Hydrology and
Earth System
Sciences

Mean transit times in headwater catchments: insights from the Otway Ranges, Australia

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Abstract. Understanding the timescales of water flow through catchments and the sources of stream water at different flow conditions is critical for understanding catchment behaviour and managing water resources. Here, tritium (^{3}H) activities, major ion geochemistry and streamflow data were used in conjunction with lumped parameter models (LPMs) to investigate mean transit times (MTTs) and the stores of water in six headwater catchments in the Otway Ranges of southeastern Australia. ^{3}H activities of stream water ranged from 0.20 to 2.14 TU, which are significantly lower than the annual average ^{3}H activity of modern local rainfall, which is between 2.4 and 3.2 TU. The ^{3}H activities of the stream water are lowest during low summer flows and increase with increasing streamflow. The concentrations of most major ions vary little with streamflow, which together with the low ^{3}H activities imply that there is no significant direct input of recent rainfall at the streamflows sampled in this study. Instead, shallow younger water stores in the soils and regolith are most likely mobilised during the wetter months.

MTTs vary from approximately 7 to 230 years. Despite uncertainties of several years in the MTTs that arise from having to assume an appropriate LPM, macroscopic mixing, and uncertainties in the ^{3}H activities of rainfall, the conclusion that they range from years to decades is robust. Additionally, the relative differences in MTTs at different streamflows in the same catchment are estimated with more certainty. The MTTs in these and similar headwater catchments in southeastern Australia are longer than in many catchments globally. These differences may reflect the relatively low rainfall and high evapotranspiration rates in southeastern Australia compared with headwater catchments elsewhere.

The long MTTs imply that there is a long-lived store of water in these catchments that can sustain the streams over drought periods lasting several years. However, the catchments are likely to be vulnerable to decadal changes in land use or climate. Additionally, there may be considerable delay in contaminants reaching the stream. An increase in nitrate and sulfate concentrations in several catchments at high streamflows may represent the input of contaminants through the shallow groundwater that contributes to streamflow during the wetter months. Poor correlations between ^{3}H activities and catchment area, drainage density, land use, and average slope imply that the MTTs are not controlled by a single parameter but a variety of factors, including catchment geomorphology and the hydraulic properties of the soils and aquifers.

1 Introduction

Determining the timescales over which precipitation is transmitted from a recharge area through a catchment to where it discharges into rivers or streams (the transit time) is important for understanding catchment behaviour and is of inherent interest to resource managers. Streams with long MTTs are connected to relatively large stores of water in the underlying aquifers (Maloszewski and Zuber, 1982; Morgenstern et al., 2010) that may sustain streamflow during droughts that last up to a few years. However, longer-term changes, such

as deforestation, agricultural development, climate change, and/or landscape change following bushfires, are likely to affect both the quality and the quantity of river flows.

Headwater streams are important as they commonly support diverse ecosystems, provide recreational opportunities and in many catchments contribute a significant proportion of the total river flow (Freeman et al., 2007). Headwater streams also differ from lowland rivers in terms of their potential water inputs. Unlike lowland rivers, which typically receive groundwater inflows from regional aquifers or near-river floodplain sediments, the sources of water in headwater streams are far less well understood. Headwater streams are commonly developed at elevations well above those of the regional water tables and/or occur on relatively impermeable bedrock. Yet such streams continue to flow even during prolonged dry periods. There are several potential water stores that could contribute to stream flow, including the soil zone, weathered or fractured basement rocks, and/or perched aquifers at the soil–bedrock interface (e.g. Sklash and Farvolden, 1979; Kennedy et al., 1986; Swistock et al., 1989; Bazemore et al., 1994; Fenicia et al., 2006; Jensco and McGlynn, 2011).

Estimates of MTTs in headwater catchments range from a few months to several decades (e.g. Soulsby et al., 2000; McGuire and McDonnell, 2006; Hrachowitz et al., 2009; McDonnell et al., 2010; Stewart and Fahey, 2010; Stewart et al., 2010; Mueller et al., 2013; Stockinger et al., 2014; Atkinson, 2014; Cartwright and Morgenstern, 2015, 2016a, b; Duvert et al., 2016). However, in many regions globally the range of MTTs in headwater catchments is not well known. Additionally, it is not always clear why MTTs vary between different areas. This lack of knowledge limits our abilities to protect and manage headwater catchments.

1.1 Estimating mean transit times (MTTs)

Groundwater follows a myriad of flow paths between the recharge areas to where it discharges into streams or rivers. Consequently, groundwater discharge does not have a discrete age but rather has a distribution of transit times. MTTs are commonly estimated using lumped parameter models (LPMs) that describe the distribution of water with different ages or tracer concentrations in simplified aquifer geometries (Maloszewski and Zuber, 1982, 1996; Maloszewski et al., 1983; Cook and Bohlke, 2000; Maloszewski, 2000; Zuber et al., 2005). LPMs represent a viable and commonly used alternative to estimating MTTs using numerical groundwater models that rely upon hydraulic parameters that are seldom known with certainty and which vary spatially. However, the LPMs are only approximations of actual flow systems and the MTTs may be broad estimates rather than specific values.

The LPMs may be utilised with stable (O, H) isotopes or major ions if the concentrations vary seasonally in rainfall (e.g. Soulsby et al., 2000; McGuire and McDonnell, 2006; Tetzlaff et al., 2007, 2009; Hrachowitz et al., 2009, 2010;

Kirchner et al., 2010). Determining MTTs from stable isotope ratios or major ion concentrations relies on tracking the delay and dampening of the seasonal variations between precipitation and discharge. However, use of these tracers typically requires sub-weekly sampling over time periods equal to or exceeding that of the transit times (Timbe et al., 2015). In addition, these tracers become ineffective when transit times exceed 4 to 5 years as the initial variations in rainfall are progressively dampened to below the point at which they can be detected (Stewart et al., 2010).

Gaseous tracers (e.g. ^{3}He, chlorofluorocarbons, or SF_6) are effective in determining residence times of groundwater (Cook and Bohlke, 2000) but are difficult to apply to surface water due to gas exchange. With a half-life of 12.32 years, tritium (^{3}H) has been used to estimate MTTs of up to 150 years (e.g. Morgenstern et al., 2010; Stewart et al., 2010). Unlike other radioactive tracers (e.g. ^{14}C), ^{3}H is part of the water molecule and its activities are affected only by radioactive decay and dispersion and not by geochemical or biogeochemical reactions in the soils or aquifers. Because ^{3}H activities are not affected by processes in the unsaturated zone, the MTTs reflect both recharge through the unsaturated zone and flow in the groundwater system.

Utilisation of ^{3}H as a tracer is facilitated by the fact that the ^{3}H activities of rainfall have been measured globally for several decades (International Atomic Energy Agency, 2016). Due to atmospheric nuclear testing, ^{3}H activities of rainfall peaked during the 1950s and 1960s (the "bomb pulse"). The bomb-pulse ^{3}H activities in the Southern Hemisphere were much lower than in the Northern Hemisphere (Tadros et al., 2014) and have now largely declined to below those of modern rainfall (Morgenstern et al., 2010). As a consequence, MTTs can generally be determined from single ^{3}H measurements (Morgenstern et al., 2010; Morgenstern and Daughney, 2012) in an analogous manner to how other radioactive isotopes (e.g. ^{14}C or ^{36}Cl) are used in regional groundwater systems. This also allows MTTs at different streamflows to be estimated (Morgenstern et al., 2010; Duvert et al., 2016; Cartwright and Morgenstern, 2015, 2016a, b).

Using LPMs to estimate MTTs has a number of uncertainties. Due to the attenuation of the ^{3}H bomb pulse in the Southern Hemisphere, the suitability of the LPM can no longer be evaluated by time-series ^{3}H measurements (Cartwright and Morgenstern, 2016a) as is still possible in the Northern Hemisphere (e.g. Blavoux et al., 2013). Hence, LPMs must be assigned based upon knowledge of the geometry of the flow system and/or information from previous time-series studies in similar catchments. While not being able to assess the form of the LPM results in uncertainties in the calculated MTTs, the MTTs are less sensitive to the choice of LPM than is the case in the Northern Hemisphere (e.g. Blavoux et al., 2013).

Rivers can receive water from numerous stores, including groundwater, tributaries, soil water, and perched aquifers, each of which may have different MTTs. The mixing of

water from different flow systems potentially produces water samples with a residence time distribution that does not correspond to those in the LPMs, and calculated MTTs are lower than actual MTTs. This is known as the aggregation error (Kirchner, 2016; Stewart et al., 2017) and it increases as the difference between the transit times of the individual endmembers increases. For transit times estimated from single ^{3}H activities, the aggregation error decreases with an increasing number of endmembers as the mixing of numerous aliquots water with different transit times is similar to what is represented by the LPMs (Cartwright and Morgenstern, 2016a).

Despite the uncertainties in calculating MTTs, because the ^{3}H activities of the remnant bomb-pulse waters have largely decayed, Southern Hemisphere waters with low ^{3}H activities have longer MTTs than waters with high ^{3}H activities. This permits relative mean transit times to be readily assessed. Because ^{3}H is radioactive, there is no requirement for flow in the catchment to be time-invariant as long as the flow path geometry remains relatively constant.

1.2 Predicting mean transit times

Fundamentally, MTTs are a function of the recharge rate, length of groundwater flow paths, and rates of groundwater flow, and parameters that control those factors will control the MTTs. Large catchments may have some long groundwater flow paths and consequently have long MTTs (e.g. McGlynn et al., 2003; Hrachowitz et al., 2010). Catchments with higher drainage densities (i.e. higher total stream length per unit area) may contain numerous short groundwater flow paths and consequently have short MTTs (e.g. Hrachowitz et al., 2009). Large groundwater storage volumes will likely also result in long MTTs (e.g. Ma and Yamanaka, 2016). Groundwater flow is likely to be more rapid through steeper catchments due to the higher hydraulic gradients, resulting in shorter MTTs (e.g. McGuire et al., 2005). Forested catchments may have higher evapotranspiration and lower recharge rates than cleared catchments (Allison et al., 1990), and the degree of forest cover exerts a control on MTTs (e.g. Tetzlaff et al., 2007). The hydraulic conductivities of the bedrock and soils are also important in controlling the timescales of water movement through catchments (e.g. Tetzlaff et al., 2009; Hale and McDonnell, 2016).

