Dear Dr. Pfister,

Thank you for your decision on our manuscript **hess-2015-320**. Please find below a revised version. As detailed in the replies to reviewers, all the reviewers' comments have been addressed in this new version. In particular, the main changes are related to:

- Rearrangement of the Introduction as recommended by Reviewer#2;
- Thorough reorganisation of the Discussion section as recommended by both reviewers, with:
    - Repositioning of several paragraphs to the Results, including details on model adjustment (new subsections in 4.1 and 4.2; new sections 4.3; 4.4; 4.5);
    - Addition of an introductory section to the Discussion to set up the conceptual framework (5.1);
    - Revision of all remaining sections;
    - Overall, the Discussion has been reduced from 4500 words to 3300 words.
- Rephrasing and shortening of the Conclusions section;
- Modification of Figures 3, 4 (colours added as requested) and 10 (error range due to chemical mass balance calculations added);
- Incorporation of all minor technical recommendations.

Please note that in the document below, all modified text is underlined; changes suggested by Reviewer#1 are marked in blue while changes suggested by Reviewer#2 are marked in red.

With my best regards,
Clément Duvert

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 ^{3}H to assess TTs of the baseflow component to streams. For catchment areas in the range 10–200 km^{2}, 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 them 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 ^{3}H 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 ^{3}H 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., Cˇejková, B., Wassenaar, L.I., 2012. Technical Note: Evaluation of between- sample memory effects in the analysis of δ2H and δ18O of water samples measured by laser spectroscopes. 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 δ18O and δ2H 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 ±1.1‰ for δ^2H and ±0.3‰ for $\delta^{18}O$.*"

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 com-ponent 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,* ***R^2 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, R^2 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.

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 δ18O (δ2H) 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 δ^2H, $\delta^{18}O$ 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* ^{3}H *time-series data,* ***in order to circumvent the bomb pulse issue. Benefiting from the much lower*** ^{3}H ***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}H = 1.51 TU). We are much more confident with the result of the second analysis (^{3}H = 1.37 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 S1 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 ^{3}H 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 τ_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.

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Time-series of tritium, stable isotopes and chloride reveal short-term variations in groundwater contribution to a stream

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Abstract

A major limitation to the accurate assessment of catchment 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. ~~Also, while catchment processes are highly non-stationary, the importance of temporal dynamics in older water TT has often been overlooked.~~ In this study we used lumped convolution models to examine time-series of tritium, stable isotopes and chloride in rainfall, streamwater and groundwater of a catchment located in subtropical Australia. Our objectives were to determine the different contributions to streamflow and their variations over time, and to understand the relationship between catchment TT and groundwater residence time. Stable isotopes and chloride provided consistent estimates of TT in the upstream part of the catchment. A young component to streamflow was identified that was partitioned into quickflow (mean TT ≈ 2 weeks) and discharge from the fractured igneous rocks forming the headwaters (mean TT ≈ 0.3 year). The use of tritium was beneficial for determining an older contribution to streamflow in the downstream area. The best fits were obtained for a mean TT of 16–25 years for this older groundwater component. This was significantly lower than the residence time calculated for groundwater in the alluvial aquifer feeding the stream downstream (≈ 76–102 years), emphasising the fact that water exiting the catchment and water stored in it had distinctive age distributions. When simulations were run separately on each tritium streamwater sample, the TT of old water fraction varied substantially over time, with values averaging 17±6 years at low flow and 38±15 years after major recharge events. This counterintuitive result was interpreted as the flushing out of deeper, older waters shortly after recharge by the resulting pressure wave propagation. Overall, this study shows the usefulness of collecting tritium data in streamwater to document short-term variations in the older component of the TT distribution. Our

results also shed light on the complex relationships between stored water and water in transit, which are highly nonlinear and remain poorly understood.

Keywords: groundwater age – catchment transit time – stream–aquifer interactions – Australia

1 Introduction

Catchment transit time (TT) can be defined as the time water spends travelling through a catchment, from infiltrating precipitation until its exit through the stream network (McDonnell et al., 2010). Because this parameter integrates information on storage, flow pathways and source of water in a single value, it has been increasingly used as a generic indicator of catchment dynamics (McGuire and McDonnell, 2006). Accurate quantification of TT is of prime importance for water resource management issues, in particular for the assessment of catchment sensitivity to anthropogenic inputs such as fertilizers or herbicides (e.g. van der Velde et al., 2010; Benettin et al., 2013), and for the provision of additional constraints on catchment-scale hydrological models (e.g. Gusyev et al., 2013). TT is estimated by relating the signature of a tracer measured in a sample taken at the outlet of a catchment to the history of the tracer input in rainfall-derived recharge water. Interpretation of TT data is often problematic because a single sample typically contains water parcels with different recharge histories, different flowpaths to the stream and thus different ages. This is exacerbated when the catchment is underlain by heterogeneous aquifers, as dispersion and mixing of different water sources can lead to very broad spectra of ages (Weissmann et al., 2002). Rather than a single scalar value, samples are therefore characterised by a TT distribution (~~TTD,~~ i.e. probability density function of the TTs contained in the sample). The residence time (RT) distribution ~~(RTD)~~ is another useful indicator that refers to the distribution of ages of water resident within the system, rather than exiting it. RT distributions are generally used to characterise subsurface water or deeper groundwater that is stored in the catchment.

~~Simple models called lumped-parameter models have been developed since the 1960s to interpret age tracer data for the assessment of TT distributions and RT distribution (Vogel, 1967; Eriksson, 1971; Maloszewski and Zuber, 1982). These models require minimal input information, and are based on the assumptions that the shape of the TT or RT distribution function is *a priori* known and that the system is at steady state. The relationship between input and output concentrations is determined analytically using a convolution integral, i.e. the amount of overlap of the TT or RT distribution function as it is shifted over the input concentration function. Some of the lumped models consider only the mechanical advection of water as driver of tracer transport (e.g. exponential model), while others also account for the effects of dispersion–diffusion processes (e.g. dispersion model). Non-parametric forms of RT distribution functions have recently been developed (Engdahl et al., 2013; Massoudieh et al., 2014a; McCallum et al., 2014), but they generally require a higher amount of input data.~~

In the last two decades, a great deal of effort has been directed to the determination of catchment TTs in a variety of streams and rivers worldwide (e.g. Maloszewski et al., 1992; Burns et al., 1998; Soulsby et al., 2000; Rodgers

et al., 2005; Dunn et al., 2010). Attempts have been made to correlate the TTs to catchment characteristics such as topography (McGuire et al., 2005; Mueller et al., 2013; Seeger and Weiler, 2014), geology (Katsuyama et al., 2010) or soil type (Tetzlaff et al., 2009; 2011; Timbe et al., 2014). Assessment of the relationship between ~~older~~ groundwater ~~residence time~~ RT and catchment TT has also been undertaken occasionally (~~Stewart and McDonnell, 1991;~~ Matsutani et al., 1993; Herrmann et al., 1999; Reddy et al., 2006~~; Muñoz-Villers and McDonnell, 2012~~). Because catchment storage is highly non-stationary, catchment TTs are known to vary over time (McDonnell et al., 2010), yet the importance of temporal dynamics in TT distributions has been overlooked until recently. One of the reasons is that this non-stationarity is not accounted for in the models commonly used in catchment TT research. In the last five years, an ever-growing number of studies has transferred its focus to assessing dynamic TT distributions (Hrachowitz et al., 2010; 2013; Roa-García and Weiler, 2010; Rinaldo et al., 2011; Cvetkovic et al., 2012; Heidbüchel et al., 2012; 2013; McMillan et al., 2012; Tetzlaff et al., 2014; Birkel et al., 2015; van der Velde et al., 2015; Benettin et al., 2015; Harman, 2015; Klaus et al., 2015a; Kirchner, 2015). Most of these studies agreed on the importance of considering storage dynamics, because the RT distribution of storage water and the TT distribution of water transiting at the outlet of the catchment are likely to be very different. Concurrently to these recent advances in catchment hydrology, groundwater scientists have also developed new theoretical bases for the incorporation of transient conditions in RT distribution functions (Massoudieh, 2013; Leray et al., 2014). Nonetheless, the determination of time-variant TT and RT distributions requires data-intensive computing, which still largely limits their use in applied studies (Seeger and Weiler, 2014).

A simple, yet still widely used alternative to more sophisticated models is the lumped-parameter modelling approach, which has been developed since the 1960s to interpret age tracer data ~~for the assessment of TT distributions and RT distributions~~ (Vogel, 1967; Eriksson, 1971; Maloszewski and Zuber, 1982). Lumped models require minimal input information, and are based on the assumptions that the shape of the TT or RT distribution function is *a priori* known and that the system is at steady state. The relationship between input and output signatures is determined analytically using a convolution integral, i.e. the amount of overlap of the TT or RT distribution function as it is shifted over the input ~~concentration~~ function. Some of the lumped models consider only the mechanical advection of water as driver of tracer transport (e.g. exponential model), while others also account for the effects of dispersion–diffusion processes (e.g. dispersion model). Non-parametric forms of RT distribution functions have recently been developed (Engdahl et al., 2013; Massoudieh et al., 2014a;

93 McCallum et al., 2014), but again, these more recent approaches require a higher amount of input data, which
94 makes the standard lumped-parameter approach a method of choice for the time being.
95 Commonly used to determine TT distributions using such models are the stable isotopes of water (^{2}H and ^{18}O).
96 Because they are constituents of the water molecule itself, ^{2}H and ^{18}O follow almost the same response function
97 as the traced material, hence are generally referred to as "ideal" tracers. Another tracer that behaves relatively
98 conservatively and has been often used in the literature is chloride. An important issue with using ^{2}H, ^{18}O and/or
99 chloride as TT indicators is that detailed catchment-specific input functions are needed (ideally at a weekly
100 sampling frequency for several years), and such data are rare globally. More importantly, Stewart et al. (2010,
101 2012) criticised the use of these tracers to assess catchment TTs, arguing that TT distributions are likely to be
102 truncated when only ^{2}H and/or ^{18}O are used. In an earlier study, Stewart et al. (2007) reported differences of up
103 to an order of magnitude between the TTs determined using stable isotopes as compared to those determined
104 using tritium (^{3}H). Later works by Seeger and Weiler (2014) and Kirchner (2015) reinforced the point that
105 "stable isotopes are effectively blind to the long tails of TT distributions" (Kirchner, 2015). The effects of older
106 groundwater contributions to streamflow have largely been ignored until recently (Smerdon et al., 2012; Frisbee
107 et al., 2013), and according to Stewart et al. (2012), new research efforts need to be focused on relating deeper
108 groundwater flow processes to catchment response. Accounting for potential delayed contributions from deeper
109 groundwater systems therefore requires the addition of a tracer, such as ^{3}H, that is capable of determining longer
110 TTs ~~to the analysis of streamwater~~.
111 ^{3}H is a radioactive isotope of hydrogen with a half-life of 12.32 years. Like ^{2}H and ^{18}O it is part of the water
112 molecule and can therefore be considered an "ideal" tracer. Fractionation effects are small and can be ignored
113 relative to measurement uncertainties and to its radioactive decay (Michel, 2005). The bomb pulse ^{3}H peak that
114 occurred in the 1960s was several orders of magnitude lower in the southern hemisphere than in the northern
115 hemisphere (Freeze and Cherry, 1979; Clark and Fritz, 1997), and the ^{3}H concentrations of remnant bomb pulse
116 water have now decayed well below that of modern rainfall (Morgenstern and Daughney, 2012). These
117 characteristics allow the detection of relatively older groundwater (up to 200 years) and, importantly, the
118 calculation of unique TT distributions from a single ^{3}H value, provided the measurement is accurate enough
119 (Morgenstern et al., 2010; Stewart et al., 2010). Other age tracers such as chlorofluorocarbons and sulfur
120 hexafluoride have shown potential for estimating groundwater RT (e.g. Cook and Solomon, 1997; Lamontagne
121 et al., 2015), however these tracers are less suitable for streamwater because of gas exchange with the
122 atmosphere (Plummer et al., 2001).

