

Reply to Anonymous Referee #1

RC C3614: Review of the paper 'Time-series of tritium, stable isotopes and chloride reveal short-term variations in groundwater contribution to a stream' by Duvert et al.

Received and published: 11 September 2015

General comment

This paper uses stable isotopes of water, chloride and tritium as tracers to compute and analyse streamflow transit time (TT) and groundwater residence time (RT) dynamics in a subtropical catchment in Australia. Given the recent attention to the analysis of TT in different environments and the potential offered by a multi-tracer approach for these investigations, the paper is of certain interest for the readers of HESS. The paper is well written. The structure is logical (besides some movements and reorganization, see my specific comments below), and the plots are generally clear (but see comments). Overall, the data interpretation is sound and the conclusions are well supported by the data.

We would like to thank Reviewer#1 for their overall positive feedback on our paper. In the following we address each of their comments (our replies to Reviewer#1 are in blue).

Specific comments

-My major concern is about the sometime quite weak discussion in certain parts of Section 5 (especially 5.4). In general, the authors, should do a better job in comparing their results with those reported in previous literature on the topic, show similarities/dissimilarities in findings, and critically discuss these. Most of all, they should stress how their results go beyond the status quo and contribute to a better understanding of streamflow TT and groundwater RT in natural catchments. In this context, some sentences about the representativeness of the study catchment for the environmental and physiographic conditions of other catchment in subtropical climates would be appreciated.

Section 5.4 is essentially a description of how the results presented in Figure 10 were obtained. The results are then discussed in Section 5.5, and compared with Morgenstern et al. (2010) and Cartwright and Morgenstern (2015). To create a better flow of ideas in this part of the Discussion, both sections will be combined in the revised manuscript. Other changes will be made to other subsections of the Discussion; see also replies to Reviewer#2 on this aspect.

A few more references and context will be added to Section 5.3 when discussing the TT of baseflow samples: "*A number of studies were carried out in the last four decades that also used ^3H to assess TTs of the baseflow component to streams. For catchment areas in the range 10–200 km², TT estimates were between 3 to 157 years (n=39; median 12 years; data presented in Stewart et al. (2010) supplemented with later papers by Morgenstern et al. (2010), Kralik et al. (2014) and Cartwright and Morgenstern (2015)). While our results compare relatively well to the literature, estimates can vary greatly even within single catchments (e.g. Morgenstern et al., 2010). Also, all reported studies were conducted in temperate regions, our work being the first one carried out in a subtropical setting.*"

More generally, very few authors have looked at variations of the TTs of baseflow, and the result that the TT of the baseflow component is higher under higher flow conditions has simply not been reported before. This finding is, as admitted by the reviewer themselves, a rather counterintuitive outcome. We will try and emphasise more how dissimilar our results are relative to previous work, and how challenging they may be for catchment process understanding. In particular, the following sentence will be added in Section 5.5: "*Importantly, the finding that TTs of the old water component increased with increasing flow has not been reported before. Our results are in stark contrast with the previous observation by Morgenstern et al. (2010)...*"

-I suggest to move Fig. 2 after Fig. 3 and perhaps Fig. 6 after Fig. 7 for a more logical organization and presentation of results. I also recommend in my comment below to move other parts of the manuscript for a more consistent and fluent paper structure.

Figures will be reordered following these suggestions, thanks.

-In general, I suggest to define the acronyms and symbols in the early part of the manuscript (typically, the introduction) and then stick to it throughout the paper. So, please, define TT, RT, TTD, RTD at the beginning and then consistently use them. Analogously, be consistent in the use of the term 'tritium' or of its symbol ' ^3H ' (I recommend to define the symbol of tritium at the beginning and then consistently use it). The same holds for the stable isotopes of water.

We will make sure that acronyms are used consistently in the new version of the manuscript.

-8040, 28. Here, and in other parts of the manuscript, I think that the use of the term 'seasonal tracer' is not clear and confusing. Please, change it or clearly state why you use this notation.