Identifying the controls on MTTs is important for understanding catchment functioning. It also potentially allows first-order estimates of MTTs to be made in similar catchments for which detailed geochemical tracer data do not exist. In some catchments, correlations between ^{3}H activities and major ion geochemistry or the runoff coefficient (the proportion of rainfall exported from the catchment by the stream) also allow first-order estimates of MTTs to be made (Morgenstern et al., 2010; Cartwright and Morgenstern, 2015, 2016a).

1.3 Objectives

This study evaluates the range of and controls on MTTs in headwater streams from the upper Gellibrand catchment of the Otway Ranges in southeastern Australia. Specifically, we test the following hypotheses. Firstly that, in common with headwater catchments elsewhere in southeastern Australia, the MTTs are several years to decades. Secondly, that the MTTs are most likely controlled by catchment attributes such as land cover, slope, or drainage density. Lastly, that shallower water stores within the catchment become progressively mobilised during higher rainfall periods contribute to streamflow at those times. We also use this study to evaluate whether there are geochemical proxies that could be used to make first-order predictions of MTTs at times when no ^{3}H data are available. Documenting MTTs is critical to understanding and protecting headwater catchments and, while this study is based on a specific area, the results have relevance to catchments globally. There is not a complete understanding of the range of MTTs in headwater catchments, nor what controls these. Thus, these are important gaps in our understanding of headwater catchments.

2 Study area

The Otway Ranges are located in southern Victoria, Australia, approximately 150 km southwest of Melbourne (Fig. 1). The region has a temperate climate, with average rainfall varying from approximately 1000 mm yr^{-1} at Gellibrand and Forrest to approximately 1600 mm yr^{-1} at Mount Sabine (Department of Environment, Land, Water and Planning, 2017) (Fig. 1) with the majority of rainfall occurring during the austral winter (July to September). Average potential evapotranspiration is 1000 to 1100 mm yr^{-1} and exceeds precipitation during the summer months (Bureau of Meteorology, 2016). The Otway Ranges occur within the Great Otway National Park, and have ecological, cultural, historical, and recreational significance. Much of the area is dominated by eucalyptus forest but also includes some commercial forestry, much of which is also eucalyptus.

The geology of the study area is described by Tickell et al. (1991). The basement comprises the Early Cretaceous Otway Group, which consists primarily of volcanogenic sandstone and mudstone with minor amounts of shale, siltstone, and coal. The Otway Group is considered to be a poor aquifer and crops out across most of the Lardners Creek and Gellibrand river catchments, as well as within the higher elevation areas of the Yahoo Creek and Ten Mile Creek catchments (Fig. 1).

The Otway Group is uncomformably overlain by Tertiary sediments of the Eastern View Formation, Demons Bluff Formation, Clifton Formation and Gellibrand Marl. The Eastern View Formation is composed of three sand and gravel units that collectively form the Lower Tertiary Aquifer. These sed-
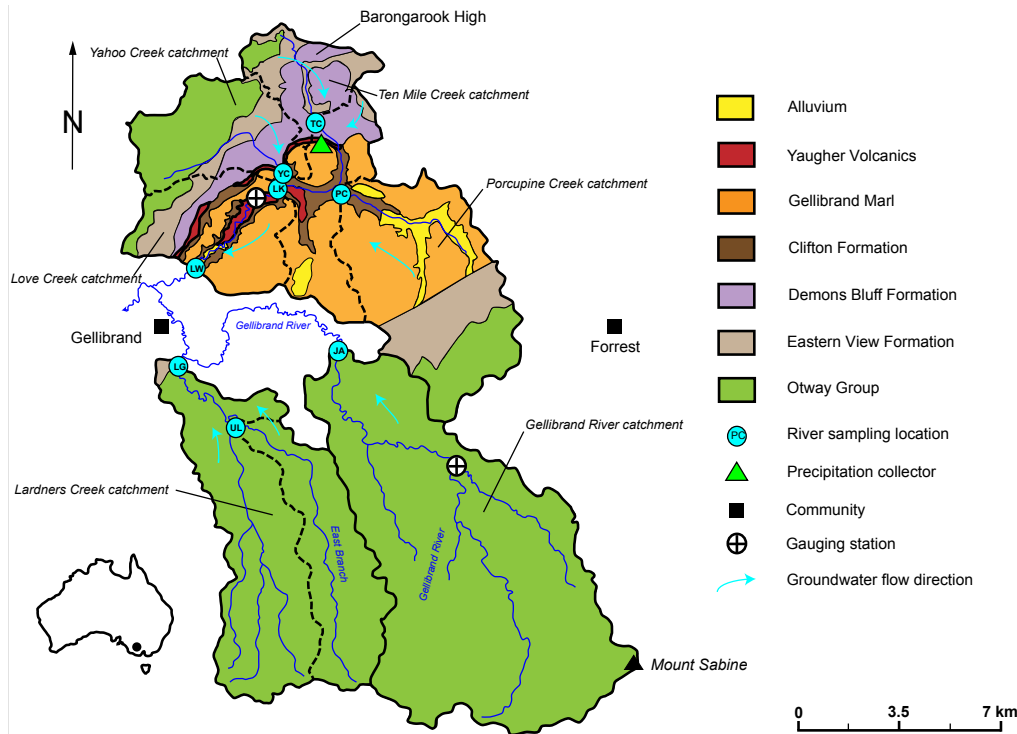
Figure 1. Map of study area showing catchments, sampling locations and bedrock geology. Inset map shows location of study area in Australia. Source: DataSearch Victoria (2015). LG = Lardners Gauge, UL = Upper Lardners, JA = Gellibrand River at James Access, PC = Porcupine Creek, TC = Ten Mile Creek, YC = Yahoo Creek, LK = Love Creek Kawarren, and LW = Love Creek Wonga. Current or discontinued gauging stations exist at all sites except for Upper Lardners.

iments crop out at various locations across the study area including at the Barongarook High (Fig. 1), which is the primary recharge area for the aquifer (Stanley, 1991; Petrides and Cartwright, 2006). The Eastern View Formation is overlain by the Demons Bluff Formation, which is a calcareous silt with negligible permeability. The formation crops out sparsely within the study area, mainly along Yahoo and Ten Mile creeks. Overlying this unit is the Clifton Formation, which is a limonitic sand and gravel aquifer. This unit crops out along Porcupine, Ten Mile, Yahoo, and Love creeks. The Clifton Formation is overlain by the Gellibrand Marl, which consists of approximately 200 to 300 m of calcareous silt. The Gellibrand Marl crops out extensively within the Love Creek and Porcupine Creek catchments and acts as a regional aquitard. Along Love Creek and parts of the Gellibrand River, the Tertiary units have been intruded by the Yaugher Volcanics, which consist primarily of basalt, tuff, and volcanic breccia. Deposits of alluvium are present along most of the stream courses, particularly Porcupine Creek and Love Creek.

Regional groundwater flows from the recharge area in the Barongarook High to the south and southwest (Leonard et al., 1981; Stanley, 1991; Atkinson et al., 2014). Additionally, localised recharge may occur elsewhere across the study area (Atkinson et al., 2014), particularly where the Eastern View

Formation crops out. Regional groundwater discharges into the Gellibrand River, Love Creek, Porcupine Creek, Ten Mile Creek and Yahoo Creek (Hebblethwaite and James, 1990; Atkinson et al., 2013; Costelloe et al., 2015). In the higher elevations of the study area, including the upper reaches of Lardners Creek, the regional water table is likely to be below the base of the streambed (Costelloe et al., 2015). Based upon ^{14}C and ^{3}H activities, residence times of the regional groundwater are between 100 and 10 000 years (Petrides and Cartwright, 2006; Atkinson et al., 2014).

The Gellibrand River (Fig. 1) flows west-southwest for approximately 100 km from its highest point in the Otway Ranges before discharging into the Southern Ocean. This study focuses on six headwater catchments of the upper Gellibrand River: Lardners Creek, Love Creek, Porcupine Creek, Ten Mile Creek, Yahoo Creek, and the Gellibrand River upstream of James Access (Fig. 1). The Lardners Creek catchment includes the whole catchment (Lardners Gauge) and a smaller upper sub-catchment (Upper Lardners) (Fig. 1). Similarly, Love Creek includes the whole catchment (Love Creek Wonga) and a smaller portion of the upper catchment (Love Creek Kawarren). Porcupine Creek, Ten Mile Creek and Yahoo Creek are also tributaries to Love Creek. Love Creek and Lardners Creek flow into the Gellibrand River near Gellibrand (Fig. 1). These headwater streams contribute a sig-

Table 1. Summary of the attributes of the upper Gellibrand River catchments.

Catchment (Fig. 1)	Drainage area (km^2)	Drainage density (m m^{-2})	Forest cover (%)	Average slope (°)	Runoff coefficient (%)
Upper Lardners (UL)	20.0	1.0×10^{-3}	92	11.0	nc*
Lardners Gauge (LG)	51.6	1.1×10^{-3}	91	11.0	33.0
Gellibrand River at James Access(JA)	81.0	9.2×10^{-4}	95	11.3	39.0
Porcupine Creek (PC)	33.6	9.5×10^{-4}	88	5.9	11.4
Ten Mile Creek (TC)	9.6	8.8×10^{-4}	88	5.7	12.0
Yahoo Creek (YC)	16.6	8.7×10^{-4}	95	8.6	10.5
Love Creek Kawarren (LK)	74.4	9.3×10^{-4}	82	6.4	10.6
Love Creek Wonga (LW)	91.7	9.2×10^{-4}	78	6.7	8.6

* Not calculated.

nificant portion of flow to the Gellibrand River, which in turn provides water for several towns, supports important aquatic and terrestrial fauna, and provides water for agriculture. Current land use in the upper Gellibrand catchment, including the cleared agricultural land which replaced the native eucalyptus forest, has been established for several decades. Despite their significance, the headwater catchments of the Otway Ranges face a number of threats, including urbanisation, further clearing of native vegetation, drought, and bushfire, all of which have the potential to impact the quantity and quality of water within the streams.