Long-term evolution of ^{3}H activity within catchments has been reported in a number of studies, both for the determination of RT in groundwater systems (e.g. Zuber et al., 2005; Stewart and Thomas, 2008; Einsiedl et al., 2009; Manning et al., 2012; Blavoux et al., 2013) and for the assessment of TT in surface water studies (Matsutani et al. 1993; Stewart et al., 2007; Morgenstern et al., 2010; Stolp et al., 2010; Stewart, 2012; Gusyev et al., 2013; Kralik et al., 2014). Most of these studies had to assume stationarity of the observed system by deriving a unique estimate of TT or RT from ^{3}H time-series data, in order to circumvent the bomb pulse issue. Benefiting from the much lower ^{3}H atmospheric levels in the southern hemisphere, Morgenstern et al. (2010) were the first to use repeated streamwater ^{3}H data to assess the temporal variations in TT distributions. Using simple lumped parameter models calibrated to each ^{3}H sample, they established that catchment TT was highly variable and a function of discharge rate. Following the same approach, Cartwright and Morgenstern (2015) explored the seasonal variability of ^{3}H activities in streamwater and their spatial variations from headwater tributaries to a lowland stream. They showed that different flowpaths were likely to have been activated under varying flow conditions, resulting in a wide range of TTs. To the extent of our knowledge, shorter term (i.e. less than monthly) variations in streamwater ^{3}H and their potential to document rapid fluctuations in the older groundwater component in streamflow have not been considered in the literature.

This study investigates the different contributions to streamflow in a subtropical headwater catchment subjected to highly seasonal rainfall, as well as their variations over time. The overarching goal is to advance our fundamental understanding of the temporal dynamics in groundwater contributions to streams, through the collection of time-series of seasonal tracers, i.e. tracers subject to pronounced seasonal cycles (^{2}H, ^{18}O and chloride), and ^{3}H. We postulate that ^{3}H time-series data may provide ~~further~~ insight into the nonlinear processes of deeper groundwater contribution to rivers, ~~but also in the limitations of using single ^{3}H samples to calculate catchment TTs~~ Specifically, the questions to be addressed are:

(i) Can simple lumped models provide reliable estimates of catchment TTs in catchments characterised by intermittent recharge and high evapotranspiration rates?

(ii) Can short-term variations in older (5–100 years) groundwater contributions be captured by ^{3}H time-series data?

(iii) How dissimilar are the RT of aquifers adjacent to streams (i.e. storage water) and the TT of streamwater (i.e. exiting water)?

2 Study area

2.1 Physical setting

The upper Teviot Brook catchment is located southwest of Brisbane (Southeast Queensland, Australia), with its headwaters in the Great Dividing Range (Fig.1). It covers an area of 95 km^2, and elevations range between 160 and 1375 metres above sea level. Climate in the region is humid subtropical with extremely variable rainfall: ~~most of which falls from November to April~~ mean annual precipitation for the catchment is 970 mm (1994–2014 period), of which 76% falls from November to April. While Teviot Brook is a perennial stream, the distribution of discharge is uneven throughout the year: 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. The headwaters support undisturbed subtropical rainforest, while the valley supports open woodland and grassland.

The first sampling location (S1) is situated in a steep, narrow valley where the stream erodes into the fractured, silica-rich igneous rocks forming the headwaters. At this upstream location, boulders, gravel and sand constitute the streambed substrate as well as near-channel deposits. The second sampling location (S2) lies further downstream where the valley is flatter and forms a wide alluvial plain. At this downstream location the stream is incised into the alluvial deposits, which at G1 are composed of fine-grained material, i.e. mostly gravel and silty clay. Underlying the alluvial deposits is a sedimentary bedrock formation (Walloon Coal Measures) consisting of irregular beds of sandstone, siltstone, shale and coal, some of which contain significant volumes of groundwater. Duvert et al. (2015a; 2015b) reported high Fe concentrations and low ^3H activities for some groundwaters of the sedimentary bedrock.

Hydraulic gradient analysis indicates that the alluvium mostly drains into the stream; hydrochemical and isotopic data also revealed a close connection between the alluvium and surface water in the Teviot Brook catchment (Duvert et al., 2015a). Borehole G1 is 13.9 m deep and it is screened from 12.3 m to its bottom, i.e. entirely within the alluvial stratum. The horizontal distance between G1 and S2 is 60 m.

2.2 Catchment hydrology

The monitoring period spans over two years, from mid-2012 to late 2014. Daily streamflow data were obtained from a gauging station operated by the Queensland Department of Natural Resources and Mines (Croftby station; 145011A) and located 2 km upstream of S2 (Fig.1). Daily precipitation data were available at three rain gauges spread across the catchment and operated by the Australian Bureau of Meteorology. Average

precipitation was calculated from the three records using the Thiessen method. Annual precipitation amounted to 1010 mm in 2012, 1190 mm in 2013 and 960 mm in 2014. The rainfall depths recorded in the headwaters were 100 to 250 mm/y higher than those in the floodplain. The maximum daily rainfall amount was 275 mm and occurred in late January 2013, with a weekly value of 470 mm for this same event (Fig.2a). This intense episode of rainfall generated a daily peak flow of 137 $m^3 s^{-1}$ upstream of S2 (Fig.2b), which corresponds to a 22-year return period event at that station – calculated by fitting long-term data to a Galton distribution. Earlier work has shown that this major event contributed significantly to recharge of the alluvial and bedrock aquifers in the headwaters (Duvert et al., 2015a; 2015b). Another high flow event occurred in late March 2014, with a daily peak flow of 39 $m^3 s^{-1}$. Generally, examination of the hydrograph reveals that extended recession periods followed peak flows. Low flow conditions ($Q < 0.01$ $m^3 s^{-1}$) occurred towards the end of the dry season, i.e. approximately from November through to January (Fig.2b). The stream did not dry up during the study period although very low flow ($Q < 0.001$ $m^3 s^{-1}$) occurred for 30 consecutive days in February–March 2014.

3 Methods

3.1 Sample collection and analysis

Bulk samples of precipitation were collected at R1 (Fig.1) at fortnightly to monthly intervals using a Palmex RS1 rainfall collector, which allows virtually evaporation-free sampling (Gröning et al., 2012). Streamwater and groundwater samples were collected at S1 and S2 (stream sampling locations) and G1 (alluvial aquifer) following the same sampling design as the rainfall samples ~~(Fig.1)~~. Samples at G1 were taken after measuring the water table level and purging a minimum of three casing volumes with a stainless steel submersible pump (Hurricane XL, Proactive). All samples were filtered through 0.45 µm membrane filters, and care was taken to seal the bottles and vials tightly to avoid evaporation.

Stable isotopes and chemical elements were measured for all samples at R1, S1, S2, and G1. ~~Tritium (^3H)~~ activity was determined at S2 for most samples, and at G1 for one sample. Chloride concentrations were measured using ion chromatography (ICS-2100, Dionex), while iron and silicon were measured using inductively coupled plasma optical emission spectrometry (Optima 8300, Perkin Elmer). Total alkalinity was measured by titrating water samples with hydrochloric acid to a pH endpoint of 4.5. Major ions were assessed for accuracy by evaluating the charge balance error, which was < 10% for all samples and < 5% for 93% of the samples. Samples were also analysed for ^2H and ^{18}O ~~oxygen ($\delta^{18}O$) and deuterium (δ^2H) stable isotopes,~~ using a Los Gatos Research water isotope analyser (TIWA-45EP). All isotopic compositions in this study are expressed

relative to the VSMOW-standard (δ notation). 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 ±1.1‰ for δ^2H and ±0.3‰ for $\delta^{18}O$. All these analyses were conducted at the Queensland University of Technology (QUT) in Brisbane. In addition, ^3H was analysed at the Australian Nuclear Science and Technology Organisation (ANSTO) in Sydney. Samples were distilled and electrolytically enriched 68-fold prior to counting with a liquid scintillation counter for several weeks. The limit of quantification was 0.05 tritium units (TU) for all samples, and uncertainty was ±0.06 TU. A sample collected in August 2013 was excluded from the dataset since it was analysed twice and yielded inconsistent results.

3.2 Tracer-based calculation of transit and residence times

3.2.1 Using stable isotopes of water and chloride

Mean TTs were determined through adjustment of a TT distribution function to observations of fortnightly input and output signatures (here the term 'signature' is meant to encompass either an ionic concentration or an isotopic composition). An input recharge function was initially computed from the measured input data that accounts for loss due to evapotranspiration (e.g. Bergmann et al., 1986; Stewart and Thomas, 2008):

$$C_r(t) = \frac{R(t)}{\bar{R}}\left(C_p(t) - \overline{C_r}\right) + \overline{C_r} \quad (1)$$

where $C_r(t)$ is the weighted input recharge signature at time t; $\overline{C_r}$ is the average recharge signature (taken at G1); $C_p(t)$ is the input rainfall signature; ~~and~~ $R(t)$ is the fortnightly recharge as calculated by the difference between precipitation and evapotranspiration; and $\bar{R}$ is the average recharge amount.

The weighted input was then convoluted to the selected TT distribution function (g) to obtain output signatures (Maloszewski and Zuber, 1982):

$$C_{out}(t) = [g * C_r](t) = \int_0^\infty C_r(t - t_e)\; g(t_e)\; e^{(-\lambda t_e)}\; dt_e \quad (2)$$

where t_e is time of entry; $C_{out}(t)$ is the output signature; $C_r(t)$ is the weighted input signature; ~~and~~ $g(t_e)$ is an appropriate TT distribution function; and $e^{(-\lambda te)}$ is the term that accounts for decay if a radioactive tracer is used (λ=0 for stable isotopes and chloride). In this study we used both the exponential and dispersion models; the reader is referred to Maloszewski and Zuber (1982) and Stewart and McDonnell (1991) for a detailed overview of TT distribution functions.

In some instances, two models were combined to represent more complex systems on the basis of our understanding of the catchment behaviour (Fig.3). This was to distinguish between a shallower and a deeper flow component with shorter and longer TT, respectively. Bimodal models were obtained by linearly combining two TT distributions:

$$C_{out}(t) = \varphi \int_0^\infty C_r(t - t_e)\ g_o(t_e)\ e^{(-\lambda t_e)}\ dt_e + (1 - \varphi) \int_0^\infty C_r(t - t_e)\ g_y(t_e)\ e^{(-\lambda t_e)}\ dt_e \quad (3)$$

where φ is the fraction of the older component ($0 < \varphi < 1$), and $g_o(t_e)$ and $g_y(t_e)$ are the TT distribution functions of the older and younger components, respectively (Fig.3). Bimodal distributions combined either two dispersion models or one exponential and one dispersion model. The mean TTs, noted τ, were then derived from the fitted distributions by calculating their first moment:

$$\tau = \int_0^\infty t\ g(t)\ dt \quad (4)$$

In the following the mean TT of the younger component is referred to as τ_y (subdivided into τ_{y1} and τ_{y2}), while the mean TT of the older component is referred to as τ_o, and the mean RT of storage groundwater is referred to as τ_r (subdivided into τ_{r1} and τ_{r2}) (Fig.3).

For chloride, the measured input and output series were highly dissimilar due to the significant effect of evaporative enrichment in soils. To get around this issue, a correction factor was applied to the predictions obtained using equations (2) and (3): $C_{out}(t)$ values were multiplied by $F = P/(P - ET)$ (i.e. ratio between precipitation and recharge over the preceding 12 months). The reasoning behind the use of this correction factor was that all chloride ions find their way through the soil, whereas much of the rainfall is evaporated off.

To estimate the fraction of older water that contributed to streamflow, a simple two-component hydrograph separation was carried out ~~(Klaus and McDonnell, 2013)~~ (Sklash and Farvolden, 1979) based on fortnightly data of each of the three seasonal tracers. This allowed obtaining time-varying values of φ:

$$\varphi(t) = \frac{\delta_{S1}(t) - \delta_{R1}(t)}{\overline{\delta_{G1}} - \delta_{R1}(t)} \quad (5)$$

where δ_{S1}, δ_{R1} and δ_{G1} are the tracer values of streamflow, rainfall and groundwater, respectively. ~~In addition, baseflow was numerically separated using the recursive digital filter described by Nathan and McMahon (1990) as a control for the tracer based partitioning results.~~ 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).

