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Sources and mean transit times of intermittent streamflow in semi-arid headwater catchments

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ABSTRACT

Determining the sources and mean transit times (MTTs) of water that generates streamflows is important for understanding and managing headwater catchments. The sources and especially the MTTs of water that contributes to streamflow in seasonally intermittent streams are far less studied than for perennial streams. Here we use major ions, dissolved organic carbon, stable isotopes, radon and tritium to quantify the sources and MTTs of intermittent streamflows in three headwater catchments (Banool, McGill and Plantation) from a semi-arid area in southeast Australia. At the start of streamflows, the MTTs of stream water varied from 25 to 42 years in the 1.51 km^2 Banool catchment, 3 to 4 years in the 3.38 km^2 McGill catchment and 9 to 14 years in the 3.41 km^2 Plantation catchment. Winter rainfall increased the relative contribution of younger waters in all three catchments. During higher winter streamflows, the MTTs of stream water reduced to ≤5 years in the Banool catchment and <1 year in the McGill and Plantation catchments. The sources of streamflow also differed between the catchments. Regional groundwater, which close to the stream has a residence time of several hundred years, dominated in the Banool catchment, whereas younger water (residence times of up to 9 years) stored in the riparian zone was the main source in the McGill and Plantation catchments. The differences in MTTs between the catchments may reflect land-use differences, especially the presence of plantation forests in the McGill and Plantation catchments. Overall, due to being less well-connected to the regional groundwater, the MTTs of these intermittent streams are far shorter than those reported for perennial headwater streams in southeast Australia.

The short MTTs indicate that these intermittent streams are vulnerable to short-term variations in rainfall.

1. Introduction

In semi-arid climates, streams in headwater catchments are commonly seasonally intermittent. They flow mainly following periods of sustained rainfall and may comprise alternating dry and flowing reaches during low-flow periods (Buttle et al., 2012; Datry et al., 2014; Stubbington et al., 2017; Goodrich et al., 2018). Headwater streams are important parts of many river networks (Meyer et al., 2007; Datry et al., 2014; Acuna et al., 2014; Stubbington et al., 2017˜) and often provide low salinity water with low nutrient loads (Jarvie et al., 2018). The observation that perennial headwater streams continue to flow during dry periods indicates that they are fed by relatively large stores of water contained in the soils, rocks, or regolith. These water sources have residence times that may be as short as a few weeks for soil water or interflow and up to several millennia for deeper groundwater (McGuire and McDonnell, 2006; Mueller et al., 2013; Peters et al., 2014; Cartwright and Morgenstern, 2015; Cartwright et al., 2018a, 2018b; Duvert et al., 2016).

Much less is known about the sources and mean transit times (MTTs) of water that initiates and sustains streamflows in seasonally intermittent streams from headwater catchments, which hinders their protection and management. Climate change and anthropogenic impacts, including forestry, agricultural land clearing and human settlements, may affect these catchments (Barmuta et al., 2009; Owuor et al., 2016). Many of these changes are predicted to increase the number and length of intermittent streams in semi-arid areas (Larned et al., 2010; Doll and ¨ Schmied, 2012; Datry et al., 2014). Because streams with longer MTTs are likely to be more resilient to short-term changes in rainfall or runoff, understanding the sources and timescales of flow in these streams is important for understanding and managing headwater catchments.

1.1. Tracing sources of stream water

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Several water sources, including runoff, soil water, perched groundwater, shallow young riparian groundwater and deeper older regional groundwater, may contribute to streamflows (Fenicia et al., 2006; Peters et al., 2014; Duvert et al., 2016; Cartwright and Morgenstern, 2018). A combination of major ions, dissolved organic carbon (DOC), stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) and radioactive isotopes (e.g., ^{222}Rn and ^{3}H) may be used to determine water sources at different stages of streamflow. Variable degrees of evapotranspiration, mineral dissolution and breakdown of soil organic matter can result in different sources of water having different concentrations of major ions or DOC (e.g., Uhlenbrook and Hoeg, 2003; Hugenschmidt et al., 2014; Cartwright et al., 2018a). Stable isotope ratios of individual runoff-forming rainfall events can be significantly different (Clarke and Fritz, 1997), and there may also be systematic seasonal or longer-term changes in the stable isotope ratios of rainfall (Hughes and Crawford, 2012). Evaporation may also alter the stable isotope ratios in near-surface waters (Clarke and Fritz, 1997). Thus, different water sources in a catchment may have different stable isotope ratios. ^{222}Rn activities are commonly several orders of magnitude higher in groundwater and soil water than surface runoff; hence, ^{222}Rn is commonly used to identify the inflows of catchment waters to streams (Cook, 2013). Additionally, because soil water, interflow and shallow groundwater are likely to be younger than deeper groundwater, ^{3}H activities also allow the sources of water in streams to be determined (Cartwright and Morgenstern, 2016b; Duvert et al., 2016; Cartwright et al., 2018a, 2018b, 2020b; Howcroft et al., 2018).

There is likely to be a difference in the dominant water sources that sustain streamflow at different stages of flow. These changes may be evident from changes in stream geochemistry (e.g., Peters et al., 2014; Duvert et al., 2016; Howcroft et al., 2018). In addition, the runoff ratio (i.e. the proportion of rainfall that is exported via the stream) may vary with streamflow (McGlynn and McDonnell, 2003). Runoff ratios at low streamflows where the stream water is largely derived from deeper near- river sources are likely to be lower than at high streamflows where shallow water sources (e.g., water from the soils or regolith) from across the catchment have been mobilised.

1.2. Mean transit times of water

The transit time may be defined as the time that water spends travelling through a catchment from where it infiltrates to where it discharges into the stream or is sampled from within the aquifers, soils or regolith. Because water travelling through the saturated and unsaturated zones follows different flow paths and undergoes dispersion and mixing, it has a range of MTTs not a discrete age (McGuire and McDonnell, 2006). While MTTs provide less information on catchment processes than the transit time distributions as a whole (McDonnell et al., 2010), they are valuable in understanding the water sources that contribute to streamflows (Peters et al., 2014; Gabrielli et al., 2017; Cartwright and Morgenstern, 2018). Lumped parameter models (LPMs) can be used to estimate MTTs and tracer concentrations (Zuber and Maloszewski, 2001; Jurgens et al., 2012). Although they assume aquifers with simple geometries, homogeneous hydraulic properties and uniform recharge, they provide estimates of MTTs that are similar to those in aquifers with more complex hydraulic properties (Cartwright et al., 2018b).

Comparison of the temporal variation of stable isotope ratios and/or major ion concentrations in rainfall and streamflows have commonly been used to estimate MTTs via LPMs (e.g., as summarised by McGuire and McDonnell, 2006). This approach requires long (ideally multi-year) sub-weekly datasets that are not common due to logistical or financial concerns. Using this approach with LPMs yields a single MTT estimate, whereas streams are more likely to have different MTTs at low and higher flows (e.g., Morgenstern et al., 2010). The approach also assumes that the flow system is time-invariant, which is not generally the case (Kirchner, 2016). Additionally, these tracers become progressively more ineffective where MTTs exceed 4 to 5 years, which is the case for many catchments in southeast Australia (Cartwright et al., 2020a), as the temporal variations are smoothed out (Stewart et al., 2010). Alternative methods, such as flux tracking (Hrachowitz et al., 2013), StorAge selection functions (e.g., Rinaldo et al., 2015; Benettin et al., 2015), and ensemble hydrographs (Kirchner, 2019; Knapp et al., 2019) may be applied to shorter geochemical records, including those from the flow periods in intermittent streams. However, they still require high- frequency (sub-weekly) tracer data and are less able to detect the input of older waters.

Especially in the southern hemisphere, Tritium (^{3}H) allows MTTs to be estimated at different flow conditions. ^{3}H is part of the water molecule and has a half-life of 12.32 years (Harris, 2000). Unlike other tracers such as ^{14}C, ^{3}He, SF_6 and the chlorofluorocarbons, ^{3}H activities are only affected by radioactive decay and dispersion and not by reactions between the water and the aquifer matrix or exchange with the atmosphere. Elevated “bomb-pulse” ^{3}H activities produced by above- ground thermonuclear tests beginning in 1963 were several orders of magnitude lower in the southern hemisphere than in the northern hemisphere (Morgenstern et al., 2010). The ^{3}H activities of catchment waters recharged during that time are now below those of present-day rainfall (Morgenstern et al., 2010; Tadros et al., 2014). While this precludes tracing the flow of bomb-pulse recharge (e.g., Brown, 1961; Allison and Hughes, 1975; Egboka et al., 1983), it does allow MTTs to be readily estimated from single ^{3}H measurements using LPMs (Morgenstern et al., 2010; Cartwright and Morgenstern, 2015).

The decline of ^{3}H activities of the remnant bomb pulse water in the southern hemisphere means that the suitability of LPMs cannot be tested using time-series ^{3}H measurements that commence now (Cartwright and Morgenstern, 2016b). Consequently, LPMs need to be adopted using a general understanding of flow system geometry or previous time-series studies in similar catchments. While this limitation and macroscopic mixing within the aquifers (aggregation) complicate the calculation of MTTs (Kirchner, 2016; Stewart et al., 2017), the fact that ^{3}H activities decrease with residence times in the catchments allows relative relationships to be established.