We agree that a definition of what we call a seasonal tracer is needed. The following statement will be added here: "*seasonal tracers, i.e. tracers subject to pronounced seasonal cycles*".

-8043, 16. The authors never mentioned iron and silicon before in the manuscript, and they appear only in Table 4. Are they really important for the results? If so, they should be introduced earlier.

Fe may be an indicator of waters that originate from the sedimentary bedrock, as shown by previous work. Si may be an indicator for waters discharging from the igneous rocks located in the headwaters. This information will be presented in the Study Area section: *“the stream erodes into the fractured, silica-rich igneous rocks forming the headwaters”* and *“Duvert et al. (2015a; 2015b) reported high Fe concentrations and low ³H activities for some groundwaters of the sedimentary bedrock.”*

-8044, 7. Please note that the term ‘concentration’ correctly applies to ions (as chloride) but not to isotopes. For these, I suggest to use the term ‘isotopic composition’. When referring to both tracers at the same time, you could use ‘tracer signature’ or a similar notation.

Thanks for pointing this out. We will use the suggested terms in the revised paper.

-8050, 13-15. It’s not clear how the authors explain more negative isotopic values in stream water than in precipitation. Please, report more solid arguments to explain this observation.

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 S1 and S2 than for rainfall, which most likely reflects the predominant contribution of depleted rainfall to recharge.”*

-8050, 18. ‘evaporation trend’: was this expected when planning the sampling site? Does the difference in elevation between S1 and S2 support this hypothesis of evaporation? There could be some lateral inflow of enriched water deriving from ephemeral tributaries that are more prone to evaporation?

These are very relevant questions. Higher evaporation in the lowlands was indeed expected due to the geomorphology of the catchment, i.e. steep riverbed slope and high amount of shading by the riparian vegetation upstream vs. flatter slope and more exposed river downstream. The elevation gradient in itself is not thought to be responsible for the difference in isotopic signature between S1 and S2, however as supposed by Reviewer#1, the contribution of evaporated tributaries has very likely enhanced this difference. A sentence will be added to address this point: *“These results are in line with field observations, showing that the streambed at S2 was characterised by gentler slope and that lateral inflows from evaporation-prone tributaries may have contributed to streamflow at this location.”*

-8052, 15. It’s not clear why the G1 sample of October 2012 suggests that groundwater in the alluvial aquifer has a modern component. Please, explain better.

This will be clarified: *“The sample collected at G1 (...) suggests that alluvial groundwater contains a substantial modern component, because its ³H concentration was only slightly below that of modern rainfall.”*

-8053, 1-3. What are A2, A1 and B1? They were not introduced before. Are they different simulations scenarios? Please, specify.

The six input time-series that were used in the simulations are presented in Table 1. A sentence will be added in the Methods subsection 3.2.2 to introduce them in more detail.

-8053, 25-8054, 12. This part should be moved to the ‘Results’ section, it’s not a discussion but just a presentation of results.

The whole Discussion section will be reorganised, with several paragraphs moved to the Methods or Results sections, as recommended by the two reviewers.

-8054, 13-8055, 2. This part should be moved to the ‘Methods’ section.

See reply above.

-8055, 3-5. This part should be moved to the ‘Results’ section.

See reply above.

-8057, 19. See comment above about iron.

Additional information will be integrated in the Study Area section (see reply above).

-8057, 26. Typically, the term ‘antecedent wetness conditions’ refers to the combined soil moisture and shallow water table levels measured before the onset of an input water (rainfall or snowmelt) event. This is not the case, since only precipitation was used. So, I suggest to replace it with ‘antecedent precipitation’.

True, we will modify the text accordingly.

More conceptually, I'm not an expert in TT analyses but I find counterintuitive the increase of TT of old water fraction with the increase of antecedent precipitation. Can the author give a robust explanation for this behaviour?

