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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 streamwater transit time (TT) stems from the use of stable isotopes or chloride as hydrological tracers, because these tracers are blind to older contributions. 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 assess the different contributions to streamflow and their variations over time, and to understand the relationships between streamwater 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  $\approx$  2 weeks) and discharge from the fractured igneous rocks forming the headwaters (mean TT  $\approx$  0.3 years). 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 the alluvial aquifer feeding the stream downstream ( $\approx$  76–102 years), outlining 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  $17 \pm 6$  years at low flow and  $38 \pm 15$  years after major recharge events. This 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.

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# 1 Introduction

Streamwater 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 (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 concentration of a tracer measured in a sample taken at the outlet of a catchment to the history of the tracer input in 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 transit time distribution (TTD, i.e. probability density function of the TTs contained in the sample). The residence time distribution (RTD) is another useful indicator that refers to the distribution of ages of water resident within the system, rather than exiting it. RTDs 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 TTDs and RTDs (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 TTD/RTD 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 inte-

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gral, i.e. the amount of overlap of the TTD/RTD 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-

5 parametric forms of RTD functions have recently been developed (Engdahl et al., 2013; Massoudieh et al., 2014b; 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 streamwater TTs in a variety of catchments worldwide (e.g. Maloszewski et al.,

10 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 groundwater residence time (RT) and

15 streamwater TT has also been undertaken occasionally (Stewart and McDonnell, 1991; Matsutani et al., 1993; Reddy et al., 2006; Muñoz-Villers and McDonnell, 2012). Because catchment storage is highly non-stationary, streamwater TTs are known to vary over time, yet the importance of temporal dynamics in TTDs has been overlooked until recently. One of the reasons is that this non-stationarity is not accounted for in the

20 lumped models. In the last five years, an ever-growing number of studies has transferred its focus to assessing dynamic TTDs (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

25 of these studies agreed on the importance of considering storage dynamics, because the RTD of storage water and the TTD 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 RTD functions (Massoudieh, 2013; Leray et al.,

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2014). However, the determination of time-variant TTDs and RTDs still requires data-intensive computing, which largely limits its use for the time being (Seeger and Weiler, 2014).

Commonly used in TT studies are the stable isotopes of hydrogen and oxygen ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ). Because they are constituents of the water molecule itself,  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  follow almost the same response function as the traced material, hence are generally referred to as “ideal” tracers. Another tracer that behaves relatively conservatively and has been largely used in the literature is chloride. Stewart et al. (2010, 2012) criticised the use of these tracers to assess streamwater TTs, arguing that TTDs are likely to be truncated when only  $\delta^2\text{H}$  and/or  $\delta^{18}\text{O}$  are used. In an earlier study, Stewart et al. (2007) reported differences of up to an order of magnitude between the streamwater TTs determined using stable isotopes as compared to those determined using tritium ( ${}^3\text{H}$ ). Later works by Seeger and Weiler (2014) and Kirchner (2015) reinforced the point that “stable isotopes are effectively blind to the long tails of TTDs” (Kirchner, 2015). The effect of older groundwater contribution to streamflow has largely been ignored until recently (Smerdon et al., 2012; Frisbee et al., 2013), and according to Stewart et al. (2012), new research efforts need to be focused on relating deeper groundwater flow processes to catchment response. Accounting for potential delayed contributions from deeper groundwater systems therefore requires addition of a tracer, such as  ${}^3\text{H}$ , that is capable of determining longer TTs to the analysis of streamwater.

Tritium is a radioactive isotope of hydrogen with a half-life of 12.32 years. Like  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  it is part of the water molecule and can therefore be considered an “ideal” tracer. Fractionation effects are small and can be ignored relative to measurement uncertainties and to its radioactive decay (Michel, 2005). In the Southern Hemisphere, the bomb pulse  ${}^3\text{H}$  peak that occurred in the 1960s was several orders of magnitude lower than in the Northern Hemisphere (Freeze and Cherry, 1979; Clark and Fritz, 1997), and the  ${}^3\text{H}$  concentrations of remnant bomb pulse water have now decayed well below that of modern rainfall (Morgenstern and Daughney, 2012). These characteristics allow the detection of relatively older groundwater (< 100 years) and the calculation of

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unique TTDs from a single  ${}^3\text{H}$  value, provided the measurement is accurate enough (Morgenstern et al., 2010; Stewart et al., 2010). Other age tracers such as chlorofluorocarbons and sulfur hexafluoride have shown potential for estimating groundwater RT (e.g. Cook and Solomon, 1997; Lamontagne et al., 2015), however these tracers are less suitable for streamwater because of gas exchange with the atmosphere (Plummer et al., 2001).

Long-term evolution of  ${}^3\text{H}$  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 assumed stationarity of the observed system by deriving a unique estimate of TT or RT from  ${}^3\text{H}$  time-series data. Morgenstern et al. (2010) were the first to use repeated streamwater  ${}^3\text{H}$  data to assess the temporal variations in TTDs. Using simple lumped parameter models calibrated to each  ${}^3\text{H}$  sample, they established that streamwater TT was highly variable and a function of discharge rate. Following the same approach, Cartwright and Morgenstern (2015) explored the seasonal variability of  ${}^3\text{H}$  activities in streamwater and their spatial variations from headwater tributaries to a lowland stream. They showed that different flowpaths were likely activated under varying flow conditions, resulting in a wide range of TTs. To the extent of our knowledge, shorter term (i.e. < monthly) variations in streamwater  ${}^3\text{H}$  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 (stable isotopes and chloride) and  ${}^3\text{H}$ . We postulate that  ${}^3\text{H}$  time-series data may provide further insight into the nonlinear processes of deeper

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groundwater contribution to rivers, but also in the limitations of using single  ${}^3\text{H}$  samples to calculate streamwater TTs. To be more specific, the questions to be addressed are:

- i. Can simple lumped models provide reliable estimates of streamwater transit times 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 tritium time-series data?
- iii. How dissimilar are the residence time of aquifers adjacent to streams (i.e. storage water) and the transit time of streamwater (i.e. exiting water)?

## 10 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<sup>2</sup>, and elevations range between 160 and 1375 m a.s.l. 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. 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 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, and hydraulic gradient analysis indicates

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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., 2015b). 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. The alluvium at borehole G1 is composed of fine-grained material, i.e. mostly gravel and silty clay. The borehole is 13.9 m deep and it is screened in the alluvial stratum from 12.3 m to its bottom. The horizontal distance between G1 and S2 is 60 m.

## 2.2 Catchment hydrology

10 The monitoring period spans over two years, from mid-2012 to late 2014. Daily streamflow data was 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 was 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 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. 3a). This intense 15 episode of rainfall generated a daily peak flow of  $137 \text{ m}^3 \text{ s}^{-1}$  upstream of S2 (Fig. 3b), 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, b). Another high flow event occurred in late March 2014, with 20 a daily peak flow of  $39 \text{ m}^3 \text{ s}^{-1}$ . Generally, examination of the hydrograph reveals that extended recession periods followed peak flows. Low flow conditions ( $Q < 0.01 \text{ m}^3 \text{ s}^{-1}$ ) occurred towards the end of the dry season, i.e. approximately from November through 25

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to January (Fig. 3b). The stream did not dry up during the study period although very low flow ( $Q < 0.001 \text{ m}^3 \text{ s}^{-1}$ ) occurred for 30 consecutive days in February–March 2014.

