

1 Dear Anonymous referee #2,

2 Thank you for your care during your reading of the manuscript, your positive remarks  
3 and your comments that will help to improve the work. Please, find here below the  
4 responses to all your comments.

5 We will take into account all your constructive feedback in the revised version of the  
6 manuscript once we receive the editor's response.

7 With kind regards,

8 The Authors

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

12 Thanks for the positive overall assessment.

13 My only two major concerns are:

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

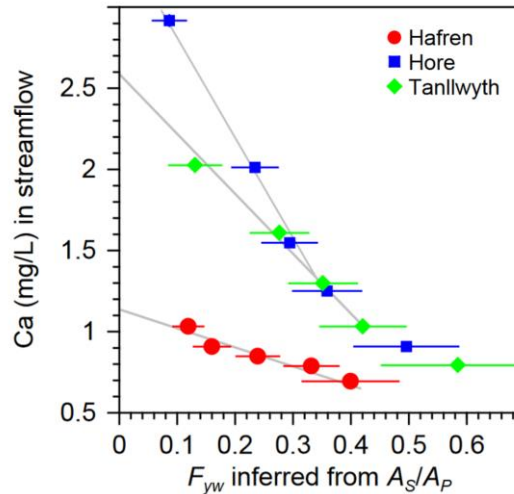
16 Thank you for this comment. In the revised version we will certainly provide more  
17 evidence of our assumptions.

18 ● The assumption 1 of considering EC as a proxy of water age derives from the  
19 following reasoning and literature:

20 *“Mineral weathering can be seen as a sequence of complex geochemical reactions*  
21 *driven by properties of fluid flow, such as the contact time between the circulating*  
22 *water and mineral surfaces...”* (Benettin et al. 2017; Benettin et al. 2015). Thus, the  
23 longer the contact time of water with rocks and soils, the higher the mineral  
24 weathering. Since EC is a bulk measure of major ions in water, the time that water  
25 is retained in a catchment before being released as streamflow (i.e., its age) is  
26 expected to be related to the ion concentrations and, accordingly, with EC. Indeed,  
27 Mosquera et al. (2016), investigating the mean transit time (MTT) of water and its  
28 spatial variability in the wet Andean páramo, found that the mean electrical  
29 conductivity is an efficient predictor of mean transit time in this high-elevation  
30 tropical ecosystem. Also, Bonacci et al. (2023), analyzing the EC measured in a  
31 karst spring, stated that EC can be used to identify the time that water spent in  
32 the karst aquifer (Bonacci et al. 2023 cum bibl.). Riazi et al. (2022), modeling the  
33 EC variation using a travel time distribution approach, assumed that the salinity  
34 of water in catchment storages is a function of water age.

- 35 ● The assumption 2 of considering  $EC_{ow}$  higher than  $EC_{yw}$  derives from the following  
36 reasoning and literature:

37 Following assumption 1, the ion concentrations (i.e., EC) in old (transit times (TT)  
38 longer than 2-3 months) water are expected to be higher than the ion  
39 concentrations (i.e., EC) in young water with shorter transit times (< 2-3 months).  
40 Moreover, young and old streamwater components can derive from different  
41 reservoirs in a catchment (Riazi et al. 2022). Among these reservoirs, old water is  
42 generally assumed to represent groundwater. This is also supported by the fact  
43 that the fraction of baseflow (representing groundwater contribution to  
44 streamflow) resulted to be complementary to young water fraction in the  
45 framework (including the three Swiss catchments of this study) investigated by  
46 Gentile et al. (2023). In this regard, different papers that characterized  
47 groundwater EC showed notable differences with EC of precipitation and  
48 meltwater. Indeed, Zuecco et al. (2018), by investigating the hydrological  
49 processes in an alpine catchment, found that EC of rain water and of recent snow  
50 is 19.2  $\mu\text{S}/\text{cm}$  and 12.2  $\mu\text{S}/\text{cm}$ , respectively. Conversely, they found that  
51 groundwater from springs had an EC of 166  $\mu\text{S}/\text{cm}$ . Moreover, by investigating  
52 the conceptualization of meltwater dynamics in an alpine catchment through  
53 hydrograph separation, Penna et al. (2017) defined the snowmelt endmember  
54 ranging from 2.9 to 15.3  $\mu\text{S}/\text{cm}$ , the glacier melt endmember ranging from 2 to 2.7  
55  $\mu\text{S}/\text{cm}$  and the groundwater endmember ranging from 210 to 317.7  $\mu\text{S}/\text{cm}$   
56 (average values from springs or streams in fall/winter). These examples are  
57 intended to show that groundwater (main source of old water) generally reveals  
58 an EC value much higher (around 10-fold) than other sources in a catchment that  
59 should preferentially contribute to the young streamwater component. Moreover,  
60 Kirchner (2016b) showed the concentrations of reactive chemical species as  
61 functions of young water fractions for streams draining three contrasting  
62 catchments at Plynlimon, Wales (Fig. 1, extracted from Figure 14 of Kirchner,  
63 2016b and modified after). Calcium concentrations (one of major ions dominating  
64 EC in natural streams, Riazi et al., 2022) in streamflow were high for low young  
65 water fractions and decreased when young water fractions increased (Fig. 1). By  
66 indicating the general trend with gray lines, it is possible to infer the calcium  
67 concentration corresponding to  $F_{yw} = 0$  (i.e., the old water end-member) which is  
68 shown to be higher than theoretical calcium concentration corresponding to  $F_{yw} =$   
69 1 (i.e., the young water end-member).



