharge in a small agricultural watershed, separated the hydrograph in event and pre-event water (assumed to be groundwater) obtaining only slight different results utilizing δ^{18}O and EC. Pellerin et al. (2008) performed HS on 19 low-to-moderate intensity rainfall events in a small urban catchment through the use of EC, silica and δ^{2}H obtaining similar outcome regardless of the tracer used. In a similar environment, Meriano et al. (2011) revealed a high level of agreement between flow partitioning results during a midsummer event using HS via δ^{18}O and EC as tracers. Camacho Suarez et al. (2015), to identify the mechanisms of runoff in a semi-arid catchment, applied HS by using both EC and δ^{18}O highlighting no major disadvantages by using EC. More recently, Mosquera

et al. (2018) used the *TraSPAN* model to simulate storm flow partitioning in a forested temperate catchment revealing similar portions of pre-event water regardless of the tracer (δ^{18}O and EC) used. Cano-Paoli et al. (2019), by investigating the streamflow separation into event and pre-event components in an alpine catchment, obtained consistent results by using δ^{18}O, δ^{2}H and EC. Lazo et al. (2023) showed that, in a tropical alpine catchment, the use of EC returned similar results of event and pre-event water than those obtained with δ^{18}O for a wide range of flow conditions reflected by the 37 monitored rainfall-runoff events. Overall, the findings of these studies suggest a quasi-conservative behaviour of EC under a wide range of hydrological and lithological conditions, also if its behaviour depends on specific characteristics (e.g., water partitioning between the surface and the subsurface, spatial distribution of minerals and subsurface properties, kinetics of rock dissolution, individual ions concentrations) of each watershed (Laudon and Slaymaker, 1997; Benettin et al., 2022; Lazo et al., 2023).”

- **The assumption of considering EC_{ow} higher than EC_{yw} has been widely supported by past papers we have included in the revised version of the manuscript. Please, see Section 3.1 of the revised version, lines from 320 to 348 that I report hereafter:**

“The application of the *EXPECT* method showed, at both daily and sampling resolution, that the old water EC endmembers, EC_{ow}^{opt} , are about one order of magnitude larger than the young water EC endmembers, EC_{yw}^{opt}, for all three experimental catchments (Table 3, Fig. 5). This result can be explained by considering that old water had longer contact with mineral surfaces in the subsurface (Benettin et al., 2015, 2017), and thus weathering-derived solute concentrations (and correspondingly EC) will be higher in old water compared to that in young water. Moreover, young and old streamwater components can derive from different reservoirs in a catchment (Riazi et al., 2022). Among these reservoirs, old water is generally assumed to represent groundwater. This is also supported by the fact that the fraction of baseflow (representing groundwater contribution to streamflow) resulted to be complementary to young water fraction in the framework (including the three Swiss catchments of this study) investigated by Gentile et al. (2023). In this regard, different papers that characterized groundwater EC showed notable differences with EC of precipitation and/or meltwater. Indeed, Zuecco et al. (2018), by investigating the hydrological processes in an alpine catchment, found that EC of rain water and of recent snow is 19.2 µS/cm and 12.2 µS/cm, respectively. Conversely, they found that groundwater from springs had an EC of 166 µS/cm. Moreover, by investigating the conceptualization of meltwater dynamics in an alpine catchment through hydrograph separation, Penna et al. (2017) defined the snowmelt endmember ranging from 2.9 to 15.3 µS/cm, the glacier melt endmember ranging from 2 to 2.7 µS/cm and the groundwater endmember ranging from 210 to 317.7 µS/cm (average values from springs or streams in fall/winter). These examples are

intended to show that groundwater (main source of old water) generally reveals an EC value much higher (around 10÷100-fold) than other sources in a catchment that should preferentially contribute to the young streamwater component. Differences in young and old water EC endmembers can also be partially justified by looking at differences in event and pre-event water EC endmembers. Indeed, old (transit times > 2-3 months) water is a large fraction of pre-event (transit times > few days) water, whereas event water (transit times < few days) is a portion of young water (transit times < 2-3 months). Due to this overlap, it would not be surprising a similarity of the old water and pre-event water EC endmembers, as well as the young water and event water EC endmembers. Cano-Paoli et al. (2019) used streamwater EC to investigate hydrological processes in alpine headwaters by separating the hydrograph into event and pre-event water. In this regard, they defined the event water end-member equal to 8 µS/cm (Penna et al., 2014) and the pre-event water endmember equal to 95 µS/cm (mean value during baseflow conditions). Laudon and Slaymaker (1997), by investigating the hydrograph separation using EC at the lower station of an alpine catchment, defined the rain water EC endmember equal to 6.15 µS/cm and the pre-event water endmember equal to 39 µS/cm. However, young and old water EC endmembers are expected to be higher than event and pre-event water EC endmembers, respectively. Accordingly, these past results taken from the scientific literature support our assumption that $EC_{yw} < EC_{ow}$."

