Reply to Anonymous Referee #2

RC C3722: Review of 12, 8035–8089, 2015 Received and published: 17 September 2015

This is an interesting study that would be of considerable value to readers of HESS. Understanding transit times in catchments is important for a range of endeavours and this study makes use of tritium, which in the southern hemisphere has become an invaluable tracer (due to the much lower bomb peak) for this purpose. The study has a really nice design whereby it is possible to use both short-term tracers (stable isotopes and Cl) and tritium – most studies have the data to use one of these approaches and few have used both.

We wish to thank Reviewer#2 for their thorough review of our work. All of their comments are addressed below and will be incorporated into a revised version of the manuscript (our replies to Reviewer#2 are in red).

While the quality of the data and interpretations are good, the paper is difficult to follow in places and the conclusions are not always well justified. Section 5 is long and could benefit from some statements explaining the aims of the various sections. Some of the material in Section 5 is also background material and data presentation; as this is a long section it would be good to remove that material and focus on what the important aspects are. Making that section clearer would improve the impact of the study.

This is a fair comment that is in agreement with the suggestions from Reviewer#1. Section 5 will be significantly reworked to improve clarity and conciseness. Several paragraphs will be moved to the Methods or Results sections, as recommended by both reviewers.

I don't particularly like lots of non-standard abbreviations in papers (while the authors will know these well, the reader often gets confused and too many makes the paper difficult to read). It would make the paper more intelligible to remove the TT's, TTD's, RTD's etc. I would also call it the "Mean Transit Time" as "Transit Time" gives the impression of a specific time rather than a range of times.

Following comments by Reviewer#1, we will be more consistent with acronyms in the new manuscript. We would like to keep the use of "TT" and "RT" as there are many occurrences all throughout the paper; however we agree to change "TTD" to "*TT distribution*" and "RTD" to "*RT distribution*" to limit the number of abbreviations used in the text.

Terminology – 18O (2H) are the tracers δ 18O (δ 2H) are the units of measurement. Thanks for this precision. We will be more consistent in the revised paper.

Specific Comments

Introduction

This section provides a good overview of the background to the study; however in places it is not clearly written. In the final version of the paper, try to make this section as clear as possible so that the reader gets a good idea of exactly what you are doing.

We are now aware that the introduction may appear unclear in places. We will try to deliver a clearer message.

I also have a few specific comments:

• Catchment transit time (rather than the streamflow transit time) is probably clearer

After a rapid search on different bibliographic databases, it indeed appears that "catchment transit time" is much more prevalent than "streamwater transit time". Thanks for the suggestion!

• The paragraph starting on line 23 of page 8037 seems out of place. It discusses details of the models while the next paragraph goes back to discussing more general aspects.

This paragraph will be moved later on in the introduction and slightly modified.

• Other issues with using Cl or stable isotopes as transit time indicators are that detailed catchment-specific input functions are needed (ideally weekly for several years) and such data are rare globally. Also use of these tracers typically gives a single transit time estimate whereas tritium can be used to estimate transit times at a range of streamflows.

These are all valuable comments; a sentence will be added in the introduction to emphasise these aspects: "An important issue with using $\delta^2 H$, $\delta^{18} O$ and/or chloride as TT indicators is that detailed catchment-specific input functions are needed (ideally at a weekly sampling frequency for several years), and such data are rare globally. More importantly, Stewart et al. (2010, 2012) criticised the use of these tracers (...)".

• Page 8040 middle paragraph. It might be good to make it clear that the reason that most studies have used the time series approach to estimate a single transit time is due to the bomb pulse problem. You mention the lower bomb pulse in the southern hemisphere in the previous paragraph and it would be good to reiterate it here.

Thanks for this suggestion; we will reiterate this aspect here: "Most of these studies had to assume stationarity of the observed system by deriving a unique estimate of TT or RT from ³H time-series data, in order to circumvent the bomb pulse issue. Benefiting from the much lower ³H atmospheric levels in the southern hemisphere, Morgenstern et al. (2010) were the first to (...)"

• Last sentence on Page 8040 is not clear (not clear what "but also in the limitations of using single 3H samples to calculate streamwater TTs" means)

This part of the sentence will be deleted in the revised manuscript.

