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Residence times and mixing of water in river banks: implications for recharge and groundwater – surface water exchange

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Abstract

The residence time of groundwater within 50 m of the Tambo River, South East Australia, has been estimated through the combined use of ^{3}H and ^{14}C. Groundwater residence times increase towards the Tambo River which implies a gaining river system and not increasing bank storage with proximity to the Tambo River. Major ion concentrations and $\delta^{2}H$ and $\delta^{18}O$ values of bank water also indicate that bank infiltration does not significantly impact groundwater chemistry under baseflow and post-flood conditions, suggesting that the gaining nature of the river may be driving the return of bank storage water back into the Tambo River within days of peak flood conditions. The covariance between ^{3}H and ^{14}C indicates the leakage and mixing between old (~ 17 200 yr) groundwater from a semi-confined aquifer and younger groundwater (< 100 yr) near the river where confining layers are less prevalent. The presence of this semi-confined aquifer has also been used to help explain the absence of bank storage, as rapid pressure propagation into the semi-confined aquifer during flooding will minimise bank infiltration. This study illustrates the complex nature of river groundwater interactions and the potential downfall in assuming simple or idealised conditions when conducting hydrogeological studies.

1 Introduction

Documenting water balances in river systems is vitally important to understanding hydrological processes and protecting and managing water resources. While surface runoff and regional groundwater inflows are the two main components of river flow, river banks or floodplain pools may act as sites of transient water storage. Bank storage represents water that infiltrates into alluvial aquifers at high river stage and subsequently returns to the river as the river stage declines (e.g., Chen and Chen, 2003; Singh, 1968; Winter, 1998). Bank storage is an important hydrological process that may considerably reduce peak river discharge during floods and maintain river discharge during periods of decreased rainfall. The volume and duration of bank storage for a given river stretch will depend on the flood peak height and flood duration, as well as the hydraulic conductivity of the alluvial aquifer and the hydraulic gradient between the aquifer and river (Chen et al., 2006).

While the concept of bank storage is well understood, quantifying the volume of water that infiltrates the banks and the duration of bank return flows is complicated. Many studies have focused on using analytical and numerical solutions to understand bank storage. Analytical solutions presented by Cooper and Rorabaugh (1963) demonstrate that the duration of bank return flow is related to the duration of the flood period and Pinder and Sauer (1971) showed that hydrographs can be modified by bank storage. Whiting and Pomeranets (1997) indicated a greater storage potential for deep narrow rivers with wider floodplains and coarse alluvial material. More recently, the potential for significant storage beneath the streambed was identified by Chen and Chen (2003), while Chen et al. (2006) showed that bank storage will return more rapidly in gaining river sections. McCallum et al. (2010) showed that when the concentration of groundwater is higher than river water, the groundwater returning to a river after bank infiltration can take months or years before returning to the concentration of regional groundwater. Bank slope has also been shown to impact bank storage, with shallower bank slope providing a greater potential for bank storage (Doble et al., 2012).

Most of these studies have concluded that bank storage periods will significantly exceed the duration of flood events. Typically bank storage return to the river will decrease exponentially after flood events, and in the case of sandy river banks with wide floodplains, residence times can be on the order of years (Doble et al., 2012; McCallum, et al., 2010; Whiting and Pomeranets, 1997). While these studies have added to our conceptual understanding of bank storage they often assume ideal or generalised conditions such as aquifer homogeneity, vertical river banks and saturated conditions (Doble et al., 2012), making them difficult to apply to many natural settings. As such, understanding the residence times of bank water may more concisely constrain the time scales and hydrogeological processes controlling bank storage. Field studies focussed

HESSD
11, 1651–1691, 2014

on bank storage and the dating of bank water near Australian rivers has been quite limited, however works by Lamontagne et al. (2011) and Cendón et al. (2010) have indicated the presence of relatively young (< 50 yr) groundwater in river banks, and Cartwright et al. (2010) has shown that preferential floodplain recharge is likely to occur near rivers during flooding. In contrast, groundwater near upland rivers in Australia has been shown to contain relatively little ^{3}H (Atkinson et al., 2013).