3.2.2 Using tritium

The occurrence of seasonal variations in rainfall ^{3}H concentrations has been widely documented (e.g. Stewart and Taylor, 1981; Tadros et al., 2014). These variations can be significant and have to be considered for achieving reliable estimates of TT distributions. Monthly ^{3}H precipitation data measured by ANSTO from bulk samples collected at Brisbane Aero were used to estimate the ^{3}H input function for the Teviot Brook catchment. Because Brisbane Aero is *ca*. 100 km northeast of Teviot Brook, the rainfall ^{3}H concentrations are likely to be significantly different between these two locations due to oceanic and altitudinal effects. According to Tadros et al. (2014), ^{3}H values for Toowoomba (i.e. located in the Great Dividing Range near Teviot Brook) were about 0.4 TU above those for Brisbane Aero for the period 2005-2011. Based on this work, an increment of +0.4 TU was applied to values measured at Brisbane Aero in order to obtain a first estimate of rainfall ^{3}H concentrations for Teviot Brook (input series A2 in Table 1). A second estimate was obtained by comparing the historical ^{3}H data between Toowoomba and Brisbane Aero for the period with overlap between the two stations, i.e. 1968-1982. All monthly values with precipitation > 100 mm, corresponding to rainfall likely contributing to recharge, were included in the analysis (n = 31). A scaling factor of 1.24 was derived from the correlation between the two stations (R^2 = 0.80). This factor was used to compute input series B2 (Table 1).

To account for losses due to evapotranspiration as rainfall infiltrates into the ground, a weighting procedure similar to the one reported by Stewart et al. (2007) was developed. Monthly ^{3}H recharge was estimated by subtracting monthly evapotranspiration from monthly precipitation, and weighting the ^{3}H rainfall concentrations by the resulting recharge. Instead of calculating single annual values, 6-months and 1-year sliding windows were used to obtain monthly values as follows:

$$C_i = \frac{\sum_{i-t}^{i} C_j \, r_j}{\sum_{i-t}^{i} r_j} \qquad (6)$$

where C_i is the monthly ^{3}H recharge for the ith month, C_j and r_j are the monthly ^{3}H precipitation and monthly recharge rate for the jth month, and t is 6 or 12 depending on the span of the sliding interval used. To avoid edge effects, a Tukey filter (Tukey, 1968) with coefficient 0.6 was applied to the sliding windows.

Input (recharge) and output (streamwater) ^{3}H concentrations were then related using the same convolution integral as the one used for stable isotopes (equations (2) and (3)), ~~except that the term $e^{(-\lambda te)}$ was added to account for radioactive decay of ^{3}H~~ with λ ~~is~~ the ^{3}H decay constant such that λ = 1.54 10^{-4} days^{-1}. To account for the uncertainty in input parameters and to assess the sensitivity of TT distribution calculations to the input function, four additional input series were derived from A2 and B2 (Table 1), and all six input series were ~~computed and~~ subsequently used in the calculations ~~(Table 1)~~. Least square regressions were used, and root

mean square errors (RMSE) were calculated to find the best data fit for each simulation using a trial and error process. All data processing and analyses were performed using Matlab version 8.4.0 (R2014b), with the Statistics toolbox version 9.1.

4 Results

~~This section provides only a summary of the obtained tracer data, and the reader can refer to the complete dataset in the supporting information.~~

4.1 Seasonal tracers in precipitation, streamwater and groundwater

Description. Stable isotope ratios and chloride signatures in precipitation were highly variable throughout the study period (Fig.2c; Fig.4). The δ^2H and $\delta^{18}O$ rainfall values ranged between -41‰ to +12‰ (average -12‰) and -6.5‰ to -0.1‰ (average -3.1‰), respectively, while chloride concentrations ranged between 0.6 to 3.2 mg L^{-1} (average 1.8 mg L^{-1}). Generally, the most significant rainfall events had isotopically depleted signatures. As an example, there was a considerable drop in all tracers during the January 2013 event (e.g. for δ^2H: decrease from -16‰ to -41‰; Fig.2c). The local meteoric water line derived from rainfall samples had an intercept of 15.8 and a slope of 8.4 (Duvert et al., 2015a), similar to that of Brisbane (Fig.4a). The stable isotope ratios measured in streamwater at S1 (Fig.2d) and S2 (Fig.2e) also covered a wide range of values, and followed similar temporal patterns to those for rainfall. However, the overall variations were less pronounced in streamwater with evident dampening of input signals. Average values were lower for S1 (δ^2H = -25‰ and $\delta^{18}O$ = -4.9‰) than for S2 (δ^2H = -20‰ and $\delta^{18}O$ = -3.7‰), both locations having lower average values than rainfall. All S1 samples aligned close to the meteoric water line, whereas most S2 samples plotted along a linear trend to the right of the line (Fig.4a). Chloride concentrations in streamwater ranged between 6.4 and 12.8 mg L^{-1} at S1, and between 35.1 and 111.1 mg L^{-1} at S2 (Figs 2d, 2e and 4b). At S2, higher chloride values were consistent with higher $\delta^{18}O$ values and *vice versa*, whereas there was a weaker correlation between the two tracers at S1 (Fig.4b). The fluctuations in stable isotopes and chloride in groundwater were considerably attenuated as compared to rain and streamwater (Fig.2f; Fig.4). The δ^2H, $\delta^{18}O$ and chloride values recorded at G1 tended to slightly decrease during the rainy season, although they stayed within the ranges -22±3‰, -3.9±0.4‰ and 60±10 mg L^{-1}, respectively (Fig.2f). Consistent displacement to the right of the meteoric line was observed for all G1 samples (Fig.4a).

Interpretation. The large temporal variability observed in rainfall isotopic and chloride records (Fig.2c) may be attributed to a combination of factors. First, ~~that include precipitation amount, but also~~ there was an apparent

seasonal cycle as values were higher in the dry season and tended to decrease during the wet season. These are well-known features for rainfall that can be related to the 'amount effect' (Dansgaard, 1964) where raindrops during drier periods experience partial evaporation below the cloud base, typical in tropical to subtropical areas (Rozanski et al., 1993). Second, more abrupt depletions of ^{2}H and ^{18}O occurred during significant precipitation events (Fig.2c), as has been reported in other parts of eastern Australia (Hughes and Crawford, 2013; King et al., 2015). 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 (Duvert et al., 2015a). Also, the position of S1 and S2 samples relative to the meteoric line (Fig.4a) indicates that fractionation due to evaporation occurred at S2, because unlike those measured at S1, isotopic ratios measured at S2 followed a clear evaporation trend. Elevated chloride concentrations are further evidence of the occurrence of evaporative enrichment downstream, with values one order of magnitude higher at S2 than at S1 (Fig.4b). These results are in line with field observations, showing that the streambed at S2 featured a gentler slope and that lateral inflows from evaporation-prone tributaries may have contributed to streamflow at this location. It can also be noted that the enrichment of chloride at S2 was much higher than that of stable isotopes (Fig.4b). This is a common observation in Australian catchments, largely attributed to high rates of evapotranspiration that concentrate cyclic salts in the unsaturated zone, thereby increasing the salinity of subsurface water before it discharges into streams (e.g. Allison et al., 1990; Cartwright et al., 2004; Bennets et al., 2006).

4.2 Tritium in precipitation, streamwater and groundwater

Description. The groundwater sample collected at G1 in October 2012 yielded a ^{3}H activity of 1.07±0.06 TU. Additional data was obtained from Please et al. (1997), who collected a sample at the same location in 1994. This earlier sample had an activity of 1.80±0.20 TU. The 20 samples of streamwater collected at S2 showed variable ^{3}H activities ranging between 1.16±0.06 and 1.43±0.06 TU (Fig.5).

In order to estimate a ^{3}H input signal for the Teviot Brook catchment, several precipitation time-series were calculated from Brisbane Aero monthly ^{3}H dataset, as detailed in Table 1. Recharge time-series were then derived from these precipitation time-series using equation (6). An example of the calculated monthly precipitation and recharge time-series for the 2003–2014 period is presented in Fig.6 for scenario A2. The ^{3}H activity in rainfall showed considerable month-to-month variability, with values ranging between 1.1 and 6.4 TU for A2, but most of the rainfall events contributing to recharge (i.e. for which monthly precipitation prevailed over monthly evapotranspiration; red circles in Fig.6) remained in the narrower range 1.5–2.5 TU.

Interpretation. The ^{3}H activity in rainfall showed considerable month-to-month variability, with values ranging between 1.1 and 6.4 TU for A2 (Fig.6). Winter (dry season) values generally were higher than summer (wet season) values, consistent with results from Tadros et al. (2014). Among the 20 ^{3}H values obtained at S2, higher values tended to coincide with higher flow conditions, although it was not systematic (Fig.5). For instance, the sample collected in January 2013 under low flow conditions yielded 1.35±0.06 TU; by contrast, the sample collected in April 2014 during the falling limb of a major runoff event yielded 1.19±0.06 TU, i.e. among the lowest values on record. Kendall's rank correlation and Pearson's coefficients were calculated between the ^{3}H measurements in streamwater and other hydrological, hydrochemical and isotopic variables (Table 2). ^{3}H activity was not significantly correlated with any of the other variables. Unlike in Morgenstern et al. (2010) and Cartwright and Morgenstern (2015), there was no strong linear relationship between flow rate and ^{3}H activity in the stream. The lack of strong correlation between ^{3}H and variables such as antecedent wetness conditions and the number of days since the last high flow event occurred, implies that more complex mechanisms governed the short-term fluctuations of ^{3}H in streamwater.

4.3 Residence time estimate for storage water

The sample collected at G1 in October 2012 (^{3}H = 1.07±0.06 TU) suggests that alluvial groundwater contains a substantial modern component, because its ^{3}H concentration was only slightly below that of modern rainfall. An earlier ^{3}H value reported by Please et al. (1997) was re-interpreted and combined with our more recent measurement to provide additional constraints on the ~~residence time (~~RT~~)~~ at G1. Two steady-state models were adjusted to the data points. The first model to be tested was a unimodal dispersion model while the second one was a bimodal exponential–dispersion model. For the bimodal model, the mean RT of younger components τ_{r1} was constrained to one year, and the fraction of younger water was constrained to 57% as these parameters provided best fits on average.

Results for both models are presented in Table 3 and the two fits using A2 as an input function are shown in Fig.7. As expected, mean RTs varied as a function of the input function chosen: values were generally lowest with A1 and B1 and highest with B3. Both models provided reasonably good fits, although for all simulations the bimodal distribution described more accurately the measured data (median RMSE 0.04 TU *vs* 0.20 TU; Table 3). Unimodal distributions had τ_r ranging between 40 (using A3 as input series) and 62 years (using B2 as input series), with a standard deviation of 7 years among all simulations. The older water fraction of bimodal models had τ_{r2} between 76 (using A1 as input series) and 102 years (using B3 as input series), with a standard deviation of nine years.

4.4 Transit time estimates using seasonal tracers

Lumped parameter models were adjusted to the stable isotope and chloride time-series at S1. Due to the limited number of fortnightly data, all values were included in the analysis, i.e. samples collected under both low baseflow and higher flow conditions. Two models were tested and compared for this purpose, a unimodal exponential model and a bimodal exponential–dispersion model (Table 4; Fig.8).

While both models provided reasonably low RMSE, unimodal models were less successful in capturing the high-frequency variations observed in output measurements (e.g. lowest values in late January and late February 2013; blue lines in Fig.8). All three tracers yielded comparable exponential TT distribution functions, with τ_y ranging between 65 and 70 days (Table 4). The bimodal models provided slightly more satisfactory fits for all tracers (black lines in Fig.8), with lower RMSE overall. Bimodal TT distribution functions derived from data at S1 had a younger fraction (27%) with τ_{y1} between 14 and 16 days, and an older fraction (73%) with τ_{y2} between 113 and 146 days (Table 4) depending on which tracer was used.