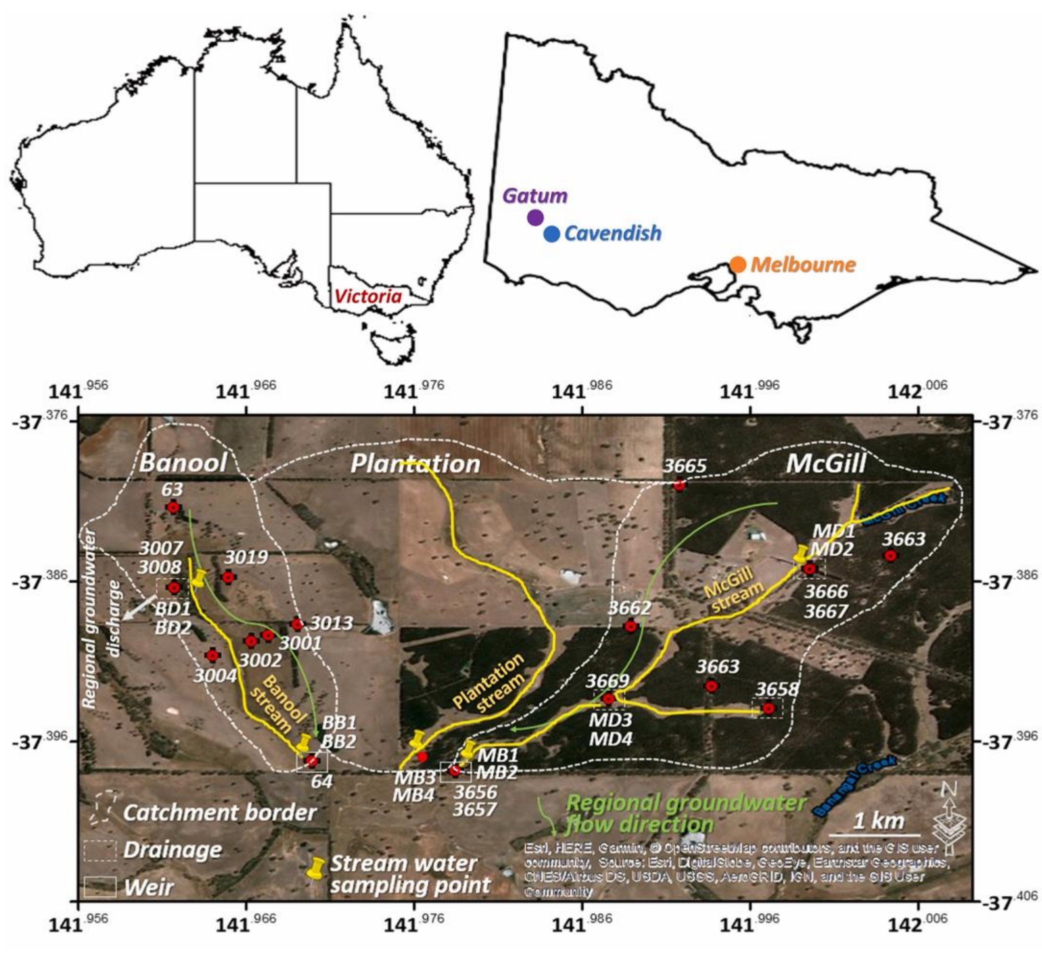
MTTs in perennial headwater catchments that range in size from a few km^2 to a few hundred km^2 in southeast Australia are commonly several years to decades, especially during baseflow conditions (Cartwright et al., 2020a). These long MTTs probably reflect the presence of deeply-weathered regolith with a large storage capacity combined with high evapotranspiration rates that result in low recharge and groundwater flow rates (Cartwright et al., 2020a). While these perennial catchments are becoming better understood, it is not clear whether the MTTs in intermittent headwater catchments will be as long. Compared with perennial catchments, intermittent catchments are less well connected to regional groundwater systems (e.g., Zimmer and McGlynn, 2018; van Meerveld et al., 2019). van Meerveld et al. (2019) proposed that the distribution of MTTs changes as intermittent streams expand and retract. However, there has been little direct quantification of the variations in the MTTs of intermittent streams at low and high flows. Additionally, whether the sources of water vary at low and high flows is also not well understood. The conclusion that streams, in general, are sustained by young near-stream catchment waters (e.g., Berghuijs and Kirchner, 2017; Rhodes et al., 2017) may be especially true in intermittent streams that are likely to be less well connected to the regional groundwater system.

1.3. Objectives

Here we examine the sources and MTTs of water in small seasonally intermittent streams from a semi-arid area of southeast Australia. We use major ions, DOC, stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) and radioisotopes (^{222}Rn and ^{3}H) to quantify the sources of stream water that initiate and maintain streamflows. We then use ^{3}H to estimate MTTs of water at different flow conditions. We hypothesise that younger near-stream sources of water will be more important in these catchments than in comparable perennial headwater catchments.

2. Study area

The study focuses on two well-instrumented catchments (Banool and McGill) at Gatum in western Victoria (Fig. 1) that contain seasonally intermittent streams. Additional limited data from an ungauged stream (referred to here as the Plantation stream) located between the Banool and McGill catchments (Fig. 1) is also presented. The Banool catchment is 1.51 km^2 and comprises mainly dryland pasture used for sheep grazing with about 3% remnant *Eucalyptus* trees. The McGill catchment is 3.38 km^2 and consists of approximately 38% grassland and 62% *Eucalyptus* plantation forest that was established in 2005 (Adelana et al., 2015). The maximum flow lengths upstream of the weirs of the Banool and McGill streams (Fig. 1) are 2.3 and 3.8 km, respectively (Adelana et al., 2015). The Plantation stream is 2.9 km long and also flows through mixed plantation forest and grassland (Fig. 1); the catchment area is 3.41 km^2. The elevation of the area ranges from 236 to 265 m AHD (Australian Height Datum). The area has cool, wet winters and hot, dry summers (Koppen-Geiger zone Bsk). The average annual rainfall at ¨ Cavendish (Station 089009) ~19 km southeast of the sites (Fig. 1) between 2010 and 2018 was ~630 mm (Bureau of Meteorology, 2020). Daily rainfall from a less-complete record from Gatum (Station 089043) is well-correlated with that at Cavendish ($r^2 = 0.96$, $p < 0.05$). Estimated average annual actual evapotranspiration rates between 2011 and 2016 were approximately 580 mm (Dresel et al., 2018). Most rainfall occurs in the austral winter (Fig. 2a), and the lowest evapotranspiration rates are between May and October (Bureau of Meteorology, 2020).



Victoria
Gatum
Cavendish
Melbourne
Banool
Plantation
McGill
Regional groundwater discharge
Banool stream
Plantation stream
McGill stream
Catchment border
Drainage
Weir
Stream water sampling point
Regional groundwater flow direction
1 km

Fig. 1. Map showing the Banool, Plantation and McGill streams with the locations of groundwater bores (numbered) and shallow piezometers (letters) at Gatum. The catchment divides are from Dresel et al. (2018). Background ArcGIS®10.5 image is from Esri, HERE, Garmin, ©OpenStreetMap contributors and the GIS User Community, Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNESAirbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community.

The bedrock in the study area comprises indurated Early Devonian ignimbrites (Cayley and Taylor, 1997) with tens-of-meters deep weathered saprolitic clay-rich regolith and ferruginous laterite duricrust (Brouwer and Fitzpatrick, 2002). Some of the drainage areas contain Quaternary alluvium with colluvium and low-permeable saprolite (Brouwer and Fitzpatrick, 2002; Adelana et al., 2015). There is a shallow (1 to 4 m deep) locally-perched groundwater system in the riparian zones, especially in the McGill and Plantation catchments (Brouwer and Fitzpatrick, 2002; Adelana et al., 2015). Although it may form a continuum, we distinguish this riparian groundwater from deeper groundwater below and outside the riparian zone (designated here as regional groundwater). As indicated in Fig. 1, the regional groundwater flows southwards in both catchments (Brouwer and Fitzpatrick, 2002; Barua et al., 2021). The pre-land clearing and present-day recharge rates are