Understanding the geochemistry of water as it enters and exits river banks is important for a range of disciplines. Hydrogeochemical processes occurring within river banks, such as the bacterial degradation of organic matter and the weathering of minerals can influence the concentrations of DOC, O_2, NO_3, Na, K and other major ions (Bourg and Bertin, 1993). Fukada et al. (2003) identified the continuing denitrification of river water as it infiltrated an alluvial aquifer and demonstrated that the chemistry of infiltrating water is likely to vary according to its residence time within the alluvial aquifer. Understanding the source and load of nutrients in rivers is fundamental in understanding their ecology (Boulton, 1993, 2005), while determining the different sources of water in the riparian zone is crucial to effective vegetation management (Cey et al., 1999; Lambs, 2004; Lamontagne et al., 2005; Woessner, 2000). Similarly, the impact of infiltrating river water on water quality in the alluvial aquifer is important when developing groundwater extraction systems for water supply (Hiscock and Grischek, 2002). Accounting for bank storage is also important in conducting groundwater discharge studies, as bank storage will chemically be similar to runoff in comparison to regional groundwater. As such the total groundwater flux to a river will be significantly underestimated if a regional groundwater end member is used during mass balance calculations and bank storage is ignored (McCallum et al., 2010; Unland et al., 2013).

This study investigates bank storage processes in areas immediately adjacent to rivers (within 50 m) by conducting field investigations on the Tambo River, Victoria, Australia. The objectives of the study are to use the geochemistry of bank water near the Tambo River over changing discharge conditions in order to (1) define the major processes controlling the chemistry of water stored in river banks (2) determine the

HESSD
11, 1651–1691, 2014

age and likely sources water stored in river banks and (3) identify the factors controlling bank storage and the scale to which bank storage is occurring. While this study uses data from specific field area, the Tambo River is similar to many others globally and the results may help in understanding bank storage processes in general.

1.1 Study area

Investigations took place on the Tambo River in the Tambo River Basin, South East Australia. The river basin extends southwards from the Eastern Victorian Uplands to the Gippsland Basin (Fig. 1). The Eastern Victorian Uplands are dominated by low-grade metamorphosed Ordovician and Devonian sandstones, shales and turbidites that have been intruded by Devonian granites (Gray and Foster, 2004). The Palaeozoic basement forms a fractured rock aquifer; however, groundwater yields are insignificant in comparison to overlying sedimentary aquifers (Birch, 2003). Coarse gravels and sands eroded from the Eastern Victorian Uplands form an alluvial aquifer in most of the major river valleys in the Gippsland Basin. The Plio-Pleistocene Haunted Hill Gravels is the shallowest aquifer over most of the Gippsland Basin and is primarily composed of quartz with some feldspar, granitic fragments, tourmaline and cassiterite (Kapostasy, 2002). The Haunted Hill Gravels are underlain by the Boisdale Formation which comprises Late Miocene to Early Pliocene sands, gravels and clays with minor Cenozoic basalts, limestone's and marls (Birch, 2003). Quaternary alluvium locally covers these formations along the river valleys. Clay layers throughout the Quaternary alluvium, Haunted Hill Gravels and Boisdale formation act as aquitards, separating a number of aquifer horizons that range from unconfined to fully confined (Hocking, 1976). These formations constitute the upper aquifers of the Gippsland Basin and are in total up to ~ 50 m thick. The deeper aquifers that do not interact with the rivers include the Ologocene-Pliocene Jemmys Point, Tambo River and Lake Wellington Formations (Leonard, 1992; Hofmann and Cartwright, 2013).

The Tambo River is perennial and flows through forest and woodland with cattle grazing on the river floodplains (Department of Agriculture, Fisheries and Forestry, 2006).

HESSD
11, 1651–1691, 2014

It discharges into the saline Lake King and the lower ~15 km of the river is estuarine. Average annual precipitation in the catchment increases from 655 mm in the upper reaches to 777 mm in the middle and lower reaches (Bureau of Meteorology, 2013). During the majority of the study period river discharge in the Tambo River ranged from 1.5 to $4.0 \times 10^5\ m^3\ day^{-1}$ (Victorian Water Resources Data Warehouse, 2013); however significant rainfall during August 2011 and March 2012 resulted in discharge events that peaked between 2.0×10^7 and $3.0 \times 10^7\ m^3\ day^{-1}$, respectively (Fig. 2).