Calibration was also carried out on the tracer time-series collected at S2 and following the same procedure (Table 4). When considering a unimodal exponential distribution, all three tracers yielded comparable TT distribution functions, with τ_y ranging between 71 and 85 days, which was slightly longer than the mean TTs calculated at S1. When considering a bimodal exponential–dispersion distribution, the younger fraction had τ_{y1} of 23 to 24 days while the older fraction had τ_{y2} of 99 to 109 days (Table 4).

4.5 Transit time estimates using tritium

4.5.1 Model adjustment to low baseflow samples

A lumped parameter model was fitted to the six ^3H samples that were taken under low baseflow conditions, i.e. $Q < 10^{-2}$ m^3 s^{-1}. The model chosen for this purpose was a bimodal exponential–dispersion model; ~~that would reflect (i) the younger contribution from the headwaters (quick flow + soil water + discharge from fractured igneous rocks) as identified in Section 4.3, and (ii) an older groundwater contribution (alluvial water + potentially bedrock seepage) to be determined. This older fraction may originate from the stored groundwater as identified in Section 5.2.~~ the fitting procedure was as follows:

- The dispersion parameter of the older component was loosely constrained to around 0.3 in order to mimic the shape of the TT distribution identified at G1 (Section 4.3). The old water fraction φ was constrained to 82%, i.e. the average value obtained for the six baseflow samples using tracer-based hydrograph separation following equation (5).

- Initial simulations were run using the six input series with no further model constraint. For the six scenarios, τ_y consistently converged to 0.33±0.08 year.

- All models were then re-run while adding the additional constraint as noted above, so that the only parameter to be determined by fitting was τ_o.

Figure 9 provides an example of the adjustment using A2 as input ^{3}H function. Reasonably good fits were obtained for all simulations (0.14 TU < RMSE < 0.16 TU), with τ_o between 15.8 and 24.5 years, average 20.1±3.9 years (Table 5).

4.5.2 Model adjustment to single tritium values

Unlike for rainfall ^{3}H values where high temporal variability was observed, the derived time-series for recharge was relatively constant over the last decade (Fig.6). This characteristic in principle allows reliable assessment of catchment TTs with single ^{3}H measurements, providing the ^{3}H remaining in the hydrosphere is too small to cause ambiguous ages, as it is in the southern hemisphere (Morgenstern et al., 2010; Stewart et al., 2010). All 20 samples collected at S2 were fitted separately using the same ~~previously established~~ lumped model for each point, so that the only parameter to be determined by fitting was the TT of the old water fraction (τ_o). The model parameters were chosen according to the best fit obtained for baseflow samples (i.e. mean TT of young component τ_y 0.33 year, dispersion parameter of old component 0.3; Section 4.5.1). In addition, for each sample the fraction of old water φ was constrained to the value obtained using tracer-based hydrograph separation according to equation (5). Conceptually, this approach appeared more meaningful than another option that would have consisted in constraining τ_o and subsequently determining the old water fractions φ, because there was no indication that τ_o remained constant over time. Simulations were carried out for all three hydrograph separation tracers and all six input series, and the sensitivity of simulations to both the ^{3}H measurement uncertainty (±0.06 TU) and the error related to the hydrograph separation procedure were also calculated.

Time-series of τ_o were derived for each input function, and Fig.10 shows the results obtained with A2 as an input series. The old water fraction φ varied between 0.39 and 1, and while there was a good agreement between the three tracers, hydrograph separation based on chloride generally yielded lower variations in φ over time (Fig.10a). ~~The separation carried out using the recursive digital filter provided comparable results to those based on seasonal tracers.~~ Generally, the older component was lowest during high flow conditions and greatest during recession periods. The simulated τ_o values varied considerably over time, and variations exceeded the uncertainties related to measurement uncertainties, chemical mass balance calculation errors and input estimates (Figs 10b, 10c, 10d). δ^{18}O was the least accurate in evaluating the variations in τ_o (wider range for the red shaded

435 area in Fig.10c), while chloride was the most accurate despite less pronounced τ_o variations (narrower range for
436 the red shaded area in Fig.10d). Yet, all three tracers provided comparable results, with a consistent shift in
437 values either upwards or downwards. As a general rule, there was a negative correlation between φ and τ_o. When
438 using A2 as input function, τ_o fluctuated between 11.9 and 58.0 years (^2H; Fig.10b), 11.6 and 63.2 years (^{18}O;
439 Fig.10c) and 11.5 and 42.1 years (chloride; Fig.10d). For clarity purposes the τ_o values reported in the text do not
440 consider errors related to measurement uncertainty. Values were highest after the major recharge events that
441 occurred in January and February 2013, with τ_o between 26.8 and 63.2 years in late February, and in April 2014,
442 with τ_o between 28.3 and 55.1 years. They were lowest during periods undergoing sustained low flow such as in
443 September 2012 (τ_o between 11.6 years for ^{18}O and 13.1 years for ^2H) and in September 2013 (τ_o between 11.5
444 years for chloride and 11.9 years for ^2H). Of note is the timing of the highest τ_o value in late February 2013, i.e.
445 one month after the major recharge episode.

446 # 5 Discussion

447 ## 5.1 Conceptual framework

448 According to our conceptual understanding of the upper Teviot Brook catchment, we have partitioned
449 streamflow into two major components (Fig.3). The first end-member represents the contribution of younger
450 waters from rapid recharge through the highly fractured igneous rocks forming the mountain front, as outlined in
451 previous studies (Duvert et al., 2015a; 2015b). This younger component was further divided into (i) quick flow
452 and (ii) relatively delayed contribution of waters seeping from the rock fractures (Fig.3). We assume that the TTs
453 of the younger end-member can be accurately described through analysis of the seasonal tracers' signal
454 dampening. Waters originating from this component typically had low total dissolved solid (TDS)
455 concentrations, although high Si concentrations at high flow.
456 The second end-member we postulate contains older waters derived from the aquifer stores located in the
457 lowland section of the study area (Fig.3). Specifically, these are waters discharging from both the alluvial aquifer
458 and the underlying sedimentary bedrock aquifer. Although a distinction between the two groundwater stores
459 would be ideal, the lack of clear differentiation between both water types led us to consider one single "older
460 water" component. We assume that the TTs of the older end-member may be accurately described through ^3H
461 data analysis. The ^3H activities in both aquifers were generally lower than those in surface water; the
462 sedimentary bedrock aquifer had on average lower ^3H values than the alluvial aquifer, and waters from both

aquifers had varying but generally high TDS concentrations (Duvert et al., 2015a). Furthermore, higher Fe concentrations were observed in the sedimentary bedrock waters shortly after recharge (Duvert et al., 2015b).

In the next sections of the Discussion, a stepwise approach is followed to evaluate the accuracy of the conceptual model outlined above. In particular, the younger and older components in streamflow are assessed and discussed in Sections 5.2 and 5.3, respectively. Section 5.4 considers the relationships between the older streamflow component and groundwater stored in the catchment. The variations over time of the TTs of the older component τ_o are then quantified and elucidated (Section 5.5). Lastly, Section 5.6 addresses the limitations of the current methodology and raises new questions for future research.

~~In this section, a stepwise approach is followed to evaluate the different contributions to streamflow, as well as their temporal dynamics. First, the variations in seasonal tracers are discussed, and the seasonal tracer time-series are used to describe the TT of a The younger component to streamflow (Section 5.1). Second, the ^{3}H data collected in groundwater are interpreted in order to assess the RT of water stored in the alluvial aquifer τ_r (Section 5.2). Third, an older component in streamwater is identified through the use of ^{3}H (Section 5.3), and the variations over time of the TTs of this older component τ_o are further quantified (Section 5.4) and elucidated (Section 5.5).~~

5.2 Identification of a younger component ~~(< 2 years)~~ in streamflow ~~using seasonal tracers~~

[The introductory paragraph was moved to Results (see 4.1; *Interpretations*)]

[The next paragraphs were moved to a new Results section (4.4)]

The younger end-member was defined by adjusting lumped models to the seasonal tracer time-series (Section 4.4, Fig.8). Among all the TT distributions described in the literature, the exponential model was selected because it 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). Importantly, this distribution assumes heavy weighting of short flowpaths, which in our case may accurately replicate the prompt response of streamflow to rainfall inputs in the headwaters.

At S1, the bimodal distribution provided the most accurate simulations (Table 4), which lends support to the occurrence of two end-members contributing to streamflow at this upstream location. The first (exponential) component may reflect quick flow and subsurface waters feeding the stream (τ_{y1} between 14 and 16 days), while the second (dispersion) component may be attributed to the contribution of waters discharging from the highly fractured igneous rocks (τ_{y2} between 113 and 146 days; Fig.8). Results at S2 were also slightly more accurate when using a bimodal distribution, suggesting a dual contribution to streamflow at S2 as well. More importantly,

493 the fits for S2 were not as accurate as those for S1, regardless of the distribution and tracer used (Table 4). This
494 reflects the likely importance of other concurrent processes in the downstream section of the catchment. Among
495 them, evaporation may be a major limitation to applying steady-state lumped models at S2. It has been reported
496 that ^{18}O is generally more sensitive to the effects of evaporation than ^{2}H (Klaus and McDonnell, 2013; Klaus et
497 al., 2015b). However, in this study there were no significant differences between TT distributions derived from
498 the two stable isotopes. Calibration of the models on chloride measurements did not yield as accurate results as
499 those for stable isotopes at S1 and to a higher extent at S2, which may be attributed to the higher effects of
500 evaporative enrichment on chloride. Based on flux tracking methods, Hrachowitz et al. (2013) showed that
501 processes such as evaporation can result in considerable biases in TT distribution estimates when using chloride
502 as a tracer.
503 It is increasingly recognised that stable isotopes cannot provide realistic estimates of longer TT waters,
504 regardless of the lumped model used (Stewart et al., 2012; Seeger and Weiler, 2014; Kirchner, 2015). In this
505 study, it is very likely that older water (i.e. > 5 years) contributed to streamflow at S2 (see Section 5.3) but also
506 possibly at S1, and only using stable isotopes and chloride does not allow detection of such contribution.
507 Therefore the ages defined above should be regarded as partial TTs that reflect the short-term and/or
508 intermediate portions of the overall TT distribution for the system, i.e. τ_y rather than τ (Seeger and Weiler, 2014).

509 **5.3 Identification of an older component ~~(5–100 years)~~ in streamflow ~~using tritium~~**

510 [The introductory paragraph was moved to Results (see 4.2; *Interpretations*)]

511 [The next paragraphs were moved to a new Results section (4.5.1)]

512 The transfer function that provided the most accurate estimates of TT for the baseflow samples at S2 was an
513 exponential–dispersion model (Section 4.5.1). While other distributions could have been tested, there is a large
514 body of literature that has reported good agreement between exponential, exponential-piston flow and dispersion
515 models calibrated to ^{3}H data (e.g. Maloszewski et al., 1992; Herrmann et al., 1999; Stewart et al., 2007;
516 Cartwright and Morgenstern, 2015). The good fits obtained using this bimodal function (Fig.9; Table 5) confirm
517 that two major water sources contributed to streamflow at S2. It can be argued that the exponential component
518 captured all young contributions from upstream, i.e. quick flow + soil water + discharge from fractured igneous
519 rocks, as identified in Section 5.2 (τ_y = 0.33 years), while the dispersion component encompassed the delayed
520 groundwater flowpaths (τ_o between 15.8 and 24.5 years). This older contribution to streamflow may originate
521 from the alluvial aquifer, potentially supplemented by seepage from the bedrock storage, as discussed in Section
522 5.1.

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 km^2, 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, this work being the first one carried out in a subtropical setting.