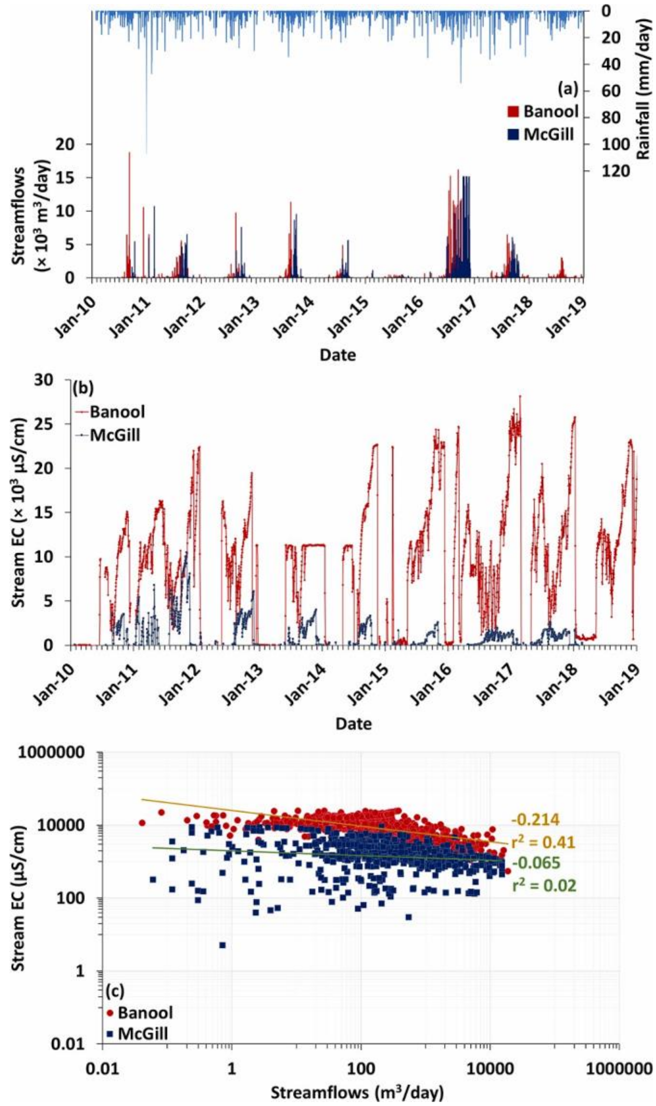


Fig. 2. (a) Daily rainfall at Cavendish (Station 089009; ~19 km southeast of the sites) and daily streamflows of the Banool and McGill streams. (b) EC values of the Banool (Jan 2010 to Dec 2018) and McGill (Jan 2010 to Nov 2017) streams. (c) Relationship between daily stream EC values and streamflows. Power-law regression lines with slopes and r^2 values are shown in yellow and green for the Banool and McGill streams, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

typically low (<14 mm/year), and the residence times of regional groundwater estimated using ^{14}C are up to 24,700 years (Barua et al., 2021).

3. Methods and materials

3.1. Water sampling

One stream water sample from the Banool weir was collected manually in May 2018. An additional thirty-one stream water samples were collected at intervals of three to ten days over a wide range of streamflows between July and November 2018 using portable ISCO 6712 and Sigma 900 auto-samplers from the weirs on the Banool (n = 15) and McGill (n = 16) streams (Fig. 1). A further two samples were collected manually from elsewhere along the streams (near bores 3007, 3666: Fig. 1), and two samples were collected from the Plantation stream (Fig. 1). Soil water samples were collected from ~1 m depth in the drainage zones and near the weirs of the Banool (n = 2) and McGill (n = 5) catchments (Fig. 1) using suction lysimeters and/or centrifuged soil samples. Regional groundwater across both Banool and McGill catchments was sampled via nineteen monitoring bores with screen depths of 1.3 to 29.7 m (Fig. 1). Shallow piezometers (~1 m deep with ~10 cm screens near their base) installed adjacent to Banool (n = 4), McGill (n = 6) and Plantation (n = 2) streams, respectively (Fig. 1) were used to sample the shallow riparian groundwater that in places is perched above the regional groundwater. Regional (n = 24) and shallow riparian groundwater (n = 24) were sampled between May and November 2018 from the screened interval using a submersible pump or bailer. At least three bore volumes of groundwater were purged prior to sampling, or the bore was dewatered and allowed to recover. Eight rain water samples were collected in narrow-mouthed containers with open funnels between June and October 2018. A one-year aggregated rainwater sample was collected between May 2018 and May 2019. Except for samples from the rainfall collectors and auto-samplers, water samples were collected in high-density polyethylene bottles and stored at ~4 °C until analysis.

The Banool and McGill catchments at Gatum were instrumented in 2010. Water levels and electrical conductivity (EC) at the weirs (Figs. 1, 2a, b) are measured at 30 min intervals using Campbell CR800 loggers. A rating curve is used to calculate streamflow from the height of the stream (Adelana et al., 2015). In 2018, the

McGill stream height was incorrectly recorded, and streamflows could not be calculated. There are also several gaps in the McGill stream height and EC record in that year; however, relative stream heights were still recorded over much of the year.

3.2. Analytical techniques

Geochemical data are presented in Table S1. EC was measured in the field using a calibrated hand-held TPS WP-81 multimeter and probe. HCO_3 concentrations with a precision of ± 5% were measured using a Hach digital titrator and reagents. Cation concentrations were analysed at Monash University using a Thermo Scientific iCAP 7000 series ICP- OES on filtered (0.45 µm cellulose nitrate filters) water samples that were acidified to pH < 2 with double distilled 16 N HNO_3. Anion concentrations were also analysed at Monash University using a Thermo Scientific Dionex ICS-1100 IC on filtered and unacidified water samples. Based on replicate analyses, the precision of cation and anion concentrations are ± 2%, and the accuracy is ± 5% based on the analysis of certified standards. Total dissolved solids (TDS) concentrations are the sum of the concentrations of major ions. Total DOC concentrations were analysed on filtered and unacidified water samples using a Shimadzu TOC-V CPH/CPN Total Organic Carbon analyser at Monash University; the detection limit is 0.2 mg/L. ^{222}Rn activities were measured in groundwater and stream water samples using a portable radon-in-air Durridge RAD-7 alpha counter and closed-loop degassing system and are expressed in Bq/m[1]. δ^{18}O and δ^{2}H values were measured at Monash University using a Thermo Finnigan Delta Plus Advantage mass spectrometer. δ^{18}O values were measured by equilibration with He-CO_2 at 32 °C for 24 hrs in a Thermo Finnigan Gas Bench while δ^{2}H values were measured by the reaction of water samples with Cr at 850 °C using a Finnigan MAT H/ Device. δ^{18}O and δ^{2}H were measured against internal standards that are calibrated using IAEA, SMOW, GISP and SLAP standards. δ^{18}O and δ^{2}H values were normalized following Coplen (1988) and are expressed relative to V-SMOW. The precision is ± 0.2‰ for δ^{18}O and ± 1‰ for δ^{2}H.

3.3. Determining mean transit times

MTTs may be estimated using LPMs via:

$$C_{out}(t) = \int_0^\infty C_{in}(t-T)e^{-\lambda T} g(T)\, dT \qquad (1)$$

(Zuber and Maloszewski, 2001; Jurgens et al., 2012). In Eq. (1), $C_{out}(t)$ is the ^{3}H activity of water at time t, C_{in} is the input of ^{3}H over time, λ is the decay constant (0.0563 per year), T is the transit time, and $g(T)$ is the transit time distribution function (Małoszewski and Zuber, 1982). There are several commonly used LPMs, and the distribution functions for these are summarised by Małoszewski and Zuber (1982), Zuber and Maloszewski (2001), Zuber et al. (2005) and Jurgens et al. (2012). The exponential mixing model (EMM) applies where the flow from the entire aquifer thickness discharges to the stream (Jurgens et al., 2012). The dispersion model (DM) is based on the one-dimensional advection–dispersion transport equation (Małoszewski and Zuber, 1982) and may be applied to a wide range of flow configurations (Jurgens et al., 2012). The transit time distribution function includes the dimensionless dispersion parameter (DP) that reflects the relative importance of dispersion to advection (Zuber and Maloszewski, 2001). This study used DP values of 0.05 to 0.5, which are applicable to hundreds-of-meters to kilometer-scale flow systems (Zuber and Maloszewski, 2001). The exponential piston-flow model (EPM) describes the flow in aquifers with both exponential and piston-flow portions, such as where there is vertical recharge through the unsaturated zone and exponential flow within the aquifer (Morgenstern et al., 2010). The transit time distribution function includes the EPM ratio that specifies the relative contribution of exponential and piston flow (Jurgens et al., 2012). The EPM model describes exponential flow where the EPM ratio equals 0 and is close to piston-flow where the EPM ratio is > 5. EPM ratios of 0.33 to 1.0 were used in this study, which represents flow systems with 75 to 50% exponential flow. These models have been successfully applied to catchments elsewhere where there are time-series data (Morgenstern et al., 2010; Blavoux et al., 2013) and other LPMs (such as the gamma model) generally yield similar estimates of MTTs (Cartwright et al., 2018a).

This study used the annual average ^{3}H activities of rainfall in Melbourne (Tadros et al., 2014; International Atomic Energy Agency, 2017) as the ^{3}H input function. The ^{3}H activities of Melbourne rainfall peaked at ~60 TU between 1950 and 1960, then declined exponentially to present-day values of 2.8 to 3.2 TU. The predicted average annual ^{3}H activity of present-day rainfall in western Victoria is 2.6 to 3.0 TU (Tadros et al., 2014), and the ^{3}H activity of the aggregated yearly (May 2018 to May 2019) rainfall sample from Gatum is ~2.8 TU (Table S1, Barua et al., 2021). Thus, a ^{3}H activity of 2.8 TU is used for present-day and pre-bomb pulse rainfall. MTTs are estimated by matching the predicted ^{3}H activities from the LPMs to the observed ^{3}H activities of the samples. The volume of groundwater (V in m^3) that contributes to streamflow (Q in m^3/day) is related to the MTT by

$$V = Q.MTT \qquad (2)$$

(Małoszewski and Zuber, 1982, 1992; Morgenstern et al., 2010; Gusyev et al., 2016).