The six catchments have areas ranging from 9.6 km^2 (Porcupine Creek) to 91.7 km^2 (Love Creek Wonga) (Table 1). Drainage densities are relatively similar and range from 8.7×10^{-4} m m^{-2} at Yahoo Creek to 1×10^{-3} m m^{-2} at Lardners Gauge and Upper Lardners (Table 1). Forest cover is lowest in the Love Creek Wonga (78 %) and Love Creek Kawarren (82 %) catchments. Forest cover in the other catchments is 88 % in the Porcupine Creek and Ten Mile Creek catchments, 91 to 92 % in the Lardners Gauge and Upper Lardners catchments, and 95 % in the Gellibrand River and Yahoo Creek catchments. Average slopes range from 5.7° (Ten Mile Creek) to 11.3° (at James Access).

3 Methods

3.1 Sampling and streamflow

River water samples were collected from eight locations in the catchments (Fig. 1). Lardners Creek was sampled at an active gauging station (Lardners Gauge) that is maintained by the Department of Environment, Land, Water and Planning (DELWP) (site 235210) and from the Lardners Creek East Branch (Upper Lardners), approximately 3.5 km upstream from Lardners Gauge. Love Creek was sampled at Kawarren (Love Creek Kawarren), approximately 1 km upstream of DELWP gauging station 235234 and at the Wonga Road crossing (Love Creek Wonga), approximately 4.5 km downstream of Kawarren. River water samples were col-

lected from the Gellibrand River, Porcupine Creek, Ten Mile Creek, and Yahoo Creek at the sites of former DELWP gauging stations (sites 235235, 235241, 235239, and 235240, respectively).

Streamflow at the time of sampling was determined for each of the eight locations with the exception of Upper Lardners, which is ungauged. Sub-daily streamflow is currently measured at Lardners Gauge (site 235210) and at Love Creek (site 235234) (Department of Environment, Land, Water and Planning, 2017) (Fig. 1). Streamflow at James Access on the Gellibrand River was estimated using a correlation ($R^2 = 0.97$, p value $= 10^{-8}$) between streamflow at the former gauging station at this location and that at the existing Upper Gellibrand River gauging station (site 235202), approximately 7 km upstream (Fig. 1). Likewise, streamflow at the Porcupine Creek, Ten Mile Creek, and Yahoo Creek sampling sites was estimated using correlations ($R^2 = 0.95$, 0.77, and 0.84, respectively, with p values $< 10^{-6}$) between streamflow at the former gauging stations at these locations and the Love Creek gauging station.

River water samples were collected from each site in July 2014, September 2014, March 2015, and September 2015 (Supplement). An additional round of river water samples was collected from Lardners Gauge, Porcupine Creek, Ten Mile Creek, and Love Creek Kawarren in November 2015. The water samples were collected from close to the centre of the streams using a polyethylene container fixed to an extendable pole. Additional data for James Access are from Atkinson (2014). A single precipitation sample was collected from Birnam in the Otway Ranges near Ten Mile Creek (Fig. 1) in September 2014 using a rainfall collector. The collector consisted of a polyethylene storage container equipped with a funnel positioned approximately 0.5 m above ground level. Prior to collection of the precipitation sample, the collector had been in the field for 78 days, during which time approximately 198 mm of rainfall was recorded at Forrest while 431 mm of rainfall was recorded at Mount Sabine (Department of Environment, Land, Water and Planning, 2017).

3.2 Geochemical analyses

The electrical conductivity (EC) and pH of the river water and precipitation samples was measured in the field using a calibrated TPS® hand-held water quality meter and probes. The EC measurements have a precision of $1\,\mu S\,cm^{-1}$. Cation concentrations were measured at Monash University using a Thermo Fischer ICP-OES on samples that had been filtered through $0.45\,\mu m$ cellulose nitrate filters and acidified to a pH < 2 using double-distilled 16 M HNO_3. Anion concentrations were measured at Monash University on filtered, unacidified samples using a Metrohm ion chromatograph. The precision of the cation and anion analyses, based upon replicate sample analysis, is ±2 % while accuracy based on analysis of certified water standards is ±5 %. HCO_3 concentrations were measured by colorimetric titration with H_2SO_4 using a Hach digital titrator and reagents and are precise to ±5 %. Concentrations of total dissolved solids (TDSs) were determined by summing the concentrations of cations and anions. Geochemical data are presented in the Supplement.

^{3}H analysis was conducted at the GNS Water Dating Laboratory in Lower Hutt, New Zealand. The samples were vacuum distilled and electrolytically enriched prior to analysis by liquid scintillation counting, as described by Morgenstern and Taylor (2009). Following further improvements the sensitivity is now further increased to a lower detection limit of 0.02 TU (tritium units) via tritium enrichment by a factor of 95, and reproducibility of tritium enrichment of 1 % is achieved via deuterium calibration for every sample. ^{3}H activities are expressed as absolute values in tritium units where 1 TU represents a ^{3}H / ^{1}H ratio of 1×10^{-18}. The precision (1σ) is ~ 1.8 % at 2 TU.

3.3 Catchment attributes

Catchment attributes (Table 1) were determined using ArcGIS 10.2 (ESRI, 2013) and datasets from DataSearch Victoria (2015). The hydrology modelling tools in ArcGIS were used to generate the stream network from a 20 m digital elevation model. A threshold catchment area of 50 Ha reproduces the observed perennial stream network of the area. Catchment areas upstream of each sampling site and drainage densities were determined using the watershed tool. Mean slopes were calculated using the spatial analysis tools. Vector-based land use datasets were converted to raster formats and reclassified. Land use was assigned as forest (native vegetation and plantations) and cleared land, which includes urban and agricultural regions. Runoff coefficients were calculated using streamflow data for each of the catchments (except Upper Lardners) for March 1986 to July 1990 (Department of Environment, Land, Water, and Planning, 2017), the only interval for which continuous streamflow data are available for each catchment. The runoff coefficient calculations assumed a uniform average annual rainfall of 1.3 m for each catchment (Bureau of Meteorology, 2016). Correlations be-

tween catchment attributes and other parameters are considered to be strong where $R^2 \geq 0.7$.

3.4 Calculating mean transit times

The lumped parameter models implemented in the TracerLPM Excel workbook (Jurgens et al., 2012) were used to estimate MTTs. The ^{3}H activity of water sampled from a stream at time $t(C_0(t))$ is related to the input (C_i) of ^{3}H via the convolution integral:

$$C_0(t) = \int_0^\infty C_i(t-T)\,g(T)e^{-\lambda T}\,dT, \qquad (1)$$

where T is the transit time, $t - T$ is the time that the groundwater entered the flow system, λ is the decay constant ($0.0563\,yr^{-1}$ for ^{3}H), and $g(T)$ is the exit age distribution function, for which closed-form analytical solutions have been derived (e.g. Maloszewski and Zuber, 1982, 1992, 1996; Kinzelbach et al., 2002). MTTs were estimated by matching the predicted ^{3}H activities from the LPMs to the observed ^{3}H activities of the samples.

As discussed earlier, the use of single ^{3}H activities to estimate MTTs requires that an LPM be assigned. Here two LPMs were utilised: the exponential piston-flow model (EPM) and the dispersion model (DM), which are among the most commonly used LPMs (McGuire and McDonnell, 2006; Stewart et al., 2010). The EPM describes flow in aquifers with both exponential and piston-flow portions. This model may be applied to unconfined aquifers where recharge through the unsaturated zone resembles piston flow and flow within the aquifer resembles exponential flow (Morgenstern et al., 2010). TracerLPM defines an EPM ratio, which represents the relative contribution of exponential and piston flow (Jurgens et al., 2012). The EPM ratio is $1/f - 1$, where f is the proportion of aquifer volume exhibiting exponential flow.

The dispersion model is based on the one-dimensional advection–dispersion equation for a semi-infinite medium (Jurgens et al., 2012). While this model can be applied to a wide variety of aquifer configurations, conceptually it is probably less realistic than other LPMs. Nonetheless, it has been successfully used to predict tracer concentrations over time in a number of flow systems (e.g. Maloszewski, 2000). Utilisation of this model requires defining a dispersion parameter, D_p, which represents the ratio of dispersion to advection.