5.4 Storage water and its relationships with the older streamflow component

~~**5.2 Identification of the residence time of storage water**~~

[The introductory paragraphs were moved to a new Results section (see 4.3)]

Simulations of groundwater RT using ^3H as a tracer are generally insensitive to the type of lumped parameter model chosen, given that ambient ^3H levels are now almost at pre-bomb levels (e.g. Stewart and Thomas, 2008). At G1, better fits were obtained for bimodal functions (Fig.7; Table 3). This may be interpreted as the probable partitioning of groundwater into one contribution of younger waters by diffuse recharge or flood-derived recharge ($\tau_{r1} \approx$ 1 year) coupled with a second contribution of older waters, potentially seeping from the underlying sedimentary bedrock aquifer ($\tau_{r2} \approx$ 80 to 100 years).

While the older component to streamflow as identified in Section 5.3 was characterised by relatively old waters with TT in the range 15.8–24.5 years, this contribution could not be directly related to the RT of storage waters ~~as defined in Section 4.2~~ (i.e. $\tau_o \neq \tau_r$). Despite the exclusive use of samples taken under low baseflow conditions to determine τ_o, the obtained values were significantly lower than the estimates of τ_{r2} for the alluvial aquifer (average 20.1±3.9 years *vs.* 88.7±9.3 years, respectively). This confirms that water stored in the catchment (resident water) and water exiting the catchment (transit water) are fundamentally different and do not necessarily follow the same variations, as recognised in recent work (e.g. Hrachowitz et al., 2013; van der Velde et al., 2015). Results from a dynamic model of chloride transport revealed that water in transit was generally younger than storage water (Benettin et al., 2015). Differences between RTs and TTs also indicate that the assumption of complete mixing was not met for the Teviot Brook catchment. This corroborates the findings from van der Velde et al. (2015), who established that complete mixing scenarios resulted in incorrect TT estimates for a catchment subjected to high seasonal rainfall variability. For instance, shallow flowpaths may be activated or deactivated under varying storage. Among the few studies that investigated the relations between catchment TT and groundwater RT based on ^3H measurements, Matsutani et al. (1993) reported that streamwater was

553 formed by a mixture of longer RT groundwater (19 years) and shorter RT soil water (< 1 year). Overall, more
554 work is needed to better define the two distributions and to assess how they relate to each other under non-
555 stationary storage conditions.

556 ~~5.4 Short-term variations in older water transit time as revealed by tritium in streamwater~~

557 [This section was moved to a new Results section (see 4.5.2)]

558 **5.5 Drivers of the variability in the older component transit time**

559 When fitting models to each ^{3}H value in streamwater, τ_o was found to vary substantially over time (Fig.10). In
560 order to better apprehend the factors influencing the variations in τ_o, the obtained values were compared to other
561 hydrological and hydrochemical variables, particularly the antecedent wetness conditions, dissolved Fe
562 concentrations and the old water discharge rate (Fig.11). Under sustained dry conditions (P_{15} < 5 mm), there was
563 no consistent relationship between τ_o and the amount of precipitation during the 15 days prior to sampling, with
564 τ_o ranging between 14.9 and 23.1 years (n = 3; Fig.11a). For higher values of P_{15} (i.e. $P_{15} \geq 10$ mm), there was a
565 positive ~~and unequivocal~~ correlation between the two variables (n = 17, R^2 for power law fit = 0.47, p-
566 value = 0.002). The TT of the old water fraction was lowest for P_{15} between 10 and 50 mm (τ_o 11.9 to 25.5
567 years), and it increased when antecedent precipitation increased (τ_o 25.6 to 58.0 years for P_{15} > 100 mm).
568 Generally, values averaged 17.0±5.6 years at low flow and 38.3±14.7 years after major high flow events. This
569 was in accordance with results from Fig.10, and suggestive of the predominant contribution of older alluvial
570 and/or bedrock waters shortly after recharge episodes. There was also a positive relationship between τ_o and Fe
571 concentrations at S2 (n = 20, R^2 for power law fit = 0.48, p-value = 0.001), with all the values > 0.2 mg L^{-1}
572 corresponding to τ_o > 30 years (Fig.11b). In contrast, no significant relationship was observed at S1, as Fe values
573 at this station ranged between < 0.01 to 0.96 mg L^{-1}. Duvert et al. (2015b) reported increasing Fe concentrations
574 after a major recharge event for some groundwaters of the sedimentary bedrock. The increase in streamflow Fe
575 might therefore be a result of enhanced discharge of these waters into the drainage network, which is coherent
576 with older τ_o values. However, other chemical parameters distinctive of the bedrock groundwaters did not
577 produce a characteristic signature in streamflow during high flow conditions. Or else, high Fe concentrations
578 may be simply due to higher weathering rates at higher flows, although this hypothesis disregards the high value
579 measured for the April 2014 sample (Fe = 4.15 mg L^{-1}) despite relatively low discharge (Q = 9.5 10^{-2} m^3 s^{-1}).
580 As discussed previously, a modification in storage due to a change in recharge dynamics may have activated
581 different groundwater flowpaths and hence water parcels with different RTs (Heidbüchel et al., 2013; van der
582 Velde et al., 2015; Cartwright and Morgenstern, 2015). When the rate of recharge was highest, flushing out of

583 waters located in the deeper, older bedrock aquifer may have been triggered by the resulting pressure wave
584 propagation. By contrast, the relatively younger τ_o observed during lower flow conditions may be attributed to
585 waters that originate from shallower parts of the alluvium and/or from subsurface layers. This is reflected in the
586 relationship between τ_o and Q_o, i.e. the portion of streamflow provided by the older component ($Q_o = Q*\varphi$;
587 Fig.11c). In this figure the groundwater end-member corresponds to τ_r (using the highest recorded Q_o through the
588 study period), while the baseflow end-member corresponds to the τ_o value calculated using the six baseflow
589 samples. The two end-members were linearly connected in an area that represents the extent of possible
590 fluctuations of τ_o, from lower old water contributions to higher old water contributions. The individual τ_o values
591 broadly followed this mixing trend (Fig.11c), which lends support to the assumptions that (i) the TT of the older
592 end-member may not be characterised by a single value but rather by a range of possible ages that fluctuate
593 depending on flow conditions, and (ii) during and shortly after higher flows, a near steady-state was reached in
594 which the TT of the old water fraction increased and approached the RT of stored water (i.e. $\tau_o \rightarrow \tau_r$). Overall,
595 the large scattering observed in Fig.11 suggests that many processes led to the variations in τ_o, and that these
596 processes were largely nonlinear.
597 Importantly, the finding that TTs of the old water component increased with increasing flow has not been
598 reported before. Our results are in stark contrast with the previous observation by Morgenstern et al. (2010) and
599 Cartwright and Morgenstern (2015) that ^{3}H-derived TTs were higher at low flow conditions and lower at high
600 flow conditions. However, these two studies did not account for a younger component to streamflow (i.e. φ was
601 effectively constrained to 1 for all samples), which may explain the disagreement with our results. Hrachowitz et
602 al. (2015) reported an increase in storage water RT at the start of the wet season in an agricultural catchment in
603 French Brittany, which they related to changes in storage dynamics (i.e. more recent water bypassing storage at
604 higher flow). The authors did not comment on potential changes in streamwater TT during the same period,
605 however.
606 We also recognise that the results reported here might be due to partially incorrect interpretation of the obtained
607 dataset: underestimation of the old water fraction φ during high flow events might be responsible for the
608 apparent positive correlation between Q_o and τ_o, although this is unlikely because the three seasonal tracers ~~and~~
609 ~~the recursive filter~~ yielded very similar flow partitions. Another potential bias in our calculations is the possible
610 lack of representation of the discharge from the fractured igneous rocks in the headwaters, which might
611 contribute significantly to the young component during high flow events. Such enhanced contribution might
612 result in slightly longer τ_y, hence shorter τ_o. Because no ^{3}H measurement was conducted at S1, this hypothesis

could not be tested further (see Section 5.2). More generally, our work emphasises the current lack of understanding of the role and dynamics of deeper groundwater contributions to streams, and suggests that more multi-tracer data is needed to better assess the TTs of the old water fraction. Our findings also indicate that the so-called "old water fraction" (also referred to as "pre-event water" or "baseflow component" in tracer studies; e.g. Klaus and McDonnell, 2013; Stewart, 2015) should not be regarded as one single, time-invariant entity, but rather as a complex component made up of a wide range of flowpaths that can be hydrologically disconnected – and subsequently reactivated – as recharge and flow conditions evolve.

5.6 Limitations of this study and way forward

Several assumptions have been put forward in this study that need to be carefully acknowledged. Firstly, there are limitations related to the use of seasonal tracers (i.e. stable isotopes and chloride):

(1) The lumped convolution approach used for the assessment of TTs of the younger contribution to streamflow relied on assumptions of stationarity. Such assumptions are very likely not satisfied in headwater catchments, particularly those characterised by high responsiveness and high seasonal variability in their climate drivers (Rinaldo et al., 2011; McDonnell and Beven, 2014). Unfortunately, the dataset obtained as part of this study did not enable characterisation of time-varying TT distribution functions, since this approach would require longer tracer records (e.g. Hrachowitz et al., 2013; Birkel et al., 2015) and/or higher sampling frequencies (e.g. Birkel et al., 2012; Benettin et al., 2013; 2015). Nonetheless, Seeger and Weiler (2014) recently noted that in the current state of research, the calculation of time-invariant TT distributions from lumped models still represents a useful alternative to more complex, computer-intensive modelling methods.

(2) Using tracers that are notoriously sensitive to evapotranspiration in environments where this process commonly occurs can be problematic. Hrachowitz et al. (2013) established that evaporation can severely affect the calculations of TTs when chloride is used as an input-output tracer. Although evapotranspiration was considered in our recharge calculations (equation (1)), a detailed analysis of catchment internal processes would be needed to verify whether evapotranspiration modifies the storage water RTs and subsequent catchment TTs. Using data from a catchment subjected to high rainfall seasonal variability, van der Velde et al. (2015) showed that younger water was more likely to contribute to evapotranspiration, which tended to result in longer catchment TTs.

(3) The partitioning of streamflow relied on the assumption that two main components contributed to streamwater, although this may not be the case at S2 because soil water may explain the higher chloride concentration and more enriched $\delta^{18}O$ observed at this location (Klaus and McDonnell, 2013; Fig.4). However,

643 we hypothesise that the occurrence of this third end-member would not significantly affect the calculation of τ_o,
644 because the TT of soil water is likely to be considerably shorter than that of the older streamflow component
645 (e.g. Matsutani et al., 1993; Muñoz-Villers and McDonnell, 2012).

646

647 Secondly, there are a number of limitations related to the use of ^3H:
648 (1) The most significant uncertainties were those related to the computed ^3H input functions. These may be
649 reduced by regularly collecting rainfall ^3H on site. The accuracy of ^3H measurements was another source of
650 uncertainty, and further improving analytical precision of ^3H activity in water samples may allow more rigorous
651 assessment of short-term TT variations (e.g. Morgenstern and Daughney, 2012).
652 (2) Changes in ^3H concentrations due to phase changes such as evaporation are commonly ignored ~~because they~~
653 ~~are usually considered negligible~~, however, high evaporation environments such as that of the lower Teviot
654 Brook catchment might significantly affect ^3H activity in streamwater. ~~If the fractionation factor for ^3H is twice~~
655 ~~that for ^2H, then an enrichment of 10‰ in δ^2H would correspond to an enrichment of 20‰ for ^3H. For a sample~~
656 ~~with an assumed ^3H activity of 1.30 TU, the measured value would then be 1.30 x 1.02 ≈ 1.33 TU. Such effect~~
657 ~~may have led to slight overestimations of the ^3H activity in low flow, high evaporation samples collected at S2.~~
658 Future research is needed to examine more thoroughly the potential interferences on ^3H due to evaporation
659 (Koster et al., 1989).
660 (3) While stationarity may be a reasonable assumption for groundwater, inter-annual variations in recharge can
661 affect RTs substantially (Manning et al., 2012). Further work aimed at providing additional constraints on RT
662 variability is therefore required, by routinely collecting age tracer data in groundwater. Massoudieh et al.
663 (2014b) showed that using multiple years of tracer records can allow more realistic quantification of the
664 uncertainty on RT distributions. Also uncertain in our work is the spatial representativeness of waters collected
665 at G1.
666 (4) Despite yielding longer TTs than seasonal tracers, the use of ^3H did not preclude the potential omission of
667 any older contribution (i.e. > 100 years) to the stream. Frisbee et al. (2013) argued that even studies based on ^3H
668 measurements might miss a significant part of the TT distributions rather than just their tail. In our case, the
669 likelihood of waters with much longer RTs seeping from the sedimentary bedrock could not be verified using ^3H
670 only. Other tracers that can capture older water footprints, such as terrigenic helium-4 (Smerdon et al., 2012) or
671 carbon-14 (Bourke et al., 2014) would need to be tested for that purpose.