Transects of groundwater monitoring bores were set up at three locations on the river banks of the Tambo River. Bores are identified by location and distance from the Tambo River, as indicated by Fig. 1 and Tables 1, 2 and 3. The transect at Bruthen is 28.5 km upstream of Lake King and consists of 3 bores installed at 5.5, 17.6 and 18.3 m distance from the river and 8.0, 5.4 and 7.1 m depth below ground surface, respectively (Fig. 1). The transect at Tambo Upper, 20.2 km upstream of Lake King, consists of 5 bores installed at 8.8, 15.0, 22.3, 23.8 and 37.9 m distance from the Tambo River and 6.7, 6.2, 23.1, 6.7 and 9.8 m depth below ground surface, respectively. The final transect at Kelly Creek, 13.8 km upstream of Lake King, consists of 4 bores installed at 7.0, 17.9, 24.9 and 26.8 m from the Tambo River at depths of 8.1, 7.8, 28 and 7.9 m , respectively. Bores at Tambo Upper have 1.5 m screens starting 1 m from the borehole bottom while all other installations have a 3 m screened section set at the bottom of the borehole. Sediment samples taken during bore installation indicate that the alluvial aquifer at all transects is dominated by coarse sands with clay rich layers variably distributed throughout the profile. As discussed below, the presence of clay layers result in the formation of semi-confined aquifers at depths of < 20 m that are separated from the surficial aquifers.

2 Methods

Bore and river elevation were determined to ±1 cm relative to the Australian Height Datum (AHD) using a Trimble digital global positioning system (DGPS). Bores were sampled using an impeller pump set at the screened section and at least 3 bore volumes were pumped before sample collection. Five sets of groundwater samples and 4 sets of river samples were collected between February 2011 and March 2012 at each transect. Sampling during February 2011, April 2011 and November 2011 represents conditions close to baseflow while sampling during August 2011 and March 2012 took place ~ 1 week after significant flooding in the catchment (Fig. 2). Rising head slug tests were conducted by pumping bores for ~ 10 min with an impeller pump at a rate of 4 L min^{-1} and then allowing groundwater heads to recover. Changes to groundwater head over the test were recorded using a Rugged TROLL 200 instrument recording pressure changes at 1 s intervals to ±1 ‰ accuracy. Hydraulic conductivity was calculated using the Hvorslev method outlined in Fetter (1994).

Electrical conductivity (EC) was measured in field to ±1 % using a calibrated TPS pH/EC meter and groundwater levels were measured using an electronic water level tape. Water samples were preserved by refrigeration in air-tight polyethylene bottles. HCO_3 and dissolved CO_2 were measured within 48 h of sample collection by titration using a HACH digital titrator with a precision of ±5 %. Samples were filtered (0.45 µ cellulose nitrate filters) and analysed for anions using a Metrohm ion chromatograph at Monash University, Clayton, with a precision of ±2 % estimated by replicate analysis. Filtered samples were acidified to pH < 2 using twice distilled 16 M nitric acid and analysed for cations by Varian Vista ICP-AES at the Australian National University or at Monash University, Clayton, using a Thermo Finnigan X series II, quadupole ICP-MS. Drift during ICP-MS analysis was corrected using internal Sc, Y, In, Bi standards, with replicate analysis returning a precision of ±5 %. Stable isotope ratios were measured at Monash University using ThermoFinnigan MAT 252 and DeltaPlus Advantage mass spectrometers. $\delta^{18}O$ values of water were measured via equilibration with He-CO_2 at 32 °C for 24–48 h in a ThermoFinnigan Gas Bench. $\delta^{2}H$ values of water were measured via reaction with Cr at 850 °C using a Finnigan MAT H/Device. $\delta^{18}O$ and $\delta^{2}H$ 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

HESSD
11, 1651–1691, 2014

expressed relative to V-SMOW where $\delta^{18}O$ and $\delta^{2}H$ values of SLAP are −55.5 ‰ and −428 ‰, respectively. The precision (1σ) of the analyses based on replicate analyses is $\delta^{18}O = \pm 0.2$ ‰, $\delta^{2}H = \pm 1$ ‰.