The average annual ^{3}H activities of modern rainfall in central and southeastern Australia are predicted to vary between 2.4 and 3.2 TU (Tadros et al., 2014). ^{3}H activities of 9- to 17-month rainfall samples from elsewhere in Victoria are between 2.72 and 2.99 TU (Atkinson, 2014; Cartwright and Morgenstern, 2015; Cartwright et al., 2018) and fall within the range of predicted ^{3}H activities for their locations. Interpolating the data from that study suggests that modern rainfall in the Otway Ranges has an annual average ^{3}H activity of
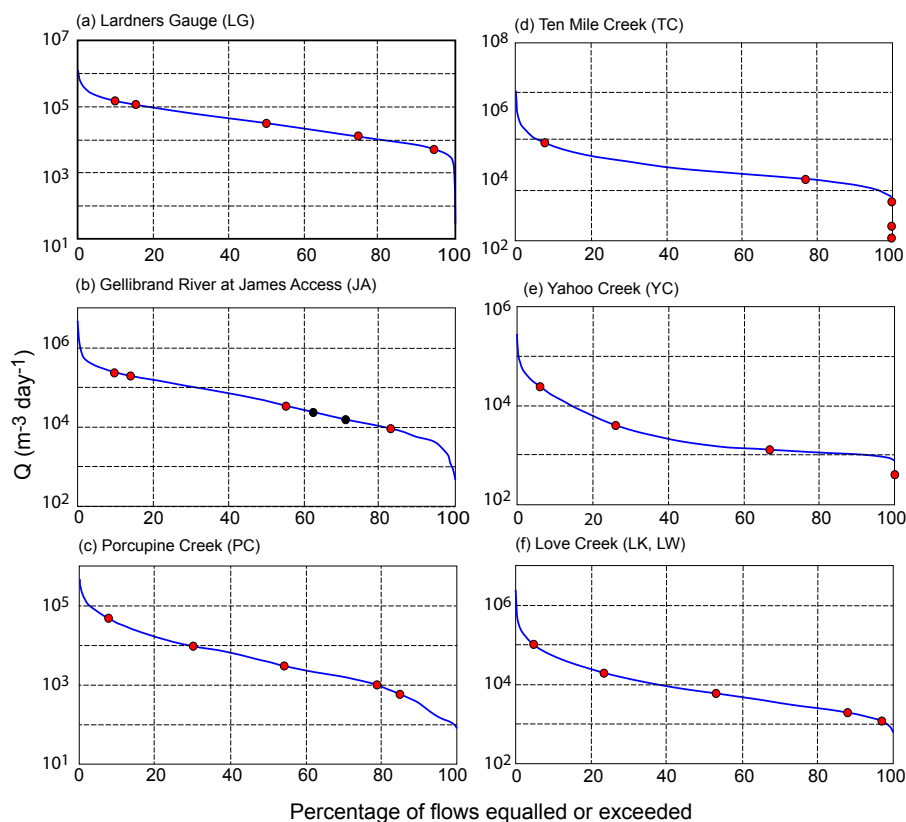
Figure 2. Streamflows at which samples were collected relative to flow duration curves for Lardners Gauge **(a)**, Gellibrand River at James Access **(b)** – additional data (black circles) from Atkinson (2014), Porcupine Creek **(c)**, Ten Mile Creek **(d)**, Yahoo Creek **(e)** and Love Creek **(f)**. Streamflow data from Department of Environment, Land, Water and Planning (2017).

~ 2.8 TU (which is slightly lower than the ~ 3.0 TU recorded at Melbourne ~ 150 km to the east of the study area). A value of 2.8 TU was used as the average annual ^{3}H activity of modern (2010 to 2016) rainfall as well as for the years prior to the atmospheric nuclear tests (pre-1951). The ^{3}H input in the intervening years is based on the ^{3}H activities of rainfall in Melbourne (International Atomic Energy Agency, 2016; Tadros et al., 2014). These were decreased by 6.7 % to account for the expected difference in ^{3}H activities in the rainfall between the Otway Ranges and Melbourne.

There are several uncertainties in the MTT calculations. The analytical uncertainty ranges between 0.02 and 0.04 TU (Supplement). To assess the effect of uncertainties in rainfall ^{3}H activities, MTTs were recalculated assuming that modern and pre-1950 rainfall had an average ^{3}H activity of either 2.4 or 3.2 TU, with the ^{3}H activities of the intervening years adjusted proportionally. As this range encompasses the estimated annual ^{3}H activities of rainfall over most of central and southeastern Australia, it allows a conservative estimate of uncertainties to be made.

The aggregation or macroscopic mixing of waters also introduces uncertainties (Kirchner, 2016; Stewart et al., 2017). Consider a stream fed by several tributaries. The expected

MTT (MTT_e) can be calculated using the streamflow data, ^{3}H activities, and MTTs of each tributary via

$$\text{MTT}_e = a\text{MTT}_1 + b\text{MTT}_2 + c\text{MTT}_3 + \ldots \tag{2}$$

(Stewart et al., 2017). In Eq. (2), a, b, and c, represent the fraction of total flow contributed by tributaries 1, 2, and 3. If the aggregation is minimal, MTT_e will be similar to that estimated from the measured ^{3}H activity via the LPM. The successful application of Eq. (2) relies on the MTTs of the different tributaries being defined by their ^{3}H activities (which in itself may not be straightforward due to aggregation within those sub-catchments). Nevertheless, it provides a broad estimate of the error due to macroscopic mixing that is otherwise difficult to assess.

3.5 Groundwater volumes

The volume (V in m^3) of groundwater stored within an aquifer that interacts with the stream (sometimes referred to as the turnover volume) is related to the MTT by

$$V = Q \cdot \text{MTT}, \tag{3}$$

where Q is streamflow (m^3 yr^{-1}) (Maloszewski and Zuber, 1982, 1992; Morgenstern et al., 2010).
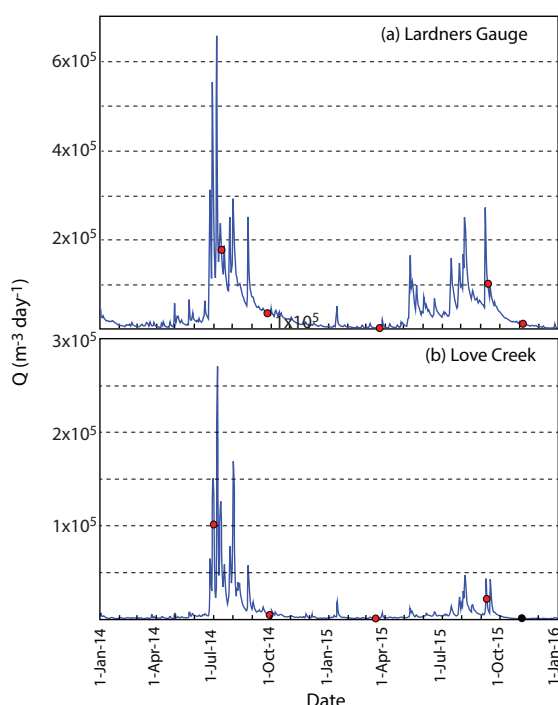
Figure 3. Hydrographs for Lardners Gauge **(a)** and Love Creek **(b)** together with the timing of sample collection. Data from Department of Environment, Land, Water and Planning (2017).

4 Results

4.1 Streamflow

Streamflow was highest during July 2014 (Supplement), ranging from $8.6 \times 10^3\,\mathrm{m^3\,day^{-1}}$ at Ten Mile Creek to $255 \times 10^3\,\mathrm{m^3\,day^{-1}}$ at James Access. Discharge was lowest during March and November 2015, ranging from $0.1 \times 10^3\,\mathrm{m^3\,day^{-1}}$ at Ten Mile Creek to $8.8 \times 10^3\,\mathrm{m^3\,day^{-1}}$ at James Access. Figure 2 illustrates the streamflows for the sampling rounds relative to the flow duration curves for the catchments. Samples were generally collected between the 10th and 100th percentiles of streamflow, which encompasses a wide range of flow conditions. Samples were collected during the recession periods after high-flow events that follow rainfall or during baseflow conditions (Fig. 3). Overland flow was not observed during any of the sampling events and small ephemeral tributaries in the catchments were dry.

Runoff coefficients range from 33 and 39 % at Lardners Gauge and James Access, respectively, to between 9 and 12 % at Porcupine Creek, Ten Mile Creek, Yahoo Creek Wonga, and Love Creek Kawarren (Table 1). The higher runoff coefficients at Lardners Gauge and James Access relative to the other catchments may be due to the fact that these rivers drain steeper catchments and are underlain almost entirely by low hydraulic conductivity Otway Group basement rocks (Fig. 1).

4.2 Tritium activities

As discussed above, the annual average ^{3}H activities of modern rainfall in much of central and southeastern Australia are between 2.4 and 3.2 TU (Tadros et al., 2014). The 78-day precipitation sample collected from near Ten Mile Creek in September 2014 had a tritium activity of 2.45 TU. This is lower than both the expected ^{3}H activities for the Otway Ranges (~ 2.8 TU: Tadros et al., 2014) and those of 9- to 12-month rainfall samples elsewhere in Victoria (2.72 to 2.99 TU: Atkinson, 2014; Cartwright and Morgenstern, 2015, 2016a; Cartwright et al., 2018). However, the Ten Mile Creek sample reflects rainfall over only part of the year and may not be representative.

Tritium activities of the rivers are < 2.14 TU, which are lower than the average annual ^{3}H activities of modern rainfall and indeed the Ten Mile Creek rainfall sample. The ^{3}H activities vary from 0.20 TU at Porcupine Creek in March 2015 to 2.14 TU at Yahoo Creek in July 2014 (Fig. 4). The higher ^{3}H activities in the rivers are within the range of ^{3}H activities of 1.80 to 2.25 TU for soil pipe water in higher elevations in the Gellibrand Catchment (Atkinson, 2014) (Fig. 4). In general, ^{3}H activities were highest at high streamflow (July 2014) and lowest at low streamflow (March and November 2015).

The ^{3}H activities of Love Creek at the upstream (Love Creek Kawarren) and downstream (Love Creek Wonga) locations in individual events varied by < 0.1 TU. The ^{3}H activities in Lardners Creek between Upper Lardners and Lardners Gauge were slightly more variable (up to 0.17 TU). The range of ^{3}H activities between the events was most variable at Porcupine Creek (0.20 to 1.97 TU), followed by Yahoo Creek (0.43 to 2.14 TU), Love Creek Kawarren (0.48 to 1.91 TU), Love Creek Wonga (0.55 to 1.88 TU), Ten Mile Creek (0.44 to 1.74 TU), Upper Lardners (1.54 to 1.99 TU), James Access (1.73 to 2.08 TU), and Lardners Gauge (1.64 to 1.97 TU) (Fig. 4). Overall, the highest ^{3}H activities were similar across all catchments but the lower ^{3}H activities varied considerably. The ^{3}H activities increase with increasing streamflow up to approximately $10^4\,\mathrm{m^3\,day^{-1}}$, above which ^{3}H activities do not increase appreciably (Fig. 4). Despite differences in catchment size, slope, geology, and land use, there is a strong correlation between ^{3}H activities and streamflow across the catchments (^{3}H $= 0.2613\ln(Q) + 0.8973$; $R^2 = 0.75$, p value $= 0.15$).

