

## ***Interactive comment on “Quantifying new water fractions and transit time distributions using ensemble hydrograph separation: theory and benchmark tests” by J. Kirchner***

**Anonymous Referee #1**

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Overview:

This article presents a new methodology called ensemble hydrograph separation. The method is distinguished from traditional hydrograph separation (i.e. 2-end-member-mixing model) in multiple ways, including (1) it utilizes differences between conservative-tracer concentrations in end members and a designated “old water” source, rather than the concentrations themselves; (2) the method recasts the end-member-mixing model based on mass balance into a linear-regression equation, which alleviates the necessary assumption of conservation of mass in the mixed flow; and (3) the method generates ensemble-average estimates of “new” water contributions to

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streamflow across extend time periods (e.g. months, seasons, and years), rather than estimates at the time scale of single storm events. The author goes on to show how discrete integral equations for conservation of tracer mass between precipitation and streamflow can similarly be recast in the form on a multiple-linear regression model. The slope coefficient in this model is shown to equate to the fractional contribution of total streamflow at a moment in time that is composed of water volumes with specific residence times. When integrated across all plausible residence times, and averaged over all relevant times, the slope coefficient allows an estimation of the ensemble-average transit-time distribution of water within streamflow (possible “forward” or “backward” TTDs, as the author shows). The author also shows how one might approximate the time variance of TTDs under different hydroclimatic conditions by applying the method to different subsets of an entire data series.

The author develops a two-store conceptual model of streamflow and conservative-solute transport for a catchment, then uses the model under various climatic forcing and parameterizations to generate benchmark ensemble TTDs and new-water estimates. The regression approaches noted above are tested to see if they can accurately recreate these independent, benchmark data sets, which they do quite well. The author concludes the article by clearly delineating how the method differs from traditional hydrograph separation and lumped-parameter-transport modeling based on time-invariant TTDs and Storage-Selection Distributions (a.k.a. SAS functions). He discusses possible interesting applications of the method.

Recommendation to the Editor:

I think this article could have a strong impact in the field of catchment hydrology. I believe it can be published with very minor revision.

The writing and visual presentation of material are excellent. I found only one certain typo (see Technical Edit #5), which is remarkable for an article of this length, and greatly appreciated. I think the most exciting possible impact of this method could be retro-

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spective application to existing data sets from myriad catchments. We have more than three decades of studies showing that “old” water is generally the majority component of the stream hydrograph, even during individual storm events. But because the rigid assumptions of two-component-mixing models are always violated in these studies, and since most of them did not report uncertainty, actual numeric estimates are dubious (as is any comparison among them). Similarly, there are nearly three decades of studies that employed lumped-parameter-transport modeling based on time-invariant TTDs to estimate mean-transit times (MTTs) of water flow through catchments in many locations. The assumption of the time-invariant TTD was always known to be a bad one (even if the analysis only considered tracer concentrations during baseflow), and is now unnecessary [G. Botter et al., 2010; Gianluca Botter et al., 2011; Harman, 2015; van der Velde et al., 2012]. As such, there is reasonable suspicion about just how accurate are all of those existing estimates of MTT. Further—and likely as a tacit acknowledgement of this poor assumption—most past studies focused on the MTT, but not the actual form of the parameterized TTD. As this author notes, the method proposed here is fairly robust in that it can be employed with tracer data sets collected at variable time intervals, and when significant parts of the time series may be missing. The method can take advantage of all these existing data sets to possibly refine our view of what MTTs are for low-order catchments in different regions, and what the form of the TTDs actually look like (at least the early-time portions of TTDs; the long tails remain difficult to constrain). I would be excited to see the results of this method being applied to all of these existing data sets, and from newer networks of catchment studies like the Critical Zone Observatories.

As one point of criticism, I would ask the author to consider, and possibly elaborate in the discussion, about what might be the advantage of this method over the contemporary methods of lumped-parameter-transport modeling based on time-variable TTDs and SAS distributions/functions? For those researchers organizing new field studies and networks of sites, and that are reasonably competent and diligent with field-data collection (i.e. avoiding lots of data gaps), is there any reason to consider this method?

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One may argue that it is not any simpler to implement, and cannot achieve similar temporal resolution when estimating time-variable TTDs and SAS distributions. As discussed by the author, application to short subsets of data (for comparison of TTDs at different times) reduces sample size and enhances uncertainty in the regression approach.