### 3 Methods

#### 3.1 Sample collection and analysis

5 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 scheme as the rainfall samples (Fig. 1). Samples at G1 were taken after  
10 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  $0.45 \mu\text{m}$  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 ( ${}^3\text{H}$ ) activity was determined at S2  
15 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 obtained by titrating water samples with hydrochloric acid to a pH endpoint of 4.5. Samples were also analysed for oxygen ( $\delta^{18}\text{O}$ ) and deuterium  
20 ( $\delta^2\text{H}$ ) stable isotopes, using a Los Gatos Research water isotope analyser. All isotopic compositions in this study are expressed relative to the VSMOW-standard. Replicate analyses indicate that analytical error was  $\pm 1.1\text{‰}$  for  $\delta^2\text{H}$  and  $\pm 0.3\text{‰}$  for  $\delta^{18}\text{O}$ . All these analyses were conducted at the Queensland University of Technology (QUT) in Brisbane. In addition, tritium was analysed at the Australian Nuclear Science and  
25 Technology Organisation (ANSTO) in Sydney. Samples were distilled and electrolytically enriched 68-fold prior to counting with a liquid scintillation counter for several

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weeks. The limit of quantification was 0.05 tritium units (TU) for all samples, and uncertainty was  $\pm 0.06$  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

#### 5 3.2.1 Using stable isotopes and chloride

Mean TTs were determined through adjustment of a TTD function to observations of fortnightly input and output concentrations. 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):

$$10 C_r(t) = \frac{R(t)}{\bar{R}} (C_p(t) - \bar{C}_r) + \bar{C}_r \quad (1)$$

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

15 The weighted input was then convoluted to the selected TTD function ( $g$ ) to obtain output concentrations (Maloszewski and Zuber, 1982):

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

where  $t_e$  is time of entry;  $C_{out}(t)$  is the output concentration;  $C_r(t)$  is the weighted input concentration; and  $g(t_e)$  is an appropriate TTD function. 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 TTD functions.

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In some instances, two models were combined to represent more complex systems on the basis of our understanding of the catchment behaviour (Fig. 2). 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 TTDs:

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

where  $\phi$  is the fraction of the older component ( $0 < \phi < 1$ ), and  $g_o(t_e)$  and  $g_y(t_e)$  are the TTD functions of the older and younger components, respectively (Fig. 2). Bimodal distributions combined either two dispersion models or one exponential and one dispersion model. The mean TTs, noted  $\tau$ , 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  $\tau_y$  (subdivided into  $\tau_{y1}$  and  $\tau_{y2}$ ), while the mean TT of the older component is referred to as  $\tau_o$ , and the mean RT of storage groundwater is referred to as  $\tau_r$  (subdivided into  $\tau_{r1}$  and  $\tau_{r2}$ ) (Fig. 2).

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 Eqs. (2) and (3):  $C_{\text{out}}(t)$  values were multiplied by  $F = \frac{P}{(P-ET)}$  (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.

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

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

where  $\delta_{S1}$ ,  $\delta_{R1}$  and  $\delta_{G1}$  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.

### 10 3.2.2 Using tritium

The occurrence of seasonal variations in rainfall  ${}^3\text{H}$  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 TTDs. Monthly  ${}^3\text{H}$  precipitation data measured by ANSTO from bulk samples collected at 15 Brisbane Aero were used to estimate the  ${}^3\text{H}$  input function for the Teviot Brook catchment. Because Brisbane Aero is ca. 100 km northeast of Teviot Brook, the rainfall  ${}^3\text{H}$  concentrations are likely to be significantly different between these two locations due to oceanic and altitudinal effects. According to Tadros et al. (2014),  ${}^3\text{H}$  values for Toowoomba (i.e. located in the Great Dividing Range near Teviot Brook) were about 20 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  ${}^3\text{H}$  concentrations for Teviot Brook (input series A2 in Table 1). A second estimate was obtained by comparing the historical  ${}^3\text{H}$  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

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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  ${}^3\text{H}$  recharge was estimated by subtracting monthly evapotranspiration from monthly precipitation, and weighting the  ${}^3\text{H}$  rainfall concentrations by the resulting recharge. Instead of calculating single annual values, 6 months and 1 yr sliding windows were used to obtain monthly values as follows:

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

where  $C_i$  is the monthly tritium recharge for the  $i$ th month,  $C_j$  and  $r_j$  are the monthly tritium precipitation and monthly recharge rate for the  $j$ th month, and  $t$  is 6 or 12 depending on the span of the sliding interval used. To avoid edge effects, a Tukey filter with coefficient 0.6 was applied to the sliding windows.

Input (recharge) and output (streamwater)  ${}^3\text{H}$  concentrations were then related using the same convolution integral as the one used for stable isotopes (Eqs. 2 and 3), except that the term  $e^{(-\lambda t_e)}$  was added to account for radioactive decay of  ${}^3\text{H}$ .  $\lambda$  is the  ${}^3\text{H}$  decay constant, such that  $\lambda = 1.54 \times 10^{-4} \text{ day}^{-1}$ . To account for the uncertainty in input parameters and to assess the sensitivity of TTD calculations to the input function, a total of six input time-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 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.

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## 4 Results

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

### 4.1 Seasonal tracers in precipitation, streamwater and groundwater

Stable isotope ratios and chloride concentrations in precipitation were highly variable throughout the study period (Figs. 3c and 4). The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  rainfall values ranged between  $-40.7$  to  $+11.7\text{‰}$  (average  $-11.5\text{‰}$ ) and  $-6.5$  to  $-0.1\text{‰}$  (average  $-3.1\text{‰}$ ), respectively, while chloride concentrations ranged between  $0.6$  to  $3.2\text{ mg L}^{-1}$  (average  $1.8\text{ mg L}^{-1}$ ). 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  $\delta^2\text{H}$ : decrease from  $-16.1$  to  $-40.7\text{‰}$ ; Fig. 3c). The local meteoric water line derived from rainfall samples had an intercept of 15.8 and a slope of 8.4 (Duvert et al., 2015b), similar to that of Brisbane (Fig. 4a). The stable isotope ratios measured in streamwater at S1 (Fig. 3d) and S2 (Fig. 3e) 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 ( $\delta^2\text{H} = -25.4$  and  $\delta^{18}\text{O} = -4.9\text{‰}$ ) than for S2 ( $\delta^2\text{H} = -20.3$  and  $\delta^{18}\text{O} = -3.7\text{‰}$ ), 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  $12.8\text{ mg L}^{-1}$  at S1, and between  $35.1$  and  $111.1\text{ mg L}^{-1}$  at S2 (Figs. 3d and e, 4b). At S2, higher chloride values were consistent with higher  $\delta^{18}\text{O}$  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 (Figs. 3f and 4). The  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  and chloride values recorded at G1 tended to slightly decrease during the rainy season, although they stayed within the ranges  $-21.5 \pm 2.7$ ,

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$-3.9 \pm 0.4\text{‰}$  and  $60 \pm 10\text{ mg L}^{-1}$ , respectively (Fig. 3f). Consistent displacement to the right of the meteoric line was observed for all G1 samples (Fig. 4a).

## 4.2 Tritium in streamwater and groundwater

The groundwater sample collected at G1 in October 2012 yielded a  ${}^3\text{H}$  activity of  $1.07 \pm 0.06\text{ TU}$ . 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  $1.80 \pm 0.20\text{ TU}$ . The 20 samples of streamwater collected at S2 showed variable  ${}^3\text{H}$  activities ranging between  $1.16 \pm 0.06$  and  $1.43 \pm 0.06\text{ TU}$  (Fig. 5).

In order to estimate a  ${}^3\text{H}$  input signal for the Teviot Brook catchment, several precipitation time-series were calculated from Brisbane Aero monthly  ${}^3\text{H}$  dataset, as detailed in Table 1. Recharge time-series were then derived from these precipitation time-series using Eq. (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  ${}^3\text{H}$  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.

