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Using tritium to document the mean transit time and sources of water contributing to a chain-of-ponds river system: Implications for resource protection☆

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ABSTRACT

Documenting the interaction between groundwater and rivers is fundamental to understanding hydrological systems. While many studies have examined the location and magnitude of groundwater inflows to rivers, much less is known about the transit times of water in catchments and from where in the aquifer the groundwater originates. Resolving those questions is vital for protecting riverine ecosystems, assessing the impact of contamination, and understanding the potential consequences of groundwater pumping. This study uses tritium (^{3}H) to evaluate the mean transit times of water contributing to Deep Creek (southeast Australia), which is a chain-of-ponds river system. ^{3}H activities of river water vary between 1.47 and 2.91 TU with lower ^{3}H activities recorded during cease-to-flow periods when the river comprises isolated groundwater-fed pools. Regional groundwater 1–2.5 km away from Deep Creek at depths of 7.5–46.5 m has ^{3}H activities of between <0.02 and 0.84 TU. The variation in ^{3}H activities suggest that the water that inflows into Deep Creek is dominated by near-river shallow groundwater with the deeper groundwater only providing significant inflows during drier periods. If the water in the catchment can be represented by a single store with a continuum of ages, mean transit times of the river water range between <1 and 31 years whereas those of the groundwater are at least 75 years and mainly >100 years. Alternatively the variation in ^{3}H activities can be explained by mixing of a young near-river water component with up to 50% older groundwater. The results of this study reinforce the need to protect shallow near-river groundwater from contamination in order to safeguard riverine ecosystems and also illustrate the potential pitfalls in using regional bores to characterise the geochemistry of near-river groundwater.

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1. Introduction

Documenting groundwater inflows to streams, lakes, and wetlands is a fundamental part of understanding catchment hydrology and a necessary step in the management and protection of surface water resources and ecosystems (Winter 1999; Sophocleous, 2002; Brodie et al., 2007). Geochemical tracers including major ions, stable isotopes, and radioactive isotopes (especially ^{222}Rn) have been successfully applied in discerning the location and magnitude of groundwater inflows to surface water bodies (e.g., Brodie et al., 2007; Cook, 2013). In certain cases it may be possible to use river geochemistry to identify specific aquifers from which the groundwater that inflows to the river was derived (Batlle-Aguilar et al., 2014; Atkinson et al., 2015). Long-lived radioisotopes (such as ^{4}He and ^{14}C) have also been utilised to detect an older component of groundwater contributing to the groundwater inflows (Gardner et al., 2011; Bourke et al., 2014). In many aquifers, however, the major ion and stable isotope geochemistry of groundwater is relatively uniform over areas of up to several hundreds of km^{2} and to depths of several tens of metres. In such cases, river geochemistry may indicate that groundwater inflows to surface water has occurred, but not distinguish from where in the aquifer the groundwater was derived. In addition, the time that groundwater

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takes to flow through the aquifer system and discharge into the surface water (the transit time) remains poorly understood in many catchments (McGuire and McDonnell, 2006; McDonnell et al., 2010).

Documenting from where in the aquifer system groundwater is derived and the transit times is important. Shallow groundwater is more susceptible to contamination; hence, if the majority of groundwater inflows are from shallow aquifers, the connected surface water bodies are at higher risk of contamination. Additionally, as the concentrations of some contaminants are attenuated by reactions within the aquifer, longer transit times may result in lower net fluxes of contaminants into the surface water. Nitrate represents the most common contaminant in agricultural areas, and nitrate concentrations in older groundwater may be reduced by denitrification (e.g., Hiscock et al., 1991). Where attenuation does not occur, the transit times controls the lag time between contamination occurring and those contaminants impacting the surface water (Morgenstern et al., 2015). Buffer zones ranging from metres to hundreds of metres are commonly set up around streams to limit the inflow of groundwater impacted by urban development; however, the efficacy of this approach requires that the connection of groundwater and stream water be well understood. Finally, understanding the potential impacts of groundwater pumping adjacent to surface water bodies requires a detailed understanding of the connections between groundwater and surface water.

Tritium (^3H) may be used to determining the transit times of shallow groundwater, soil water, or surface water (e.g., Cook and Bohlke, 2000; Morgenstern et al., 2010; Cartwright and Morgenstern, 2015; Morgenstern et al., 2015). Since it is part of the water molecule, ^3H activities are not impacted by geochemical or biological reactions in the aquifers or soils and depend only on the initial activities and the residence times in the catchment. Other potential tracers that may be used to determine transit times of young waters such as ^3He, the chlorofluorocarbons, or SF_6 are dissolved gases that degas to the atmosphere and are difficult to use in surface water systems (McGuire and McDonnell, 2006). Because ^3H activities are not impacted by exchange with soil gasses, ^3H transit times reflect the passage of water through the both unsaturated and saturated zones.

Using models that describe the distribution of flow paths within an aquifer (Cook and Bohlke, 2000; Maloszewski, 2000; McGuire et al., 2005), ^3H activities may be used to estimate transit times of waters that are up to ~100 years old. Globally, the ^3H activities in rainfall over the last several decades are well known (e.g. International Atomic Energy Association, 2016) and many region-specific compilations exist (e.g., the Tadros et al., 2014 compilation for Australia). Rainfall ^3H activities peaked in the 1950s–1960s due to the atmospheric nuclear tests that increased atmospheric ^3H activities (commonly termed the "bomb-pulse"). The ^3H activities of bomb-pulse rainfall in the southern hemisphere were several orders of magnitude lower than those in the northern hemisphere (e.g., Clark and Fritz, 1997) and the ^3H activities of this water have now decayed below those of modern rainfall. This situation permits unique transit times to be estimated from single ^3H measurements, which in turn does not require an assumption that the flow in catchments is steady state (Morgenstern et al., 2010). By contrast, the ^3H activities of remnant bomb pulse waters in the northern hemisphere are currently above those of modern rainfall, which requires time-series of ^3H activities to be used to estimate transit times (Morgenstern et al., 2010).

1.1. Objectives

This study examines the transit times of water contributing to Deep Creek (Maribyrnong Catchment) in southeast Australia, which is a chain-of-ponds river system that receives groundwater inflows (Cartwright and Gilfedder, 2015). Specifically ^3H is used to determine mean transit times of the river water at a variety of streamflows, including the cease-to-flow conditions when the river consists of isolated groundwater-fed pools. These transit times are compared with those of groundwater to assess the proportion of deeper (7.5–46.5 m) regional groundwater that inflows into the river at different flow conditions. Resolving the mean transit times and the proportion of deeper groundwater that infiltrates the pools is important for managing and protecting Deep Creek and its riverine ecosystems.

While based on a specific river system, the issues discussed here are generally applicable. In common with many catchments globally, Deep Creek has limited groundwater monitoring bores and most of these bores are located a few (in this case 1 to 2.5) kilometres from the river and at depths of several metres. This bore network permits a broad understanding of the groundwater system but not a detailed understanding of groundwater-river interaction.