Section 2

This section presents most of the relevant background information for the study. It would be helped by a few more specific details, for example "Climate in the region is humid subtropical with extremely variable rainfall, most of which falls from November to April. While Teviot Brook is a perennial stream, the distribution of discharge is uneven throughout the year" would more informative with some value for rainfall and discharge.

Information on rainfall and discharge variability will be included in Section 2.1: "mean annual precipitation is 970 mm (1994–2014 period), of which 76% falls from November to April." and "the mean annual discharge is 120 mm (1994–2014 period), with highest and lowest streamflow occurring in February (average 40 mm) and September (average 2 mm), respectively."

Some other comments:

• The end of Section 2.1 is a bit confused – the discussion alternates between details of the geology and information on the bore construction, it needs to be reorganised so that the information is grouped better.

The sequence will be amended to create better flow in writing. Information will be ordered as follows: (1) streambed morphology; (2) geology of the alluvium; (3) geology of the sedimentary bedrock; (4) hydraulic gradients and bore details.

• In Section 2.2 you discuss the recent rainfall but given that the transit times are likely to be longer than a few years, the longer-term average rainfall is also important and should be specified.

As per a previous comment, the long-term average rainfall will be added earlier in Section 2.1.

Section 3

• Section 3.1 not clear what "Streamwater and groundwater samples were collected... ...following the same sampling scheme as the rainfall samples (Fig. 1)" means (Fig. 1 is a map not a description of the sampling methodology. The term "*sampling scheme*" will be replaced by "*sampling design*" and the reference to Fig.1 will be deleted.

• The statement (page 8044) "A sample collected in August 2013 was excluded from the dataset since it was analysed twice and yielded inconsistent results" is a concern – how many of your samples were repeated (and what was the agreement).

Unfortunately this sample was the only one to be repeated, because it clearly appeared as an outlier in the first sample run (${}^{3}\text{H} = 1.51 \text{ TU}$). We are much more confident with the result of the second analysis (${}^{3}\text{H} = 1.37 \text{ TU}$), however without additional examination we are unable to totally rule out the first measurement. In a conservative approach we preferred to exclude the sample altogether.

• Section 3.1. Make sure that you list the uncertainties for all the analytical techniques, you have it for some not for others.

The uncertainties related to ionic concentration measurements will also be provided.

• There is a potential problem with the use of digital filters and chemical mass balance (end of Section 3.2.1). Digital filters separate baseflow and quickflow BUT importantly the baseflow is all delayed sources of water (eg bank return flow, interflow, groundwater inputs etc); the Nathan & McMahon paper discusses this. Chemical mass balance probably partitions interflow and bank return flow into the event water component (see discussion in McCallum et al. 2009, Water Resour. Res., 46, W07541, doi:10.1029/2009WR008539 and Cartwright et al. 2014, Hydrol. Earth Syst. Sci., 18, 15–30, 2014, doi:10.5194/hess-18-15-2014). While it is good to integrate these techniques into the study, you need to consider exactly what they tell you. I'd suggest only incorporating one of these (perhaps the CMB as it is a chemical technique that is easier to compare with your geochemical data).

Very interesting comment, thank you. We agree to integrate only the tracer-based hydrograph separation method to the final version of the paper. A short discussion will be added that addresses this point: "The use of a chemical mass balance approach to partition streamflow was preferred over recursive digital filtering (Nathan and McMahon, 1990), because the former method is less likely to include delayed sources, such as bank return flow and/or interflow, in the older water component (Cartwright et al., 2014)."

• Section 3.2.2. With the explanation of the LPM equations, it would be clearer if they were written out in full (ie with the decay term) and then you explain that that term is not needed for the stable isotopes. This way it is clearer where in the equation the decay term fits.

The radioactive decay term will be added to equations 2 and 3 as suggested.

Section 4

• Is there any reason that you need to present data even in a summary table that you don't use? If you are going to present these data, you need to say more about it than "there are some extra data in a table" which tells us little about the data is and why it is important.

As it is not essential to the paper, this supplement will not be included in the final version of the manuscript. Interested readers will still be able to retrieve data from the paper published in HESSD.

• Section 4.1. d2H values should be quotes as whole numbers and d18O values to 1 decimal place in accordance with their precision.

OK, this will be modified.

• Some of the material that appears in Section 5 (eg the variation of stable isotopes and Cl in rainfall) are descriptive and would be better in this section.