Moreover, Kirchner (2016b) showed the concentrations of reactive chemical species as functions of young water fractions for streams draining three contrasting catchments at Plynlimon, Wales (Fig. 1, extracted from Figure 14 of Kirchner, 2016b and modified after). Calcium concentrations (one of major ions dominating EC in natural streams, Riazi et al., 2022) in streamflow were high for low young water fractions and decreased when young water fractions increased (Fig. 1). By indicating the general trend with gray lines, it is possible to infer the calcium concentration corresponding to $F_{yw} = 0$ (i.e., the old water end-member) which is shown to be higher than theoretical calcium concentration corresponding to $F_{yw} = 1$ (i.e., the young water end-member).

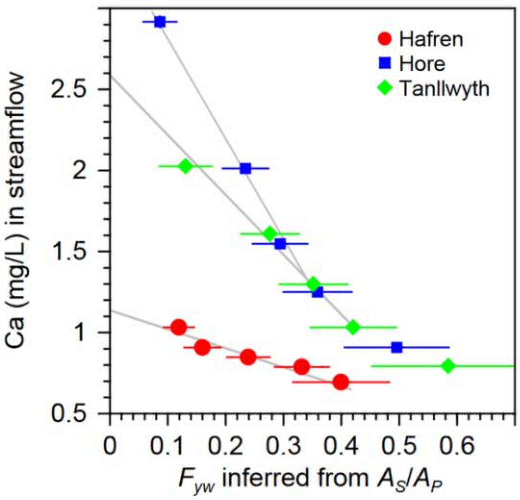


Fig 1. Calcium concentration as functions of young water fractions for three contrasting catchments at Plynlimon, Wales.

Image source: Figure 14 of 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., modified after.

2) the authors could discuss how their method can be applied to other basins beyond their experimental watersheds.

Thank you for this comment.

In the revised version, we expanded the section 3.3 of the preprint and we have renamed it as “"Limitations of the EXPECT method and recommendations for future applications". Please, see lines from 470 to 490 we report hereafter:

“While the *EXPECT* method can offer valuable insights into the young water fraction’s discharge sensitivity and its time-variability, it is not without its limitations. The assumption of considering EC as a proxy of streamwater age may not hold true in all hydrological systems. For example, human activities, such as mining, irrigation or wastewater inputs can alter the streamwater EC in unpredictable ways. Another example involves catchments with highly soluble rocks in the aquifers (e.g., limestone or gypsum), that are susceptible to dissolution by water. It has been shown that EC can increase with *Q* in some karst systems due to remobilization of the circulating water in the fractured areas (Balestra et al., 2022). Therefore, the F_{yw}-EC relationship (Eq. 3) can be very different from that in our three study catchments that are mainly groundwater influenced. Indeed, also an early study advised to be mindful of EC behaviour since it depends on specific characteristics of each catchment (Laudon and Slaymaker, 1997). Accordingly, for future applications of the method presented in this paper, we

recommend to start visualizing the relationship between flow-specific young water fractions and flow-specific electrical conductivities with the aim of constructing a site-specific mixing relationship, as suggested by Kirchner (2016b). Please, note that this relationship could be potentially different from an exponential mixing model. Indeed, the use of the exponential mixing model is not pretended to be the definitive answer to the problem of choosing the right mixing model for flow partitioning in young and old water. Accordingly, if the most suitable mixing model turns out to be different from an exponential mixing model, the equations presented in this study will need to be adapted to the specific case study. However, the method's application scheme for calibrating the endmembers can still be employed. Nevertheless, in some catchments with short and sparse isotope timeseries, flow-specific young water fractions cannot be estimated reliably (von Freyberg et al., 2018b). von Freyberg et al. (2018a) were able to estimate reliable flow-specific young water fractions for nine Swiss catchments that disposed of isotope timeseries 4 to 5 years-long with a minimum number of samples from 81 to a maximum of 140, where streamwater grab samples were collected approximately fortnightly. Thus, we suggest an isotope data set with these characteristics to construct a reliable site-specific mixing model with both flow-specific EC and F^{Q}_{yw}."