We agree with Reviewer#1 that this result is counterintuitive, and we have already given an explanation for the behaviour, e.g. in Section 5.5: P8058 L15 – P8059 L7, or in the Abstract: P8036 L19–24. In brief, we suggest that deeper, older waters are flushed out shortly after major recharge events due to the pressure wave propagation that results from infiltrating water. At this stage of the project it is difficult to provide definitive interpretations of these observations, and further studies in the catchment might be better placed to develop a conceptual model with more confidence.

-8059,17-8060,2. This part should be moved to the next section (Limitations...).

This section will be reworked as well.

Minor comments and technical corrections

8036, 1-6. A link is missing between the concept about the major limitation and the temporal dynamics of TT. The authors could even remove the first two sentences and simply start with 'In this study. . .'

We would prefer to keep these two introductory concepts as they provide some important background to the study. The second sentence will be modified to better relate the two concepts: *"A major limitation to the accurate assessment of streamwater transit time (TT) stems from the use of stable isotopes or chloride as hydrological tracers, because these tracers are blind to older contributions. Yet, capturing the temporal dynamics in the older contribution TT is essential, because catchment processes are highly non-stationary."*

8037, 8. 'inputs': such as? Please, specify.

The sentence will be changed to: *"anthropogenic inputs such as fertilizers or herbicides"*.

8037, 12. 'recharge water'. Specify if you mean only liquid precipitation or also, as a term in a general context, snowmelt, glacier melt ect. Or state that given the climatic characteristic of the study area, you only mean rainfall (if this is the case).

We will add to the text: *"in rainfall-derived recharge water"*.

8037, 26. Here, and later in the manuscript: avoid using the '/' sign meaning 'or' because it could be confused with a ratio.

Thanks for this suggestion, the '/' will be replaced with 'or'.

8038, 17. Include a reference after 'highly non-stationary'.

"McDonnell et al. (2010)" will be added here.

8038, 18. Put a fullstop after 'time' and split the sentence in two.

We think this sentence is easily readable as a whole, and would prefer not to modify it.

8039, 4-5. Replace 'hydrogen and oxygen' with 'water'. Moreover, use the notation 'delta' when referring to the isotopic measurements, but not in a general context as here.

OK.

8040, 13. The acronym 'RT' was not defined before.

'RT' was actually defined before, see P8038 L14.

8041, 3-9. See my specific comment above about the non-consistent use of TT, RT and 3H.

As mentioned before, acronyms will be used consistently in the modified manuscript.

8042, 11 and 13. Replace 'was' with 'were' ('data' is plural).

OK.

8042, 19. Fig. 2 should be cited before Fig. 3. In this case, for logical reasons, I suggest to move the current Fig. 2 after the current Fig. 3.

Figures 2 and 3 will be swapped.

8043, 20. Please, specify the version, since there is quite some differences between earlier and newer generation of LGR isotope analysers. Moreover, since the author are talking about typical analytical error, they should mention if any lab procedure to achieve the maximum accuracy and precision (see, for example, Wassenaar et al., 2014) and to minimize the memory effect (see Penna et al., 2012 for both commercially available laser isotope analyzers, see van Geldern and Barth, 2012 for only one brand) was applied. Particularly, the first two reported references could be cited here.

Penna, D., Stenni, B., Šanda, M., Wrede, S., Bogaard, T.A., Michelini, M., Fischer, B.M.C., Gobbi, A., Mantese, N., Zuecco, G., Borga, M., Bonazza, M., Sobotková, M., Čejková, B., Wassenaar, L.I., 2012. Technical Note: Evaluation of between-sample memory effects in the analysis of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of water samples measured by laser spectrometers. *Hydrology and Earth System Sciences* 16, 3925–3933. doi:10.5194/hess-16-3925-2012

Van Geldern, R., Barth, J.A.C., 2012. Optimization of instrument setup and post-run corrections for oxygen and hydrogen stable isotope measurements of water by isotope ratio infrared spectroscopy (IRIS). *Limnology and Oceanography: Methods* 10, 1024–1036. doi:10.4319/lom.2012.10.1024