Section 5 will be significantly rearranged, with paragraphs belonging to the Results being removed from it.

Section 5

This section goes through the data in a logical manner, but in several places you need clearer / fuller explanations to be convincing. There is a lot in this section and it is not always easy to follow, for example you use different LPM models for the young and old water fractions (Sections 5.1 & 5.3) and reading through Section 5.5 it is not clear whether you need another water store (water from the sedimentary aquifer) as well as the quickflow component and water from the alluvial sediments. I think that I agree with most of what is in this section but it is difficult to follow and I'd suggest re-ordering this material as follows:

1. Firstly set up the conceptual model. Currently you introduce information such as the changes in Fe concentrations late in this section to support the conceptualisation, but they really are what allow you to conceptualise the system in the first place.

2. Follow the conceptualisation with the discussion of the young and old water modelling; in this way it makes more sense as the reader has a clear picture of what the system looks like.

3. Try to avoid general comments in this section (it is long enough as it is). For example the comments on stable isotopes at the end of Section 5.1 belong in the introduction and are distracting here.

4. Do more to lead the reader through each section. For example you talk about correlations in several of the sections and while you describe whether correlations exist, you never really make it clear what the purpose of assessing the correlations is.

A lot of thought has gone into interpreting the data but a reader not familiar with tritium and LPM's would find it hard to follow, which lessens the impact of the study.

All these comments relate to a rearrangement of the Discussion. On the basis of Reviewer#2's suggestions, Section 5 will be substantially reworked in order to make it easier to follow for the readership. In particular, we will outline the conceptual framework as an introduction to the section; move several paragraphs to the Results; elaborate on the choice of different lumped parameter models; and, where possible, shorten some of the information.

Some other specific comments:

• Page 8050. Why are the stable isotope ratios in the rivers lower than in rainfall (does this hint at a problem with representative sampling of rainfall either in time or space)?

Here we should have specified that this observation applies to most, but not all, samples. During major precipitation events the isotopic signature in rainfall is more depleted than the one measured in streamwater. Essentially, the rainfall isotopic variations are dampened in the stream. The text will be modified to clarify: "In streamwater, isotopic ratios were generally lower for SI and S2 than for rainfall, which most likely reflects the predominant contribution of depleted rainfall to recharge."

• Page 8050. The assertion that evaporation increases Cl concentrations and changes the stables may be true, but looking at your data the change in stable isotopes implies evaporation of only a few% which would not change the Cl concentrations significantly (is that the case?). As with a number of the ideas in this section, you can be more rigorous in your discussion.

As seen in Fig. 4b, the enrichment of Cl at S2 is clearly much larger than that of the stable isotopes (an order of magnitude *vs* a few %). This is a common observation in Australian rivers and aquifers. It has been attributed to high rates of evapotranspiration, which concentrate cyclic salts in the unsaturated zone, hence increasing the salinity of soil water before it discharges into streams (e.g. among many others, Allison et al., 1990; Cartwright et al., 2004; Bennets et al., 2006). As a result, there are generally no clear relationships between stable isotope enrichment and Cl enrichment. This aspect will be briefly discussed in the updated version of the manuscript.

• Pages 8050-8051. Somewhere you need to justify your choice of LPM models. The exponential model is probably OK but many studies (eg the several by Morgenstern) use an exponential-piston flow model with the piston flow component used to simulate the recharge through the unsaturated zone. Discuss this a bit more fully.

In Section 5.1, the idea was to characterise the TTs of the younger water fraction, and two models were compared for this purpose, i.e. an exponential model and a bimodal exponential-dispersion model.

The exponential model was selected because it is especially suitable for interpreting catchment TTs: this distribution considers all possible flowpaths to the stream – the shortest flowpath having a TT equal to zero and the longest having a TT equal to infinity (e.g. Stewart et al., 2010). This was deemed appropriate given the highly responsive flow dynamics governing the Teviot Brook catchment. The addition of a piston flow component to the model would likely have been unsuccessful in capturing the prompt response of streamflow to rainfall inputs. This will be specified in the revised version of the paper.