## 5 Discussion

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 younger component to streamflow  $\tau_y$  (Sect. 5.1). Second, the  ${}^3\text{H}$  data collected in groundwater are interpreted in order to assess the RT of water stored in the alluvial aquifer  $\tau_r$  (Sect. 5.2). Third, an older component in streamwater is identified through

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the use of  ${}^3\text{H}$  (Sect. 5.3), and the variations over time of the TTs of this older component  $\tau_o$  are further quantified (Sect. 5.4) and elucidated (Sect. 5.5).

## 5.1 Identification of a younger component (< 2 years) in streamflow using seasonal tracers

5 The large temporal variability observed in rainfall isotopic and chloride records (Fig. 3c) may be attributed to a combination of factors that include precipitation amount, but also an apparent seasonal cycle. 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

10 experience partial evaporation below the cloud base, typical in tropical to subtropical areas (Rozanski et al., 1993). Depletion of stable isotopes during significant precipitation events (Fig. 3c) has been reported in other parts of eastern Australia (Hughes and Crawford, 2013; King et al., 2015). In streamwater, average isotopic ratios were lower for S1 and S2 than the weighted average for rainfall, which most likely reflects

15 the predominant contribution of depleted rainfall to recharge (Duvert et al., 2015b). 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

20 downstream, with values one order of magnitude higher at S2 than at S1 (Fig. 4b).

In order to define a first end-member – which would represent the contribution of younger water from rapid recharge through the highly fractured igneous rocks in the headwaters (Duvert et al., 2015b), 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

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(Table 2; Fig. 7). 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. 7). All three tracers yielded comparable exponential TTD functions, with  $\tau_y$  ranging between 65 and 70 days (Table 2). The bimodal models provided slightly more satisfactory fits for all tracers (black lines in Fig. 6), with lower RMSE overall. Bimodal TTD functions derived from data at S1 had a younger fraction (27 %) with  $\tau_{y1}$  between 14 and 16 days, and an older fraction (73 %) with  $\tau_{y2}$  between 113 and 146 days (Table 2) depending on which tracer was used. Better fits for these bimodal functions than for exponential models lend support to the occurrence of two end-members contributing to streamflow at S1. This is in agreement with our conceptual understanding of the upstream hydrological functioning, where streamflow may be partitioned into (i) quick flow and subsurface waters discharging into the stream, and (ii) delayed contribution of waters seeping from the highly fractured igneous rocks.

Calibration was also carried out on the tracer time-series collected at S2 and following the same procedure (Table 2). When considering a unimodal exponential distribution, all three tracers yielded comparable TTD functions, with  $\tau_y$  ranging between 71 and 85 days, which was slightly longer than the mean TTDs calculated at S1. When considering a bimodal exponential–dispersion distribution, the younger fraction had  $\tau_{y1}$  of 23 to 24 days while the older fraction had  $\tau_{y2}$  of 99 to 109 days (Table 2). Again, results were slightly more accurate when using a bimodal distribution, suggesting a dual contribution to streamflow at S2 as well. More importantly, the fits for S2 were not as accurate as those for S1, regardless of the distribution and tracer used. This reflects the likely importance of other concurrent processes in the downstream section of the catchment. Among them, evaporation may be a major limitation to applying steady-state lumped models at S2. It has been reported that  $\delta^{18}\text{O}$  is generally more sensitive to the effects of evaporation than  $\delta^2\text{H}$  (Klaus and McDonnell, 2013; Klaus et al., 2015b). However, in this study there were no significant differences between TTDs derived from the two stable isotopes. Calibration of the models on chloride measurements did not

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yield as accurate results as those for stable isotopes at S1 and to a higher extent at S2, which may be attributed to the higher effects of evaporative enrichment on chloride. Based on flux tracking methods, Hrachowitz et al. (2013) showed that processes such as evaporation can result in considerable biases in TTD estimates when using chloride as a tracer.

It is increasingly recognised that stable isotopes cannot provide realistic estimates of longer TT waters, regardless of the lumped model used (Stewart et al., 2012; Seeger and Weiler, 2014; Kirchner, 2015). In this study, it is very likely that “older water” (i.e. > 5 years) contributed to streamflow at S2 (see Sect. 5.3) but also possibly at S1, and the sole use of stable isotopes and chloride did not allow detection of such contribution. Therefore all the mean TTs defined above should be regarded as partial mean TTs that reflect the short-term and/or intermediate portions of the overall TTD, rather than actual mean TTs (Seeger and Weiler, 2014).

## 5.2 Identification of the residence time of storage water

The sample collected at G1 in October 2012 ( ${}^3\text{H} = 1.07 \pm 0.06 \text{ TU}$ ) suggests that groundwaters stored in the alluvial aquifer contain a substantial modern component. An earlier  ${}^3\text{H}$  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 distribution model while the second one was a bi-modal exponential–dispersion model. Simulations using  ${}^3\text{H}$  as a tracer are generally insensitive to the type of lumped parameter model chosen, given that ambient tritium levels are now almost at pre-bomb levels (e.g. Stewart and Thomas, 2008). Therefore the choice of a priori distributions may not affect the results significantly. For the bi-modal model, the mean RT of younger components  $\tau_{r1}$  was constrained to 1 year, and the fraction of younger water was constrained to 57 % as these parameters provided best fits on average.

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Results for both models are presented in Table 3 and the two fits using A2 as an input function are shown in Fig. 8. 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 vs. 0.20 TU; Table 3). Unimodal distributions had  $\tau_r$  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  $\tau_{r2}$  between 76 (using A1 as input series) and 102 years (using B3 as input series), with a standard deviation of 9 years. The better fits obtained for bimodal functions (e.g. in Fig. 8) may be interpreted as the probable partitioning of groundwater at G1 into one contribution of younger waters by diffuse recharge or flood-derived recharge (mean RT  $\approx$  1 years) coupled with a second contribution of older waters, potentially seeping from the underlying sedimentary bedrock aquifer (mean RT  $\approx$  80 to 100 years). It was reported that the  ${}^3\text{H}$  activity in the sedimentary bedrock aquifer was on average lower than the  ${}^3\text{H}$  activity in the alluvial aquifer (Duvert et al., 2015b).

Although the assumption of steady state is more likely to hold for groundwater systems than for streamwater, the somewhat reduced number of samples was a limitation for a definitive assessment of the RT of storage water at G1. Using a 13 yr record of  ${}^3\text{H}$  (and other age tracers) in a mountainous aquifer, Manning et al. (2012) showed that temporal variations in RT could be significant even for groundwater, and that these variations can be related to variations in recharge due to changing climatic conditions.

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

The  ${}^3\text{H}$  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  ${}^3\text{H}$  values obtained at S2, higher values tended to coincide

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with higher flow conditions, although it was not systematic (Fig. 5). For instance, the sample collected in January 2013 under low flow conditions yielded  $1.35 \pm 0.06$  TU; by contrast, the sample collected in April 2014 during the falling limb of a major runoff event yielded  $1.19 \pm 0.06$  TU, i.e. among the lowest values on record. Kendall's rank correlation and Pearson's coefficients were calculated between the  ${}^3\text{H}$  measurements in streamwater and other hydrological, hydrochemical and isotopic variables (Table 4). Tritium 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  ${}^3\text{H}$  activity in the stream. The lack of strong correlation between  ${}^3\text{H}$  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  ${}^3\text{H}$  in streamwater.