(5) Another issue that has been raised recently is the potential aggregation biases affecting the calculation of TT distributions in complex systems (Kirchner, 2015). Based on the use of seasonal tracers, the author demonstrated that mean TTs are likely to be underestimated in heterogeneous catchments, i.e. those composed of subcatchments with contrasting TT distributions. A similar benchmark study should be undertaken for ^{3}H in order to verify whether TTs derived from ^{3}H measurements in heterogeneous catchments are also biased.

6 Conclusions

Based on time-series observations of seasonal tracers (stable isotopes and chloride) and ^{3}H in a subtropical mountainous catchment, we assessed the different contributions to streamflow as well as the variations in catchment TT and groundwater RT. Calibrating lumped parameter models to seasonal tracer data provided consistent estimates of TTs in the upstream part of the catchment, where evaporation was not a major process. ~~A young component to streamflow was identified that was partitioned into quickflow (mean TT ≈ 2 weeks) and discharge from the fractured igneous rocks forming the headwaters (mean TT ≈ 0.3 year).~~ In the downstream location, lumped models reproduced the tracers' output signals less accurately, partly because evapotranspiration complicated the input–output relationships, but also because of the increased hydrological complexity ~~due to higher heterogeneity~~ at this scale (i.e. interactions with deeper storage ~~alluvial~~ waters ~~and potentially deeper sedimentary bedrock waters~~).

In this context, the use of ^{3}H time-series was highly beneficial for (i) determining an older groundwater contribution to streamflow in the downstream area, and (ii) providing insight into the temporal variations of this old water fraction. ~~The best fits to ^{3}H baseflow values were obtained when considering a younger component with mean TT ≈ 0.3 year, which reflected the upstream contributions previously quantified, and an older groundwater component with mean TT ≈ 16–25 years. The latter value was significantly lower than the RT calculated for the shallow alluvial aquifer feeding the stream downstream (RT ≈ 76–102 years).~~ The old water fraction TT was significantly younger than the RT of groundwater stored in the catchment, ~~Such discrepancy between groundwater RT~~, which ~~and TT of the older component streamwater~~ outlines the necessary distinction between transit and storage waters in catchment process conceptualisation. ~~and the non-stationary catchment flow processes that govern the variations in TTs.~~ When simulations were run separately on each ^{3}H streamwater sample, the TT of old water fraction was found to vary substantially over time, with values averaging 17±6 years at low flow ~~(antecedent precipitation < 10 mm)~~ and 38±15 years after major recharge events ~~(antecedent precipitation > 100 mm)~~ – other parameters being held constant. These variations ~~were highly nonlinear and~~

~~broadly correlated with antecedent wetness conditions and recession dynamics~~ were interpreted as the activation of longer, deeper flowpaths carrying older waters when the rate of recharge was highest.

Overall, this study suggests that collecting high-resolution ^{3}H data in streamwater can be valuable to document short-term variations in the TT of old water fraction. If confirmed by further studies and corroborated by the use of other dating tracers, the occurrence of fluctuations in older contributions to streamflow may have important implications for water resource management and particularly contamination issues, because these fluctuations may control the time scales of retention and release of contaminants. It is therefore essential to collect longer-term experimental data that will contribute to identifying older groundwater contributions and to quantifying them with more confidence.

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973 2005.

974 Table 1. Description of the different ^{3}H input series computed for the Teviot Brook catchment

Input series	Description of input parameters
A1	Brisbane Aero ^{3}H values +0.3 TU (= A2 input series -25%)
A2	Brisbane Aero ^{3}H values +0.4 TU
A3	Brisbane Aero ^{3}H values +0.5 TU (= A2 input series +25%)
B1	Brisbane Aero ^{3}H values *1.20 TU (= B2 input series -95% confidence interval on the Toowoomba vs. Brisbane correlation)
B2	Brisbane Aero ^{3}H values *1.24 TU
B3	Brisbane Aero ^{3}H values *1.28 TU (= B2 input series +95% confidence interval on the Toowoomba vs. Brisbane correlation)

975

976 Table 2. Kendall's τ and Pearson's r correlation coefficients between tritium and other variables at S2.

Variable	r	τ
Mean daily discharge ($m^3 s^{-1}$)	0.47	0.06
δ^2H (‰)	-0.27	-0.06
$\delta^{18}O$ (‰)	-0.23	0.02
Cl (mg L^{-1})	-0.12	0.03
Si (mg L^{-1})	0.35	0.11
Alkalinity (mg L^{-1})	-0.32	-0.13
Fe (mg L^{-1})	0.25	0.11
Antecedent P in the last 15 days (mm)	0.32	-0.01
Last day with P > 2 mm (-)	0.11	0.03

977

978 No value was statistically significant at $p < 0.05$ for both tests.

Table 3. Results of model simulations of residence time for G1 using ^{3}H ~~as an age tracer~~.

Input series	Unimodal DM			Bimodal EM–DM			
	τ_r (years)	D_P	RMSE (TU)	τ_{r1} (years)	τ_{r2} (years)	D_P	RMSE (TU)
A1	46.9	0.70	±0.19	1	75.8	0.29	±0.02
A2	48.2	0.71	±0.18	1	82.9	0.30	±0.01
A3	39.8	0.71	±0.18	1	89	0.28	±0.03
B1	48.5	0.69	±0.22	1	86.8	0.30	±0.06
B2	61.6	0.70	±0.20	1	95	0.29	±0.05
B3	54.6	0.69	±0.21	1	102.5	0.29	±0.05

DM stands for dispersion model; EM–DM stands for exponential–dispersion model; D_P stands for dispersion parameter. For the EM–DM, τ_{r1} was constrained to 1 year, and the raction of younger water was constrained to 57%.

984 Table 4. Results of model simulations of transit time for S1 and S2 using ^{2}H, ^{18}O and chloride.

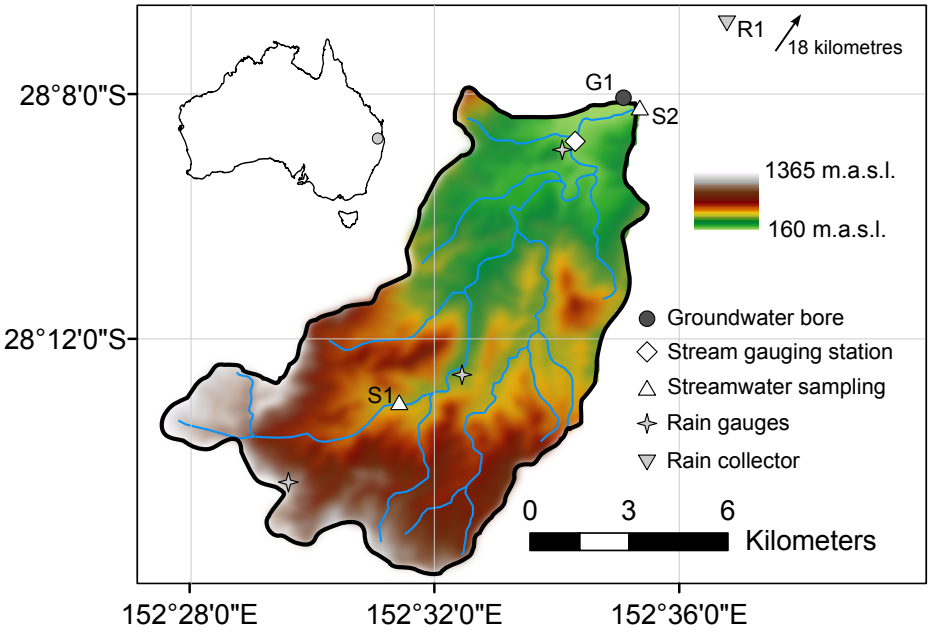
		Unimodal EM		Bimodal EM–DM		
Sampling location	Tracer	τ_y (days)	RMSE	τ_{y1} (days)	τ_{y2} (days)	RMSE
S1	oxygen-18	69	± 0.09‰	15	121	± 0.08‰
	deuterium	65	± 0.58‰	14	113	± 0.52‰
	chloride	70	± 0.28 mg L^{-1}	16	146	± 0.26 mg L^{-1}
S2	oxygen-18	85	± 0.16‰	23	109	± 0.16‰
	deuterium	71	± 0.75‰	24	99	± 0.72‰
	chloride	76	± 4.89 mg L^{-1}	24	106	± 4.68 mg L^{-1}

985
986 EM stands for exponential model; EM–DM stands for exponential–dispersion model. For the EM–DM, the
987 dispersion parameter of the second mode was 0.3 and the fraction of younger water was 27%.

Table 5. Results of model simulations of transit time for S2 under low baseflow conditions (i.e. daily Q < 0.01 $m^3 s^{-1}$), using ^3H ~~as an age tracer~~ and an exponential–dispersion model.

Input series	τ_o (years)	RMSE (TU)
A1	15.8	±0.15
A2	20.2	±0.15
A3	24.5	±0.15
B1	15.8	±0.14
B2	19.8	±0.16
B3	24.4	±0.16

The mean TT of younger components (τ_y) was constrained to 0.33 year, the dispersion parameter of older components was constrained to 0.3, and the ratio of older water was constrained to 82%.



994

995 Figure 1. Upper Teviot Brook catchment and location of sampling sites. The stream gauging station corresponds
996 to Teviot Brook at Croftby (145011A; operated by the Queensland Department of Natural Resources and
997 Mines). The rainfall gauges correspond to Wilsons Peak Alert (040876), Carneys Creek The Ranch (040490) and
998 Croftby Alert (040947), all run by the Bureau of Meteorology.