1.2. Setting

Deep Creek (Fig. 1) is a tributary of the Maribyrnong River in central Victoria, Australia, that comprises numerous 1–2 m deep and up to 15 m wide pools connected by narrower river sections (Cartwright and Gilfedder, 2015), a form commonly referred to as chain-of-ponds or swampy meadows (Mactaggart et al., 2008). The floodplain of the Deep Creek catchment comprises lava flows of the Quaternary to Recent basaltic Newer Volcanics that are overlain by thin Recent alluvium and colluvium deposits. The Newer Volcanics landscape is relatively young and irregular with lakes and pools developed where lava flows fill pre-existing drainage lines (Joyce, 1988). Groundwater in the Newer Volcanics in general is preferentially recharged through scoria deposits that have high permeabilities and groundwater flow is hosted both in fractures and more permeable units (Tweed et al., 2007). Underlying the Newer Volcanics is a basement of indurated Ordovician-Silurian turbidites, Devonian granites, and Devonian granodiorites. The basement rocks host groundwater flow in fractures and weathered zones that are developed close to the present day or pre-Newer Volcanics land surfaces.

The average annual rainfall at Lancefield (Fig. 1) is ~680 mm (Bureau of Meteorology (2016). June, July, and August are the wettest months (65–70 mm rainfall each month). Rainfall in the late austral summer and autumn (February–April) is typically 35–40 mm and potential evapotranspiration rates exceed rainfall at those times (Bureau of Meteorology (2016)). Streamflows in Deep Creek are highest in the winter months (Fig. 2) and Deep Creek commonly does not flow over the summer months. In drier years (e.g., 2015), there may only be continuous flow for a few weeks in late winter or spring (Fig. 2); however, most of the pools along Deep Creek persist during the no-flow periods and are the habitat of the Yarra pygmy perch (*Nannoperca obscura*), which is a threatened native fish species with limited distribution (Hammer et al., 2010).

Due to the paucity of bores, groundwater flow in this region is only broadly understood. Groundwater is recharged on the hills and flows towards Deep Creek. The presence of springs at the edge of and within the floodplain in parts of the upper catchment (Melbourne Water, 2016a) imply that groundwater locally discharges close to the river. From a combination of major ion, stable isotope, and ^{222}Rn geochemistry, Cartwright and Gilfedder (2015) concluded that the river between Cobar and Darraweit Guim (Fig. 1) was largely gaining and that the permanent pools represent points of groundwater discharge.

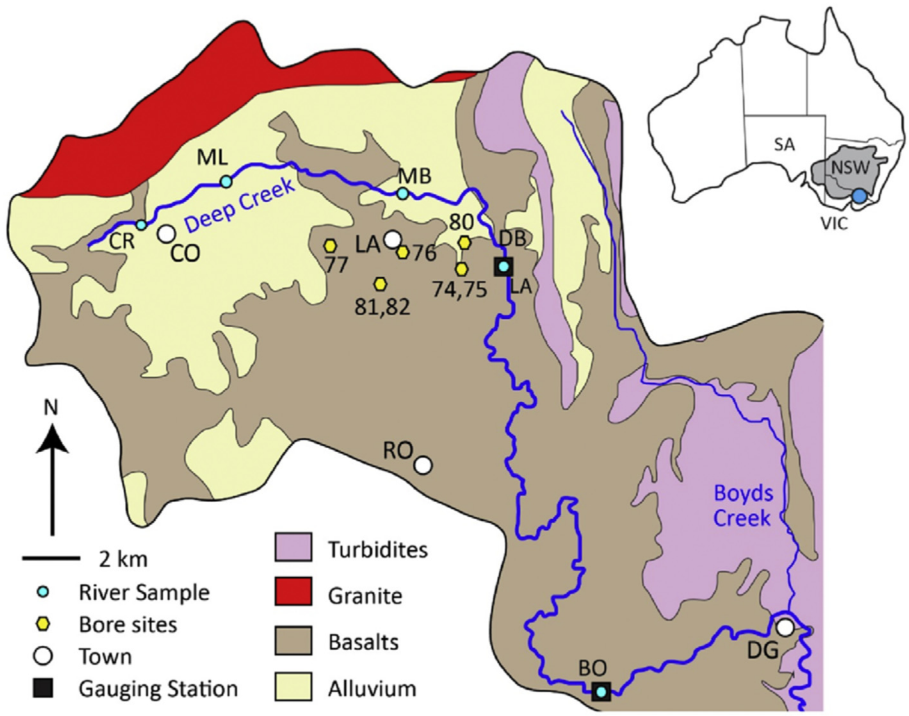

Fig. 1. Map of Deep Creek catchment (after Cartwright and Gilfedder, 2015). River sampling sites are Croziers Lane (CR), Doggetts Bridge (DB), Mooneys Lane (ML), Mustys Bridge (MB), and Bolinda (BO). Gauging stations are Bolinda (BO) and Lancefield (LA). Towns are Cobar (CO), Darraweit Guim (DG), Lancefield (LA), and Romsey (RO). Bore numbers are preceded by 1449.

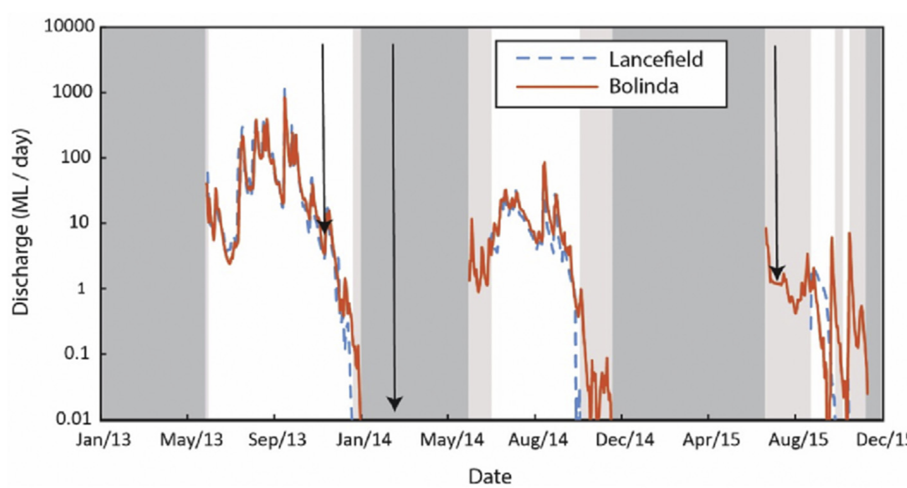

Fig. 2. Streamflows at the Lancefield and Bolinda gauges (Fig. 1) between January 2013 and December 2015; data from Department of Environment, Land, Water and Planning (2016) and Melbourne Water (2016b). Shaded areas are periods when the river has ceased to flow (dark shading – no flow at Lancefield or Bolinda; light shading – flow at Bolinda but no flow at Lancefield). Arrowed lines show the timing of the river sampling.

2. Methods

2.1. Sampling

Deep Creek was sampled in three rounds between November 2013 and July 2015 at five sites between Cobar in the upper catchment and Bolinda (Fig. 1). Streamflows in this part of the catchment are measured at gauging stations at Lancefield and Bolinda (Department of Environment, Land, Water, and Planning, 2016; Melbourne Water 2016b: Fig. 1). In November 2013 streamflow was recorded at both Lancefield (3.91 ML/day) and Bolinda (5.57 ML/day) (Fig. 2) and most of the pools were connected. In February 2014 Deep Creek comprised a chain of disconnected pools and there was no streamflow at either Lancefield or Bolinda (Fig. 2). In July 2015 there was streamflow at Bolinda (1.40 ML/day) but not at Lancefield implying that connection between the pools was developing at the start of winter.