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

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**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.**

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**Differences in young and old water EC end-members can also be partially justified by looking at differences in event and pre-event water EC endmembers. For example, Cano-Paoli et al. (2019) used the 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  $\mu\text{S}/\text{cm}$  (as in Penna et al. 2014) and the pre-event water endmember equal to 95  $\mu\text{S}/\text{cm}$  (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  $\mu\text{S}/\text{cm}$  and the pre-event water endmember equal to 39  $\mu\text{S}/\text{cm}$ . Old (TT > 2-3 months) water is a large fraction of pre-event (TT > few days) water, whereas event water (TT < few days) is a portion of young water (TT < 2-3 months). Due to this overlap (schematized in Fig. 2), would not be surprising a similarity of old and pre-event water EC endmembers, as well as young and event water EC endmembers. However, young and old water EC endmembers are expected to be higher than event and pre-event water EC endmembers, respectively.**

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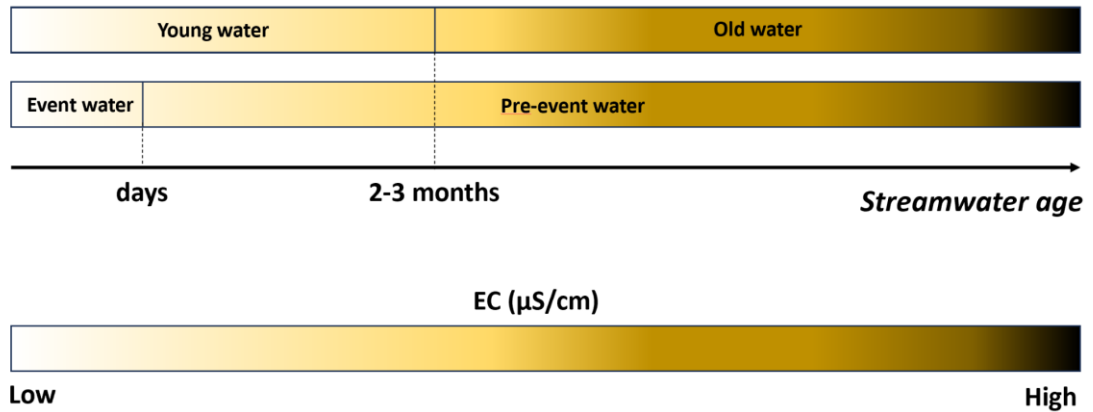
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**Fig. 2. Conceptualization of EC variations with streamwater age highlighting the overlap between old and pre-event water, as well as young and event water.**

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- **The assumption 3 of using an exponential mixing model that describes how the young water fraction varies with EC in streamwater can be further justified by looking at the relation between flow-specific young water fractions ( $F_{yw}^Q$ ) and flow-specific electrical conductivity (see Fig. 1 in the first response to Anonymous referee #1) that we will include in the revised version of the manuscript.**

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

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**Thank you for this comment.**

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**We could expand the section 3.3 of the preprint renaming it as ““Limitations of the EXPECT method and recommendations for future applications” in the revised version.**

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**We can add a paragraph at the end of section 3.3, briefly outlining the application to other basins beyond our experimental watersheds. We will better explain that a good starting point to choose the mixing model between young water fraction and EC is to visualize the relationship between flow-specific young water fractions and flow-specific electrical conductivities, as suggested in Kirchner (2016b). 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. However, also if there will be changes in the mathematics, the general method structure to calibrate the endmembers can be applied. Please, note that in some catchments with short and sparse isotope timeseries, flow-specific young water fractions cannot be estimated reliably (von Freyberg et al. 2018).**