1. Lines 52-55, readers may seek more detailed descriptions for the terms 'unweighted,' 'flow-weighted,' and 'time-weighted.'

We have inserted complete information about these terms in the supplementary material and we add the reference to supplementary material at line 67. In order to avoid confusion, we have only used the term "unweighted" in the revised version. Thank you for this.

2. Lines 85-86, what do you mean by the 'uncertainty of the discharge sensitivity of the young water fraction'?

The estimation of the discharge sensitivity of young water fraction is described in the supplementary material and (briefly) in lines from 69 to 82. Referring to the supplementary material, by fitting Eq. (S4) directly to the streamwater isotope values by using the IRLS method it is possible to estimate the parameters F^*_0 and S^*_d, as well as their associated standard errors. When we talk about the 'uncertainty of the discharge sensitivity of the young water fraction' we are referring to these standard errors. In Table 4 of the revised version we show that with the EXPECT method we reduce the standard errors of such parameters.

3. Table 2, are the numbers of ^{18}O samples and EC samples the same?

We have explained this at lines 293-298 of the revised version:

"At SR, please note that the "EC samples" are not referring to physical samples in this specific application. Accordingly, $EC(t_i)$ and $Q(t_i)$ are obtained by sub-setting those EC and Q values from the daily time series that correspond to the time of isotope sampling. In this sense, we can say that the number of EC samples and isotope samples is the same. Nevertheless, the method can be potentially applied at SR in catchments in

which EC is only measured from water samples. At SR, $F_{yw}(t_i)$ values are estimated only for those days on which an isotope sample was taken.”

4. Eqs. 2.1-2.2, I would appreciate more details on the estimation of As, A*s and Ap.

As for your first minor comment: we have inserted complete information about these terms in the supplementary material and we add the reference to supplementary material at line 67.

5. Figure 5, could you explain what Qmed and Q50/50 represent?

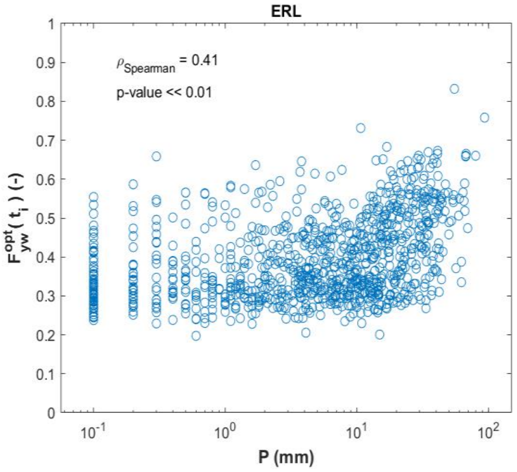
We have added what Q_{med} and $Q_{50/50}$ represent in the figure caption. Thank you for this.

6. Figure 6, is the variable snow depth represented as HS in the figure? Please specify the years in each of the panels.

Yes, HS and “snow depth” are the same variable. We did not realize that we have used two different names in the figure. We have added “(HS)” in the legend after “snow depth” and we have specified the years in each of the panels. Thank you for your comment.

7. Figure 7, why not include a scatter plot for F_{yw} and P, which might better illustrate the correlation?

The first attempt of Figure 7 was a scatter plot. However, it was not so evident the threshold-like behavior, while it is clear with a binned scatter plot. However, we report hereafter the scatter plot to show how the figure looks like with the representation you suggest:



8. Line 395, 'significantly reduced the uncertainty of'—how can we observe this reduction in uncertainty from the results section? Please provide more details in the text.

Following our answer to your second minor comment: in Table 4 of the revised version, we show that with the *EXPECT* method we reduce the standard error of the same parameters that can also be obtained with the method presented in Gallart et al. (2020), i.e., the existing method used to estimate the discharge sensitivity of young water fraction.