4.3 Major ion geochemistry

River water geochemistry is similar across all catchments and is dominated by Na, Cl, and HCO_3 (Supplement). TDS concentrations are generally less than $100\,\mathrm{mg\,L^{-1}}$ at Lardners Gauge, Upper Lardners, and James Access but typically exceed $200\,\mathrm{mg\,L^{-1}}$ in Love Creek Wonga, Love Creek Kawarren, Porcupine Creek, Ten Mile Creek, and Yahoo Creek. TDS concentrations increase downstream in Lardners
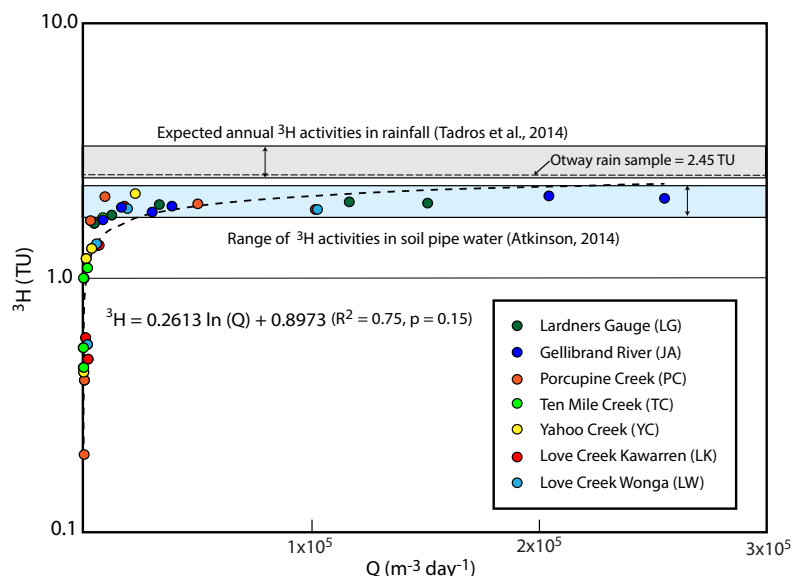
Figure 4. ^{3}H activities of stream water as a function of streamflow for all catchments except Upper Lardners which is ungauged. ^{3}H data from Supplement, streamflow data from Department of Environment, Land, Water and Planning (2017) or calculated as discussed in the text. Shaded boxes show the expected annual average of rainfall ^{3}H activities from Tadros et al. (2014) and soil waters from Atkinson (2014).
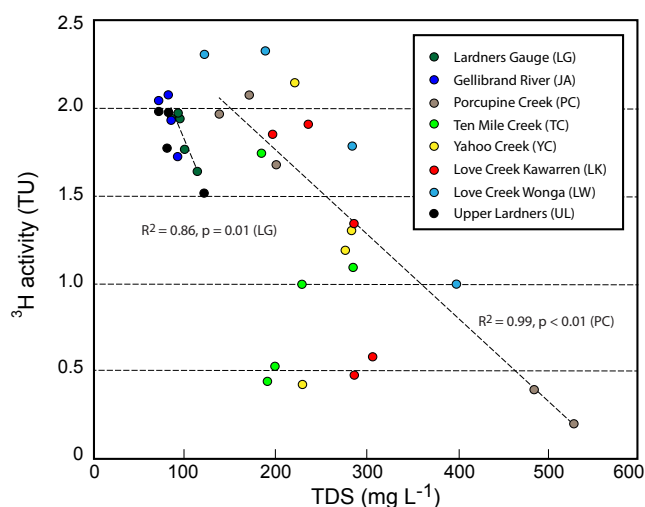

Figure 5. ^{3}H activities as a function of TDS for all catchments (data from Supplement). Strong inverse correlations between ^{3}H activities and TDS exist for Lardiners Gauge and Porcupine Creek.

and Love creeks and are inversely correlated with streamflow in all catchments.

At Love Creek, Ten Mile Creek, Yahoo Creek, and Upper Lardners, there is no correlation between ^{3}H activities and EC, TDS, or major ion concentrations (Fig. 5). However, at Porcupine Creek, there is a strong correlation ($R^2 > 0.95$, p value < 0.01) between ^{3}H activities and EC, TDS, and all major ion concentrations with the exception of chloride, nitrate, and sulfate. In addition, there is a strong correlation

($R^2 = 0.86$, p value $= 0.01$) between ^{3}H activities and TDS at Lardners Gauge (Fig. 5).

At Upper Lardners, James Access, and Ten Mile Creek, there is a strong correlation ($R^2 > 0.8$, p values < 0.11) between nitrate concentration and ^{3}H activities (Fig. 6a). The range of nitrate concentrations (0.08 to 2.0 mg L^{-1}) were relatively similar during each sampling event across all catchments except for in July 2014, when nitrate concentrations exceeded 3 mg L^{-1} at Love Creek Kawarren and Love Creek Wonga. A similar correlation exists between sulfate concentrations and ^{3}H activities at James Access and at Upper Lardners, but not at Ten Mile Creek (Fig. 6b). However, sulfate concentrations at these locations are lower than they are in the other catchments.

5   Discussion

The combination of streamflow, ^{3}H activities, major ion geochemistry, and catchment attributes allows aspects of the behaviour of the upper Gellibrand catchments to be understood. This section addresses the changing stores of water in the catchments, the range and uncertainties of MTTs, and whether MTTs can be predicted from catchment attributes or geochemical data.
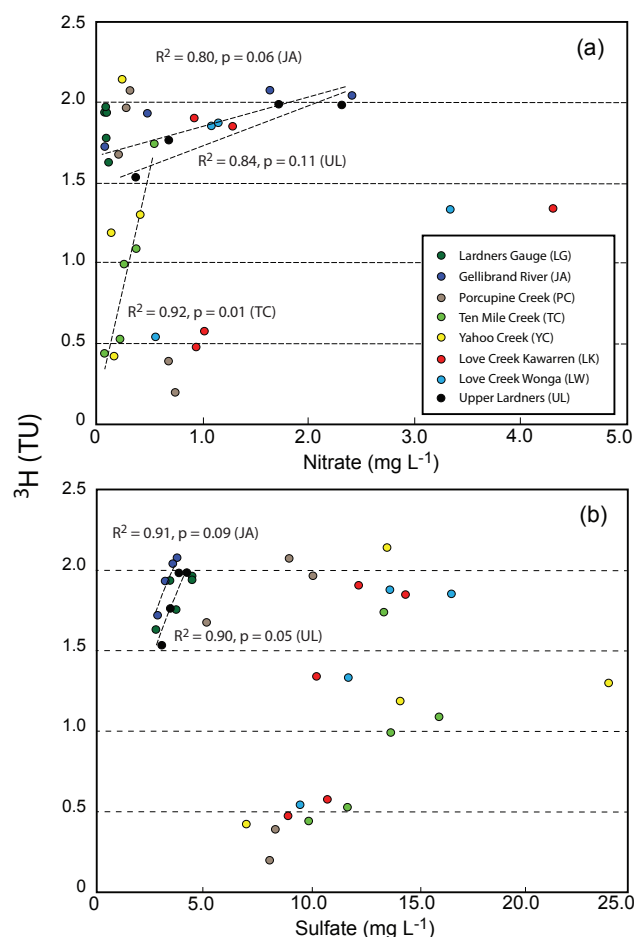
Figure 6. ^{3}H activities as function of nitrate concentrations **(a)** and sulfate concentrations **(b)**. Data from Supplement. Strong ($R^2 > 0.7$) correlations indicated.

5.1 Sources of river inflows

It is important to determine how the water stores that contribute to streamflow change between high and low flows. Groundwater inflows are most probably the dominant source of water during the summer months. However, at times of higher streamflow there may be mobilisation of younger shallower water stores (e.g. water from the soils or the regolith) as the catchment wets up (e.g. Hrachowitz et al., 2013; Cartwright and Morgenstern, 2015, 2016a) or mixing between baseflow and recent rainfall (e.g. Morgenstern et al., 2010). The river water samples were collected during baseflow conditions or during recession periods after high streamflows that follow rainfall (Fig. 3) when recent rainfall is less likely to directly contribute to streamflows. That the major ion geochemistry varies little with streamflow also suggests that there is not significant dilution of groundwater inflows with recent rainfall during the sampling periods (e.g. Sklash

and Farvolden, 1979; Kennedy et al., 1986; Jensco and McGlynn, 2011; Cartwright and Morgenstern, 2015).

Together, these observations suggest that there is no significant direct input of recent rainfall during the sampling periods. The flow system is concluded to be a continuum that is dominated by older groundwater inflows at low flows while progressively shallower and younger stores of water (such as soil water or perched groundwater) are mobilised during wetter periods. The observations that nitrate and sulfate concentrations in several of the catchments are higher at high streamflows (Fig. 6) may reflect the input of contaminants from recent agricultural activities to the streams. This observation agrees with the conceptualisation that shallower stores of water in the catchment, which are more likely to be impacted by contamination, are mobilised during the wetter periods of the year.

5.2 Mean transit times

If the conceptualisation of the flow system is correct, MTTs may be calculated using a single LPM. If there were some dilution by recent rainfall, using a single LPM yields the minimum MTT of the baseflow component (Morgenstern et al., 2010). MTTs in the headwaters catchments were estimated using the EPM and the DM. For the EPM, EPM ratios of 0.33 (75 % exponential flow), 1.0 (50 % exponential flow) and 3.0 (25 % exponential flow) were adopted. The EPM model accords with the expected geometry of flow in the catchment (vertical recharge through the unsaturated zone followed by flow along flow paths of varying length), and EPM models with these EPM ratios have reproduced the ^{3}H time series in headwater catchments with similar geometries elsewhere (Maloszewski and Zuber, 1982; Morgenstern and Daughney, 2012; Blavoux et al., 2013; Morgenstern et al., 2010). For the DM, D_p values of 0.05 and 0.5 were adopted, which are appropriate for kilometre-scale flow systems (Zuber and Maloszewski, 2001; Gelhar et al., 1992). Utilisation of a variety of LPMs allows the impact of the assumed model on the MTTs to be assessed.