4. Results

4.1. Streamflows, EC and radon

Although experiencing large variability, the Banool and McGill streams generally start to flow in mid-May and continue flowing until October with peak flows in August to September (Dresel et al., 2018). In 2018, the Banool stream started to flow in mid-May soon after a rainfall event of 36 mm in 48 hrs; the McGill stream commenced flowing in mid- July during a 7-day period where 50 mm of rainfall (Bureau of Meteorology, 2020). Due to higher rainfall and lower evapotranspiration rates, streamflows are higher during the winter months (Fig. 2a). Between 2010 and 2018, the annual streamflows were 1.26×10^4 to 2.41×10^5 m^3 in the Banool stream, and from 2010 to 2017, the annual streamflows were 7.29×10^3 to 6.35×10^5 m^3 in the McGill stream. Except in 2016, which had a higher than average annual rainfall (~800 mm: Bureau of Meteorology, 2020), annual streamflows of the Banool stream were higher than the McGill stream (Dresel et al., 2018). In 2018, the annual Banool streamflow was 6.33×10^4 m^3, and the highest daily streamflow was 3.02×10^3 m^3 in August (Fig. 3a). The level of

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[1] H activities were measured at the Institute of Geological and Nuclear Sciences (GNS) in New Zealand. Water samples were vacuum distilled, electrolytically enriched, and ^{3}H activities were measured by liquid scintillation using Quantulus ultra-low-level counters (Morgenstern and Taylor, 2009). ^{3}H activities are expressed in tritium units (TU), where 1 TU corresponds to a ^{3}H/^{1}H ratio 1×10^{-18}. The relative uncertainties and quantification limits are ± 2% and 0.02 TU, respectively.

the McGill stream was also higher during the winter months (Fig. 3b). The streamflow patterns of the Plantation stream are similar to the Banool and McGill streams.

The Banool stream flows for about half of the year, while McGill streamflow only occurs over about three months (Figs. 3 and 4). Monthly runoff ratios were generally high from August to September (Fig. 4). 2016, which as discussed above was a year of higher rainfall, had the highest runoff ratios during the monitoring period. In the Banool catchment, the runoff ratios ranged from 2 to 16% in the winter months of 2018 (Fig. 4). Streamflows in the larger McGill catchment are generally lower than in the Banool catchment (Fig. 2a), leading to lower runoff ratios in 2018 in the McGill catchment.

Groundwater elevations gradually increase following winter rainfall and decrease over the summer months (Dresel et al., 2018; Barua et al., 2021). Vertical head gradients at paired bores 3007 and 3008 in the Banool catchment (Fig. 1) are upwards. Water levels in the adjacent piezometers BD1 and BD2 (Fig. 1) are commonly above the ground level, and the soils around these piezometers are generally water-saturated. In contrast, groundwater levels at all bores in the McGill catchment, even adjacent to the stream, are a few metres below ground level, and head gradients in paired bores 3666 & 3667 and 3656 & 3657 (Fig. 1) are downward.

Daily stream EC values between 2010 and 2018 ranged from 5.49×10^2 to 2.57×10^4 μS/cm and from 5.10 to 9.25×10^3 μS/cm in the Banool and McGill streams, respectively (Fig. 2c). EC values were generally low during high streamflows and gradually increased after the peak streamflows (Fig. 2a, 2b). The trends in log EC vs. log streamflow (Fig. 2c) have slopes that are close to 0. Simple dilution of a constant inflow of saline baseflow with low salinity rainfall would produce log EC vs. log streamflow trends close to − 1 (Godsey et al., 2010), and the data are more consistent with the displacement of moderately saline water from within the catchments into the streams at higher streamflows. The stream waters have ^{222}Rn activities of 1710 to 3180 Bq/m^3 (Table S1). Whereas, the riparian zone groundwater and regional groundwater have ^{222}Rn activities of 1510 to 155,000 Bq/m^3 and 1320 to 145,000 Bq/m^3, respectively (Table S1).

4.2. Major ions and dissolved organic carbon

Overall, the TDS concentrations and major ion geochemistry of stream water overlap with those of soil water, riparian zone groundwater and regional groundwater (Table S1; Fig. 5a–h, S1). However, there are subtle differences in the major ion geochemistry of different water types between the catchments that can help to understand the origins of streamflow. In the Banool catchment, the concentrations of TDS and major ions (e.g., Na, Mg, SO_4 and Br) in stream water, riparian zone groundwater and regional groundwater are similar. By contrast, the stream water and most of the riparian zone groundwater in the McGill catchment have lower major ion concentrations than the regional groundwater. DOC concentrations also vary between different waters in the Banool, McGill and Plantation catchments (Table S1, Fig. 5i, 5j). The stream waters have DOC concentrations of 18 to 33 mg/L that are similar to those of most of the riparian zone groundwaters (12 to 63 mg/ L). Regional groundwater generally has lower DOC concentrations (1.4 to 30 mg/L), with the highest concentrations in the shallow parts of the aquifer between 1.3 and 2.5 m depths (Table S1).