In order to characterise a potential older contribution to the stream at S2, a lumped parameter model was fitted to the six samples that were taken under low baseflow conditions, i.e.  $Q < 0.01 \text{ m}^3 \text{ s}^{-1}$ . 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 Sect. 5.1, 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 Sect. 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 TTD identified at G1 (Sect. 5.2). The old water fraction  $\phi$  was constrained to 82 %, i.e. the average value obtained for the six baseflow samples using tracer-based hydrograph separation following Eq. (5).
- Initial simulations were run using the six input series with no further model constraint. For the six scenarios,  $\tau_y$  consistently converged to  $0.33 \pm 0.08$  years.

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- 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  $\tau_o$ .

Figure 9 provides an example of the adjustment using A2 as input  ${}^3\text{H}$  function. Reasonably good fits were obtained for all simulations ( $0.14 \text{ TU} < \text{RMSE} < 0.16 \text{ TU}$ ), with  $\tau_o$  between 15.8 and 24.5 years, average  $20.1 \pm 3.9$  years (Table 5). It can be argued that the exponential component with first moment 0.33 years captures all young contributions as identified in Sect. 5.1. While the second component was characterised by much older waters, this contribution could not be directly related to the RT of storage waters as defined in Sect. 5.2 (i.e.  $\tau_o \neq \tau_r$ ). Despite the exclusive use of samples taken under low baseflow conditions for this calibration, the obtained  $\tau_o$  were significantly lower than the estimates of  $\tau_{r2}$  for the alluvial aquifer (average  $20.1 \pm 3.9$  vs.  $88.7 \pm 9.3$  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 streamwater TT and groundwater RT based on  ${}^3\text{H}$  measurements, Matsutani et al. (1993) reported that streamwater was formed by a mixture of longer RT groundwater (19 years) and shorter RT soil water (< 1 year). Overall, more work is needed to better define the two distributions and to assess how they relate to each other under non-stationary storage conditions.

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

Unlike for rainfall  ${}^3\text{H}$  values where high temporal variability was observed, the derived time-series for recharge were relatively constant over the last decade (Fig. 6). This characteristic in principle allows reliable assessment of streamwater TTs with single  ${}^3\text{H}$  measurements, providing the  ${}^3\text{H}$  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 ( $\tau_o$ ). The model parameters were chosen according to the best fit obtained for baseflow samples (i.e. mean TT of young component  $\tau_y$  0.33 years, dispersion parameter of old component 0.3; Sect. 5.3). In addition, for each sample the fraction of old water  $\phi$  was constrained to the value obtained using tracer-based hydrograph separation according to Eq. (5). Conceptually, this approach appeared more meaningful than another option that would have consisted in constraining  $\tau_o$  and subsequently determining the old water fractions  $\phi$ , because there was no indication that  $\tau_o$  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 the  ${}^3\text{H}$  measurement uncertainty ( $\pm 0.06$  TU) was also tested for each sample.

Time-series of  $\tau_o$  were derived for each input function, and Fig. 10 shows the results obtained with A2 as an input series. The old water fraction  $\phi$  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  $\phi$  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  $\tau_o$  values varied considerably over time, and variations exceeded the uncertain-

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ties related to measurement errors and input estimates (Fig. 10b–d). All three tracers provided similar results, with a consistent shift in values either upwards or downwards. As a general rule, there was a negative correlation between  $\phi$  and  $\tau_o$ . When using A2 as input function,  $\tau_o$  fluctuated between 11.9 and 58.0 years ( $\delta^2\text{H}$ ; Fig. 10b), 11.6 and 63.2 years ( $\delta^{18}\text{O}$ ; Fig. 10c) and 11.5 and 42.1 years (chloride; Fig. 10d). For clarity purposes the  $\tau_o$  values reported in the text do not consider errors related to measurement uncertainty). Values were highest after the major recharge events that occurred in January and February 2013, with  $\tau_o$  between 26.8 and 63.2 years in late February, and in April 2014, with  $\tau_o$  between 28.3 and 55.1 years. They were lowest during periods undergoing sustained low flow such as in September 2012 ( $\tau_o$  between 11.6 years for  $\delta^{18}\text{O}$  and 13.1 years for  $\delta^2\text{H}$ ) and in September 2013 ( $\tau_o$  between 11.5 years for chloride and 11.9 years for  $\delta^2\text{H}$ ). Of note is the timing of the highest  $\tau_o$  value in late February 2013, i.e. one month after the major recharge episode. These are rather unexpected results that may be interpreted as the activation of longer, deeper flowpaths carrying older waters shortly after high flow events.

## 5.5 Drivers of the variability in older water transit time

In order to better apprehend the factors influencing the variations in  $\tau_o$ , the obtained values were compared to other hydrological and hydrochemical variables, particularly the antecedent wetness conditions, dissolved Fe concentrations and the old water discharge rate (Fig. 11). Under sustained dry conditions ( $P_{15} < 5\text{ mm}$ ), there was no consistent relationship between  $\tau_o$  and the amount of precipitation during the 15 days prior to sampling, with  $\tau_o$  ranging between 14.9 and 23.1 years ( $n = 3$ ; Fig. 11a). For higher values of  $P_{15}$  (i.e.  $P_{15} \geq 10\text{ mm}$ ), there was a positive and unequivocal correlation between the two variables ( $n = 17$ ). The transit time of old water fraction was lowest for  $P_{15}$  between 10 and 50 mm ( $\tau_o$  11.9 to 25.5 years), and it increased when antecedent wetness conditions increased ( $\tau_o$  25.6 to 58.0 years for  $P_{15} > 100\text{ mm}$ ). Generally, values averaged  $17.0 \pm 5.6$  years at low flow and  $38.3 \pm 14.7$  years after major high flow

events. This was in accordance with results from Fig. 10, and suggestive of the predominant contribution of older alluvial and/or bedrock waters shortly after recharge episodes. There was also a positive relationship between  $\tau_o$  and Fe concentrations at S2, with all the values  $> 0.2 \text{ mg L}^{-1}$  corresponding to  $\tau_o > 30$  years (Fig. 11b). In contrast, no significant relationship was observed at S1, as Fe values at this station ranged between  $< 0.01$  to  $0.96 \text{ mg L}^{-1}$ . Duvert et al. (2015a) reported increasing Fe concentrations after a major recharge event for some groundwaters of the sedimentary bedrock. The increase in streamflow Fe might therefore be a result of enhanced discharge of these waters into the drainage network, which is coherent with older  $\tau_o$  values. However, other chemical parameters distinctive of the bedrock groundwaters did not produce a characteristic signature in streamflow during high flow conditions. Or else, high Fe concentrations may be simply due to higher weathering rates at higher flows, although this hypothesis disregards the high value measured for the April 2014 sample ( $\text{Fe} = 4.15 \text{ mg L}^{-1}$ ) despite relatively low discharge ( $Q = 0.095 \text{ m}^3 \text{ s}^{-1}$ ).