River water was sampled from the centre to the stream using an open sampler fixed to an extendable pole. Groundwater was sampled from observation bores that have 1–3 m long screens using an impeller pump (shallower bores) or a piston pump (deeper bores) set at the screened interval and at least three bore volumes of water was extracted prior to sampling. Rainfall represents sequentially collected and aggregated samples.

2.2. Analytical techniques

Samples for ^3H were analysed at GNS, New Zealand by liquid scintillation spectrometry using Quantulus ultra-low-level counters following vacuum distillation and electrolytic enrichment (Morgenstern and Taylor, 2009). ^3H activities (Tables 1 and 2) are expressed in tritium units (TU) where 1 TU represents a $^3H/^1H$ ratio of 1×10^{-18}. A detection limit of 0.02 TU is achieved via tritium enrichment by a factor of 95, and deuterium-calibration of every sample results in reproducibility of tritium enrichment of 1%. Precision (1σ) is ~1.8% for samples of >1 TU.

HCO_3 concentrations with a precision of ±5% were measured within 12 h of collection using a Hach digital titrator and reagents. Major ion concentrations were analysed at Monash University using a ThermoFinnigan ICP-OES (cations) and a ThermoFischer ion chromatograph (anions). Samples for cation analysis were filtered through 0.45 μm cellulose nitrate filters and acidified to pH < 2 using 16M HNO_3. Samples for anion analysis were filtered but unacidified. The precision of the ICP-OES and ion chromatograph analyses based on replicate analysis of samples is ±2% and the accuracy based on analysis of certified water standards is ±5%. Absolute charge balance errors are up to 7% with a median of 3%. Major ion geochemistry data is presented in Tables 1 and 2

Stable isotope ratios of water (Tables 1 and 2) were measured at Monash University using Finnigan MAT 252 and ThermoFinnigan DeltaPlus Advantage mass spectrometers. $\delta^{18}O$ values were measured via equilibration of water with He-CO_2 at 32 °C for 24–48 h in a ThermoFinnigan Gas Bench. δ^2H values were measured by reaction of water with Cr at 850 °C in a Finnigan MAT H/Device. $\delta^{18}O$ and δ^2H values were measured relative to internal standards that were calibrated using IAEA SMOW, GISP, and SLAP standards. Data were normalised following Coplen (1988) and are expressed relative to V-SMOW where $\delta^{18}O$ and δ^2H values of SLAP are −55.5‰ and −428‰, respectively. Precision (σ) based on replicate sample analysis is 0.15‰ for $\delta^{18}O$ and 0.1‰ for δ^2H.

2.3. Estimating mean transit times using ^3H

Groundwater in catchments follows flow paths of varying length and thus the water discharging into streams or sampled from bores has a range of transit times (e.g., Cook and Bohlke, 2000; McGuire and McDonnell, 2006). Mean transit times were calculated using lumped parameter models that are based on simplified aquifer geometries (Cook and Bohlke, 2000; Maloszewski, 2000; Zuber et al., 2005) as implemented in the TracerLPM Excel workbook (Jurgens et al., 2012). These lumped parameter models assume that groundwater flow paths do not vary over time and that all the water that infiltrates transits through the unsaturated zone adds to the groundwater. The ^3H activity in water at the catchment outflow (or sampled from a bore) at time t ($C_o(t)$) is related to the input of ^3H over time (C_i) via the convolution interval:

$$C_o(t) = \int_0^\infty C_i(t-\tau)g(\tau)e^{-\lambda\tau}d\tau \tag{1}$$

where τ is the transit time, t-τ is the time that the water entered the flow system, λ is the ^3H decay constant (0.0563 yr^{-1}), and $g(\tau)$ is the system response function that describes the distribution of flow paths and transit times in the aquifer.

The exponential flow model estimates mean transit times in homogeneous unconfined aquifers of constant thickness that receive uniform recharge and where water from the entire aquifer thickness discharges to the stream or is sampled by the bore. Piston flow assumes that all flow paths are the same length and that there is no mixing, so all water discharging to the stream or sampled by a bore at any given time has the same transit time. The exponential-piston flow model describes mean transit times in aquifers that have both regions of exponential and piston flow. The exponential-piston flow model may also be applied to groundwater sampled from bores from unconfined to semi-confined aquifers where the bores are screened below the water table such that they do not capture water with very short residence times (Cartwright and Morgenstern, 2012; Morgenstern et al., 2015). The system response function for the exponential-piston flow model is:

$$g(\tau) = 0 \quad \text{for } \tau < \tau_m(1-f) \tag{2a}$$

$$g(\tau) = (f\tau_m)^{-1}e^{-\tau/f\tau_m + 1/f - 1} \quad \text{for } \tau > \tau_m(1-f) \tag{2b}$$

where τ_m is the mean transit time and f is the proportion of the

Table 1
Geochemistry of river water from Deep Creek.

Site[a]	EC	Discharge	^3H	$\delta^{18}O$	δ^2H	HCO_3	Cl	Br	NO_3	SO_4	Na	Mg	K	Ca
	μS/cm	ML/day	TU	‰	‰	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
7/11/2013														
Croziers Rd	635		2.731 ± 0.048	−2.7	−21	172	139	0.55	1.95	0.83	97.9	28.3	2.1	17.3
Mooneys	580		2.718 ± 0.047	−2.9	−23	75	156	0.47	3.66	3.89	83.5	24.2	2.7	14.5
Mustys	598		2.773 ± 0.048	−3.2	−25	102	141	0.43	0.37	5.36	73.6	20.7	2.6	13.1
Doggetts	586	3.91	2.886 ± 0.049	−3.0	−23	125	136	0.39	0.53	5.65	71.7	20.3	2.8	13.5
Bolinda	642	5.57	2.826 ± 0.048	−2.9	−22	135	136	0.36	0.18	7.95	67.6	24.4	2.8	17.4
19/2/2014														
Croziers Rd	1279		2.546 ± 0.044	2.6	2	59	351	1.09	0.03	0.47	147.5	45.0	4.2	25.9
Mooneys	1384		2.557 ± 0.045	3.2	5	127	324	0.89	0.25	13.09	136.9	49.0	11.3	30.7
Mustys		Dry												
Doggetts	1077	0	2.425 ± 0.042	1.9	−3	182	225	0.66	0.60	14.95	112.0	35.8	10.3	25.8
Bolinda	1055	0	2.455 ± 0.043	2.1	0	189	213	0.71	0.09	5.86	107.3	41.9	4.7	27.0
22/7/2015														
Croziers Rd	1467		1.472 ± 0.026	−4.4	−29	87	440	1.63	0.39	8.3	189	46.4	5.0	25.6
Mooneys	1570		1.715 ± 0.029	−4.0	−26	82	464	1.54	0.48	26.6	190	50.1	6.1	28.8
Mustys	1854		2.315 ± 0.040	0.7	−6	142	534	2.31	0.24	12.0	234	60.2	5.6	36.8
Doggetts	695	0	2.914 ± 0.050	−3.4	−22	70	169	0.59	0.39	22.7	76.7	18.3	2.7	14.2
Bolinda	1993	1.40	1.963 ± 0.034	−0.1	−13	108	562	2.19	0.55	25.6	230	80.2	4.6	36.5

[a] Sites on Fig. 1.

