Response to the interactive comment of N. Roulet on

"New water fractions and transit time distributions at Plynlimon, Wales, estimated from stable water isotopes in precipitation and streamflow" by Julia L. A. Knapp et al.

We want to thank Nigel Roulet for reviewing our manuscript and for providing helpful comment. Please find our responses to the comments below. The comments provided by Prof. Roulet are shown in italics, and our responses in regular font. Changes we will make in the revised manuscript are underlined.

This a well-written and well-argued paper. It will be a valuable contribution the runoff literature, particularly the interpretation of separating storm flow components. The authors use a high temporal resolution isotope and chloride data set for several catchments in Plynlimon, Wales to address a number of questions related to the separation of new (event) water from older 'stored' water in runoff. They calculate transit times, fraction of event water, and spectral filtering to attempt to tease out catchment transport and storage processes. The paper uses inference from the outflow record and has no physical information to actually figure out transport and storage.

The results are not overly surprising – one needs to define well what one is analyzing and the appropriateness of various define characteristics are assessed relative to the research questions being asked. This seems obvious. The sensitivity of the results to the frequency of sampling is also not surprising but this is a nice empirical analysis of the effect. This study is a good example of the importance of stored water to storm runoff. It is also show a reassuring similarity between isotopic tracers – the isotopes producing essential the same result but Cl yields less event water than the isotopes. I suspect this is because the rain water signal for Cl is derived rather than directly measured as an input signal. This is not the case with the isotopes.

The paper is timely. As the authors state the high resolution data set they use is unique but with new, reasonably priced, technologies for measuring isotopes in a semi-continuous manner coming on line, the issues this paper raises will be very important.

We thank Prof. Roulet for the positive assessment of the manuscript.

Pg 3 – In 1 "gold standard". There is no such thing in hydrology for this kind of word. One would have to understand the flow system to get one. Even in the constructed settings the variability is a problem. Not sure this term is useful – will it ever be obtained?

We agree that (unfortunately) no "gold standard" tracer exists in hydrology (and our point was that neither isotopes nor chloride fills this role). We will change the sentence to <u>"..., as both tracers suffer from different shortcomings</u>" in the revised version of the manuscript.

Pg 3 - Ln 20 - 25. This statement is correct but could be a little more forwarding looking to the future.

We assume that "more forward looking to the future" refers to the more widespread availability of isotope measurements, including new technology enabling the semicontinuous measurements of stable water isotopes in a more automated manner. This in an important point, and we will include this in the revised version of the manuscript, albeit not at this point in the introduction, but in the conclusion (p.19, I.3, following "... we conclude that stable water isotopes provide a more reliable basis for quantifying catchment transport timescales."): "..., especially in the light of novel technology, enabling semi-continuous measurements of stable water isotopes in an automated manner (e.g., von Freyberg et al., 2017)."

Pg 11 In 1 hints at this future. Why not be explicit?

We agree that the advancements with regard to stable water isotope technology should be mentioned explicitly. This section of the manuscript, however, refers to the analysis of chloride data. Instead, we will include a note toward the end of the paper. Please see our response to the previous comment for details.

Pg 11 – In 19-21. Not sure I understand why you did not filter the CI? Something is not making sense to me here.

We did not filter the weekly chloride samples, because we expected the effect of dry deposition to be less important in these samples. For one, the funnel was smaller, meaning more absolute amount of rain was needed to make up a measurable sample than for the 7-hourly sampling. Therefore, any dry deposition was much more diluted in the weekly sampling compared to the 7-hourly sampling. Due to the longer sampling interval, we also expected dry deposition to have some effect on nearly every sample. Therefore, it would also have been more difficult to identify samples with a substantial effect of dry deposition and exclude them based on empirical criteria. For these reasons, we decided to merely perform a general outlier removal on the weekly chloride data to remove samples with unrealistically high concentrations.

Pg 13 – In 22-26 The filtering issue again. How good it is depends on how you can eliminate the dry deposition issue. Can you elaborate?

This is correct. Following suggestions from the first reviewer of this manuscript, we have decided to add additional detail on the dry deposition filtering in Sect. 5.3. We will expand this additional comment to include the point made by Prof. Roulet: "<u>The analysis thus showed that chloride may be a suitable passive tracer, if potential effects of dry deposition are removed. The extent of the suitability of chloride as a tracer consequently depends on how well dry deposition effects can be identified and removed. However, it is important to note that the filtering approach for dry deposition</u>

employed here was not empirically validated and was not based on physical effects like wind speed or direction. Furthermore, the removal of dry-deposition affected samples leads to a reduced mass recovery. In the ensemble hydrograph separation approach, this has only a small effect, as only the correlation between the input and output signal is assessed. In other approaches, however, a correct mass balance is essential. Therefore, we argue that the stable water isotope data provide a better and more reliable data set to quantify catchment characteristics as well as mixing and storage processes."

Pg 14 Ln 8-15 Same issue. Not sure why the dry deposition would make the new fraction smaller?

As explained in the manuscript, dry deposition leads to some few precipitation samples with unrealistically high concentrations. This has the effect of stretching the x-axis of the regression whose slope yields the new water fraction. As the x-axis becomes more and more extended by these high-concentration outliers, the regression slope becomes lower and lower, and consequently the calculated new water fraction is smaller.

Pg. 14 In 26-34. This seems obvious and suggests that operational definitions need to be specified so in the future we know what we are comparing. Why not be more explicit in the definition of thresholds.

This paragraph discusses the precipitation threshold. As described in the manuscript, explicitly defining the threshold is not feasible, as it "depends on the frequency and intensity of rain events, as well as the sampling frequency". Strictly defining the magnitude of the threshold is therefore not a good idea. However, if different systems are compared, the precipitation thresholds should be comparable, e.g. lead to the exclusion of similar percentages of total precipitation. We will add this to the revised manuscript (at the end of line 29): "<u>If different systems are compared, we recommend choosing a precipitation threshold that will exclude similar fractions of precipitation volumes and isotope samples. In our case, the precipitation threshold of 0.1 mm h⁻¹ led to an exclusion of..."</u>

Referenced Literature

von Freyberg, J., Studer, B., and Kirchner, J. W.: A lab in the field: high-frequency analysis of water quality and stable isotopes in stream water and precipitation, Hydrol. Earth Syst. Sci., 21, 1721-1739, <u>https://doi.org/10.5194/hess-21-1721-2017</u>, 2017.