Samples for ^{14}C and ^{3}H analysis were collected during the April 2011 sampling period (Fig. 2). ^{3}H water samples were distilled and electrolytically enriched prior to analysis by liquid scintillation (Morgenstern and Taylor, 2009). The ^{3}H concentrations were expressed in tritium units (TU) with uncertainties ranging from ~ 25 % at the quantification limit (0.13 TU) to < 6 % for ^{3}H concentrations above 1.5 TU. For ^{14}C analysis, the total DIC was converted to CO_2 by acidifying the samples with H_3PO_4 and extracting the liberated CO_2 gas using a custom built extraction line. The CO_2 sample was then heated in a sealed glass tube, containing baked CuO and Ag and Cu wire at 600 °C for 2 h – to remove any sulfur compounds that may have been liberated – and followed by graphitisation, graphite targets were analysed by AMS at ANSTO's STAR accelerator following Fink et al. (2004). The activity of ^{14}C is expressed as per cent of modern carbon (pMC) following Stuiver and Polach (1977). The average error associated with radiocarbon measurements is 0.3 %.

3 Results

3.1 Groundwater elevations and hydraulic conductivities

Groundwater elevation at Bruthen varied between 7.45 m (AHD) in April 2011 and 8.89 m in August 2011. There was less than 6 cm difference across the transect during any given sampling period. Groundwater elevation in B1 and B2 were within 3 cm of each other during all sampling periods, while B3 was 2 to 6 cm higher than B1 and B2 (Fig. 3). Groundwater elevation at Bruthen was higher than river elevation during all sampling periods. Rising head slug tests at this transect indicate a hydraulic conductivity of ~ 8.5×10^{-3} m s^{-1}.

Groundwater elevation in the shallow bores at Tambo Upper ranged from 3.30 m in April 2011 to 4.80 m in August 2011. Elevations in TU5, TU2 and TU1 in individual campaigns were within 3 to 5 cm of each other. Groundwater elevations at TU4 were the lowest in the transect, averaging 3.92 m over the study, approximately 9 cm lower than the average levels in TU1, TU2, and TU5 (Fig. 3). The deeper bore (TU3D) was artesian during all sampling periods; this bore samples a deeper, semi-confined aquifer that has higher elevations than the surficial aquifer. During February and April 2011, groundwater elevations in this bore were 4.85 and 4.69 m, respectively, while in all other sampling periods the elevation exceeded that of the casing (5.04 m). Groundwater elevation at Tambo Upper was greater than river elevation during all periods except April 2011. Slug tests at this transect indicate hydraulic conductivity's ranging from 5.1×10^{-4} to $8.6 \times 10^{-5}\,\mathrm{m\,s^{-1}}$ in the surficial aquifer, and $1.9 \times 10^{-5}\,\mathrm{m\,s^{-1}}$ in the semi-confined aquifer.

At Kelly Creek, groundwater levels in the shallower bores ranged from 3.07 m in April 2011 to 3.68 m in August 2011 (Fig. 3). Groundwater levels in these bores generally decreased with proximity to the river during all sample periods except April 2011. Groundwater levels in the deeper bore at Kelly Creek (KC3D) were higher than the shallow bores, ranging from 3.82 m in February 2011 to 4.33 m in November 2011. Slug tests at this transect indicate hydraulic conductivity ranging from 2.4 to $3.4 \times 10^{-5}\,\mathrm{m\,s^{-1}}$.