Wassenaar, L.I., Coplen, T.B., Aggarwal, P.K., 2014. Approaches for Achieving Long-Term Accuracy and Precision of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for Waters Analyzed using Laser Absorption Spectrometers. *Environmental Science & Technology* 48, 1123–1131. doi:10.1021/es403354n

Thanks for this advice. The version of our LGR isotope analyser will be provided: “(TIWA-45EP)”. In addition, a reference will be added with the following text: “All isotopic compositions in this study are expressed relative to the VSMOW-standard. Between-sample memory effects were minimised by pre-running all samples and subsequently re-measuring them with decreasing isotopic ratios, as recommended in Penna et al. (2012). Replicate analyses indicate that analytical error was $\pm 1.1\%$ for $\delta^2\text{H}$ and $\pm 0.3\%$ for $\delta^{18}\text{O}$.”

8044, 5. Add ‘of water’ after ‘isotopes’
OK.

8044, Eq. 1. I understand what the term at the denominator is but, please, define it. 8044, Eq. 2. Please, define ‘g’.
Sure, ‘R’ will be defined. Also, please note that ‘g’ is already defined P8044 L15.

8046, 2. The reference is not appropriate, because that paper is a nice review paper that includes many different methods. I suggest to remove that reference and use a classical, more appropriate one such as Pinder and Jones (1969) or Sklash and Farvolden (1979).

Pinder G. F., Jones J. F., 1969. Determination of ground-water component of peak discharge from chemistry of total runoff. *Water Resources Research*, 5(2), 438–445, doi: 867 10.1029/WR005i002p00438.

Sklash M. G., Farvolden R. N., 1979. Role of groundwater in storm runoff. *Journal of Hydrology*, 43(1–4), 45–65, doi: 10.1016/0022-1694(79)90164-1.

Thank you for suggesting these references. “Sklash and Farvolden (1979)” will be cited instead of “Klaus and McDonnell (2013)”.

8047, 12. Include reference to Tukey filter.
OK.

8047, 21. Please, specify that the fit is a data fit.
OK.

8050, 5-9. Reformulate so that the explanation of the ‘amount effect’ and the reference come after the first mention at line 6.
This section will be altered and the reference to Dansgaard (1964) will be introduced earlier on.

8053, 24. Remove ‘(5-100 years)’.
OK. To be consistent, “(< 2 years)” will also be removed P8050 L3.

8057, 23. ‘unequivocal’ is a vague term. Please, remove and give n, R² and p-value.
This term will be replaced by “n=17, R² for power law fit = 0.47, p-value = 0.002”.

8058, 3. ‘positive relationship’: give n, R² and p-value.
The following information will be added: “n=20, R² for power law fit = 0.48, p-value = 0.001”.

8078, Table 5. In the caption, remove ‘as an age tracer’.
OK.

8079, Fig. 1. Remove all sentences but the first from the caption. That information should go to the text.
We consider that this is not fundamental information for the wider HESS audience, and for the sake of conciseness we prefer to provide these details in the figure caption only.

8081, Fig. 3. This figure would greatly benefit from the use of color. Moreover, change the legend using the delta notation for the isotopes.
Figure 3 will be modified following the reviewer’s recommendations.

8082, Fig. 4. This figure would greatly benefit from the use of color as well. Moreover, use different symbols for S2 and S3.

Figure 4 will be modified following the reviewer's recommendations.

8084, Fig. 6. What is A2?

Table 1 gives a description for A2. As previously mentioned, a sentence will be added in the Methods section to provide more details on the six input time-series.

8088, Fig. 10. Remove the reference, it's already reported in the text.

As per a comment from Reviewer#2, the recursive digital filter calculation will be removed from the revised manuscript.

Thanks again to Reviewer#1 for their time and constructive review.