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I also have some smaller comments as follows:

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

120 **We have inserted complete information about these terms in the supplementary material,**  
121 **but we missed adding a reference to supplementary material at line 55. We will add this**  
122 **reference. We will also specify that time-weighted or unweighted young water fractions**  
123 **are synonymous). Thank you for this.**

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

126 **The discharge sensitivity of young water fraction estimation is described in the**  
127 **supplementary material of the preprint. By fitting Eq. (S4) directly to the streamwater**  
128 **isotope values by using the IRLS method it is possible to estimate the parameters  $F^*_0$  and**  
129  **$S^*_d$ , as well as their associated standard errors. When we talk about the 'uncertainty of**  
130 **the discharge sensitivity of the young water fraction' we are referring to these standard**  
131 **errors. In Table 4 of the preprint we show that with the *EXPECT* method we reduce the**  
132 **standard errors of such parameters.**

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

134 **Please, consider that we are not referring to physical samples. We have a daily EC time**  
135 **series obtained from averaging 10-minute data from an EC probe in the stream. When**  
136 **we apply the *EXPECT* method at the “sampling resolution”, we subset those EC values**  
137 **from the daily time series that correspond to the time of isotope sampling. In this sense**  
138 **we can say that we have the same number of EC and isotope samples. We will clarify this**  
139 **better in the text. Thank you.**

140 4. Eqs. 2.1-2.2, I would appreciate more details on the estimation of  $A_s$ ,  $A^*_s$  and  $A_p$ .

141 **As for your first minor comment: we have inserted complete information about these**  
142 **terms in the supplementary material, but we missed adding a reference to supplementary**  
143 **material at line 150. We will add this reference.**

144 5. Figure 5, could you explain what  $Q_{med}$  and  $Q_{50/50}$  represent?

145 **We will add what  $Q_{med}$  and  $Q_{50/50}$  represent in the figure caption. Thank you for this.**

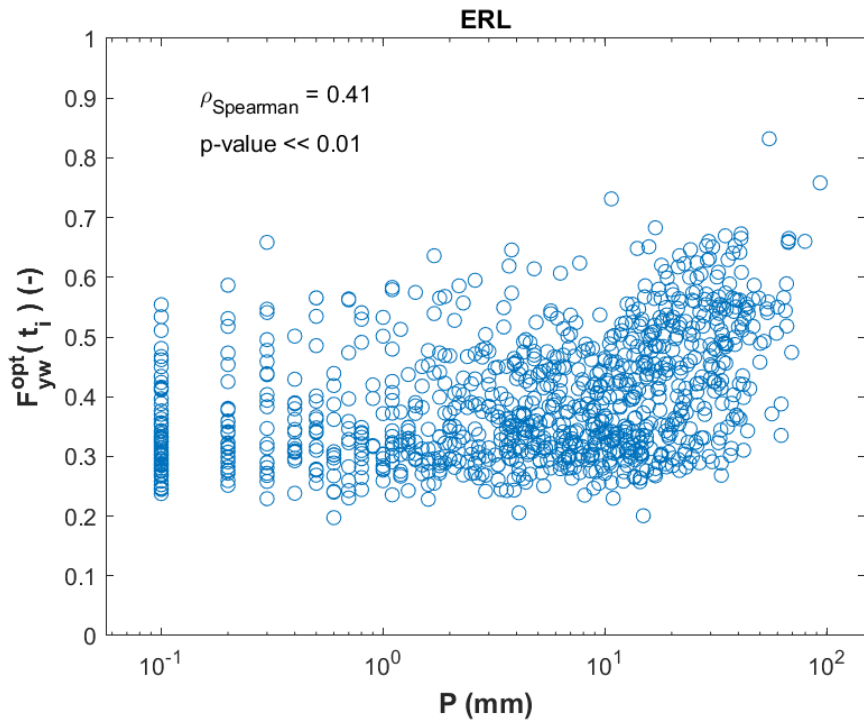
146 6. Figure 6, is the variable snow depth represented as  $H_S$  in the figure? Please specify the  
147 years in each of the panels.

148 **Yes,  $H_S$  and “snow depth” are the same variable. We did not realize that we have used**  
149 **two different names in the figure. We will add “( $H_S$ )” in the legend after “snow depth”.**  
150 **Thank you for having noticed this.**

151 **We will specify the years in each of the panels.**

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

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



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

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

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167 **References:**

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