As discussed previously, a modification in storage due to a change in recharge dynamics may have activated different groundwater flowpaths and hence water parcels with different RTs (Heidbüchel et al., 2013; van der Velde et al., 2015; Cartwright and Morgenstern, 2015). When the rate of recharge was highest, flushing out of waters located in the deeper, older bedrock aquifer may have been triggered by the resulting pressure wave propagation. By contrast, the relatively younger  $\tau_o$  observed during lower flow conditions may be attributed to waters that originate from shallower parts of the alluvium and/or from subsurface layers. This is reflected in the relationship between  $\tau_o$  and  $Q_o$ , i.e. the portion of streamflow provided by the older component ( $Q_o = Q \cdot \phi$ ; Fig. 11c). In this figure the groundwater end-member corresponds to  $\tau_r$  (using the highest recorded  $Q_o$  through the study period), while the baseflow end-member corresponds to the  $\tau_o$  value calculated using the six baseflow samples. The two end-members were linearly connected in an area that represents the extent of possible fluctuations of  $\tau_o$ , from lower old water contributions to higher old water contributions. The individual  $\tau_o$  values broadly followed this mixing trend (Fig. 11c), which lends support

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to the assumptions that (i) the TT of the older end-member may not be characterised by a single value but rather by a range of possible ages that fluctuate depending on flow conditions, and (ii) during and shortly after higher flows, a near steady-state was reached in which the TT of the old water fraction increased and approached the RT of stored water (i.e.  $\tau_o \rightarrow \tau_r$ ). Overall, the large scattering observed in Fig. 11 suggests that many processes led to the variations in  $\tau_o$ , and that these processes were largely nonlinear.

Importantly, our results differ from the previous observation by Morgenstern et al. (2010) and Cartwright and Morgenstern (2015) that  ${}^3\text{H}$ -derived TTs were higher at low flow conditions and lower at high flow conditions. However, these two studies did not account for a younger component to streamflow (i.e.  $\phi$  constrained to 1 for all samples), which may explain the disagreement with our results. We also recognise that the results reported here might be due to partially incorrect interpretation of the obtained dataset: underestimation of the old water fraction  $\phi$  during high flow events might be responsible for the apparent positive correlation between  $Q_o$  and  $\tau_o$ , although this is unlikely because the three seasonal tracers and the recursive filter yielded very similar flow partitions. Another potential bias in our calculations is the possible lack of representation of the discharge from the fractured igneous rocks in the headwaters, which might contribute significantly to the young component during high flow events. Such enhanced contribution might result in slightly longer  $\tau_y$ , hence shorter  $\tau_o$ . Because no  ${}^3\text{H}$  measurement was conducted at S1, this hypothesis could not be tested further (see Sect. 5.1). 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; 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

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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 TTD 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 TTDs 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 (Eq. 1), a detailed analysis of catchment internal processes would be needed to verify whether evapotranspiration modifies the storage water RTs and subsequent streamwater TTs. Using data from a catchment subjected to high rainfall seasonal variability, van der Velde et al. (2015)

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showed that younger water was more likely to contribute to evapotranspiration, which tended to result in longer streamwater TTs.

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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  $\delta^{18}\text{O}$  observed at this location (Klaus and McDonnell, 2013; Fig. 4). However, we hypothesise that the occurrence of this third end-member would not significantly affect the calculation of  $\tau_o$ , because the TT of soil water is likely to be considerably shorter than that of the older streamflow component (e.g. Matsutani et al., 1993; Muñoz-Villers and McDonnell, 2012).

10

Secondly, there are a number of limitations related to the use of  ${}^3\text{H}$ :

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1. The most significant uncertainties were those related to the computed  ${}^3\text{H}$  input functions. These may be reduced by regularly collecting rainfall  ${}^3\text{H}$  on site. The accuracy of  ${}^3\text{H}$  measurements was another source of uncertainty, and further improving analytical precision of  ${}^3\text{H}$  activity in water samples may allow more rigorous assessment of short-term TT variations (e.g. Morgenstern and Daughney, 2012).

20

2. Changes in  ${}^3\text{H}$  concentrations due to phase changes such as evaporation are commonly ignored because they are usually considered negligible. However, high evaporation environments such as that of the lower Teviot Brook catchment might significantly affect  ${}^3\text{H}$  activity in streamwater. If the fractionation factor for  ${}^3\text{H}$  is twice that for  ${}^2\text{H}$ , then an enrichment of 10‰ in  $\delta^2\text{H}$  would correspond to an enrichment of 20‰ for  ${}^3\text{H}$ . For a sample with an assumed  ${}^3\text{H}$  activity of 1.30 TU, the measured value would then be  $1.30 \times 1.02 \approx 1.33$  TU. Such effect may have led to slight overestimations of the  ${}^3\text{H}$  activity in low flow, high evaporation samples collected at S2. Future research is needed to examine more thoroughly the potential interferences on  ${}^3\text{H}$  due to evaporation.

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3. While stationarity may be a reasonable assumption for groundwater, inter-annual variations in recharge can affect RTs substantially (Manning et al., 2012). Further work aimed at providing additional constraints on RT variability is therefore required, by routinely collecting age tracer data in groundwater. Massoudieh et al. (2014a) showed that using multiple years of tracer records can allow more realistic quantification of the uncertainty on RTDs.

4. Despite yielding longer TTs than seasonal tracers, the use of  ${}^3\text{H}$  did not preclude the potential omission of any older contribution (i.e.  $> 100$  years) to the stream. Frisbee et al. (2013) argued that even studies based on  ${}^3\text{H}$  measurements might miss a significant part of the TTDs rather than just their tail. In our case, the likelihood of waters with much longer RTs seeping from the sedimentary bedrock could not be verified using  ${}^3\text{H}$  only. Other tracers that can capture older water footprints, such as terrigenic helium-4 (Smerdon et al., 2012) or 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 TTDs 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 TTDs. A similar benchmark study should be undertaken for  ${}^3\text{H}$  in order to verify whether TTs derived from  ${}^3\text{H}$  measurements in heterogeneous catchments are also biased.

## 6 Conclusions

Based on time-series observations of seasonal tracers (stable isotopes and chloride) and tritium ( ${}^3\text{H}$ ) in a subtropical mountainous catchment, we assessed the different contributions to streamflow as well as the variations in streamwater transit time (TT) and groundwater residence time (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  $\approx$  2 weeks) and discharge from the fractured igneous rocks forming the headwaters (mean TT  $\approx$  0.3 years). 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 alluvial waters and potentially deeper sedimentary bedrock waters).

In this context, the use of  ${}^3\text{H}$  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  ${}^3\text{H}$  baseflow values were obtained when considering a younger component with mean TT  $\approx$  0.3 years, which reflected the upstream contributions previously quantified, and an older groundwater component with mean TT  $\approx$  16–25 years. The latter value was significantly lower than the RT calculated for the shallow alluvial aquifer feeding the stream downstream (RT  $\approx$  76–102 years). Such discrepancy between groundwater RT and TT of the older component streamwater outlines the necessary distinction between transit and storage waters, and the non-stationary catchment flow processes that govern the variations in TTs. When simulations were run separately on each  ${}^3\text{H}$  streamwater sample, the TT of old water fraction was found to vary substantially over time, with values averaging  $17 \pm 6$  years at low flow (antecedent precipitation  $< 10$  mm) and  $38 \pm 15$  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.

Overall, this study suggests that collecting high-resolution  ${}^3\text{H}$  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 im-

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5 plications 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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**Table 1.** Description of the different  ${}^3\text{H}$  input series computed for the Teviot Brook catchment.

Input series	Description of input parameters
A1	A2 – 25 %
A2	Brisbane Aero ${}^3\text{H}$ values + 0.4 TU
A3	A2 + 25 %
B1	B2 – 90 % CI slope
B2	Brisbane Aero ${}^3\text{H}$ values $\times$ 1.24 TU
B3	B2 + 90 % CI slope

CI refers to the confidence interval on the Toowoomba vs. Brisbane Aero regression slope.

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**Table 2.** Results of model simulations of transit time for S1 and S2 using  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  and chloride.