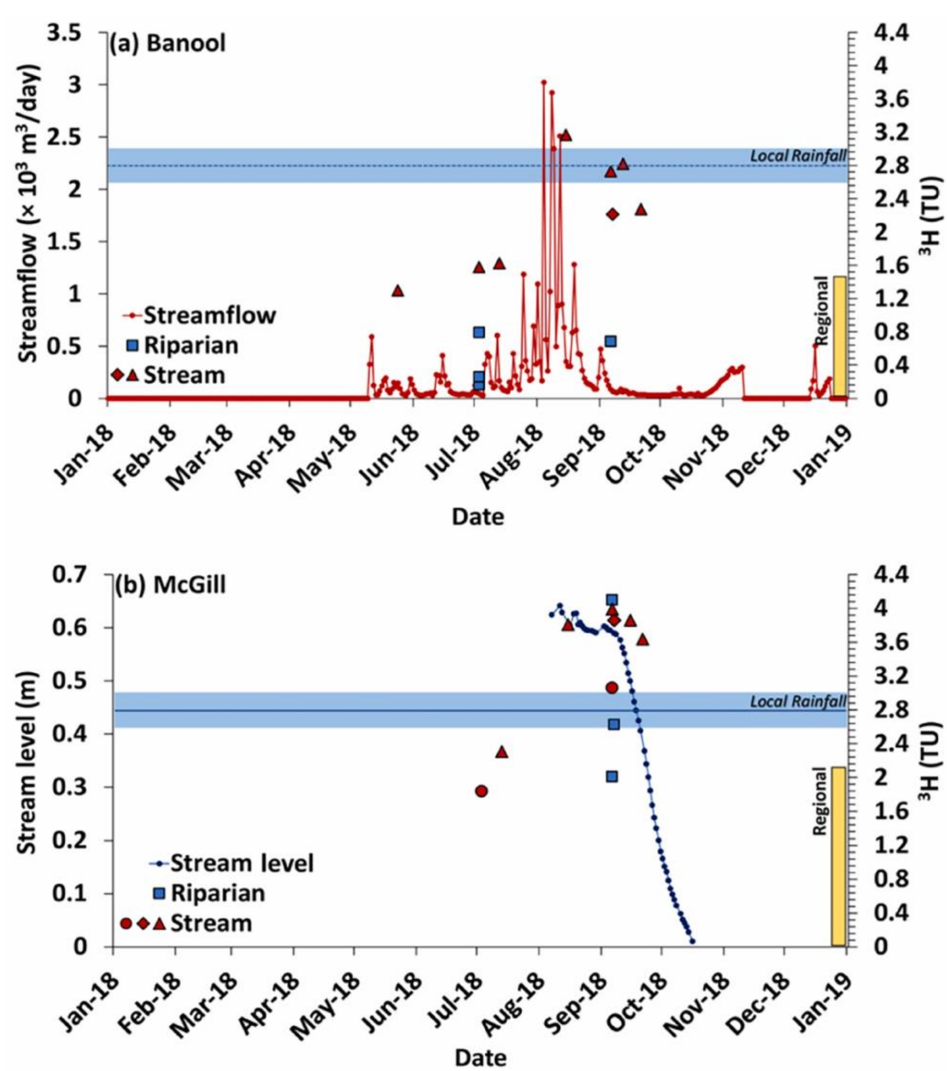

Fig. 3. 2018 streamflow and stream level and [1] H activities in waters from the riparian zones and streams in the Banool (a) and McGill (b) catchments (Fig. 1). Diamond symbols indicate samples from elsewhere along the streams and circle symbols are the Plantation stream water samples. The yellow bar indicates the range of ^{3}H activities in regional groundwater (data from Table S1). The shaded band represents estimated ^{3}H activities of present-day rainfall (2.6 to 3.0 TU: Tadros et al., 2014) and the dashed line is the measured ^{3}H value of local rainfall. Data from Table S1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.3. Stable isotopes The δ^{18}O and δ^{2}H values of different catchment waters and rainfall are summarized in Fig. 6. δ^{18}O and δ^{2}H values of local rain water are − 5.7 to 2.8‰ and − 31 to 21‰, respectively. The stream water has a wide range of δ^{18}O (-4.3 to 1.1‰) and δ^{2}H (-28 to 6‰) values that define a slope of 6.5, implying that these waters have undergone evaporation (Clarke and Fritz, 1997). The δ^{18}O and δ^{2}H values of riparian zone groundwater are − 4.9 to − 1.1‰ and − 37 to − 13‰, respectively, and those of the soil waters are − 4.6 to − 3.2‰ and − 36 to − 17‰, respectively. The regional groundwater has less variable δ^{18}O values of − 5.5 to − 4.3‰ and δ2H values of − 34 to − 27‰ that group around the weighted average δ^{18}O and δ^{2}H values of Melbourne rainfall (δ^{18}O = 5.03‰ and δ^{2}H = 28.4‰: Hughes & Crawford, 2012). As with the major ions and DOC, the δ^{18}O and δ^{2}H values of riparian zone groundwater in the Banool catchment are similar to those of regional groundwater. By contrast, in the McGill catchment, most of the riparian zone groundwater has higher δ^{18}O and δ^{2}H values than the regional groundwater. The δ^{18}O and δ^{2}H values of soil waters in both the Banool and McGill catchments overlap with those of stream water, riparian zone groundwater and regional groundwater.

4.4. Tritium activities

The Banool stream water has ^{3}H activities of 1.30 to 3.17 TU, and the McGill stream water has ^{3}H activities of 2.31 to 3.99 TU (Fig. 3). ^{3}H activities in the Plantation stream are between 1.84 and 3.06 TU (Fig. 3). At any time, the ^{3}H activities of water at the weirs and water from elsewhere along the streams are similar (Table 1, Fig. 3). ^{3}H activities are lowest at the start of streamflows and highest during high winter streamflows (Fig. 3). The highest ^{3}H activities are higher than those of measured and predicted average annual rainfall in this area (~2.8 TU), but are similar to those of winter rainfall in southeast Australia. Those rains typically have high ^{3}H activities due to the transport of water vapor with high ^{3}H activities from the stratosphere to the troposphere (Morishima et al., 1985; Ehhalt et al., 2002; Tadros et al., 2014).

[1] H activities of the regional groundwater are generally much lower than those in the streams (<0.02 to 2.14 TU: Table S1, Fig. 3). Shallow (1.3 m depth) regional groundwater from the discharge area in the Banool catchment has a ^{3}H activity of 1.10 TU. Other regional groundwater with ^{3}H activities of > 1 TU is from the recharge areas at the edges of the catchments (e.g., bore 63 at Banool and bores 3662, 3658 at McGill: Table S1, Fig. 1). Groundwater with ^{3}H activities of 1.01 to 2.14 TU is also present adjacent to the McGill stream near the weir (bores 3656 and 3657: Table S1, Fig. 1), which is also an area where recharge occurs (Barua et al., 2021). In the Banool catchment, groundwater from the riparian zone has ^{3}H activities of 0.16 to 0.79 TU (Table S1, Fig. 3) that overlap with those of the regional groundwater. By contrast, the riparian zone groundwater in the McGill and Plantation catchments has ^{3}H activities of 2.01 to 4.10 TU (Table S1, Fig. 3) that are

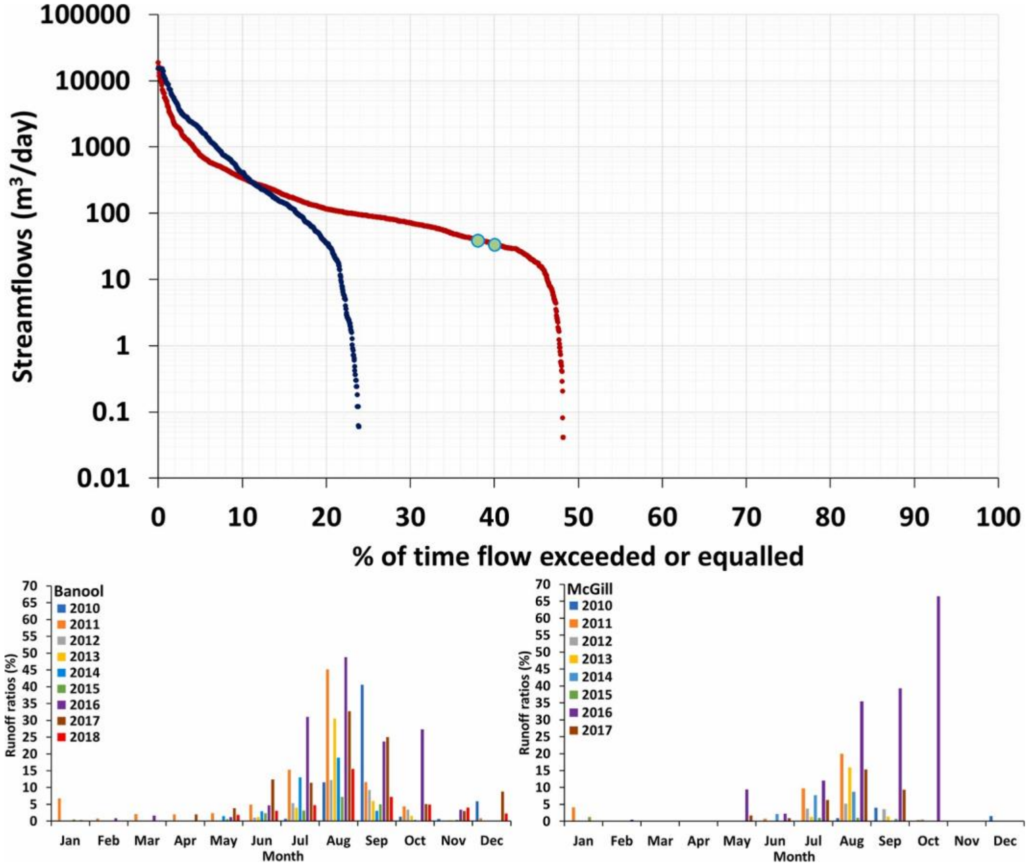

Fig. 4. Flow duration curves at Banool (Jan 2010 to Dec 2018) and McGill (Jan 2010 to Nov 2017). The circle symbols represent conditions of stream water sampling. The bottom figures show monthly ratios of streamflow and rainfall in the Banool and McGill catchments.

generally higher than the regional groundwater (Table S1, Fig. 3). Aside from one sample, ^3H activities of groundwater in the riparian zone are lower than those of present-day local rainfall (Table S1, Fig. 3). Locally high ^3H activities in riparian zone groundwater probably reflect preferential recharge by winter rainfall with higher ^3H activities (Fig. 3).

5. Discussion

5.1. Mean transit times of intermittent streamflow and groundwater

The MTTs of streamflow in the Banool stream at the time when streamflow starts in May were 25 to 42 years (Table 1, Fig. 7). The McGill and Plantation streams did not start flowing until early July and their MTTs at that time were 3 to 4 years and 9 to 14 years, respectively (Table 1, Fig. 7). MTTs of the Banool stream in early July were reduced to between 14 and 26 years. At high streamflows in August to September, the Banool stream waters had MTTs of ≤ 5 years, and the waters from the McGill and Plantation streams had MTTs of < 1 year (Table 1, Fig. 7). The high ^3H activities (>2.8 TU) imply that there is a significant component of the water that originated from winter rainfall that as noted above has higher than average ^3H activities. In turn, this suggests that MTTs at that time are less than a few months (Table 1, Fig. 7). The riparian zone groundwaters had MTTs of up to a few hundreds of years in the Banool catchment, up to 1 year in the McGill catchment and up to 9 years in the Plantation catchment (Table 1, Fig. 7). While the deeper regional groundwater has MTTs of up to 24,700 years (as discussed above), the shallow regional groundwater, especially in the Banool catchment, is much younger (Barua et al., 2021) and has ^3H activities that overlap with the riparian zone groundwater (Table S1, Fig. 5). The MTTs of groundwater from 1.3 m depth at Banool (bore 3008: Fig. 1) are 70 to 420 years, and groundwater from 2.5 m depth at McGill (bore 3657: Fig. 1) has MTTs of 80 to 330 years (Barua et al., 2021).