3.2 Electrical conductivity

Groundwater EC values at Bruthen ranged from 136 to 607 $\mu\mathrm{S\,cm^{-1}}$. Groundwater at B3 was generally the most saline, ranging from 261 to 607 $\mu\mathrm{S\,cm^{-1}}$, while that from B1 ranged from 136 to 293 $\mu\mathrm{S\,cm^{-1}}$. Shallow groundwater at Tambo Upper was more saline than that from Bruthen, ranging from 717 $\mu\mathrm{S\,cm^{-1}}$ to 2682 $\mu\mathrm{S\,cm^{-1}}$. Shallow groundwater at Tambo Upper was also generally more saline closer to the river than further from the river, averaging 2110 $\mu\mathrm{S\,cm^{-1}}$ at TU1 and TU2 over the study period, compared to 980 $\mu\mathrm{S\,cm^{-1}}$ at TU4 and TU5. Deeper groundwater at Tambo Upper was

HESSD
11, 1651–1691, 2014

consistently the most saline in the transect, ranging from 2490 µS cm^{-1} in April 2011 to 3250 µS cm^{-1} in August 2011. Groundwater at Kelly Creek was generally more saline than Tambo Upper, with EC's ranging from 2000 to 2777 µS cm^{-1} over the study period. Groundwater EC was less variable at Kelly Creek and did not generally increase or decrease with proximity to the Tambo River.

3.3 Stable isotopes

δ^{18}O and δ^{2}H values generally plot close to the both local and global meteoric water lines (LMWL and GMWL); however river water at Kelly Creek during February 2011 plots to the right of the GMWL (Fig. 4). δ^{18}O values at Bruthen ranged from −4.3 to −7.5 ‰ and were generally higher closer to the river at B1 (average = −4.8 ± 0.4 ‰) than those further from the river at B2 and B3 (average = −5.3 ± 2.2 ‰). Stable isotope values were less variable at Tambo Upper with δ^{18}O values ranging from −5.3 to −6.3 ‰. Groundwater at TU3D, TU1 and TU2 was generally more depleted in ^{18}O (average δ^{18}O = −6.0 ± 0.2 ‰) than at TU4 and TU5 (average δ^{18}O = −5.6 ± 0.2 ‰). Shallow groundwater at Kelly Creek showed little variability in δ^{18}O values ranging from −5.3 to −5.8 ‰ over the study. As with EC, δ^{18}O values showed little variation across the transect, with average δ^{18}O values closest to the river at KC1 (−5.5 ± 0.2 ‰) and further from the river at KC2 and KC3 (−5.6 ± 0.1 ‰) within instrumental error. Deeper groundwater at Kelly Creek had slightly lower δ^{18}O values (average δ^{18}O = −5.9 ± 0.5 ‰) than the shallow groundwater. River water had lower δ^{18}O values than groundwater during all sampling periods except February 2011. During this period, δ^{18}O values of river water increased form −5.7 ‰ at Bruthen to −3.4 ‰ at Kelly Creek. Stable isotopes showed less variation in river water at other times during the study, with δ^{18}O values ranging from −7.9 to −7.5 ‰.

HESSD
11, 1651–1691, 2014

3.4 ^3H and ^{14}C

Both ^3H and ^{14}C activities in April 2011 were the highest in groundwater from Bruthen, ranging from 2.7 to 2.8 tritium units and 98.0 to 99.3 pMC, respectively. ^3H activities were higher in groundwater further from the river at Tambo Upper at TU4 and TU5 (^3H activities 1.6 and 1.2 tritium units, respectively) compared to groundwater closer to the river at TU1 and TU2 (^3H activities 0.40 and 0.36 tritium units, respectively). ^3H activities in deep groundwater at TU3D were below detection. ^{14}C activities show a similar variation, with higher activities at TU4 and TU5 (94.5 and 79.2 pMC) compared to groundwater at TU1 and TU2 (35.4 and 38.0 pMC). Deeper groundwater at TU3D had lower ^{14}C activities (10.6 pMC). ^3H activities in groundwater at Kelly Creek decreased from 0.51 tritium units at KC4 to 0.40 and 0.36 tritium units at KC1 and KC2, respectively. ^{14}C activities follow a similar trend, decreasing from 84.2 pMC at KC4 to 80.4 pMC at KC1.

3.5 Major ions

Despite sampling groundwater from similar aquifers, there are considerable differences in the geochemistry of groundwater from the three transect locations.