Last, the author makes one conclusion that I would disagree with, and that I believe might negatively influence subsequent applications of this method to field data (see specific comments 4 and 10). I ask the author to consider these comments and possibly revise their remarks. I also thought there were a few instances where the citation of other relevant works could be improved (see specific comments 9, 12, and 13).

Specific Comments:

(1) Page 5; line 24: Another complication would seem to be the fact that  $CQ(j)$  will be strongly temporally correlated with  $CQ(j-1)$ . Most perennial streams will be hydraulically connected to a riparian aquifer, and receiving discharge from that aquifer so long as the stream is gaining. The water volume in that aquifer may be 1 or 2 orders of magnitude greater than the volume of water associated with typical precipitation events.  $CQ(j-1)$  (i.e., old water) and  $CQ(j)$  should then be strongly temporally correlated. In other cases  $C_{new}(j)$  might also be strongly temporally correlated with  $CQ(j)$ , for example, in catchments with widespread impervious surfaces that induce infiltration-excess-overland flow. Whether or not the latter type of temporal correlation would exist would also depend on the temporal resolution of sampling. Is this potential for temporal correlation within the explanatory and dependent variables problematic for the linear regression approach here?

(2) Page 6, line 3-5: What would qualify as small? The condition in line 5 would not necessarily be true would it? In the case of stable-isotopes as tracers, if 1) rainfall is distributed uniformly throughout the year, 2) there is seasonal variation in the mean  $C_{new}(j)$ , and 3) streamflow is generated preferentially by precipitation that falls in the

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cold season, then this difference would not be expected to be zero, would it? These conditions are fairly common.

(3) Page 13, lines 8-10: Could you comment on the rationale for randomly assigning  $\delta^2\text{H}$  values to precipitation in this way, in light of the fact that actual  $\delta^2\text{H}$  values are often correlated with cumulative rainfall amounts/unit time? I ask only because the existence of this correlation would seemingly have bearing on condition 2 on page 6. If cumulative rainfall amount during a storm is not correlated with  $\delta^2\text{H}$ , then in principle either very negative  $\delta^2\text{H}$  values, or values near zero (a plausible upper boundary of the variable's range), could be observed for large storms that generate greater  $F_{\text{new}}$ . In that case condition 2 on page 6 might be questionable. Seemingly the random assignment here in some sense violates that condition, yet the results in Figures 1 and 2 are quite good?

(4) Page 26, lines 28-30 and Page 27, lines 1-3: Worst-case scenario based on what? Estimates of actual evaporative enrichment measured in surficial soil water? Or plausible ranges from models [e.g. Allison et al., 1983; Barnes and Allison, 1983]? Certainly in semi-arid environments, or where vegetation is interspersed (e.g. tree plantations or agricultural settings) there could be more than 20 ‰ enrichment of soil water before it percolates below the root zone. The fractionation effect could vary strongly at daily and weekly time scales depending on storm frequency and intensity, and potential evaporation (from plant surfaces and surficial soil). The fractionation effect could in fact be strongly correlated with storm size—not a constant offset or random fluctuation that introduce no bias. And of course this simulation makes no consideration of spatial variability of the fractionation effect, which might occur due to substantial land-cover variability (e.g. catchments with mixed bare-soil and vegetated cover; wetland-meadow-forest transitions; partially snow-covered with spatially- and temporally-variable melt dynamics, etc.). Finally, it's worth noting that the isotope composition of infiltrating water can be different than precipitation (greater or lesser) due to evaporation from, or storage within, plant canopies [Allen et al., 2016]. These

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effects can be of variable sign and magnitude during individual storms. I would argue it is these storm-specific effects that matter—not an average offset over the long term—because these storm-specific effects influence the individual values of  $C_{\text{new}}$  – Cold in the regression model.

I think the concluding statement about this analysis (page 27, lines 1-3) should be more suggestive than definitive. People will read this and make the convenient assumption that a single precipitation collector is all that is needed in the field, rather than the more labor-intensive alternative of having multiple precipitation/throughfall/snowfall collectors (to capture some essence of spatial variability, and thus leading to more samples to analyze in the lab). This is an aspect of the method that should at least be examined in a few field studies in catchments that vary climatically and ecologically, rather than assumed unimportant based on this useful, but inconclusive, simulation. The same problem exists among most historical studies of mean transit times in forested catchments: the input data sets in the convolution integral are all biased to some unknown degree due to the spatial heterogeneity of storage, throughfall, and evaporation.