5.2. Uncertainties in MTT estimates

There are several uncertainties in the estimated MTTs. The differences in the MTTs from the individual LPMs increase at lower ^3H activities (Table 1, Fig. 7). For water with a ^3H activity of 0.5 TU, the range of MTTs estimated from the LPMs used in this study is ± 94 years (±55%); whereas, for water with ^3H activities of 1.5 TU and 2.5 TU, the range is ± 13 years (±43%) and ± 1 year (±50%), respectively. Uncertainties in the ^3H activities of rainfall will also influence the MTT estimates. Recharge of groundwater or soil water may occur mainly by early spring or winter rainfall (Morgenstern et al., 2010; Blavoux et al., 2013; Cartwright et al., 2018a). As discussed above, this rainfall may have higher ^3H activities, in which case the MTTs would be slightly older than those estimated in Table 1 and Fig. 7. The variability in the estimated ^3H activity of modern rainfall in this area (2.8 ± 0.2 TU: Tadros et al., 2014) represents a 7% uncertainty. Applying the same uncertainty to the whole ^3H input function results in variations of MTTs for waters with ^3H activities of 0.5, 1.5 and 2.5 TU calculated using the EPM model with an EPM ratio of 0.33 of 6 to 8 years (5–7%), 5 to 6 years (22–26%) and 1 to 2 years (50–51%), respectively. Uncertainties in MTTs from the other LPMs are similar. Analytical uncertainties (Table S1) result in an uncertainty in MTTs of 2 to 3%.

The MTT calculations assume that there is a single reservoir of water contributing to the streams. The EC vs. streamflow trends (Fig. 2c) implies that there is no simple mixing of rainfall with more saline water in the catchments; however, some mixing of waters (aggregation) in the catchments may occur. Uncertainties caused by such aggregation are difficult to assess (Kirchner, 2016; Stewart et al., 2017). The effect of aggregation is highest where two water sources with widely different MTTs mix in approximately equal proportions (Stewart et al., 2017). However, for ^{3}H activities, the effect of aggregation becomes less where there is a mixing of several waters with a range of MTTs (Cartwright and Morgenstern, 2016a). Previous studies have estimated that the uncertainty due to aggregation may be up to ± 15% (Cartwright and Morgenstern, 2016a; Howcroft et al., 2018).

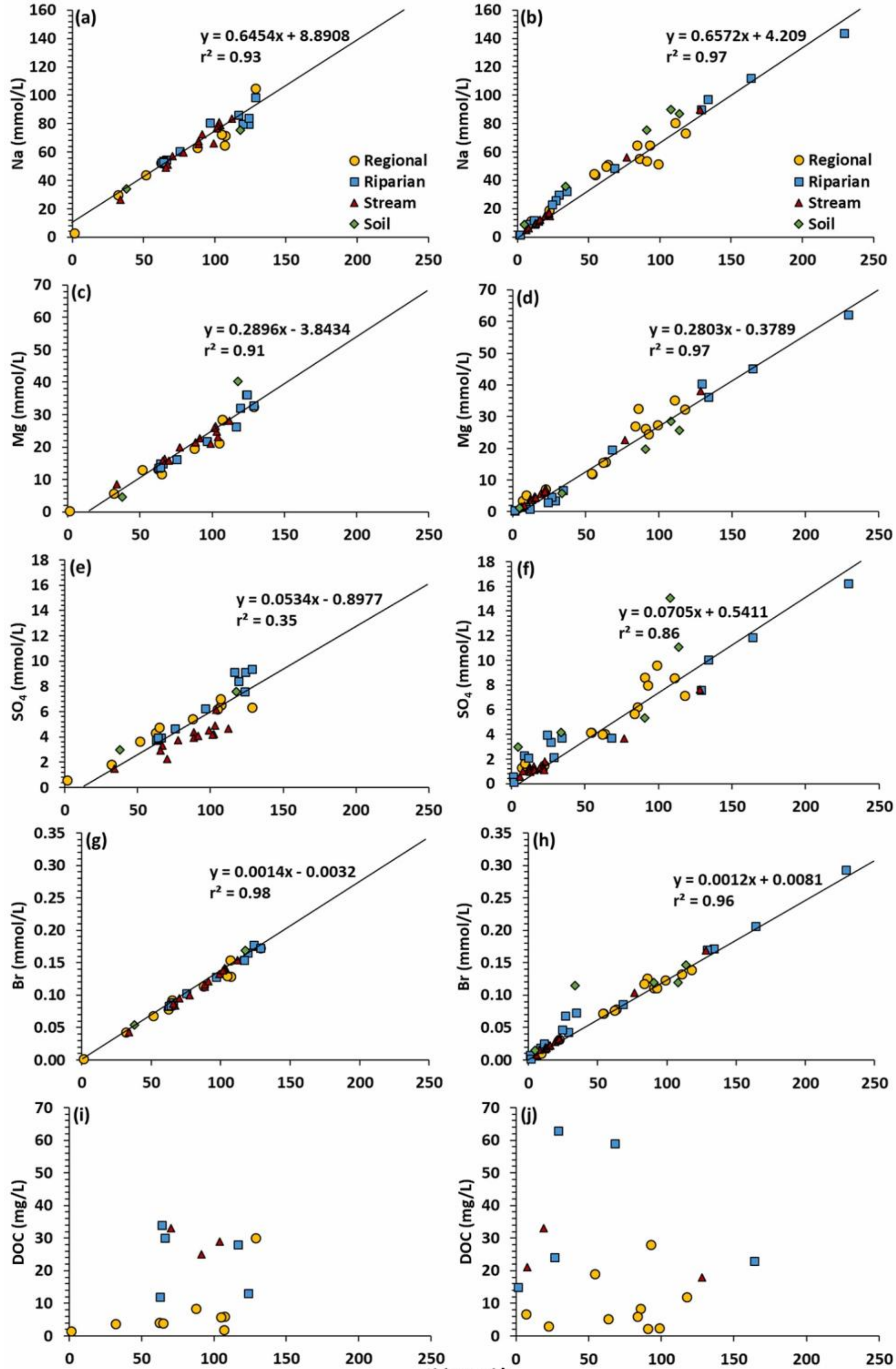

Fig. 5. Concentrations of Na, Mg, SO_4, Br and DOC vs Cl concentrations in waters from Banool (left), and McGill and Plantation (right). Data from Table S1.

Assuming that all the uncertainties are unrelated and have Gaussian distributions, the net uncertainty, estimated as $\sqrt{(\sigma_1^2 + \sigma_2^2 + \sigma_3^2 \ldots)}$, are between 50 and 70%. While these uncertainties are considerable, they do not change the conclusion that: (1) the waters from the streams and riparian zones have a wide range of MTTs from less than a few months to several decades; (2) the MTTs are longer at the start of streamflows; and (3) the MTTs in the Banool catchment are significantly longer than those in the McGill and Plantation catchments.

5.3. Sources of stream water

The MTTs of stream water when the streams start flowing are several years to decades, implying that the streamflows are not initiated by the