Table 2
Geochemistry of groundwater from the Deep Creek catchment.

Bore[a]		Screen[b]	^{3}H	δ^{18}O	δ^2H	HCO_3	Cl	Br	NO_3	SO_4	Na	Mg	K	Ca
		m	TU	‰	‰	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
144974	N. Volcanics	15–18	bd[c]	−3.5	−25	247	324	1.21	1.87	3.2	147	66.3	6.9	21.6
144975	Castlemaine	43.5–46.5	bd	−3.9	−31	319	367	1.17	1.51	6.8	163	93.4	7.7	28.0
144976	Alluvium	7.5–10.5	0.842 ± 0.026	−4.1	−31	187	138	0.52	6.76	4.0	87.2	29.0	6.6	18.4
144977	Castlemaine	43–46	bd	−3.9	−30	132	221	0.85	2.36	1.6	133	36.2	8.8	10.1
144980	Castlemaine	7.5–10.5	0.122 ± 0.017	−3.8	−27	335	171	0.51	0.40	2.3	93.6	65.2	2.5	18.0
144981	N. Volcanics	43.5–46.5	0.127 ± 0.015	−3.9	−31	301	240	0.82	0.02	2.9	125	55.4	9.3	20.3
144982	N. Volcanics	26–29	bd	−3.5	−24	252	326	1.32	6.55	4.2	152	63.9	13.3	19.8

[a] Bore localities on Fig. 1.
[b] Screened interval.
[c] Below detection (<0.02 TU).

aquifer volume that exhibits exponential flow. The exponential-piston flow model is equivalent to the piston flow model at $f = 0$ and to the exponential model at $f = 1$. TracerLPM specifies the ratio of exponential to piston flow as the EPM ratio (equivalent to $1/f - 1$).

The dispersion model is based on the one-dimensional advection-dispersion equation for which the system response function is:

$$g(\tau) = \frac{n}{\tau\sqrt{4\pi D_P \tau/\tau_m}} e^{-\left(\frac{(1-\tau/\tau_m)^2}{4D_P\tau/\tau_m}\right)} \tag{3}$$

where D_P is the dispersion parameter. D_P is the inverse of the Peclet Number and equivalent to $D/(v\,x)$, where v is velocity (m day^{-1}), x is distance (m), and D is the dispersion coefficient (m^2 day^{-1}). While the dispersion model is considered a less realistic conceptualisation of groundwater flow paths, it does reproduce the observed distribution of transit times in many catchments (Maloszewski, 2000).

The partial exponential model may also be used to calculate transit times in groundwater sampled from bores. The system response function for this model is:

$$g(\tau) = \left(\frac{z*}{z} + 1\right)\tau_a{}^{-1} e^{-\tau/\tau_a} \tag{4}$$

where z represents the screened interval of the bore, z* the distance above the screen that is unsampled, and τ_a is the mean transit time of the water in the whole aquifer, which is given by:

$$\tau_a = \frac{\tau_m}{1 - \ln\left(1 - \frac{z^*}{z+z^*}\right)} \tag{5}$$

TracerLPM specifies the PEM ratio as z*/z. If the bores are screened across the entire saturated thickness of the aquifer, $z^* = 0$ and $\tau_a = \tau_m$ resulting in this model becoming equivalent to the exponential model. For bores that sample only part of the aquifer, the mean transit times are similar to those obtained from the exponential piston flow model (Jurgens et al., 2012).

3. Results

3.1. Major ions and stable isotopes

The total dissolved solids (TDS) concentrations of Deep Creek river water vary from 360 to 1030 mg/L with higher TDS concentrations recorded in February 2014 and July 2015 when the river was not continuously flowing. Na is the major cation in surface water (67–77% of cations on a molar basis) followed by Mg (17–23%) and Ca (6–10%); Cl (58–90%) and HCO_3 (10–42%) are the major anions (Fig. 3). While the river geochemistry data discussed by Cartwright and Gilfedder (2015) did not include HCO_3, the relative concentrations of the other cations and anions were similar to those in this study. Groundwater TDS concentrations range from 480 to 990 mg/L. The relative concentrations of the major cations (Na: 57–78%; Mg: 19–33%; Ca: 3–8%) and the major anions (Cl: 48–69%; HCO_3: 31–52%) in the groundwater overlap with those of the river water (Fig. 3). Molar Cl/Br ratios of the river water (570–860) and groundwater (600–760) also overlap. Additionally, there is no significant difference in the major ion geochemistry of groundwater from the different aquifers.

The δ^{18}O and δ^2H values of the river water define a single array with a slope of 4.5 (Fig. 4) that intercepts the meteoric water line at close to the weighted average δ^{18}O and δ^2H values of rainfall in Melbourne ($\delta^{18}O = -28.4$‰ and $\delta^2H = -5$‰: Cartwright et al., 2012), which is 80 km to the southeast. Overall, the stable isotope ratios of the river water reflect evaporation (Gonfiantini, 1986; Clark and Fritz, 1997), with the highest degrees of evaporation (greatest displacement from the meteoric water line) recorded in February 2014 when the river comprised isolated pools. Groundwater has δ^{18}O and δ^2H values that overlap with those of the least evaporated river water (Fig. 4). The δ^{18}O and δ^2H values of the river water and groundwater are similar to those reported by Cartwright

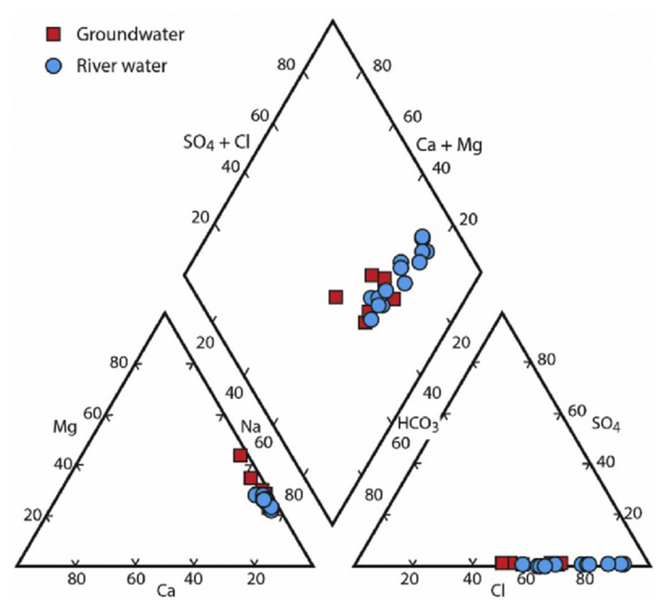

Fig. 3. Trilinear diagram summarising major ion geochemistry of groundwater and river water (data from Tables 1 and 2). Ratios are molar.