(5) Page 29, line 10: Could you clarify here if lag time  $m$  corresponds to the most distant past time when a measurement of CP is available, or can the value of  $m$  be chosen even among those past times when CP was measured? You seem to be implying the latter case, but I don't understand why you would potentially lump multiple measured values of CP into the Colder term, rather than using the values individually in the regression analysis. Perhaps this is clarified later on in the text.

(6) Page 40, lines 15-20: This seems related to the question I posed in specific comment 1. If that is correct, perhaps you could foreshadow for the reader at that location in the text that this issue is discussed later.

(7) Page 45, lines 15-25: Could you clarify in this case how the parameter  $m$  is determined? Seemingly if you want to isolate some subsets of the time series of  $Q$  for comparison of the average-backward TTDs, for example,  $Q$  during September versus

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April at Smith River, the CQj and distribution of water ages at any time during either interval could be strongly influenced by CP that occurred over many historical time intervals prior to September or April.

(8) Page 47, figures 16a,b: Regarding the orange line, it's interesting and counter-intuitive to me that these average TTDs would show that volume fractions of Q with ages of only a few days would be (slightly) more probable than volume fractions of Q with ages of several days to weeks. It rains so infrequently during the summer, most often there would be little to no water at all within the catchment that had residence time of only a few days. I would think there should be a slight increasing trend in these probabilities from left to right on the transit-time axis, up to a point where the trend then turns back downward. Is this possibly because those few storms that do occur during the summer (and deliver some water to the stream with age of only a few days) represent a disproportionately large fraction of total Q over the summer months?

(9) Page 49, line 4: Certainly there are several good examples of where storage dependence has been examined, even one case in the same climate as the Smith River. These are worth acknowledging [Benettin et al., 2013; Harman, 2015; Heidebuchel et al., 2013; Heidebuchel et al., 2012; Rodriguez et al., 2018; van der Velde et al., 2010; van der Velde et al., 2012].

(10) Page 51, line 19: I would argue that point 5 here should perhaps be omitted. While suggestive, I don't think the simulation that leads to this conclusion is a very realistic representation of isotope fractionation effects over time or space. See specific comment 4 above. Also, while I'm no proponent of traditional hydrograph separation, I don't think the first sentence in point 5 is really true. The method is not necessarily vulnerable to biases in tracer measurements resulting from fractionation. If fractionation has occurred in the end member, the effect should be apparent in the measured delta values. Fractionation doesn't inhibit accurate quantification of the tracer concentration in the end member.

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(11) Page 52, lines 7-9: Perhaps put "time-invariant" in italics here for emphasis, since the focus of both of those papers was of course to demonstrate that, while potentially more temporally stable than TTDs, even SAS distributions should be considered time-variant in most cases.

(12) Page 52, lines 11-14: And note some important works preceding those you have cited [e.g. Ali et al., 2014; Fiori and Russo, 2008; Fiori et al., 2009; Rinaldo et al., 2011; Russo and Fiori, 2009].

(13) Page 52, lines 15-19: This paper [Pangle et al., 2017] provides a clear illustration of your point, where multiple hydrologic variables, and a tracer breakthrough curve, can be simulated quite accurately with traditional flow and transport models, while still not accurately reproducing the known age distributions of water in the flow out of the system.

### Technical Edits:

(1) Page 2, equation 2: Should you have subscript j along with subscripts "new" and "old" attached to C terms in equations 2 and 3? In practice they are not uniquely measured at every time step, but must at least be assumed at each time step.

(2) Page 61, equation A5: Is it redundant to use overbars and angled brackets on the same term?

(3) Figures 4, 6, and 8: Some kind of discontinuity in the vertical axes of the some of the graphs. Maybe due to pdf rendering? Not important, just bringing it to attention in case it can be easily fixed.

(4) Page 28, line 24: Should the subscripts be j here rather than i? Since times associated with sampling P have been denoted with i whereas those for Q with j?

(5) Page 30, line 17: Looks like a typo on the subscript of second term on the right-hand side of the equal sign.

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