Groundwater from Bruthen is a HCO_3-Ca-Na type (Fig. 5). The concentration of most major cations at Bruthen decrease with increasing Cl concentrations, however K has a weak positive correlation with Cl (Fig. 6). Molar Na : Cl ratios at Bruthen generally range from 2 to 4 during periods of lower rainfall in the catchment (February 2011, April 2011 and November 2011), and are generally below 1 during periods of increased rainfall (August 2011 and March 2012). Molar Cl:Br ratios at Bruthen increase from 140 to over 1000 with increasing Cl concentrations (Fig. 6).

Groundwater from Tambo Upper is a Cl-Na-Ca type (Fig. 5). At Tambo Upper Na and K concentrations increase and Ca and Mg concentrations decrease with increasing Cl concentrations (Fig. 8). Groundwater further from the river at Tambo Upper (TU4 and TU5) has Cl concentrations below 10 mmol L^{-1}, K concentrations below

HESSD
11, 1651–1691, 2014

0.2 mmol L^{-1} and Na concentrations below 7 mmol L^{-1} (Table 1). Deeper groundwater from Tambo Upper (TU3D) has Cl concentrations greater than 15 mmol L^{-1}, K concentrations greater than 0.8 mmol L^{-1} and Na concentrations greater than 16 mmol L^{-1}. Groundwater closer to the river at Tambo Upper (TU1 and TU2) contains concentrations of Na, K, Mg and Ca that are an intermediate between that of TU3D and groundwater at TU4 and TU5.

Shallow groundwater at Kelly Creek is Cl-Ca-Na type. At Kelly Creek, shallow groundwater has Cl concentrations that range from 11.6 to 20.1 mmol L^{-1} and Ca concentrations that range from 3.1 to 8.5 mmol L^{-1} (Fig. 7). Ca, Na, K, and Mg concentrations generally increase with Cl concentrations. Deeper groundwater from Kelly Creek shows similar trends in major ion concentrations to shallower groundwater, however the relative proportion of Na and Mg is higher and the relative proportion of Ca is lower. Molar Cl : Br ratios in groundwater at Kelly Creek increase from ~ 650 to ~ 1000 while Na : Cl ratios decrease from 1.4 to 0.4 as Cl concentrations increase.

4 Discussion

The following section focusses on identifying the source of water stored in the banks of the Tambo River. Through groundwater dating, the prevalence of bank storage is evaluated and patterns in groundwater recharge and flow are identified. These evaluations are further coupled with major ion and stable isotope analysis under changing hydrological conditions, in order to identify processes controlling the chemistry of bank water and the potential impacts to river and groundwater quality.

4.1 Hydrogeochemical processes

Higher Na : Cl ratios at Bruthen and Kelly Creek during periods of lower rainfall suggests that longer groundwater residence times facilitate greater water-rock interaction and the dissolution of Na bearing minerals such as plagioclase (Edmunds, 2009;

HESSD
11, 1651–1691, 2014

Herczeg et al., 2001). The increase in Cl : Br ratios at Bruthen and Kelly Creek with increasing Cl concentrations (Figs. 6 and 7) indicates an input of Cl rather than evapotranspiration (which would not impact Cl : Br ratios). An absence of evaporation is also supported by δ^2H and δ^{18}O values at Bruthen which plot close to the local meteoric water line rather than along evaporation trends (Fig. 4) (Cartwright et al., 2010; Herczeg et al., 2001). Increased Cl : Br ratios may result from halite (NaCl) dissolution which could also shift Na : Cl ratios towards 1 as Cl concentrations increase.

However, there are no obvious stores of halite in the catchment and Na:Cl ratios of <1 at Kelly Creek are difficult to explain by halite dissolution. An alternative source of Cl is KCl fertilizers that are used locally (Department of Environment and Primary Industries, 2013). K : Cl ratios decrease with increasing Cl concentrations at Bruthen (Fig. 6), however, K is non-conservative and may be removed from the soil profile by vegetation (e.g., Schachtman and Schroder, 1994). It is also possible that groundwater has interacted with weathered and potentially parent shale, where K could be sorbed by illite (Griffioen, 2001). In any case, the observation that increased Cl concentrations coincide with increased rainfall suggest that infiltration facilitates the transport of Cl from land surface and/or the soil profile into shallow groundwater (Panno et al., 2006).