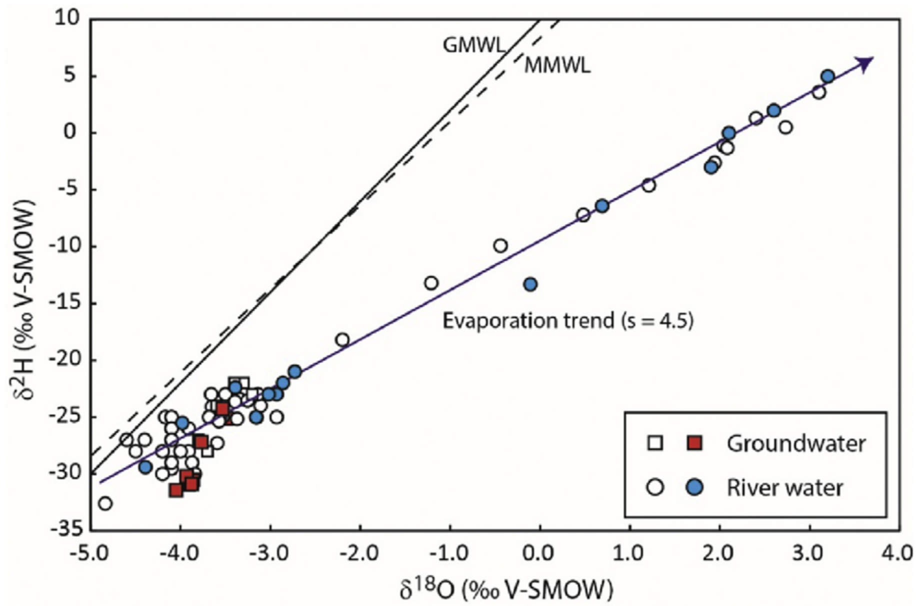

Fig. 4. $\delta^{18}O$ vs $\delta^{2}H$ values of groundwater and river water from Deep Creek. GMWL is the global meteoric water line (e.g. Clark and Fritz, 1997), MMWL is the Melbourne Meteoric Water Line (Hughes and Crawford, 2012). Data from Tables 1 and 2 and Cartwright and Gilfedder (2015) (open symbols).

and Gilfedder (2015) (Fig. 4).

3.2. ^{3}H activities

Modern rainfall in southeast Victoria is estimated to have a ^{3}H activity of 2.8–3.2 TU (Tadros et al., 2014). Aggregated samples of rainfall from southeast Australia collected as part of this and other studies fall within that range. These include: a 12 month sample collected in August 2015 from Yarra Junction ~80 km to the southeast of Deep Creek ($^{3}H = 2.76$ TU); a 9 month sample collected in July 2013 from Melbourne ~80 km to the southeast of Deep Creek ($^{3}H = 2.72$ TU); and three samples from Mount Buffalo 90 km to the east of Deep Creek collected in December 2013 (17 month, $^{3}H = 2.99$ TU: Cartwright and Morgenstern, 2015), February 2015 (12 month $^{3}H = 2.85$ TU: Cartwright and Morgenstern, 2015), and November 2015 (9 month, $^{3}H = 2.88$ TU).

^{3}H activities of groundwater range from below detection (<0.02 TU) to 0.84 TU (n = 7, median = <0.02 TU) (Table 2, Fig. 5). Two of the above-background ^{3}H activities are from the shallowest groundwater (7.5–10.5 m depth); however, the other groundwater sample with an above background ^{3}H activity is from 43.5 to 46.5 m. The ^{3}H activities of river water range from 2.73 to 2.89 TU (n = 5) in November 2013, from 2.43 to 2.56 TU (n = 4) in February 2014, and from 1.47 to 2.91 TU (n = 5) in July 2015 (Table 1, Fig. 5). For the dataset as a whole, the median ^{3}H activity of the river water is 2.55 TU, and the higher ^{3}H activities of river water from Deep Creek overlap with those of the rainfall (Fig. 5). For the ^{3}H activities of the groundwater and the river water, p values from two-tailed t tests are <<0.01, implying that the difference between these two populations is significant well beyond the 99% confidence interval. Deep Creek at Doggetts Bridge records the highest ^{3}H activities in both November 2013 and July 2015; however, apart from this there is no consistent pattern of variation of river ^{3}H activities. There is a broad correlation ($R^2 = 0.6$) between ^{3}H activities and TDS

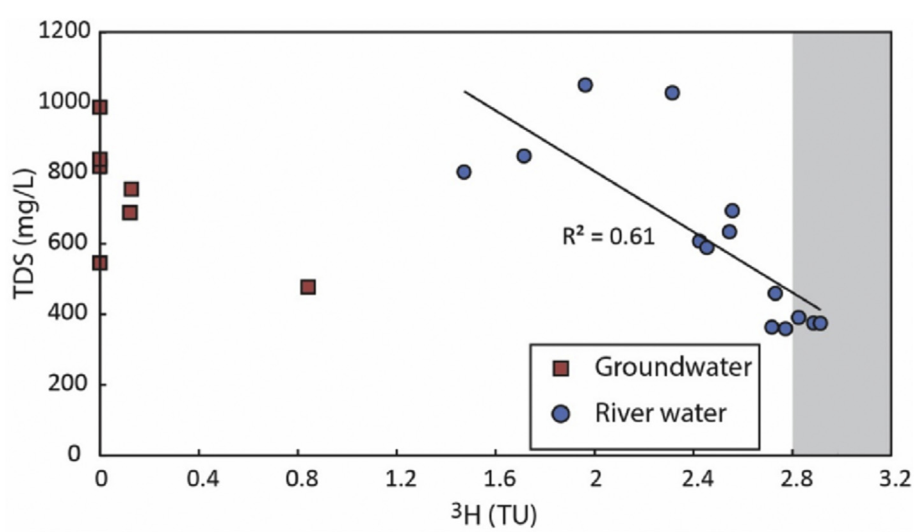

Fig. 5. ^{3}H activities vs. TDS concentrations of groundwater and river water from Deep Creek (data from Tables 1 and 2).

concentrations (Fig. 5).

4. Discussion

The combination of major ion geochemistry, stable isotope ratios, and ^{3}H activities allow the sources and mean transit times of groundwater that inflows into Deep Creel to be understood.

4.1. Sources of groundwater inflows

Despite their only being a few groundwater samples, the major ion geochemistry of the groundwater from the different aquifers is similar, and the groundwater geochemistry is similar to that of the river water (Tables 1 and 2, Fig. 3). As discussed above, the similarity of the major ion geochemistry between groundwater and river water was one of the lines of evidence that is consistent with Deep Creek receiving groundwater inflows (Cartwright and Gilfedder, 2015). The major ion geochemistry cannot, however, be used to determine from where the groundwater is derived. Likewise, the $\delta^{18}O$ and $\delta^{2}H$ values of groundwater from the different aquifers are similar and overlap with those of the least evaporated river water (Fig. 4). As with the major ion geochemistry, these data are consistent with there being groundwater inflows to Deep Creek but do not indicate from where in the aquifer system the groundwater is derived.

By contrast, the observation that the regional groundwater has significantly lower ^{3}H activities (<0.84 TU) than the river water (1.47–2.91 TU) implies that it does not contribute significantly to the river, even when Deep Creek comprises a series of disconnected pools. Two end-member models that may be used to estimate the contribution of groundwater of different ages to the river are: 1) the discharge of groundwater with a continuum of transit times; and 2) binary mixing of an older groundwater component with recent rainfall (or young groundwater) (Fig. 6).