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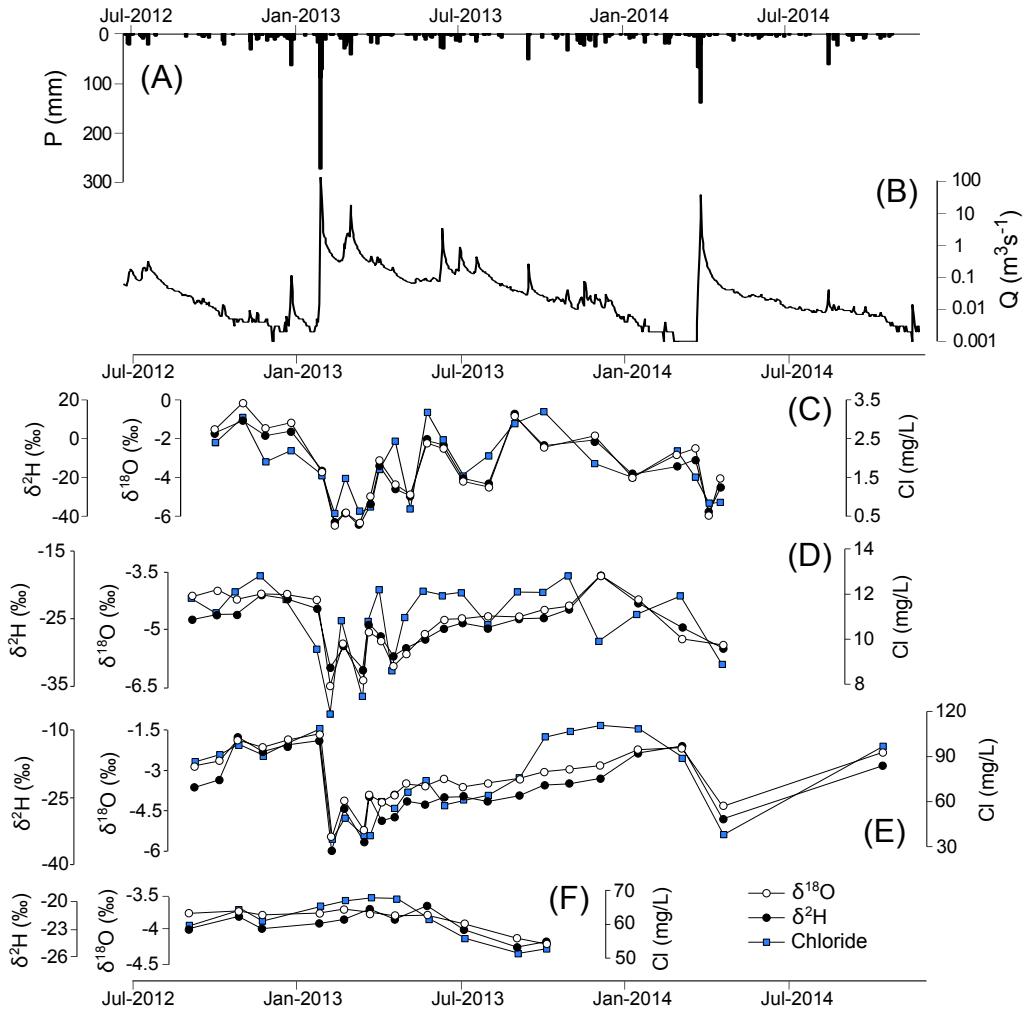
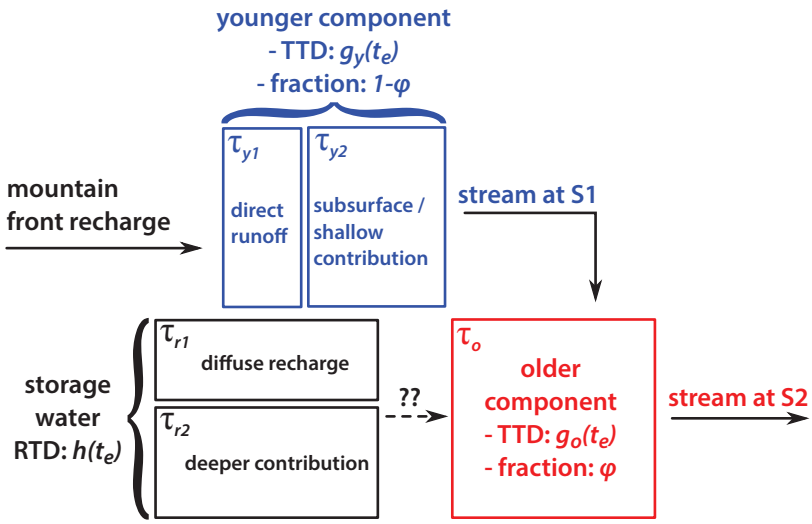


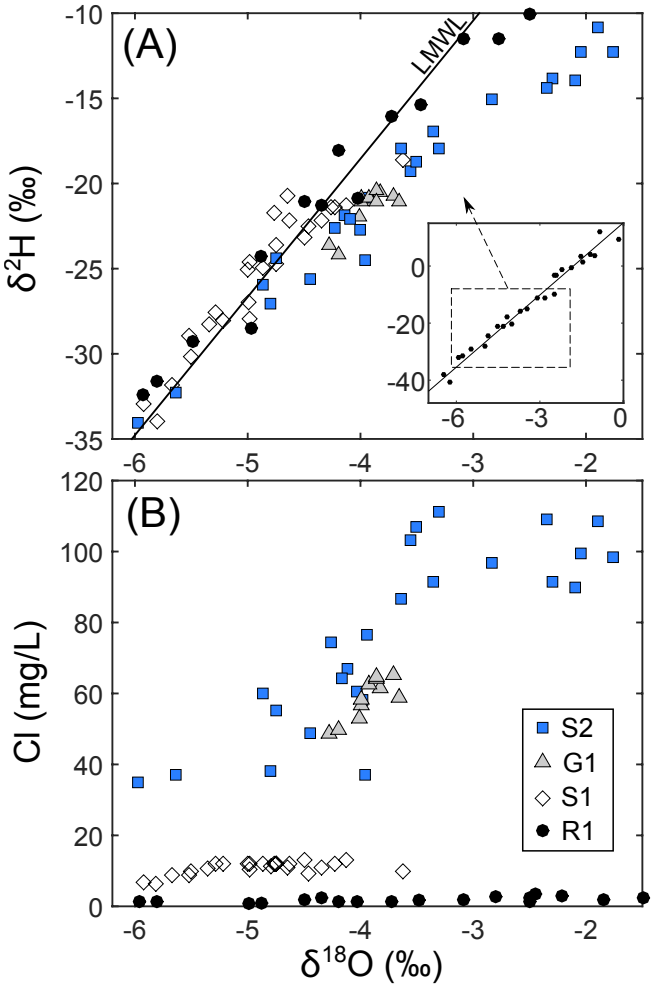
Figure 2. Time-series of Thiessen-averaged precipitation (a), daily discharge at Croftby (DNRM station 145011A) (b), and δ^2H, $\delta^{18}O$ and chloride at R1 (rainfall) (c), S1 (d) and S2 (streamwater) (e), and G1 (groundwater) (f). Note that the y-axes of δ^2H, $\delta^{18}O$ and chloride have different scales for each individual plot.



1004

1005 Figure 3. Conceptual diagram showing the flow components and their transit times to be characterised in this

1006 study.



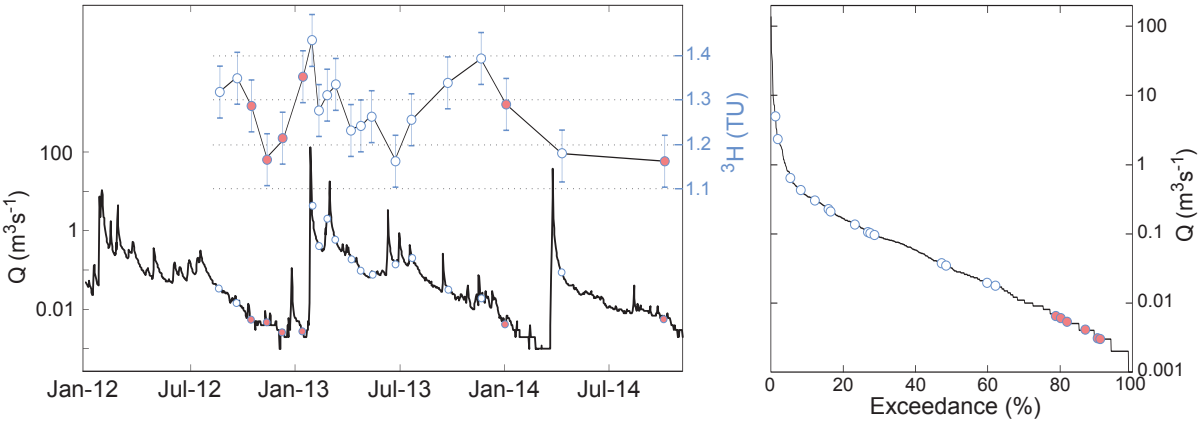
1007

1008 Figure 4. Relationships between (a) deuterium and oxygen-18 and (b) chloride and oxygen-18 for rainfall,

1009 streamwater and groundwater of the Teviot Brook catchment. The local meteoric water line plotted in (a) follows

1010 the equation $\delta^2H = 8.4\ \delta^{18}O + 15.8$ (Duvert et al., 2015a).

1011



1012

1013 Figure 5. Time-series of ^{3}H activity at S2 and daily discharge data (left). Flow duration curve at S2 (right). The

1014 six red circles correspond to samples used to fit the low baseflow model (see Fig.9). The whiskers correspond to

1015 measurement uncertainty (±0.06 TU for all samples).

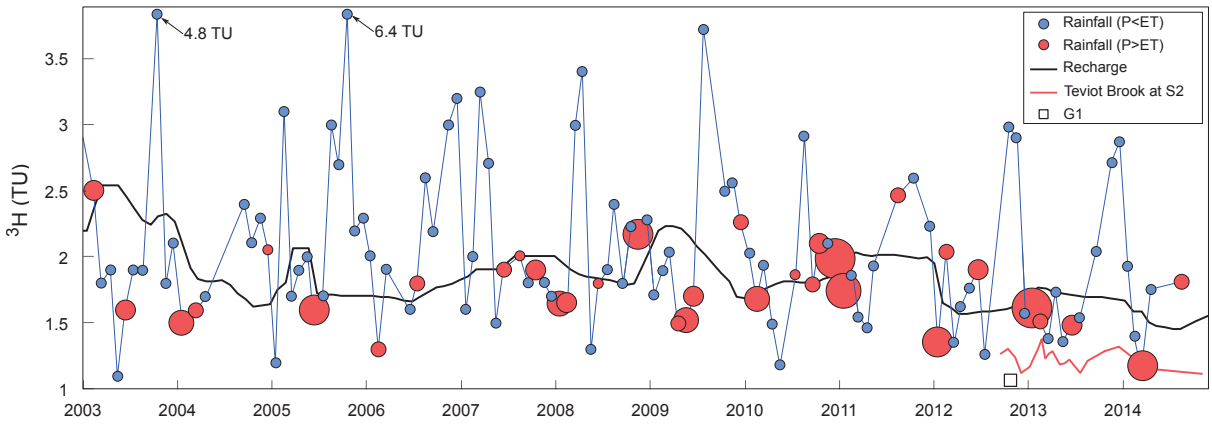
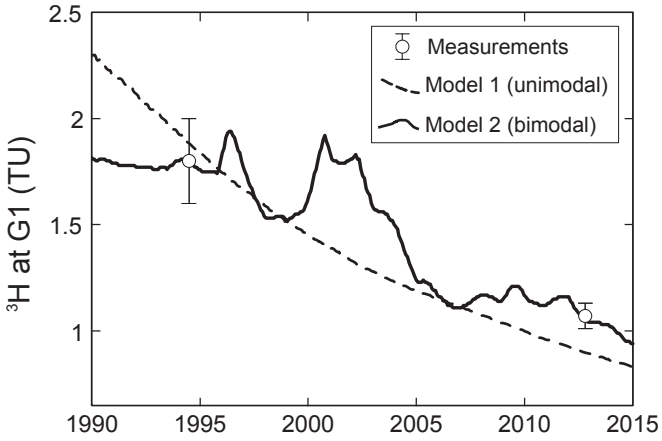


Figure 6. Temporal evolution of input ^{3}H in precipitation (circles) and recharge (black line) for the Teviot Brook catchment considering the A2 scenario. The plotted circles correspond to rainfall collected at Brisbane Aero and adjusted to Teviot Brook according to A2. The recharge time-series was obtained using equation (6) and a 12-month sliding window. The marker size for rainfall contributing to recharge (red circles) reflects the recharge rate.



1022

1023 Figure 7. Fits of two models at G1 using A2 as input ^{3}H series. The unimodal model is a dispersion model with
1024 first moment 48.2 years and dispersion parameter 0.71. The bimodal model is an exponential–dispersion model:
1025 a younger component (exponential distribution; fraction 57%) with first moment 1 year and an older component
1026 (dispersion distribution; fraction 43%) with first moment 82.9 years and dispersion parameter 0.30. The 1994
1027 measurement is from Please et al. (1997).