At Tambo Upper, the groundwater from TU1, TU2 and TU5 has Cl concentrations consistent with the mixing between deep groundwater from TU3D (Cl concentrations of 17.11 to 27.03 mmol L^{-1}) and shallow groundwater from TU4 (Cl concentrations of 3.94 to 6.24 mmol L^{-1}) (Fig. 8). Molar Na : Cl ratios and K : Cl ratios in the deeper groundwater are generally higher, while Ca : Cl and Mg : Cl ratios are generally lower than in the shallow groundwater. This suggests a greater dissolution of Na and K minerals in the deeper aquifer as a result of higher residence times, while the dissolution of Ca and Mg minerals such as gypsum and calcite is minimal. Shallow groundwater from TU4 has higher Mg : Cl and Ca : Cl ratios than the deeper groundwater and lower Na : Cl and K : Cl ratios than the deeper groundwater. The geochemistry of the shallow groundwater throughout the rest of the transect may be explained by mixing trend between shallow and deep groundwater (Fig. 8). This especially occurs during

HESSD
11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

the wetter periods of August 2011 and March 2012, suggesting that hydraulic loading of the deeper, semi-confined aquifer is driving increased leakage of deep groundwater into the overlying alluvial aquifer.

4.2 Aquifer interactions

The ^{14}C and ^{3}H activities in groundwater may be predicted from their atmospheric concentrations and groundwater residence times. The activities of these isotopes in the atmosphere were elevated due to nuclear tests that occurred mainly in the 1960s (the so-called "bomb pulse"). For this study, calculations are based on a rainfall weighted ^{3}H activity of 3.2 tritium units for the period July 2005 to June 2011 in the Melbourne area (Tadros et al., 2014), and we assume that pre-bomb pulse tritium activities are similar to these as indicated by Allison and Hughes (1977). Unlike ^{3}H, ^{14}C activities of atmospheric CO_2 were similar in the northern and southern hemispheres (Fontes, 1983). The data of Hau et al. (2013) were used for ^{14}C activities of precipitation from 1950 to 2011. Pre 1950, ^{14}C activities are assumed to have decreased from 100 pMC in 1905 to 97.5 pMC in 1950 due to fossil fuel burning (Suess, 1971).

Le Gal La Salle et al. (2001) presented a renewal rate model where the shallow aquifer is treated as a reservoir in which each year a certain proportion of water leaks to deeper groundwater and is replaced by recharge. The ^{3}H or ^{14}C activity in groundwater at time t (C_t) is given by:

$$C_t = (1 - R_n)C_{t-1}e^{-\lambda} + R_nC_i \tag{1}$$

where λ is the decay constant (5.63×10^{-3} yr^{-1} for ^{3}H , 1.21×10^{-4} yr^{-1} for ^{14}C), C_i is the activity of ^{3}H or ^{14}C in precipitation in year i and R_n is the aquifer renewal rate.

The assumption that the aquifer acts as a single well-mixed homogeneous zone is unlikely to apply to anything but the top few metres of an aquifer. Lumped-parameter models may also be used to describe groundwater flow in shallow unconfined aquifers and semi-confined aquifers (Małoszewski and Zuber, 1991, 1982; Morgenstern, 2010; Zuber et al., 2005). Piston flow models assume that no mixing takes place between recharge and water in the aquifer, and is suitable for settings where dispersion is low. Conversely, the exponential flow model assumes a vertical stratification of groundwater ages in an aquifer and is suitable for the sampling of fully penetrating wells or surface water bodies fed by aquifers receiving homogeneous recharge. This study uses the exponential piston flow model (EPFM) which combines a portion of piston flow followed by a portion of exponential flow and is appropriate for unconfined to semi-confined aquifers screened below the water table, such that precludes sampling of groundwater with very short residence times (Morgenstern, 2010; Cartwright and Morgenstern, 2012).