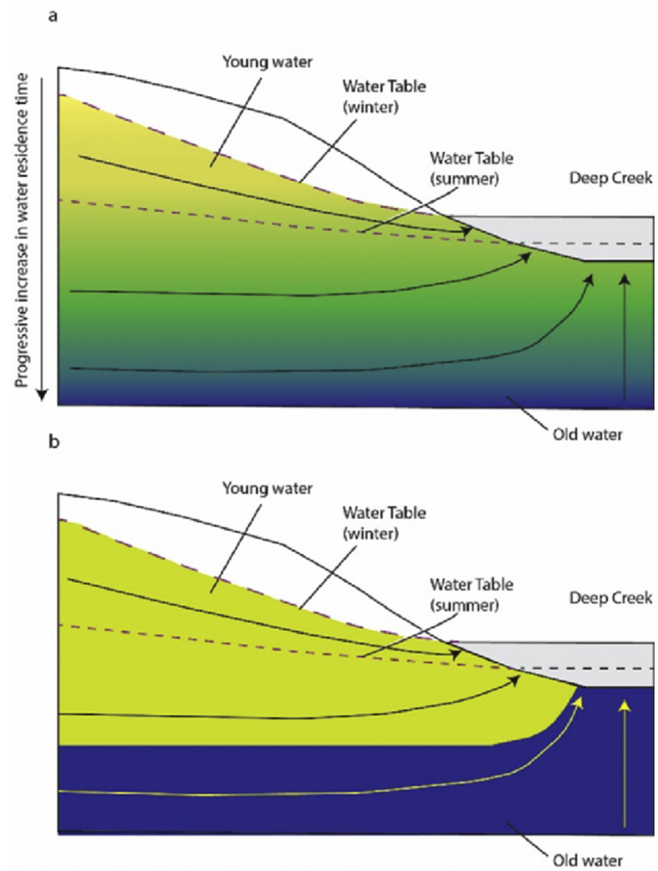

Fig. 6. Schematic representation of the two flow models discussed in the text. **6a**. Groundwater with a continuum of residence times inflows into Deep Creek. **6b**. Binary mixing between old and younger groundwater inflows. Shallower groundwater flow paths become inactive in summer.

4.2. Continuum model

The continuum model envisages that the flow system contains a single store of water and that the mean transit times of water contributing to the river increase as the catchment dries up because the younger shallow water has discharged from the system (Fig. 6a). While groundwater flow in unconfined shallow aquifers may approximate exponential flow, recharge through the unsaturated zone most likely resembles piston flow. Thus, following similar studies elsewhere (Morgenstern and Daughney, 2012; Cartwright and Morgenstern, 2015; Morgenstern et al., 2015), mean transit times were initially estimated using the exponential-piston flow model (Eqs (1) and (2)). Initial calculations assumed an EPM ratio of 0.33 ($f = 0.75$); a similar flow model successfully reproduces time-series of ^{3}H activities in groundwater in New Zealand (Morgenstern and Daughney, 2012). It was assumed that present-day recharge has a ^{3}H activity of 3 TU, which is consistent with the predicted ^{3}H activities of rainfall in southeast Australia (Tadros et al., 2014). The average annual ^{3}H activities of rainfall in Melbourne from the IAEA GNIP program (International Atomic Energy Association, 2016) were used as the ^{3}H activities of recharge back to the 1960s. A ^{3}H activity of 3 TU was also used for the pre bomb-pulse recharge.

Estimated mean transit times in Deep Creek range from <1 year to 31 years (Table 3). There are several sources of uncertainty in these mean transit times. Firstly the lumped parameter models have idealised geometry that is assumed not to have changed over time. Fig. 7a shows mean transit times calculated using the same ^{3}H input from the exponential flow model, the exponential-piston flow model with an EPM ratio of 1 ($f = 0.5$), and the dispersion flow model with $D_P = 0.1$, which is an appropriate value for flow systems of this scale (Maloszewski, 2000). For this suite of models, the range of mean transit times for a water with a ^{3}H activity of 2.5 TU is ~0.6 years. Most of the river samples from November 2013 and February 2014 have ^{3}H activities >2.5 TU, and the uncertainties in mean transit times resulting from the adoption of different models are smaller. For a water with a ^{3}H activity of 1.5 TU (which corresponds to the lowest river ^{3}H activity in July 2015), the same models yield mean transit times that vary by ~13 years (Fig. 7a). Propagating the analytical uncertainty in ^{3}H activities (Table 2) results in uncertainties in mean transit times of ±0.6 years for a water with a ^{3}H activity of 2.5 TU and ±1.6 years for a water with a ^{3}H activity of 1.5 TU.

Uncertainties in the ^{3}H activity of modern recharge also translate into uncertainties in the mean transit times, predominantly for the waters with high ^{3}H activities. If recharge is seasonal, it may have different ^{3}H activities to that of average rainfall. Specifically preferential recharge by late winter and early spring rainfall is likely to have higher than average ^{3}H activities as this is the time of maximum transport of water vapour with high ^{3}H activities from the stratosphere to the troposphere (Tadros et al., 2014). Increasing the ^{3}H activity of recharge to 3.2 TU, which is at the upper end of the estimated range of rainfall (Tadros et al., 2014), increases the calculated mean transit time of water with a ^{3}H activity of 2.5 TU by ~1 year. Using a ^{3}H activity of 2.8 TU, which corresponds to the lower end of the estimated and measured rainfall ^{3}H activities, would reduce the calculated mean transit time by a similar amount (Fig. 7, Table 3). However, given that the river water commonly has

Table 3
Calculated mean transit times from the Deep Creek catchment.

	Mean Transit Times (years)						
	EPM (0.33)[a]	EM	DM (0.1)	EPM (1.0)	PEM (2.0)	EPM (0.33)[b]	EPM (0.33)[c]
River							
7/11/2013							
Croziers Rd	1.9	2.1	1.7	1.8		0.5	3.3
Mooneys	2.0	2.2	1.8	1.9		0.5	3.4
Mustys	1.5	1.7	1.4	1.4		0.2	2.9
Doggetts	0.7	0.7	0.7	0.7		nc[d]	2.0
Bolinda	1.1	1.2	1.1	1.1		nc	2.5
19/02/2014							
Croziers Rd	3.9	4.2	3.7	3.6		2.0	5.0
Mooneys	3.7	4.1	3.5	3.4		1.9	4.9
Doggetts	5.4	5.9	5.5	5.2		3.9	6.3
Bolinda	5.0	5.4	5.0	4.8		3.4	6.0
22/07/2015							
Croziers Rd	31.3	38.4	30.6	26.1		31.2	31.4
Mooneys	20.6	24.4	15.6	16.1		20.4	20.6
Mustys	6.1	6.9	5.8	5.6		4.6	6.8
Doggetts	0.5	0.5	0.5	0.5		nc	1.7
Bolinda	12.3	15.8	11.0	11.4		11.2	13.0
Groundwater[e]							
114976	75	97	69	82	79	75	75
144980	194	225	124	104	100	194	194
144981	190	223	120	101	99	190	190

[a] Flow models: EPM = Exponential-piston (EPM ratio in brackets); EM = Exponential; DM = Dispersion (Dp in brackets); PM = Partial Exponential (PEM ratio in brackets).
[b] EPM flow model assuming ^{3}H of modern recharge = 2.8 TU.
[c] EPM flow model assuming ^{3}H of modern recharge = 3.2 TU.
[d] Not calculated, ^{3}H activity >2.8 TU.
[e] Bores with ^{3}H below detection omitted.