Calculated MTTs ranged from approximately 7 years at Yahoo Creek in July 2014 to 230 years at Porcupine Creek in March 2015 (Table 3). In general, the lowest MTTs were estimated from the EPM with EPM ratio = 3.0 while the highest MTTs were estimated using the DM with $D_p = 0.5$. Because of the remnant bomb-pulse ^{3}H, a few samples with ^{3}H activities between 1.2 and 1.7 TU yield MTTs that are non-unique for models with high piston flow components (i.e. the EPM with EPM ratio = 3.0 and the DM with $D_p = 0.05$; Table 3, Fig. 7). The choice of the LPM has little impact on MTTs for ^{3}H activities greater than 1 TU (Fig. 7). However, as ^{3}H activities decrease, the relative difference between the MTTs from the different LPMs increases. At the lowest ^{3}H activity of 0.20 TU, the difference between the MTT estimates is approximately 164 years.
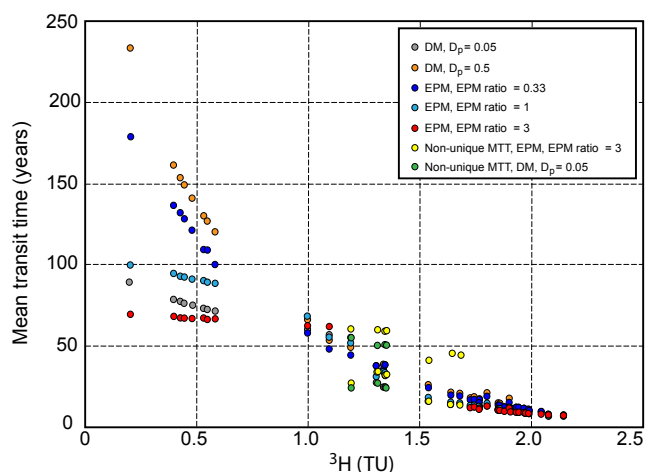
Figure 7. Estimated MTTs vs. [3]H activities in the stream waters calculated using the exponential piston-flow model (EPM) with EPM ratios of 0.33, 1.0, and 3.0 and the dispersion model (DM) with D_p values of 0.05 and 0.5. Data from Supplement and Table 3.

MTTs for Lardners Gauge, Upper Lardners, and James Access were similar, and are between 7 and 26 years. In contrast, MTTs for Porcupine Creek ranged from approximately 7 to 230 years, while those for Ten Mile Creek, Yahoo Creek, Love Creek Wonga, and Love Creek Kawarren ranged from approximately 13 to 150, 7 to 15, and 10 to 140 years, respectively. In all catchments, the longest MTTs are recorded at the lowest streamflows (March 2015) while the shortest MTTs occur at the highest streamflows (July 2014 and September 2015) (Fig. 8). At Lardners Gauge, James Access, Porcupine Creek, and Love Creek, the samples collected at the highest flow rates have MTTs that are slightly longer than those of the samples collected at the second highest streamflow (Fig. 8). Whether this reflects changes to the flow system or is due to uncertainties in the MTT estimates is not certain.

The volume of water in the aquifers that contributes to the streamflow may be estimated from Eq. (3). Both the Lardners Gauge and the Love Creek Wonga catchments have active streamflow monitoring, and the calculations are carried out for these catchments. Using the relationships between MTT and streamflow (Fig. 8) and streamflow data for 2014 and 2015 (Department of Environment, Land, Water, and Planning, 2017), the average MTT for the two catchments is estimated to be 29.7 years (Love Creek Wonga) and 10.8 years (Lardners Gauge). For the average annual streamflow over those 2 years, the turnover volumes are 2.6×10^5 m[3] (Love Creek Wonga) and 4.5×10^5 m[3] (Lardners Gauge). These volumes are small relative to the likely volumes of water stored in the catchments. For the catchment areas (Table 1) and a porosity of 0.1 to 0.3, which is appropriate for most soils and aquifers, this volume of water could be stored in a layer that is 0.01 to 0.1 m thick.

5.3 Uncertainties in MTT estimates

The uncertainties in the MTTs arising from the analytical uncertainties (Supplement) range from ±0.9 years for the sample with the highest ^{3}H activity to ±10 years for the sample with the lowest ^{3}H activity. These equate to relative uncertainties of ∼ ±10 %. Having to assume an LPM reflects a major uncertainty for calculating the MTTs, especially for waters with ^{3}H activities < 1 TU (Fig. 7). For a water with a ^{3}H activity of 2 TU, the uncertainty in MTTs is ±1.2 years (±13 %), while for waters with ^{3}H activities of 1 and 0.5 TU they are ±5 years (±8 %) and ±31 years (±30 %), respectively. The EPM with an EPM ratio of 3.0 and the DM with a D_p value of 0.05 have a large component of piston flow and are possibly less realistic representations of the flow systems; however, the differences between the MTTs estimated using the other LPMs are still considerable.

The influence of uncertainties in the ^{3}H input was assessed by varying the modern and pre-bomb-pulse ^{3}H activities between 2.4 and 3.2 TU and adjusting the ^{3}H activities in the intervening years accordingly. As discussed above, this encompasses the predicted range of average annual ^{3}H activities in most of central and southeastern Australia. These calculations used the EPM with an EPM ratio of 1.0 but the effect is similar in the other models. The relative difference between MTTs is generally highest when ^{3}H activities exceed 1 TU (Fig. 9). For ^{3}H activities of 2 TU, the uncertainty in MTTs is ±5 years (±54 %), while for waters with ^{3}H activities of 1 and 0.5 TU they are ±10 years (±15 %) and ±5 years (±5 %), respectively.

[3]H activities in rainfall can vary seasonally. Catchments with MTTs in excess of a few years do not preserve seasonal variations in stable isotope ratios or major ion concentrations (Stewart et al., 2010). In a similar way, the seasonal variation in rainfall ^{3}H activities are unlikely to be preserved in the catchment waters (Morgenstern et al., 2010). Thus, using annual ^{3}H activities as the input is appropriate. However, if recharge has a strong seasonality, its ^{3}H activities may be different from those of annual rainfall. Rainfall in the Otway Ranges is distributed throughout the year and it is likely that some recharge occurs throughout the year. Less recharge probably occurs during summer due to some rainfall being lost to evapotranspiration. However, as is the case elsewhere in the Southern Hemisphere (Morgenstern et al., 2010), the ^{3}H activities in summer rainfall are closely similar to the average annual ^{3}H activities (Tadros et al., 2014; International Atomic Energy Agency, 2017). The observation that the ^{3}H activities of summer (December to February) rainfall at Mount Buffalo in northeastern Victoria were similar (2.86 TU) to those of two annual rainfall samples (2.99 and 2.85 TU) support this assertion (Cartwright and Morgenstern, 2015). With such a seasonal distribution of ^{3}H activities, the uncertainties in MTTs resulting from using the average annual ^{3}H activities are less than those that arise from the general uncertainty in the ^{3}H input function.
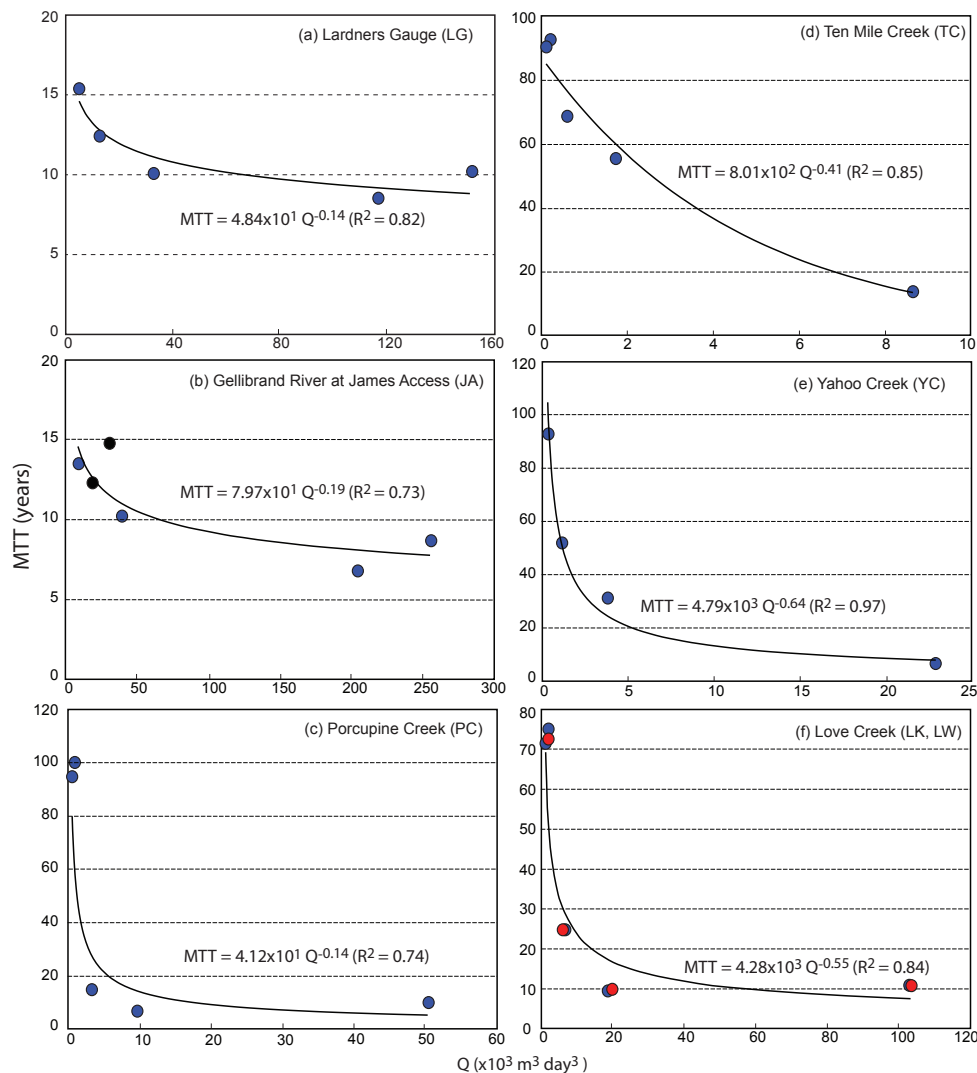
Figure 8. MTTs calculated using the EPM model with an EPM ratio of 1.0 (Table 3) as a function of streamflow (Q) for Lardners Gauge **(a)**, Gellibrand River at James Access **(b)** – black circles are data from Atkinson (2014), Porcupine Creek **(c)**, Ten Mile Creek **(d)**, Yahoo Creek **(e)**, and Love Creek **(f)** – blue circles are Love Creek Kawarren and red circles Love Creek Wonga. Curves are exponential trend lines. Streamflow data from Department of Environment, Land, Water and Planning (2017) or calculated as discussed in the text.