Sampling location	Tracer	Unimodal EM		Bimodal EM–DM		
		$\tau_y$ (days)	RMSE	$\tau_{y1}$ (days)	$\tau_{y2}$ (days)	RMSE
S1	$\delta^{18}\text{O}$	69	$\pm 0.09\text{‰}$	15	121	$\pm 0.08\text{‰}$
	$\delta^2\text{H}$	65	$\pm 0.58\text{‰}$	15	113	$\pm 0.52\text{‰}$
	chloride	70	$\pm 0.28\text{ mg L}^{-1}$	16	146	$\pm 0.26\text{ mg L}^{-1}$
S2	$\delta^{18}\text{O}$	85	$\pm 0.16\text{‰}$	23	109	$\pm 0.16\text{‰}$
	$\delta^2\text{H}$	71	$\pm 0.75\text{‰}$	24	99	$\pm 0.72\text{‰}$
	chloride	76	$\pm 4.89\text{ mg L}^{-1}$	24	106	$\pm 4.68\text{ mg L}^{-1}$

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

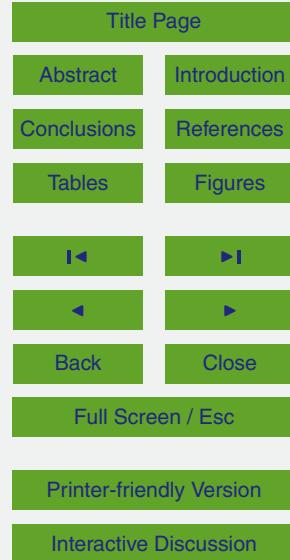
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**Table 3.** Results of model simulations of residence time for G1 using  $^{3}\text{H}$  as an age tracer.

Input series	Unimodal DM			Bimodal EM–DM			RMSE (TU)
	$\tau_r$ (years)	$D_P$	RMSE (TU)	$\tau_{r1}$ (years)	$\tau_{r2}$ (years)	$D_P$	
A1	46.9	0.70	$\pm 0.19$	1	75.8	0.29	$\pm 0.02$
A2	48.2	0.71	$\pm 0.18$	1	82.9	0.30	$\pm 0.01$
A3	39.8	0.71	$\pm 0.18$	1	89.0	0.28	$\pm 0.03$
B1	48.5	0.69	$\pm 0.22$	1	86.8	0.30	$\pm 0.06$
B2	61.6	0.70	$\pm 0.20$	1	95.0	0.29	$\pm 0.05$
B3	54.6	0.69	$\pm 0.21$	1	102.5	0.29	$\pm 0.05$

DM stands for dispersion model; EM–DM stands for exponential–dispersion model;  $D_P$  stands for dispersion parameter. For the EM–DM,  $\tau_{r1}$  was constrained to 1 years, and the fraction of younger water was constrained to 57 %.



**Table 4.** Kendall's  $\tau$  and Pearson's  $r$  correlation coefficients between  ${}^3\text{H}$  and other variables at S2.

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

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

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

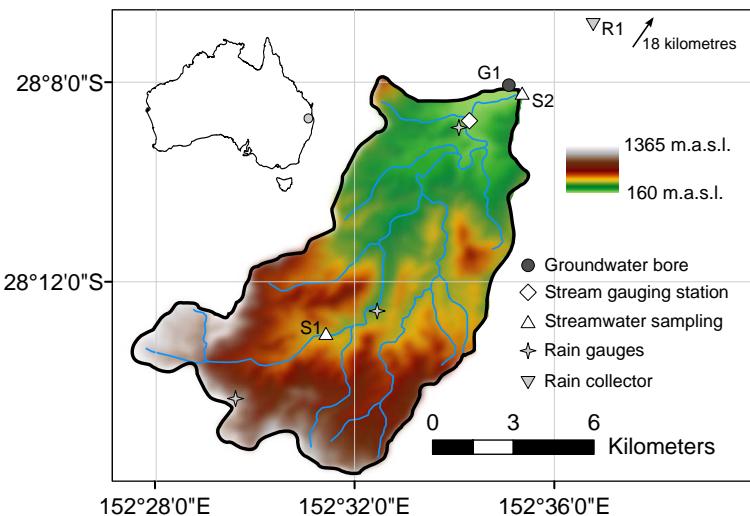
Input series	$\tau_0$ (years)	RMSE (TU)
A1	15.8	$\pm 0.15$
A2	20.2	$\pm 0.15$
A3	24.5	$\pm 0.15$
B1	15.8	$\pm 0.14$
B2	19.8	$\pm 0.16$
B3	24.4	$\pm 0.16$

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

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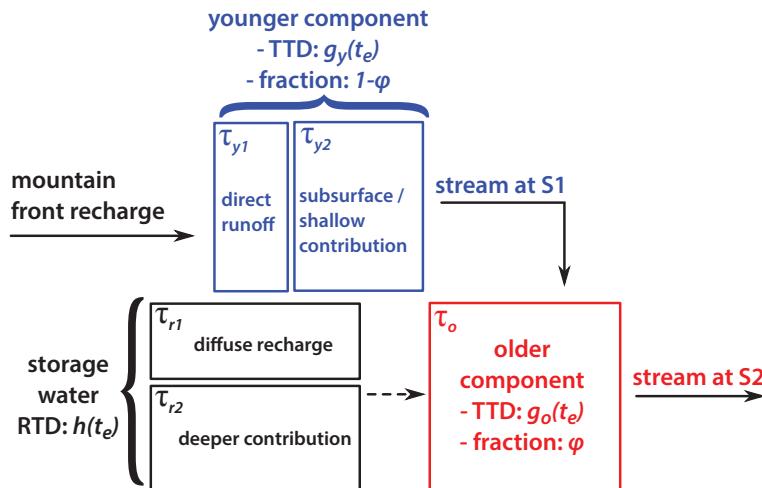


**Figure 1.** Upper Teviot Brook catchment and location of sampling sites. The stream gauging station corresponds to Teviot Brook at Croftby (145011A; operated by the Queensland Department of Natural Resources and Mines). The rainfall gauges correspond to Wilsons Peak Alert (040876), Carneys Creek The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

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**Figure 2.** Conceptual diagram showing the flow components and their transit times to be characterised in this study.