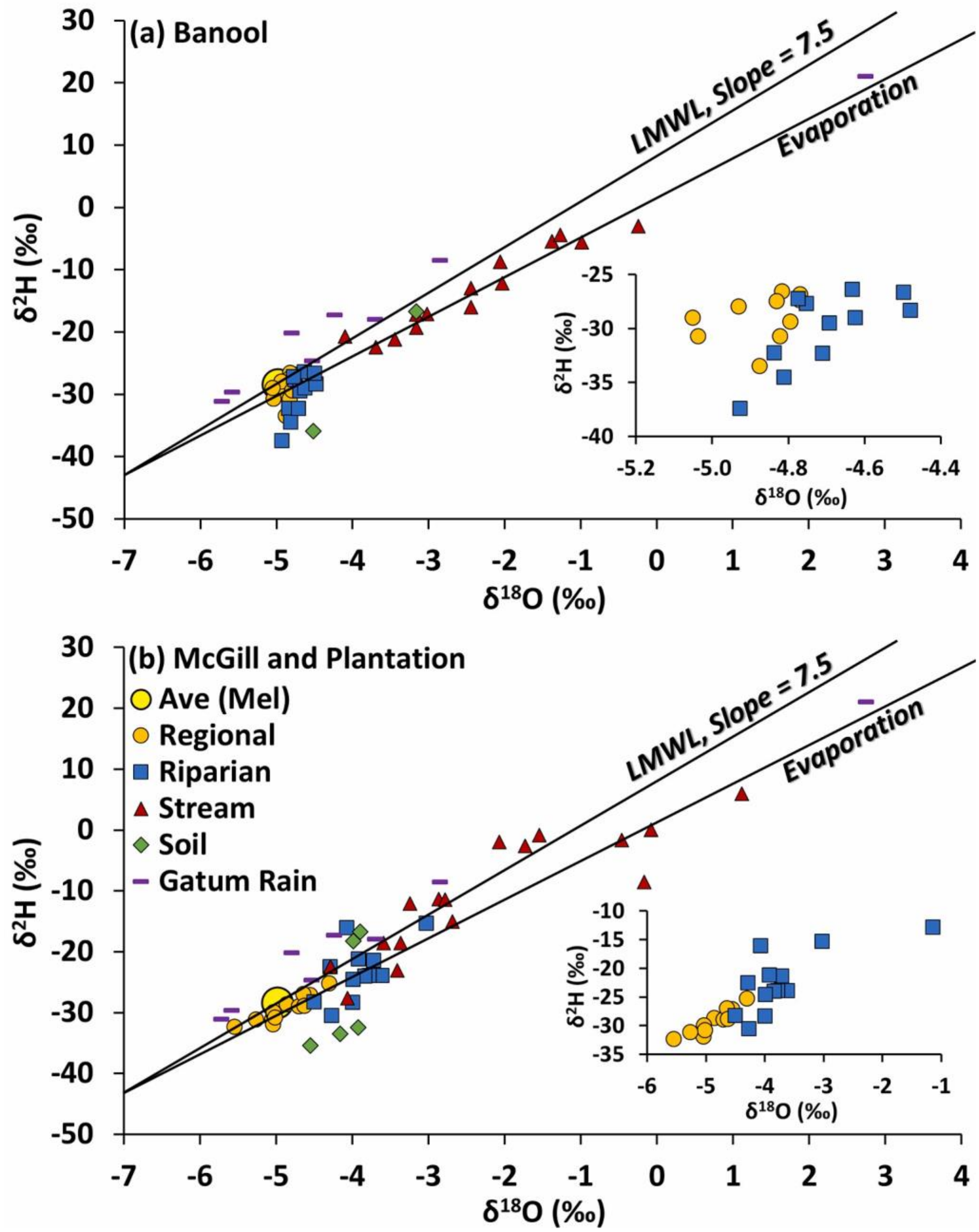

Fig. 6. $\delta^{18}O$ and $\delta^{2}H$ values of waters from (a) Banool, and (b) McGill and Plantation (data from Table S1). Insets show samples close to the average rainfall for clarity. The weighted average $\delta^{18}O$ and $\delta^{2}H$ values (Ave (Mel)) and local meteoric water line (LMWL) for Melbourne rainfall are from Hughes & Crawford (2012).

direct input of recent rainfall. The high stream EC values (Fig. 2b, c), major ion concentrations (Fig. 5a–h, S1) and ^{222}Rn activities (Table S1) also imply that the streams are not fed only by surface runoff. However, the sources of water differ between the catchments (Fig. 8).

The following observations imply that regional groundwater discharge occurs across the Banool catchment. Water elevations in piezometers BD1 and BD2 (Fig. 1) are commonly above the ground surface, especially during the autumn and winter months and the geochemistry of that water is closely similar to the regional groundwater. Additionally, the area around those piezometers is permanently wet. Furthermore, groundwater elevations are close to or above ground level in bores close to the stream, and head gradients near the stream are upwards.

The riparian zone groundwater in this catchment has ^{3}H activities of 0.16–0.79 TU that are similar to those of the shallower regional groundwater (Fig. 3a). This and the similarities in major ion and DOC concentrations and stable isotope ratios between riparian zone groundwater and regional groundwater (Figs. 5, 6a, S1) imply that the shallow riparian zone groundwater in this catchment probably forms a continuum with the regional groundwater. Thus, regional groundwater may contribute significantly to streamflow (Fig. 8a), especially at the start of flows in May when ^{3}H activities in the stream are lowest (1.30 TU). This conclusion is also consistent with the volume of water that is required to generate streamflow at the onset of streamflow in May, calculated using Eq. (2). In the Banool catchment, the MTTs of 25 to 42 years (9125 to 15330 days) and streamflow in May of 1.46×10^{2} m^{3}/day (Table 1) imply a volume of 1.33×10^{6} to 2.24×10^{6} m^{3} (Eq. (2)). The length of the Banool stream is 2300 m. Assuming that the thickness and width of the riparian zone are 2 and 20 m, respectively, and the mean sediment porosity is 0.15 (Adelana et al., 2015), the estimated volume of water stored in the riparian zone is 1.38×10^{4} m^{3}, which is two orders of magnitude smaller than the volume of water sustaining streamflow at this time. Increasing the assumed volume of the riparian zone or the porosity probably cannot resolve this discrepancy.

By contrast, regional groundwater elevations in the McGill

Table 1

^{3}H activities and estimated MTTs in riparian groundwater and stream water.

Sampling date	Sample[a] ID	Q m^3/day	^{3}H TU	DM (0.05)[b] Years	DM (0.5)	EPM (0.33)	EPM (1.0)	EMM
Banool catchment								
Riparian groundwater								
3/07/2018	BD1		0.16 ± 0.02	96	260	192	105	587
3/07/2018	BD2		0.26 ± 0.02	88	209	174	102	360
3/07/2018	BB1		0.79 ± 0.02	66	86	74	80	94
6/09/2018	BB2		0.69 ± 0.02	70	103	86	87	115
Stream water 24/05/2018								
	BS	146	1.30 ± 0.03	25	38	35	31	42
3/07/2018	BS	40.5	1.58 ± 0.03	16	22	20	17	26
13/07/2018	BS	167	1.62 ± 0.03	14	20 <1	18 <1	15 <1	24 <1
15/08/2018	BS	351	3.17 ± 0.05	<1c				
6/09/2018	BS	88.8	2.73 ± 0.04	<1	<1	<1	<1	<1
7/09/2018	BS*	63.7	2.21 ± 0.04	4	5	5	4	5
12/09/2018	BS	61.0	2.82 ± 0.04	<1	<1	<1	<1	<1
21/09/2018	BS	33.2	2.27 ± 0.04	4	5	4	4	4
McGill catchment								
Riparian groundwater								
6/09/2018	MD2		4.10 ± 0.06	<1	<1	<1	<1	<1
7/09/2018	MD4		2.63 ± 0.05	1	1	1	1	1
Stream water 13/07/2018								
	MS		2.31 ± 0.04	3	4	3	3	4
15/08/2018	MS		3.81 ± 0.06	<1	<1	<1	<1	<1
6/09/2018	MS		3.99 ± 0.06	<1	<1	<1	<1	<1
7/09/2018	MS*		3.86 ± 0.06	<1	<1	<1	<1	<1
15/09/2018	MS		3.86 ± 0.06	<1	<1	<1	<1	<1
21/09/2018	MS		3.64 ± 0.06	<1	<1	<1	<1	<1
Plantation catchment								
Riparian groundwater								
6/09/2018	MB3		2.01 ± 0.04	6	9	8	7	9
Stream water 3/07/2018								
	PS		1.84 ± 0.04	9	12	11	9	14
6/09/2018	PS		3.06 ± 0.05	<1	<1	<1	<1	<1

a: Riparian zone groundwater and stream water sampling locations shown in Fig. 1; BS* and MS* represent samples collected elsewhere along the two streams. **b:** Lumped parameter models: DM = dispersion model, EPM = exponential piston model, EMM = exponential mixing model; values of the dispersion parameter and EPM ratios are in brackets. **c:** Very young water (winter rainfall with MTTs of less than a few months).

catchment are generally below the ground surface, implying that there is no widespread discharge of regional groundwater. In this catchment, ^{3}H activities, major ion and DOC concentrations and stable isotope ratios differ between riparian zone groundwater and regional groundwater (Fig. 3b, 5, 6b, S1), implying that they are separate water sources. The much shorter MTTs at the start of McGill streamflow (up to 4 years) also imply that the riparian zone groundwater rather than the regional groundwater contributes to the early streamflow (Fig. 8b). The annual flow in the McGill stream is generally lower than the Banool stream, and the riparian zones probably contain a sufficient volume of water to generate McGill streamflow. The Plantation stream has MTTs of up to 14 years, which again may indicate the involvement of mainly shorter- lived water sources rather than the regional groundwater (Fig. 8b). The relatively high ^{3}H activities (1.01–2.14 TU) of the regional groundwater near the McGill stream (bores 3656 and 3657: Fig. 1) probably reflect recharge of the groundwater by the stream as the water table is below the stream bed in this area.

Higher runoff ratios in August to September (Fig. 4) and MTTs ≤ 5 years imply that the winter rainfall progressively mobilises waters from younger sources as the catchments wet up to sustain high winter streamflows. The soil water, which has similar major ion concentrations and stable isotope ratios to the stream water (Figs 5, 6, S1), may also be one of the sources of stream water at this time (Fig. 8). In the Banool stream in September, the MTTs of 4 to 5 years (1460–1825 days) and streamflow of 3.30×10^{1} to 6.30×10^{1} m^3/day (Table 1) yields an estimated volume of water to sustain streamflow of 4.85×10^{4} to 1.17×10^{5} m^3 (Eq. (2)). Estimating volumes at the peak of streamflows is more difficult. However, assuming MTTs of 1 week to 1 month and using the highest streamflow of 3.51×10^{2} m^3/day (Table 1, Fig. 3a), gives volumes of 2.46×10^{3} to 1.05×10^{4} m^3 (Eq. (2)). These volumes of water are also larger than that estimated to be contained in the riparian zone, implying that the stream water is derived from a broader zone in the catchment.

The differences between the water sources in the catchments may be due to land-use differences. The McGill and Plantation catchments contain a high coverage of plantation forests, whereas the Banool catchment is dominantly pasture (Fig. 1). Higher vegetation water uses in the winter months at the McGill catchment (Adelana et al., 2015; Dresel et al., 2018) might have lowered the regional groundwater levels causing a disconnection between the regional groundwater and the streams. While this may be expected, the pre-planation flow regime or geochemistry of the McGill stream is not well understood, and it is difficult to test.