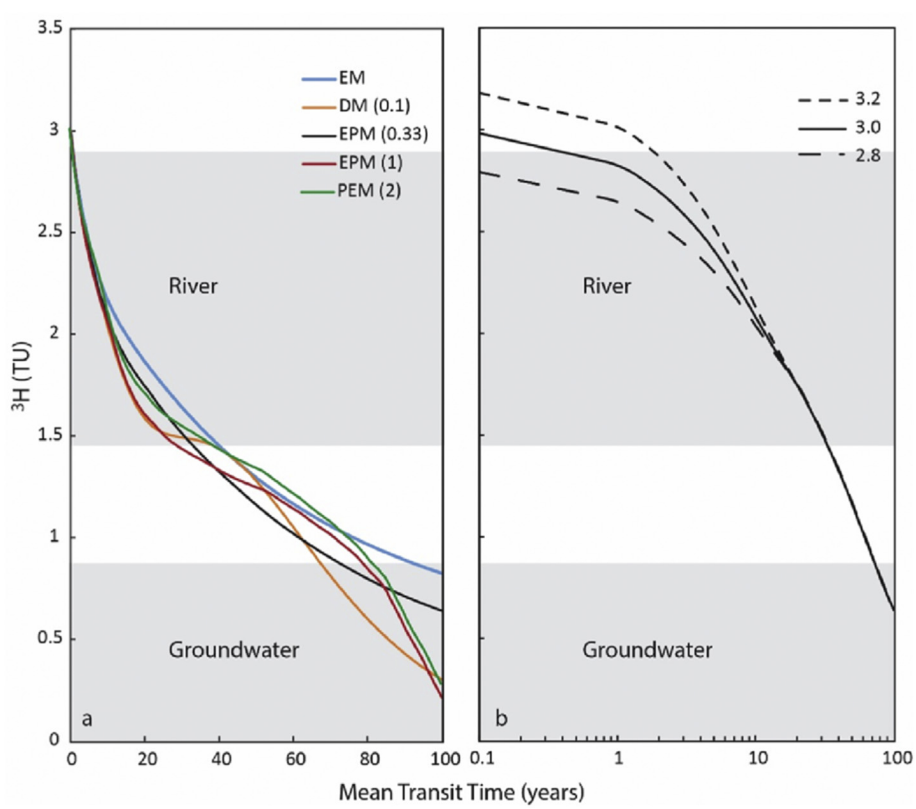

Fig. 7. a. Comparison of mean transit times from different lumped parameter models, calculated using Eqs (1)–(3) assuming a ^{3}H activity of recharge of 3.0 TU. DM: Dispersion model with D_p = 0.1. EM: Exponential flow model. EPM: Exponential-piston flow model with EPM ratio = 0.33 and 1.0. PEM: Partial exponential model with PEM ratio = 2. **7b**. Mean transit times from the exponential flow model (EPM ratio = 0.33) with ^{3}H activities of modern recharge ranging from 2.8 to 3.2 TU. Shaded fields show ^{3}H activities in the river water and groundwater (data from Tables 1 and 2).

a ^3H activity of >2.8 TU (Fig. 5), it is unlikely that the ^3H of recharge could be that low. The impact of uncertainties in the ^3H activity of modern recharge on the mean transit time decrease as ^3H activities decline. For water with a ^3H activity of 1.5 TU the difference in mean transit times resulting from adopting ^3H activities of recharge of between 2.8 and 3.2 TU is < 0.1 years (Fig. 7b).

While there is uncertainty in the actual mean transit times, relative differences in the mean transit times are less impacted. Because the remnant bomb-pulse ^3H activities in the southern hemisphere are lower than those of modern rainfall, calculated transit times are less model dependant and lower ^3H activities imply that the water is older. The uncertainty in the ^3H activity of modern recharge impact all the estimates of mean transit times in the region, while uncertainties as to the most appropriate flow model may affect the estimates of mean transit times between sites (if the geometry of the flow system is spatially variable) but will not affect the differences in estimated mean transit times at the same site at different times.

A similar approach may be made to assessing the mean transit times of the groundwater. Using the same input assumptions as above and the exponential-piston flow model with an EPM ratio of 0.33, the shortest mean transit time (for groundwater from bore 144976) is 75 years. Applying the partial exponential flow model with a PEM ratio of 2, which is appropriate for many of the groundwater bores, yields a similar mean transit time of 79 years, while the other lumped parameter models yield mean transit times between 69 and 97 years (Table 3). Since the bores only sample groundwater from part of the aquifer, the exponential model, which yields the longest mean transit times, is less likely to be applicable. For water with ^3H activities below the detection limit of 0.02 TU, the mean transit times calculated using the exponential piston flow model (EPM ratio = 0.33) are >220 years while those calculated using the partial exponential flow model are >130 years.

The estimated mean transit times of the groundwater are more sensitive to the assumed flow models than those of the younger river water as the predicted mean transit time from the different models diverge significantly at low ^3H activities (Fig. 7, Table 3). Regardless of the uncertainties in the calculations, however, it is clear that the deeper regional groundwater has mean transit times of at least several decades that are significantly longer than those of the water in the river. In turn this implies that little of the deeper groundwater contributes to the river even during the cease-to-flow periods. This may be illustrated by calculating the fraction of old water in the river at different mean transit times and for the different flow models (Fig. 8). For a mean transit time of 5 years (corresponding to February 2014), <<1% of the water is > 50 years old. For a mean transit time of 30 years (corresponding to the longer mean transit times in July 2015), 1–4% of the water is > 100 years old and 8–19% of the water is > 50 years old.

4.3. Binary mixing

The binary mixing model conceives that the flow system consists of discrete stores of deeper older regional groundwater and shallower younger water. Separation of the groundwater in this manner may occur if the shallower groundwater is contained in the near-river alluvial sediments while the deeper groundwater is derived from the underlying basalts or basement rocks. The young water store may also comprise surface runoff, soil water, bank storage or interflow. These two stores are conceived to both contribute to the river (Fig. 6b) with the proportion of water from the shallower younger store decreasing as the catchment dries up over summer. The diminishing input of shallow young water during summer would be expected to occur as the water table falls and/or due to the draining of water contained within the banks, soils, or regolith. Assuming a ^3H activity of the young water component of 3 TU (which is consistent with the rainfall ^3H activities and close to the highest river TU activities) and an older groundwater ^3H activity of 0 TU, the ^3H activities of the river water could be explained by the older groundwater component comprising up to 51% of the water in the river (Fig. 9) with a median estimate of 15%. The highest estimated old groundwater input is for July 2015 at Croziers Rd (^3H activity = 1.47 TU). Varying the ^3H activities of the two end