When using 3 H as a tracer, the simulations are generally insensitive to the type of model chosen for the TT distribution: there is abundant literature that reports good agreement between exponential, exponential-piston flow and dispersion models calibrated to 3 H data (e.g. among many others Maloszewski et al., 1992; Herrmann et al., 1999; Stewart et al., 2007; Cartwright and Morgenstern, 2015). This aspect will also be evoked in the manuscript.

• There appears to be no attempt at error propagation. You could try sensitivity analyses based on:

- Propagation of analytical uncertainties for 3H (1)
- Assessing the uncertainties around the chemical mass balance (2)
- Comparing alternative lumped parameter models (3)

(1) The propagation of ³H analytical uncertainty on τ_o calculations has actually been carried out (see whisker plots in Figure 10).

(2) This is a good suggestion; the uncertainties related to the calculation of φ (chemical mass balance approach) will be estimated according to the method described in Genereux (1998), and then propagated to the calculation of $\tau_{o.}$ Figure 10 and the corresponding section of the Discussion will be modified accordingly.

(3) With regards to the suggestion of comparing alternative lumped parameter models, see comment above.

• Page 8059, line 8. Is this the case; the Morgenstern et al. (2010) paper does discuss young water inputs (see pg. 2029) and applied a binary model.

Unfortunately there is no such page number in Morgenstern et al. (2010). Our guess is that Reviewer#2 is referring to Figure 9c in that same paper (P2297), which presents a conceptual model with total catchment fluxes partitioned between an older water component or baseflow (76%) and a younger water component or quickflow (24%). Please note that the partitioning presented in that diagram is an average value which the authors have obtained by separating streamflow over a 6-year data series using a numerical filter (see P2295). However, this information has not been used to constrain the two fractions of a bimodal model as we did in our work. Furthermore, the only distribution used by Morgenstern et al. (2010) for TT calculations was an exponential piston flow model, which is not a bimodal distribution.

• Section 5.6. The section on evaporation impacts on tritium is superfluous (or could be dealt with in a sentence). Again in this section try to focus on the most important things, you don't have to discuss everything in detail. This bullet point will be substantially reduced in the final version.

Section 6

In this section try not to repeat the specific conclusions but to draw out the more general aspects of the study. Some of the discussion in Section 5.6. might be better in the conclusions. As with the other sections try to focus on what is most important.

The conclusion will be reworked and slightly condensed.

Figures

Figures 3 & 4 would be better with larger symbols and/or colour Figures 3 and 4 will be modified following the reviewer's recommendations (also pointed out by Reviewer#1).

Again, we acknowledge Reviewer#2 for their feedback. We will now focus on incorporating the reviewers' comments as well as any other comment that may arise in the discussion process.

References

Allison, G.B., Cook, P.G., Barnett, S.R., Walker, G.R., Jolly, I.D., Hughes, M.W., 1990. Land clearance and river salinisation in the western Murray Basin. J. Hydrol. 119, 1–20.

Bennetts, D.A., Webb, J.A., Stone, D.J.M., Hill, D.M., 2006. Understanding the salinisation process for groundwater in an area of south-eastern Australia, using hydrochemical and isotopic evidence. J. Hydrol. 323, 178–192.

Cartwright, I., Weaver, T.R., Fulton, S., Nichol, C., Reid, M., Cheng, X., 2004. Hydrogeochemical and isotopic constraints on the origins of dryland salinity, Murray Basin, Victoria, Australia. Appl. Geochem. 19, 1233–1254.

Cartwright, I., Gilfedder, B., Hofmann, H., 2014. Contrasts between estimates of baseflow help discern multiple sources of water contributing to rivers. Hydrol. Earth Syst. Sci. 18, 15–30.

Genereux D., 1998. Quantifying uncertainty in tracer-based hydrograph separations. Water Resour. Res. 34, 915–919.

Herrmann, A., Bahls, S., Stichler, W., Gallart, F., Latron, J., 1999. Isotope hydrological study of mean transit times and related hydrogeological conditions in Pyrenean experimental basins (Vallcebre, Catalonia). Integrated Methods in Catchment Hydrology — Tracer, Remote Sensing and New Hydrometric Techniques. IAHS Pub. 258, 101–110.

Maloszewski, P., Rauert, W., Trimborn, P., Herrmann, A., Rau, R., 1992. Isotope hydrological study of mean transit times in an alpine basin (Wimbachtal, Germany). J. Hydrol. 140, 343–360.