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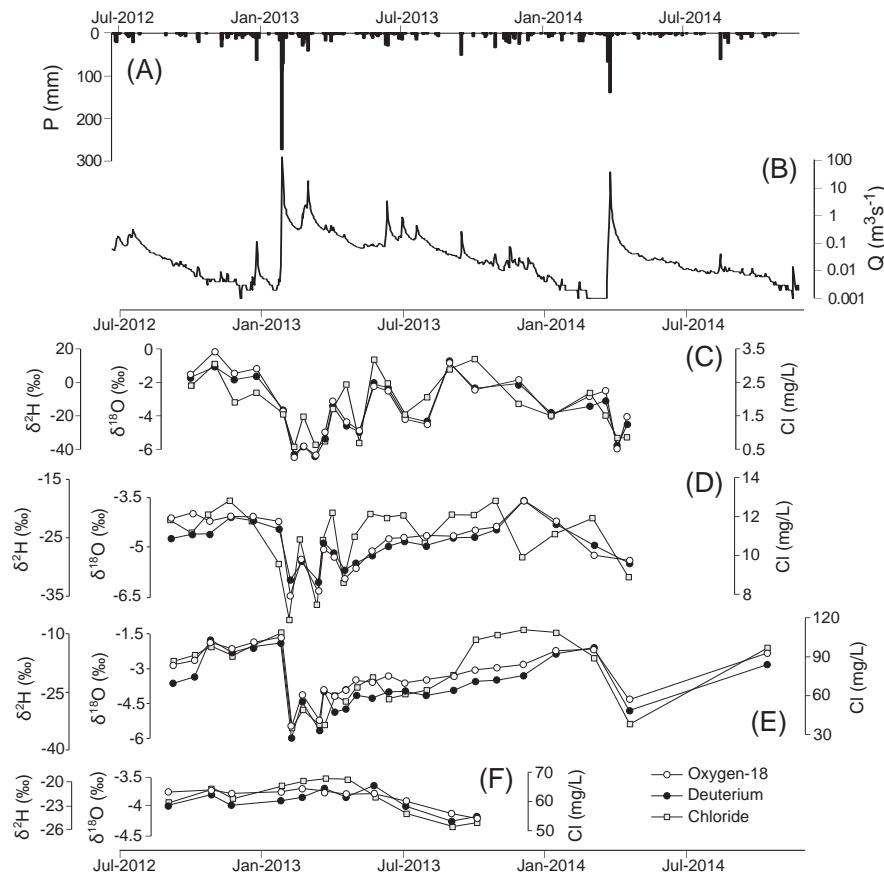
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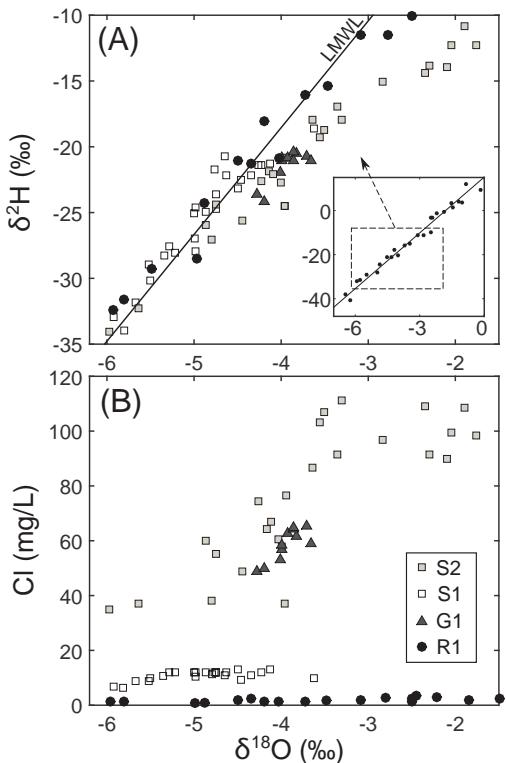
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**Figure 3.** Time-series of Thiessen-averaged precipitation (**a**), daily discharge at Croftby (DNRM station 145011A) (**b**), and  $\delta^{2\text{H}}$ ,  $\delta^{18\text{O}}$  and chloride at R1 (rainfall) (**c**), S1 (**d**) and S2 (streamwater) (**e**), and G1 (groundwater) (**f**). Note that the y axes of  $\delta^{2\text{H}}$ ,  $\delta^{18\text{O}}$  and chloride have different scales for each individual plot.

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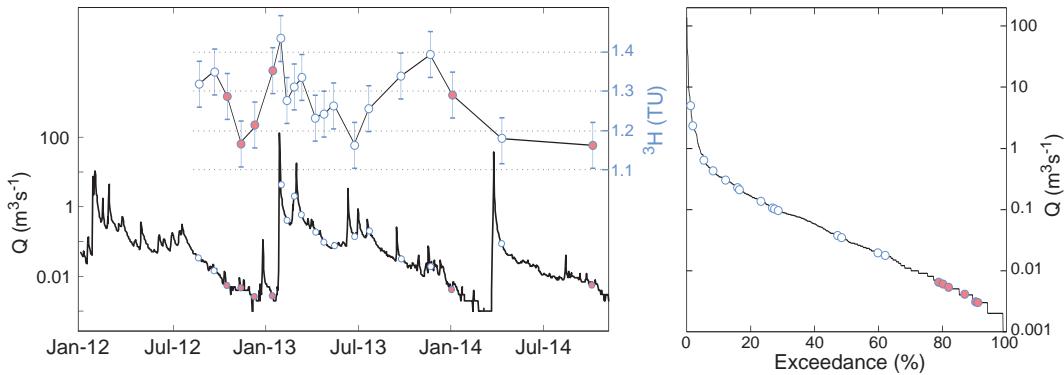
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**Figure 4.** Relationships between **(a)**  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  and **(b)** chloride and  $\delta^{18}\text{O}$  for rainfall, streamwater and groundwater of the Teviot Brook catchment. The local meteoric water line plotted in **(a)** follows the equation  $\delta^2\text{H} = 8.4 \cdot \delta^{18}\text{O} + 15.8$  (Duvert et al., 2015b).

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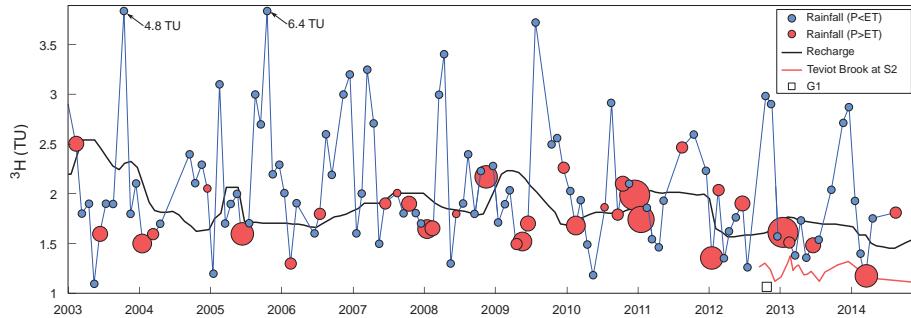


**Figure 5.** Time-series of  ${}^3\text{H}$  activity at S2 and daily discharge data (left panel). Flow duration curve at S2 (right panel). The six red circles correspond to samples used to fit the low baseflow model (see Fig. 9). The whiskers correspond to measurement uncertainty ( $\pm 0.06$  TU for all samples).

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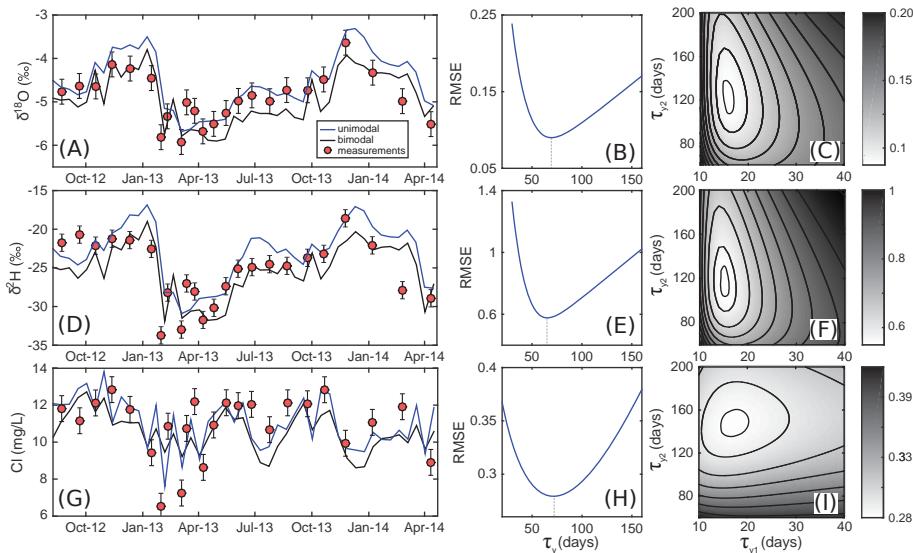


**Figure 6.** Temporal evolution of input  ${}^3\text{H}$  in precipitation (circles) and recharge (black line) for the Teviot Brook catchment considering the A2 scenario. The plotted circles correspond to rainfall collected at Brisbane Aero and adjusted to Teviot Brook according to A2. The recharge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

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**Figure 7.** Exponential (blue) and exponential–dispersion (black) models calibrated to the  $\delta^{18}\text{O}$  (a),  $\delta^2\text{H}$  (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  $\tau_y$  for the three tracers (b, e, h). RMSE of the exponential–dispersion model (27 % younger component; dispersion parameter 0.3) as a function of mean transit times of the younger ( $\tau_{y1}$ ) and older ( $\tau_{y2}$ ) 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 2.