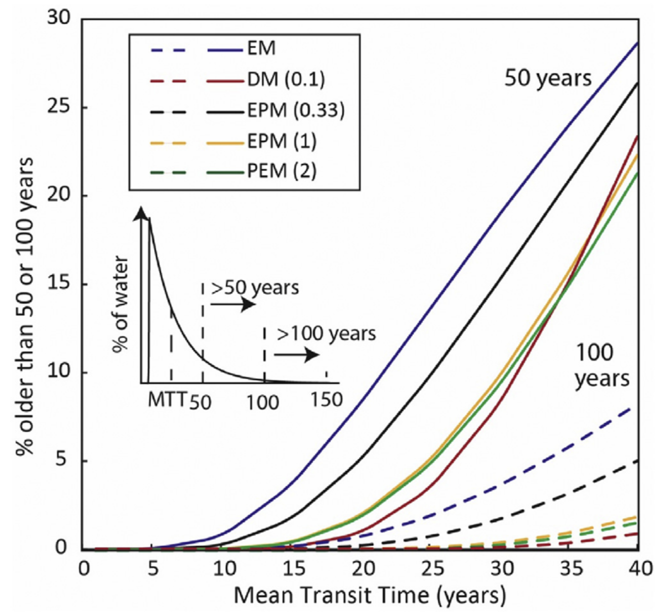

Fig. 8. Percentage of water older than 50 or 100 years calculated for different flow models and a range of mean transit times. DM: Dispersion model with D_p = 0.1. EM: Exponential flow model. EPM = Exponential-piston flow model with EPM ratio = 0.33 and 1.0. PEM: Partial exponential flow model with PEM ratio = 2. Inset shows schematically the percentage distribution of water aliquots of different ages in the exponential piston flow model (EPM ratio = 0.33) with a mean transit time (MTT) of 25 years.

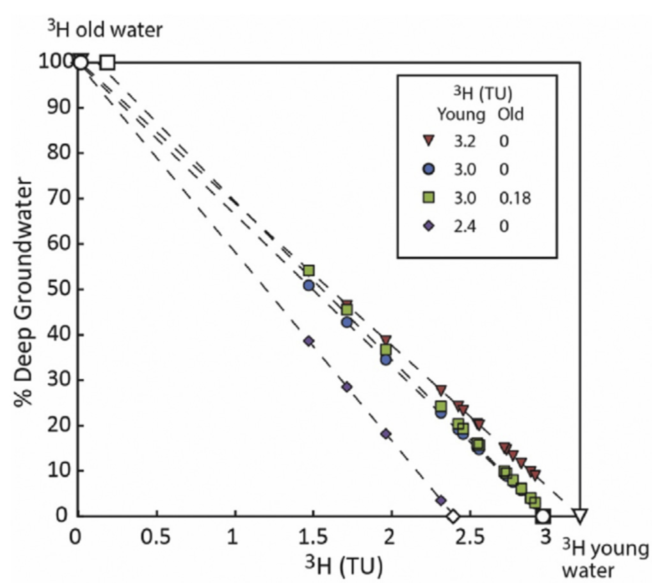

Fig. 9. Proportion of deep groundwater required to produce the observed ^3H activities of Deep Creek (filled symbols) by binary mixing of a young and older groundwater component with different ^3H activities (open symbols).

members produces some differences in these estimates. For example, assuming that the ^{3}H activity of younger water component was 3.2 TU (the higher estimate of rainfall ^{3}H activities) results in median and maximum estimates of the contribution of the older groundwater component of 20% and 54%, respectively. Assuming that the groundwater has a ^{3}H activity of 0.12 TU (which is the highest ^{3}H activity of the groundwater in the Castlemaine Group and the Newer Volcanics) results in median and maximum estimates of the contribution of the older water component of 16% and 53%, respectively. Aside from the Doggetts Bridge site, the highest contributions of deeper groundwater to Deep Creek are again in July 2015.

In reality the flow system may be intermediate between the continuum case and binary mixing (e.g., mixing of two water stores where the upper water store has a range of residence times). In this case the proportion of older water required to reduce the ^{3}H activities in the pools by mixing is lower. For example, if the shallower water store during the drier summer periods had a ^{3}H activity of 2.4 TU (approximately the ^{3}H activity in February 2014), the lowest recorded ^{3}H activity in the river of 1.47 TU would be achieved by mixing of ~40% of older groundwater with a ^{3}H activity of 0 TU (Fig. 9). Overall, while there are uncertainties in these calculations, the binary mixing model also implies that the deeper groundwater only significantly contributes to the river during prolonged cease-to-flow periods.

4.4. Temporal changes

Both the single store and binary mixing models imply that, except for at Doggetts Bridge, there is a greater inflow of older groundwater into Deep Creek during July 2015 than at during the other periods. In July 2015 there had been no streamflow at Lancefield since December 2014 (Melbourne Water, 2016b), and the upper catchment of Deep Creek consisted of disconnected pools that had been isolated for several months. Prolonged cease-to-flow periods occur during times of low rainfall. At such times there is little surface runoff or interflow and much of the recently-recharged younger water in the catchment has likely already been discharged into the river and removed by evaporation. As the water in the pools evaporates, continued inflow of deeper older groundwater will result in the average age of the water in the pools progressively increasing, these processes result in the inverse correlation between ^{3}H activities and TDS concentrations (Fig. 5). The high ^{3}H activities at Doggetts Bridge (which is a site of groundwater inflows: Cartwright and Gilfedder, 2015) probably reflect a larger reservoir of shallow younger water combined with limited deeper groundwater discharge in this area; however, the underlying causes for this are not known.

5. Conclusions and implications

The use of ^{3}H as a tracer has allowed groundwater-river interaction in Deep Creek to be better understood. Deep Creek receives groundwater inflows at all flow conditions and during the cease-to-flow periods comprises groundwater-fed disconnected pools (Cartwright and Gilfedder, 2015). However, except locally during prolonged cease-to-flow periods, the deeper regional groundwater sampled by bores a few kilometres from Deep Creek is a relatively minor component of the river water. That most of the water in the river has relatively short mean transit times implies that the groundwater inflows are derived largely from the shallow near-river aquifers together with water from the unsaturated zone and surface runoff during rainfall events. The lack of systematic down catchment variation in ^{3}H activities is also consistent with the river being largely connected to local groundwater systems. If the pools were connected to the regional groundwater, the mean transit times would be expected to be similar or increase down the catchment. This detailed understanding of groundwater-surface water interaction could not be gleaned from the major ion or stable isotope geochemistry or from the available groundwater and surface water elevations.

Understanding the relationship between groundwater and surface water is important for managing and protecting Deep Creek. Given that groundwater inflows to the river are largely derived from the shallow near-river aquifers, protecting these aquifers from contaminants is critical for protecting the riverine ecosystems. More generally, this study illustrates the utility of ^{3}H, especially in the southern hemisphere, in the study of connected groundwater and surface water systems and in providing additional understanding from where in the aquifers the groundwater is derived. This study also highlights the potential problems in using regional groundwater bores to characterise the geochemistry of the groundwater that interacts with the river. If the near-river lithologies are similar to those away from the river, the major ion concentrations will likely be similar. However, the concentration of other chemical components such as ^{222}Rn or nutrients may be more variable, which introduces uncertainties in mass balance or flux calculations.

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