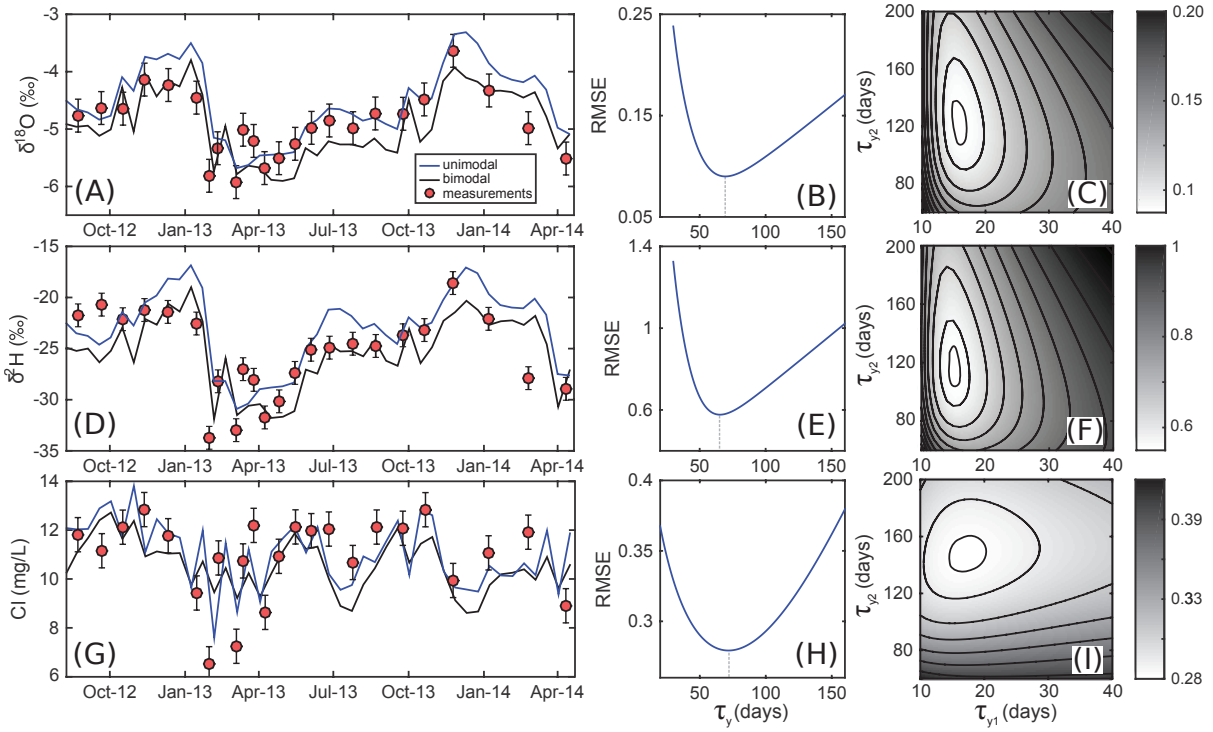
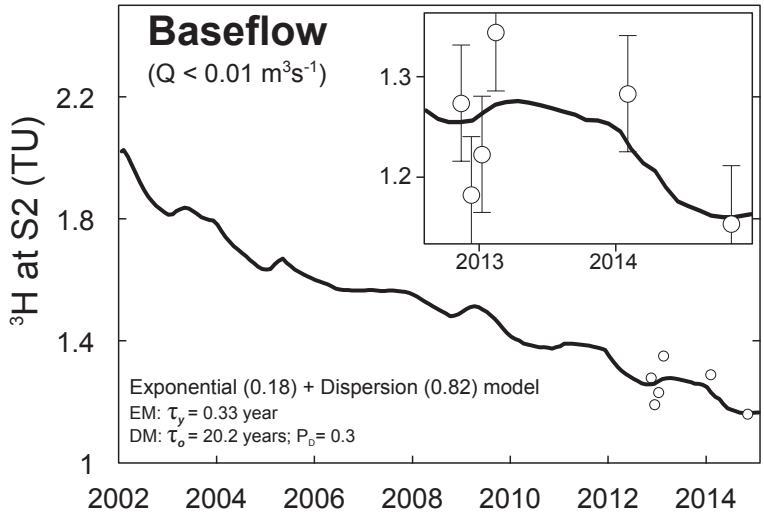


Figure 8. Exponential (blue) and exponential–dispersion (black) models calibrated to the oxygen-18 (a), deuterium (d) and chloride (g) time-series at S1. Whiskers correspond to the measurement uncertainty as given in the Methods section. Root mean square errors (RMSE) of the exponential model as a function of τ_y for the three tracers (b, e, h). RMSE of the exponential–dispersion model (27% younger component; $P_D = 0.3$) as a function of mean transit times of the younger (τ_{y1}) and older (τ_{y2}) fractions for the three tracers (c, f and i). Lighter colours are for lower RMSE, and the smallest contours correspond to the range of acceptable fit, arbitrarily defined as the values for which the RMSE are lower than the lowest RMSE obtained with the exponential models. Results for these simulations are reported in Table 4.



1037

1038 Figure 9. Bimodal model fitted to the ^{3}H activities at S2 under low baseflow conditions (i.e. daily $Q < 10^{-2}$ m^3 s^{-1}

1039). A2 was used as input ^{3}H series for this case. Results using other input series are listed in Table 5.

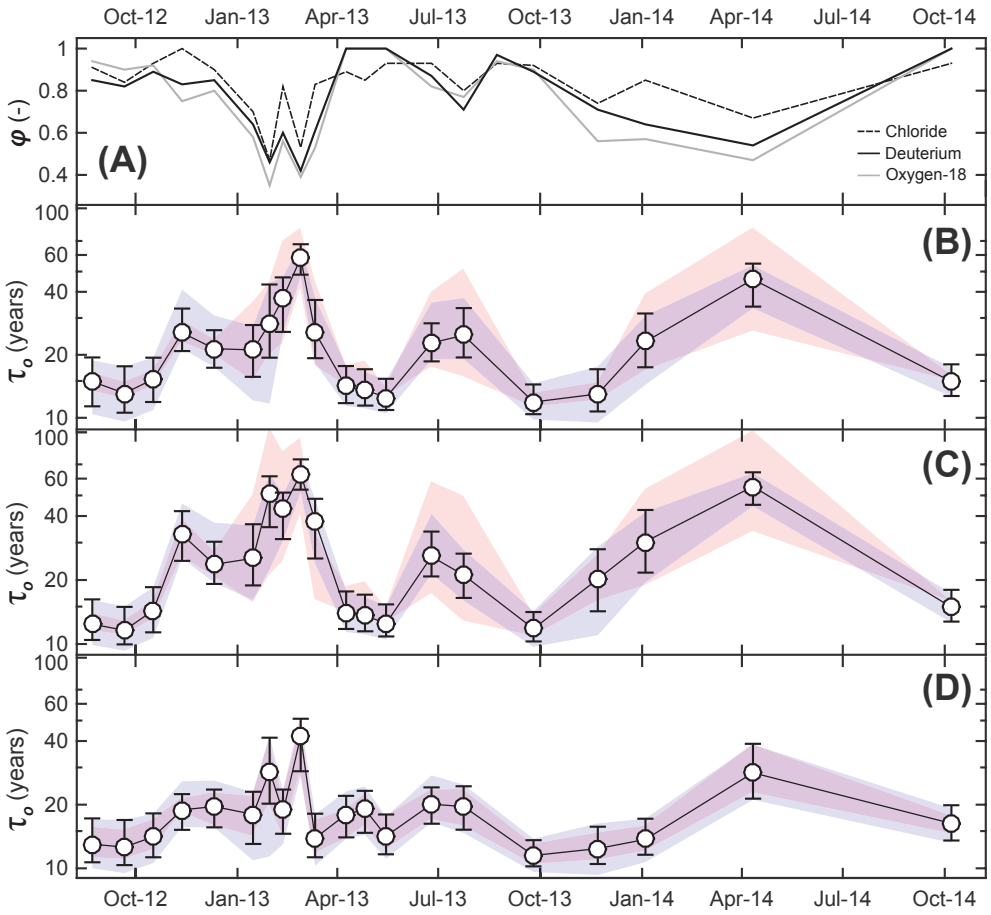


Figure 10. Variations in the older component fraction φ according to the three seasonal tracers (using equation (5)) ~~and a recursive digital filter (Nathan and McMahon, 1990)~~ (a). Variations in the TT of older fraction τ_o at S2 based on hydrograph separation using ^{2}H (b), ^{18}O (c) and chloride (d). Values in (b), (c) and (d) were obtained through the adjustment of exponential–dispersion models to each ^{3}H sample separately, and using A2 as input series and a 12-month sliding window. Whiskers represent the error range due to the measurement uncertainty on each sample (i.e. ±0.06 TU). The blue shaded areas represent the range of values due to uncertainties in the estimation of recharge input (i.e. for the six ^{3}H input time-series), while the red shaded areas represent the range of error related to the calculation of φ, which was estimated according to the method described in Genereux (1998) and propagated to the calculation of τ_o.

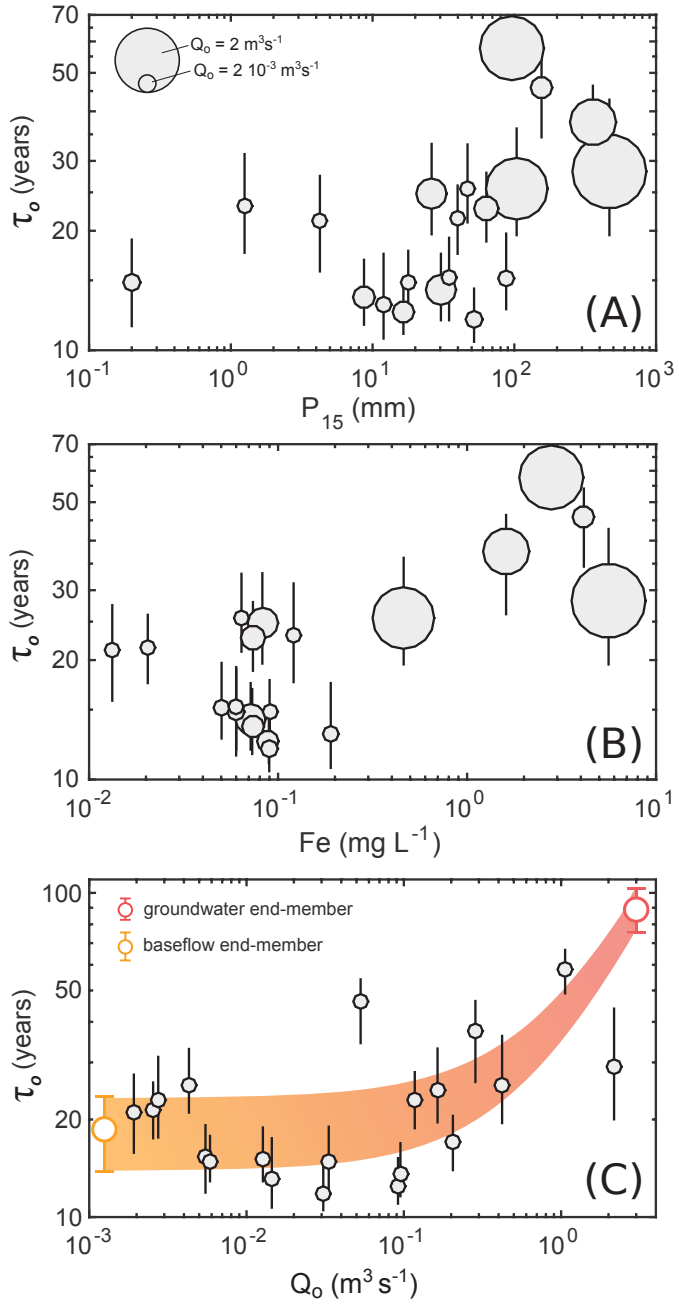


Figure 11. Relationship between the transit time of old water fraction (τ_o) and antecedent precipitation P_{15}, i.e. precipitation depth over the catchment during the 15 days prior to sampling (a). Relationship between τ_o and dissolved Fe concentrations (b). Relationship between τ_o and Q_o ($Q_o = Q * \varphi$) (c). Values were obtained using A2 as input series and deuterium as a hydrograph separation tracer. Whiskers correspond to simulations using upper and lower measurement uncertainty errors. The size of markers in (a) and (b) provides an indication on the value of Q_o during sampling. In (c), the groundwater (red) end-member corresponds to the residence time calculated at G1, while the baseflow (orange) end-member corresponds to the transit time of the old water fraction calculated at S2 using the six baseflow samples. The shaded area in (c) represents simple linear mixing between the two end-members.