6. Conclusions Runoff ratios, major ions, DOC, stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) and radioisotopes (^{222}Rn and ^{3}H) demonstrate that different water sources generate and then sustain streamflows in these seasonally intermittent catchments. Older regional groundwater and shallow younger water sources (such as riparian zone groundwater) are locally involved in the generation of early streamflow, while winter rainfall displaces increased volumes of younger waters to sustain streamflows during the winter months. As is the case elsewhere (e.g., Berghuijs and Kirchner, 2017; Rhodes et al., 2017; Zimmer and McGlynn, 2018; van Meerveld et al., 2019), young water sources appear to be very important during higher streamflows in these catchments.

Documenting water sources sustaining streamflows in headwater streams yields some general information on transit times (e.g., shallow sources of water, such as soil water and interflow, are generally younger

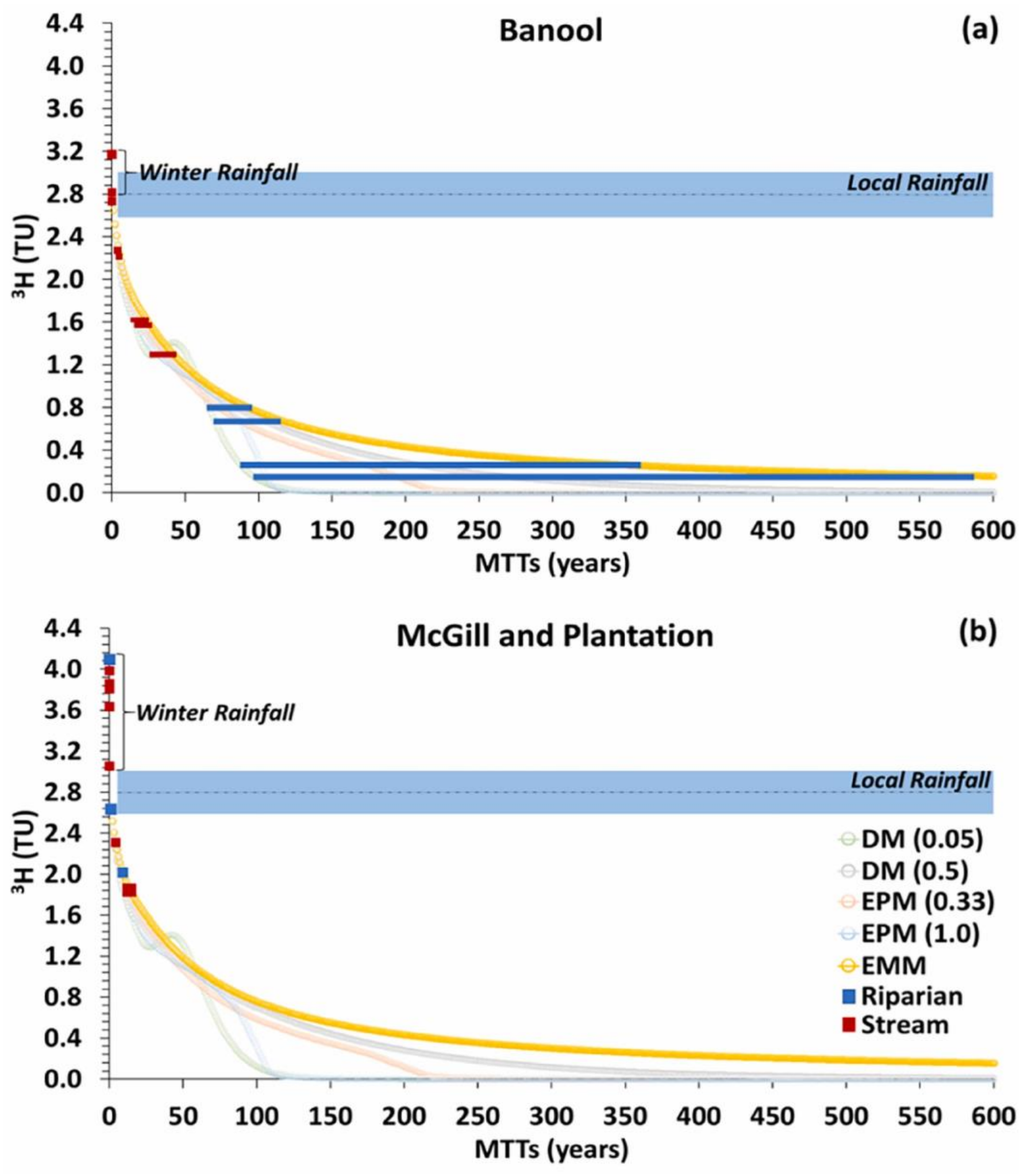

Fig. 7. Estimated MTTs of riparian zone groundwaters and stream waters using different LPMs for (a) Banool, and (b) McGill and Plantation. DM = dispersion model, EPM = exponential piston model, EMM = exponential mixing model. The dispersion parameter and EPM ratio are in brackets. The dashed line represents the measured ^{3}H of local rainfall (Table S1) and shaded band represents the likely range of ^{3}H values in present-day rainfall (Tadros et al., 2014). Samples with higher ^{3}H activities than average rainfall may represent winter rainfall.

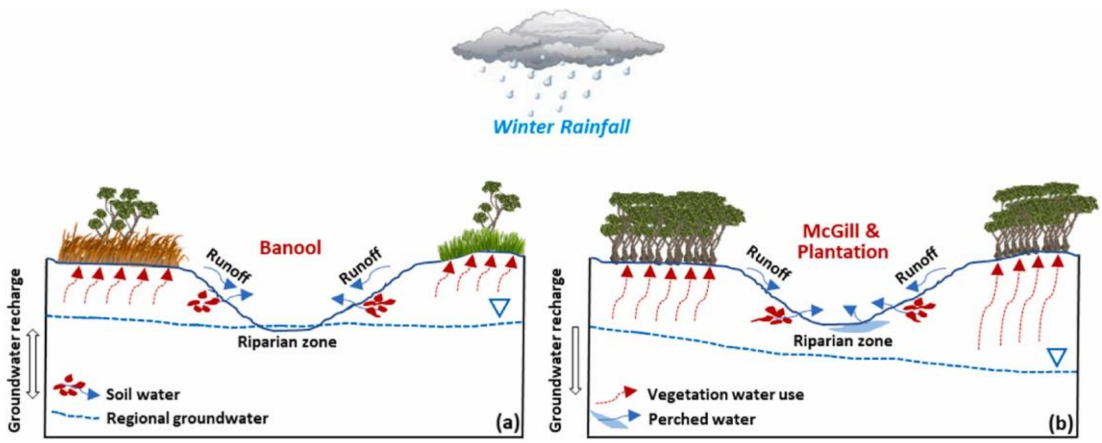

Fig. 8. Conceptual model showing the sources of water generating Banool, McGill and Plantation streamflows.

than deeper groundwater). However, quantifying the MTTs in intermittent headwater streams allows comparison with perennial headwater catchments to be made. Streams in perennial headwater catchments in southeast Australia are generally sustained by inflows of long-lived (years to centuries) waters at most streamflows (Duvert et al., 2016; Cartwright et al., 2020a, 2020b), and none have ^{3}H activities that are higher than those of average local rainfall. This is the case for even small catchments with similar areas to those of the Banool, McGill and Plantation catchments (and catchment size does not correlate with MTTs in the perennial streams: Cartwright et al., 2020a). In contrast, the intermittent headwater streams in this study are generally sustained by shorter-lived sources of water, especially at high streamflows following winter rainfall. These catchments have similar rainfall and comprise deeply-weathered rocks that may store large volumes of water similar to many other catchments in southeast Australia. However, unlike the perennial catchments, the regional groundwater in intermittent catchments is less likely to be connected to the streams, thus removing a major source of older water. If intermittent streams are generally sustained by water with relatively short MTTs, their streamflows will be less buffered against the impact of year-on-year variations in rainfall than in perennial streams. However, the MTTs are still relatively long at low streamflows compared with predictions in temperate and glaciated northern hemisphere catchments (e.g., van Meerveld et al., 2019), possibly reflecting the relatively large volumes of storage in the weathered regolith. If the proportion of intermittent streams increase (Larned et al., 2010; Doll and Schmied, 2012; Datry et al., 2014¨), the MTTs of water sustaining streamflows may decrease. This will potentially impact on the resilience of these streams to rainfall variations and the timescales of contaminant transport to the streams.

CRediT authorship contribution statement

Shovon Barua: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Ian Cartwright:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing. **P. Evan Dresel:** Conceptualization, Funding acquisition, Investigation, Writing – review & editing. **Uwe Morgenstern:** Investigation, Methodology, Writing – review & editing. **Jeffrey J. McDonnell:** Conceptualization, Funding acquisition, Methodology, Writing – review & editing. **Edoardo Daly:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.jhydrol.2021.127208.

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