The impact of macroscopic mixing was estimated using Eq. (2) and the streamflow data and MTTs for Porcupine, Ten Mile, and Yahoo creeks that flow into Love Creek upstream of Love Creek Kawarren (Fig. 1). The analysis used the EPM with an EPM ratio of 1.0 (Table 3), but again similar results were obtained with the other LPMs. Based on the streamflow data, these three streams contribute 77 to 82 % of total stream flow at Love Creek Kawarren (Table 3). The remaining portion of flow in Love Creek is assumed to be contributed by undefined inputs such as groundwater inflow and inputs from smaller tributaries. It was assumed that there was one unidentified input, the ^{3}H activity of which was estimated by the difference between the weighted ^{3}H activities of Porcupine, Ten Mile, and Yahoo creeks and the ^{3}H ac-

tivity at Love Creek Kawarren. The MTT of this input was determined from the ^{3}H activity using the EPM.

In March 2015, the estimated MTT calculated using the LPM at Love Creek Kawarren was higher than MTT_e calculated using Eq. (2) by 3.7 years or 4 % (Table 4). At other times, the differences were 3.9 to 7.4 years (18 to 37 %). These calculations may not truly address aggregation as there may be more than one unidentified additional store of water and there may be aggregation within the individual subcatchments (which impacts their estimated MTTs). Nevertheless, they do indicate that the potential uncertainties in MTTs due to aggregation are potentially several years (as discussed by Stewart et al., 2017). For waters with similar ^{3}H activities, Cartwright and Morgenstern (2016a) estimated
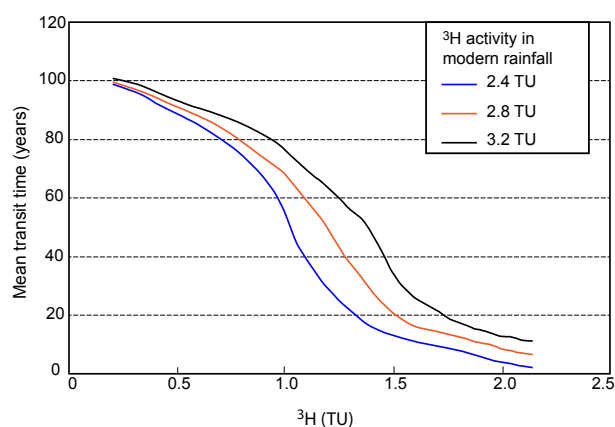
Figure 9. Impact of varying rainfall ^{3}H inputs on MTTs calculated using the EPM model with an EPM ratio of 1.0. The three rainfall inputs modern and pre bomb-pulse ^{3}H activities of 2.4, 2.8, and 3.2 TU and the ^{3}H activity of the bomb-pulse rainfall was varied by a similar proportion as discussed in the text.

that the aggregation error may be up to 20 % where two waters with MTTs of 10 and 50 years or 1 and 5 years mixed but noted that this error became progressively lower if more stores of water with a similar range of MTTs mixed.

If the uncertainties are uncorrelated, the overall uncertainty is given by the square root of the sum of the squares of the individual uncertainties. The analysis assumes that uncertainties due to analytical uncertainties and aggregation are uniformly 10 and 20 %, respectively, and the uncertainties from the range of LPMs and the ^{3}H input of rainfall are as discussed above. For a water with a ^{3}H activity of 2 TU, the overall uncertainty in MTTs are approximately ± 60 % (± 5.4 years), whereas for waters with ^{3}H activities of 1 and 0.5 TU they are ± 28 % (± 17 years) and ± 38 % (± 35 years), respectively.

While these uncertainties are considerable, the observation that the ^{3}H activities of the streams are locally 10 % of those of modern rainfall (and far less than the rainfall ^{3}H activities at the peak of the bomb pulse) necessitates that the MTTs must be several decades. Because the aggregation error, which is probably the most difficult to assess, results in MTTs being underestimated (Kirchner et al., 2016; Stewart et al., 2017) some MTTs may be longer than calculated. Relative differences in MTTs between and within catchments may be estimated with more certainty. Because the catchments are located in a relatively small area, the ^{3}H inputs are likely to be closely similar. Thus, uncertainties in the ^{3}H input are thus less likely to impact the comparison of MTTs between catchments. Additionally, as the geometry of the flow system in each catchment is unlikely to vary substantially at different streamflows, not being able to assess the suitability of the LPM has less impact on the relative differences in MTTs at different streamflows in the same catchment.

Table 2. Correlation between catchment attributes and ^{3}H activities for the upper Gellibrand River catchments.

Catchment attribute	Sampling date	R^2
Area	Jul 2014	0.01
	Sep 2014	0.26
	Mar 2015	0.06
	Sep 2015	0.57
Drainage density	Jul 2014	0.00
	Sep 2014	0.58
	Mar 2015	0.40
	Sep 2015	0.40
Runoff coefficient	Jul 2014	0.10
	Sep 2014	0.66
	Mar 2015	0.94
	Sep 2015	0.19
Forest cover	Jul 2014	0.51
	Sep 2014	0.15
	Mar 2015	0.24
	Sep 2015	0.01
Slope	Jul 2014	0.39
	Sep 2014	0.55
	Mar 2015	0.87
	Sep 2015	0.15

5.4 Predicting mean transit times

There are weak ($R^2 \leq 0.7$) or no correlations between ^{3}H activities and catchment area, drainage density, or forest cover (Table 2). There is a strong correlation between ^{3}H activities and average slope ($R^2 = 0.87$, p value 0.01) during March 2015, when streamflow was lowest but not at other times. The variability of MTTs from James Access, Lardners Gauge, and Upper Lardners (which occur on the Otway Group: Fig. 1) and from Porcupine Creek, Yahoo Creek, Love Creek, and Ten Mile Creek (which have similar lithologies in their catchments: Fig. 1) indicates the MTTs are not simply related to the geology. A combination of the catchment properties together with the hydraulic properties of the soils and aquifers or evapotranspiration rates likely control the MTTs. The hydraulic properties and evapotranspiration rates are probably spatially variable and are difficult to estimate, which makes it difficult to assess their influence. The observation that relationships between ^{3}H activities and streamflow in all the catchments are similar (Fig. 4) suggests that the MTTs at high flows reflect the inflow of water from the shallower water stores which will be largely independent of the catchment attributes.

There are strong positive correlations between ^{3}H activities and the runoff coefficient ($R^2 = 0.94$, p value $= 0.27$) (Fig. 10). This may be due to both the runoff coefficient and MTTs being controlled by the rates of recharge and ground-

Table 3. Summary of calculated mean transit times (MTTs) for the upper Gellibrand River catchments.

Location (Fig. 1)	Date (dd/mm/yyyy)	Q^a $10^3\,\mathrm{m}^3\,\mathrm{day}^{-1}$	^{3}H (TU)	MTT (years) EPM[b] 0.33	1.0	3.0	DM[c] 0.05	0.5
Upper Lardners (UL)	10/07/2014	–	1.99	9.9	9.6	8.8	9.0	11.2
	28/09/2014	–	1.77	15.7	12.9	11.8	12.2	17.6
	20/03/2015	–	1.54	24.2	18.5	(16.2, 41.4)[d]	16.3	26.2
	10/09/2015	–	1.99	8.8	8.2	8.6	8.3	9.9
Lardners Gauge (LG)	10/07/2014	151.3	1.94	10.8	10.2	9.3	9.6	12.3
	28/09/2014	32.8	1.94	10.6	10.1	9.2	9.5	12.1
	20/03/2015	5.0	1.64	19.8	15.4	(14.1, 45.7)	14.2	21.6
	10/09/2015	116.6	1.97	9.1	8.5	8.7	8.6	10.2
	04/11/2015	12.7	1.77	13.8	12.4	11.2	11.6	15.8
Gellibrand River at James Access (JA)	13/03/2012	18.5	1.90	15.5	12.3	11.8	11.7	17.7
	26/04/2012	30.4	1.80	19.2	14.8	13.1	13.4	21.4
	10/07/2014	255.2	2.04	8.7	8.7	8.1	8.2	9.7
	28/09/2014	39.1	1.93	10.8	10.2	9.4	9.7	12.4
	20/03/2015	8.8	1.73	16.2	13.5	12.2	12.6	18.2
	10/09/2015	204.4	2.08	7.3	6.8	7.7	7.0	8.1
Porcupine Creek (PC)	10/07/2014	50.4	1.97	10.3	9.8	9.0	9.2	11.7
	27/09/2014	3.3	1.68	19.3	14.9	(13.9, 44.7)	13.8	21.0
	20/03/2015	1.0	0.20	179	100	69.5	89.6	234
	10/09/2015	9.7	2.08	7.3	6.8	7.7	7.0	8.1
	04/11/2015	0.6	0.40	137	94.8	68.4	78.7	162
Ten Mile Creek (TC)	10/07/2014	8.6	1.74	17.1	13.6	12.5	12.7	18.8
	27/09/2014	0.6	1.00	58.3	68.5	62.5	60.1	66.3
	20/03/2015	0.2	0.44	128	92.5	67.2	76.4	150
	10/09/2015	1.7	1.09	48.3	55.5	62.0	57.0	53.5
	04/11/2015	0.1	0.53	109	90.3	67.2	73.3	130
Yahoo Creek (YC)	11/07/2014	23.0	2.14	6.9	6.8	7.2	7.0	7.6
	28/09/2014	1.2	1.19	44.7	52.0	(60.6, 27.4)	(55.3, 24.8)	49.2
	20/03/2015	0.4	0.43	132	93.1	67.4	77.2	154
	10/09/2015	3.9	1.30	34.8	31.3	(34.3, 60.0)	(27.6, 50.7)	37.9
Love Creek Kawarren (LK)	10/07/2014	102.9	1.85	13.3	11.5	10.5	10.9	15.0
	27/09/2014	6.7	1.34	35.3	33.5	(32.3, 59.2)	(24.8, 51.2)	38.4
	20/03/2015	2.0	0.48	121	91.2	67.0	75.1	141
	10/09/2015	18.6	1.91	10.4	9.8	9.5	9.5	11.9
	04/11/2015	1.2	0.58	100	88.6	66.8	71.5	120
Love Creek Wonga (LW)	10/07/2014	103.5	1.86	13.1	11.4	10.4	10.8	14.8
	28/09/2014	6.0	1.34	35.7	34.2	(32.1, 59.3)	(24.8, 51.4)	38.8
	20/03/2015	2.0	0.55	109	89.4	66.4	72.6	127
	10/09/2015	19.6	1.88	11.0	10.4	9.8	9.9	12.6

