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) 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. Of course, this discussion will be useful to journal readers, but it is also crucial for us to take a critical look at our research.

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

We will incorporate all your constructive feedback in the revised version of our manuscript if we receive a positive editor's response.

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 would like to incorporate the figure representing flow-specific electrical conductivity vs flow-specific young water fractions (see Fig. 1 of AC1) in Section 2.2 (similarly to Figure 14 of Kirchner, 2016b). From this figure it is possible to visualize the relationship between electrical conductivity and young water fraction. Indeed, we observe that the decrease of EC with increasing young water fraction is well described by the exponential model.

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. As we have reported in our answers (AC1) to your comments (RC1), we felt supported in the use of EC by previous published papers stating that not-conservative tracers can be used to create mixing relationship with young water fraction (Kirchner, 2016b) and that results achieved with EC are consistent with those obtained with stable water isotopes (Riazi et al. 2022). Please, see the quote from Kirchner (2016b) and Riazi et al. (2022) that summarize these points with related scientific references:

"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 Fyw 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)."

Kirchner (2016b)

"EC has been used successfully as a tracer in various previous studies and has compared favourably with results from stable isotopes (Blume et al., 2008; Cano-Paoli et al., 2019; Laudon & Slaymaker, 1997; Meriano et al., 2011; Mosquera et al., 2018). Nevertheless, there are also so characteristics of EC that mean it does not meet the definition of an ideal conservative tracer. One issue is that, as noted above, EC is the net effect of a variety of ions that are influenced by various factors other than age, including geochemical processes within the catchment, leading to some uncertainty regarding its usefulness. For example, ion exchange and weathering likely mean that the ionic composition of water is non-conservative, meaning that EC is also likely to behave non-conservatively (Singha et al., 2011). Nevertheless, taken together, these past studies suggest that EC may provide useful information on water age and hence conditioning travel time model simulations to EC may prove useful."

Riazi et al. (2022)

Accordingly, although EC is not a conservative tracer, it has been used in the past to infer information on water age with successful results. Our results also confirm that, despite the EC limitations (that must be highlighted to use it with care), EC can be used to achieve reliable information on water age.

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. Yes, there are many symbols in our work and a "List of symbols" could be very useful for the readers: we did not think about it. We will add a

"List of symbols" in the revised version of our manuscript if we receive a positive editor response.

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 will specify what the term "old" means in the revised version of the manuscript. We will do this in the "List of symbols" as you have suggested. We already thought about the use of a different word (e.g., "elderly water fraction = 1 - young water fraction"), but we definitely used the term "old" since it is the term commonly used in past papers about young water fraction.

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 will improve our manuscript.

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:

Data translates to us what nature is saying since we do not speak the language of nature. As with every translation, it is not perfect, but data is the starting point for our research. Sometimes data is sufficient to infer something useful and reliable about how nature works. Some other time, we have to elaborate data by using some methods. Elaborating data (e.g., assuming that input concentration can be represented as a sine curve having the same amplitude over different years) is necessary to extract further information from data or simply to quantify the information that would remain otherwise qualitative. 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. MTT is subject to the aggregation error. Thus, Kirchner (2016a) proposed a new metric (the young water fraction) that is not affected by this error (thus, it better preserves the information that measured data can provide us).

About hydrologic nonstationarity, Kirchner (2016b) demonstrates that *“young water fractions can also be estimated separately for individual flow regimes”* and that *“one can also estimate the chemical composition of idealized “young water” and “old water” end-members, using relationships between young water fractions and solute concentrations across different flow regimes”.*

Following the statements of Kirchner (2016b), we designed the *EXPECT* method. With the *EXPECT* method it is possible to estimate the discharge sensitivity of young water fraction differently from the method presented in Gallart et al. (2020). These are two distinct methods with two different uncertainties that can, at the latest, be compared. In this regard, we compared the discharge sensitivity estimated with the *EXPECT* method with past estimates of discharge sensitivity (estimated in Gallart et al. 2020) and with flow-specific young water fractions (estimated in von Freyberg et al. 2018).

- **Our discharge sensitivity estimates are consistent with past discharge sensitivity estimates (estimated in Gallart et al. 2020 with a different method) and with past estimates of flow-specific young water fractions.**
- **The standard errors of the parameters S^*_d and F^*_0 are lower than those obtained by using the method of Gallart et al. (2020).**
- **We have obtained additional information on young water and old water EC endmembers.**
- **The mathematical (biunivocal) relationship between F_{yw} and Q of Gallart et al. (2020) does not consider possible hysteretic behavior between discharge and young**

water fractions during rainfall and after events (Benettin et al. 2017). With the *EXPECT* method we can potentially take into account this behavior by using daily young water fractions estimated from daily EC (that is subject to hysteretic behavior).

- **We can investigate the short-term variability of young water fractions.**
- **We jointly use stable water isotopes and EC. The latter is not a conservative tracer, but it is measured data that can give information (with some uncertainties) about the water age (Riazi et al. 2022 cum bibl.).**

From these points we conclude that we are providing a novel method that could potentially provide new insights for new knowledge.

Finally, we want to underline that when we talk about water age, we are always dealing with "estimates" since water age cannot be measured. What we can do is to estimate water age based on the use of tracers (stable water isotopes and EC in our study) that can be measured. Indeed, our daily young water fraction estimates cannot be validated by using "water age measurements". However, in the obtained numbers you can trust since we successfully validated our results by using past estimates of flow-specific young water fractions (estimated in von Freyberg et al. 2018) and of discharge sensitivity (estimated in Gallart et al. 2020), both used as a benchmark.

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.

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., all the streamwater is old water and you can measure the old water endmember), see also Kirchner (2016b):

"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)."

From results of flow-specific young water fraction (see Fig. 4 of the preprint), at very low and very high flow conditions the young water fraction resulted to be roughly equal to 0.2 and 0.5, respectively, in the three study catchments. This suggests that the streamflow is (very likely) always a mixture of young and old water. Thus, you will never be able to directly measure the old water endmember in the stream. However, the old water EC endmember we have obtained from calibration in the ERL catchment:

- **is higher than the maximum EC value measured in the stream during the whole observation period. This makes sense: if streamflow is always a mixture of young and old water, the old water EC endmember is necessarily higher than the maximum EC measured in the stream.**
- **is consistent with EC of around 500 µS cm^{-1} in groundwater, measured in the deepest monitoring well (6.8 m) in the catchment during fall-winter (see lines 246-249 of the preprint)**

We can do a similar reasoning for young water. Thank you for the reference of data on Central European precipitation. We will include in our discussion that the young water fraction can contain some soil water with higher EC.

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 (EC^Q) versus flow specific young water fractions (F^Q_{yw}) or median discharge in each flow regime (Q^Q). Accordingly, EC^Q 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 EC^Q vs F^Q_{yw} is 0.83, while that obtained by fitting a linear model on EC^Q vs Q^Q is 0.59. This result suggests that the young water fraction explains a larger portion of EC variance than discharges in the ERL catchment.

References:

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