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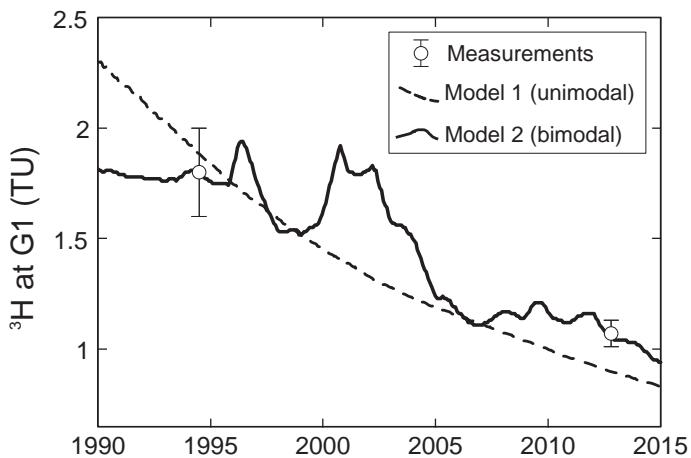
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**Figure 8.** Fits of two models at G1 using A2 as input  ${}^3\text{H}$  series. The unimodal model is a dispersion model with first moment 48.2 years and dispersion parameter 0.71. The bimodal model is an exponential–dispersion model: a younger component (exponential distribution; fraction 57 %) with first moment 1 years and an older component (dispersion distribution; fraction 43 %) with first moment 82.9 years and dispersion parameter 0.30. The 1994 measurement is from Please et al. (1997).

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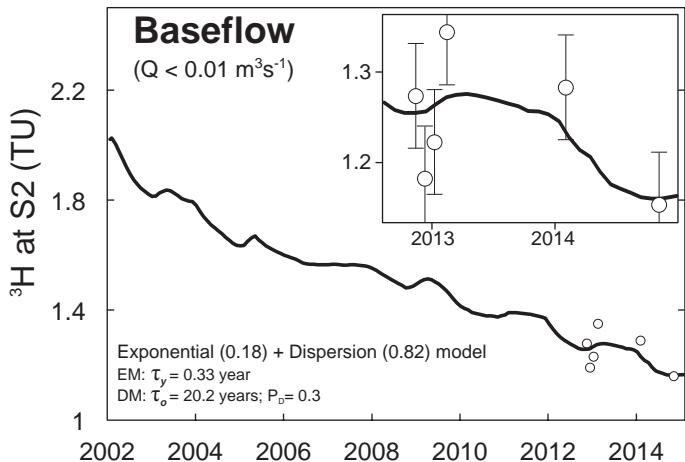
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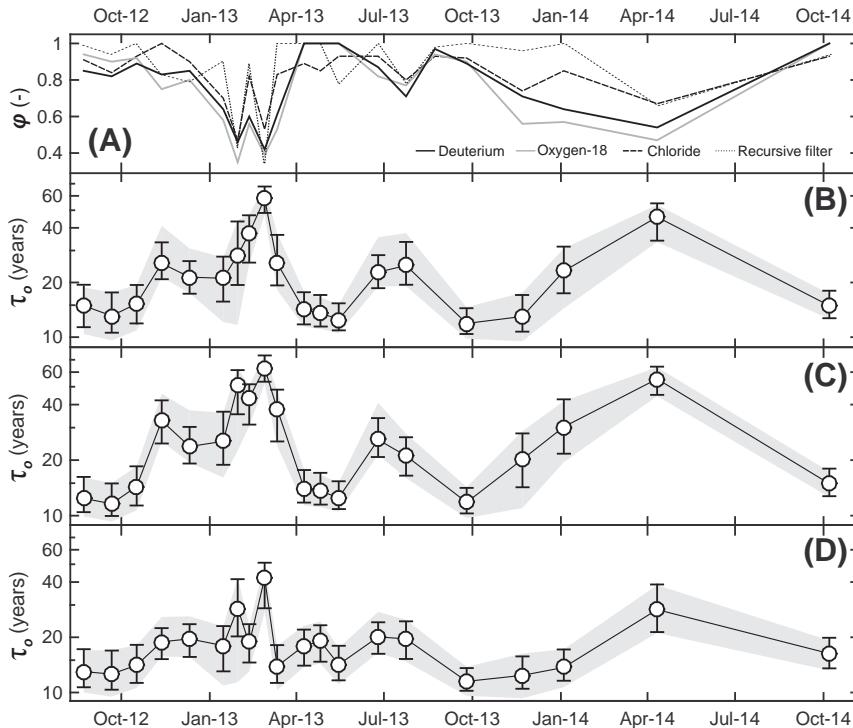
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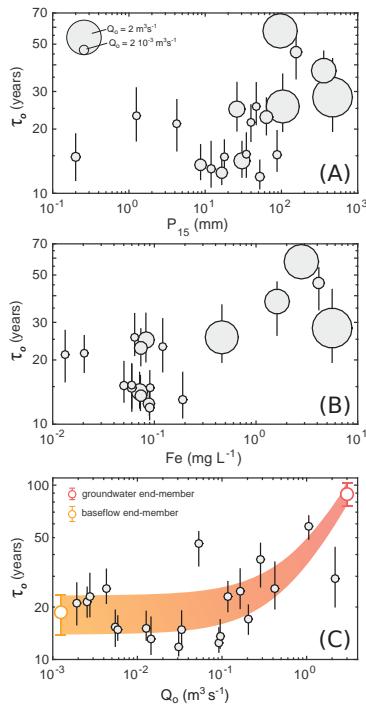
**Figure 9.** Bimodal model fitted to the  ${}^3\text{H}$  activities at S2 under low baseflow conditions (i.e. daily  $Q < 0.01 \text{ m}^3 \text{s}^{-1}$ ). A2 was used as input  ${}^3\text{H}$  series for this case. Results using other input series are listed in Table 5.



**Figure 10.** Variations in the older component fraction  $\phi$  according to the three seasonal tracers (using Eq. 5) and a recursive digital filter (Nathan and McMahon, 1990) **(a)**. Variations in the transit time of older fraction at S2 based on hydrograph separation using  $\delta^{2\text{H}}$  **(b)**,  $\delta^{18\text{O}}$  **(c)** and chloride **(d)**. Values in **(b-d)** were obtained through the adjustment of exponential-dispersion models to each  ${}^3\text{H}$  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.  $\pm 0.06$  TU). The grey shaded area represents the range of values due to uncertainties in the estimation of recharge input (i.e. for the six  ${}^3\text{H}$  input time-series).

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**Figure 11.** Relationship between the transit time of old water fraction ( $\tau_o$ ) and antecedent precipitation  $P_{15}$ , i.e. precipitation depth over the catchment during the 15 days prior to sampling (a). Relationship between  $\tau_o$  and dissolved Fe concentrations (b). Relationship between  $\tau_o$  and  $Q_o$  ( $Q_o = Q \cdot \phi$ ) (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.