[a] Discharge. [b] Exponential piston-flow model with EPM parameter of 0.33, 1, and 3. [c] Dispersion model with dispersion parameter of 0.05 and 0.5. [d] Non-unique MTTs.

water flow. The Lardners Gauge and James Access sites have much higher runoff coefficients than the other catchments, and the correlation with ^{3}H activities may reflect the difference between the two groups of catchments. If this is the case, the runoff coefficient may be useful in determining gross rather than subtle differences in MTTs.

EC and streamflow were measured on a monthly basis at the gauging station on Porcupine Creek (site 235241) between January 1990 and January 1994 (Department

of Environment, Land, Water and Planning, 2017). A strong correlation between MTTs and EC at this location (MTT $= 1.362\,e^{0.0061\cdot\mathrm{EC}}$: $R^2 = 0.96$, p value $= 10^{-8}$) allows MTTs at this site to be estimated over this 4-year period (Fig. 11). The estimated MTTs range from 3 to 50 years, with the longest MTTs corresponding to low summer flows and the shortest MTTs during high winter flows. Although based upon a limited number of samples, these results demonstrate
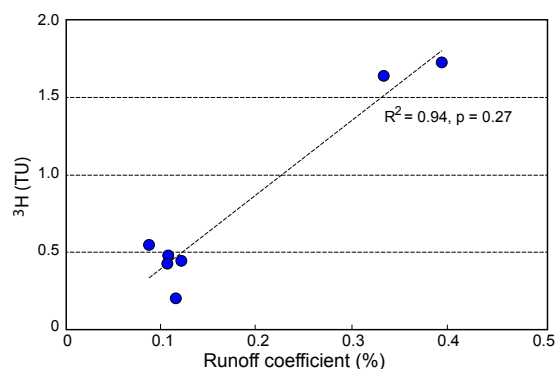
Figure 10. ^{3}H activities vs. runoff coefficients for the March 2015 samples (data from Table 1 and Supplement). Although a strong correlation ($R^2 = 0.94$) exists, it may be a result of the grouping of the samples.
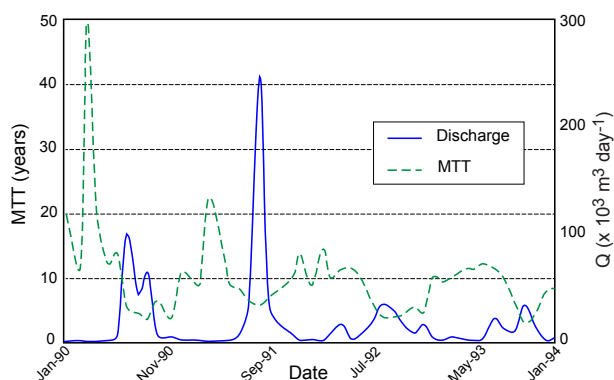

Figure 11. Variation in MTT as a function of streamflow at Porcupine Creek for January 1990 to January 1994 calculated using the relationship between EC and ^{3}H activity (Supplement) and monthly EC data from the Department of Environment, Land, Water and Planning (2017). Streamflow data also from Department of Environment, Land, Water and Planning (2017).

the high variability of transit times within the catchment and the value of finding proxies for ^{3}H.

6 Summary and conclusions

The calculated MTTs in the six headwater catchments in the Upper Gellibrand catchment of Otway Ranges vary from approximately 7 to 230 years, verifying the hypothesis that these streams are sustained by relatively old water. While there are significant uncertainties in the MTT estimates, the conclusion that they range from years to several decades and are longer at low streamflows is robust. Similar MTTs are recorded in other catchments in southeastern Australia (e.g. Cartwright and Morgenstern, 2015, 2016a, b). Especially at low streamflows, the MTTs are far longer than in most headwater catchments worldwide (e.g. Stewart et al., 2010) and

Table 4. Estimates of the difference between calculated mean transit times (MTTs) and that estimated from the mixing of waters from different tributaries at Love Creek Kawarren.

Sample date	MTT (years)	
10/07/2014	MTT$_e$[a]	15.4
	Sample MTT[b]	11.5
	Difference (years)	3.9
	Difference (%)	25.5
27/09/2014	MTT$_e$	40.9
	Sample MTT	33.5
	Difference (years)	7.4
	Difference (%)	18.1
20/03/2015	MTT$_e$	87.4
	Sample MTT	91.2
	Difference (years)	3.8
	Difference (%)	4.4
10/09/2015	MTT$_e$	15.5
	Sample MTT (years)	9.8
	Difference (years)	5.7
	Difference (%)	36.7

[a] Estimated from the tributary inputs (Eq. 2). [b] Estimated using the EPM (1.0) lumped parameter model (Table 3).

are some of the longest yet recorded. The average MTT of 15 ± 22 years calculated by Stewart et al. (2010) was for MTTs based on ^{3}H activities, which makes it directly comparable with MTTs from the south Australian catchments.

Understanding the reasons for the difference in MTTs between catchments is important for understanding catchment behaviour. The catchments in southeastern Australia have similar dimensions, slopes, and stream densities to those elsewhere, making it unlikely that the differences in MTTs result from catchment geomorphology. The Gellibrand catchments have only thin near-river alluvial sediments, thus diminishing the likelihood of bank storage and return flows of young waters during the recession from the high streamflows. However, many headwater catchments globally lack extensive alluvial sediments. The hydraulic properties of the soils and aquifers may also result in slow recharge rates and long MTTs. These are very poorly known and it is difficult to assess their influence.

Due to the high transpiration rates of eucalyptus forests, recharge rates in Australian catchments are generally lower than elsewhere globally (Allison et al., 1990). However, the observation that there is no correlation between the percentage of forest cover and MTTs in the upper Gellibrand catchments where land clearing occurred several decades ago is problematic for proposing this as a simple control. Despite being in the more temperate region of southeastern Australia, the average rainfall in the Otway Ranges of 1000 to 1600 mm yr^{-1} is modest compared with upland areas in many parts of the world and the average evapotranspiration

rate of 1000 to 1100 mm yr^{-1} includes a sizeable component of evaporation (which is more prevalent on the cleared land) (Bureau of Meteorology, 2016). The long MTTs in the catchments from southeastern Australia may, therefore, reflect the low rainfall and high evaporation and/or transpiration rates that limit recharge.

The long MTTs are significant for understanding and managing the catchments. Firstly, there are likely to be long-lived stores of water in these catchments that can sustain the streams during droughts that last up to a few years, although longer-term changes (such as land use change or climate change) may eventually affect the streamflows. The long MTTs also imply that any contaminants in groundwater are likely to be released into the streams over years to decades (e.g. Morgenstern and Daughney, 2012). The locally higher nitrate and sulfate concentrations at high streamflows may reflect the input of contaminants from recent agricultural activities to the streams via the younger groundwater that is mobilised at those times.

Even at baseflow conditions, it was not possible to simply predict the MTTs across the catchments from catchment attributes or the geochemistry, although local correlations exist (this refutes one of the hypotheses). The MTTs are most likely controlled by a combination of catchment attributes and also soil properties, hydraulic conductivities, and evapotranspiration rates. This is in keeping with the observation that previous studies have identified correlations between a range of parameters and MTTs (i.e. no single attribute appears to provide the dominant control on MTTs across different regions). Characterising hydraulic properties and evapotranspiration rates on a catchment-wide scale is difficult, which limits the ability to predict MTTs. The runoff coefficient that is a reasonable indicator of MTTs elsewhere in southeastern Australia (Cartwright and Morgenstern, 2015) was the best predictor of MTTs. This may reflect the fact that both the runoff coefficient and MTTs are controlled by recharge and groundwater flow rates.

This study illustrates that, while broad ranges of MTTs may be estimated using ^{3}H, precise determination of MTTs is difficult. Additionally, it highlights the challenge in understanding the reasons for the long MTTs in the Australian catchments compared with headwater catchments elsewhere. The potential controls on MTTs is catchments are numerous, and more studies in catchments with different climate, land use, geomorphology, and geology are needed if the desire to be able to predict catchment behaviour regionally or globally is to be realised.

The Supplement related to this article is available online at https://doi.org/10.5194/hess-22-635-2018-supplement.

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