For the EPFM C_t is given by:

$$C_t = \int_0^\infty C_i(t-\tau)g(\tau)e^{(-\lambda\tau)}\mathrm{d}\tau \tag{2}$$

where τ is the transit time and $g(\tau)$ is the system response function. The system response function is given by:

$$g(\tau) = 0 \quad \text{for} \quad \tau < T(1-f) \tag{3a}$$

$$g(\tau) = (fT)^{-1}e^{(-\tau/(ft_t)+1/f-1)} \quad \text{for} \quad \tau > T(1-f) \tag{3b}$$

where T is the mean residence time and f is the ratio of exponential flow to piston flow for the total flow volume (Cartwright and Morgenstern, 2012; Zuber et al., 2005). f has been estimated at 0.8 for shallow bores neighbouring the Tambo River on the basis of bore depth, screen length and aquifer lithology.

While the exact model adopted results in different estimates of groundwater residence times, the predicted variation in ^{14}C and ^{3}H activities are similar in all flow models that involve attenuation of the bomb-pulse peak of ^{3}H and ^{14}C during flow. The covariance of ^{14}C and ^{3}H activities constrains mixing within the groundwater system

HESSD
11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

(Le Gal La Salle et al., 2001; Cartwright et al., 2007, 2012). Mixing between recently-recharged groundwater and older groundwater with low ^{14}C and negligible ^{3}H activities will displace water compositions to the left of the predicted a^{14}C vs. ^{3}H trends. Closed-system calcite dissolution lowers a^{14}C but which does not impact ^{3}H concentrations produces a similar displacement. The co-variance between ^{3}H and ^{14}C for groundwater samples is shown in Fig. 9, with the expected trends for Eq. (1).

This indicates that groundwater from Bruthen has a relatively high renewal rate compared to groundwater from Kelly Creek and < 20 % closed system calcite dissolution, as is consistent with aquifers dominated by siliclastic sediments (Vogel, 1970; Clark and Fritz, 1997). By contrast, groundwater from TU1, TU2 and TU5 at Tambo Upper follow a trend consistent with the mixing between groundwater in the shallow aquifer that has higher renewal rates (TU4), and groundwater in the deeper semi-confined aquifer that has lower renewal rates (TU3D) (Fig. 9). The trend indicates increased leakage from the deeper aquifer into the surface aquifer closer to the river at TU1 and TU2. This is consistent with higher groundwater levels and electrical conductivities at TU1 and TU2 (Fig. 3) that would result from increased connectivity with artesian groundwater in the deeper, semi-confined aquifer. This connection may have resulted from erosion of the clay layers closer to the Tambo River during periodic flooding.

4.3 Groundwater residence times and mixing

Groundwater residence times were calculated using the ^{3}H activities and the EPFM with $f = 0.8$. Groundwater from Bruthen has relatively short residence times of 2 to 4 yr. Groundwater from Kelly Creek has longer residence times (96 to 100 yr), which is consistent with the higher degrees of mineral dissolution at Kelly Creek discussed previously. Groundwater from TU4 at Tambo Upper has an intermediate residence time of 27 yr. The ^{3}H and ^{14}C activities of these samples are similar to what is expected where there has been minimal mixing between older and younger groundwater (c.f. Le Gal La Salle et al., 2001). To assess the sensitivity of these results, f values in this study were varied between 0.6 and 1.0. This results in variations of < 0.1 yr at Bruthen

HESSD
11, 1651–1691, 2014

and < 15 yr at Kelly Creek. Uncertainties in groundwater age based on the uncertainty of ^3H activities were < 1 yr at Bruthen (based on an uncertainty of 0.14 tritium units) and < 1.5 yr at Kelly Creek (based on an uncertainty of 0.04 tritium units). As deeper groundwater from Tambo Upper site is ^3H free, residence times were calculated from ^{14}C activities. Making the assumption of 15 % calcite dissolution, age estimates based on Clarke and Fritz (1997, their Eq. 2, p. 206) are ~ 17 200 yr.

The relatively young groundwater residence times from the shallow aquifers implies that groundwater recharge in the area is dominantly local, probably within a few hundreds of meters of the Tambo River. Mean groundwater residence times from the Bruthen bores are similar and within analytical uncertainty, preventing calculation of horizontal flow velocities. Mean groundwater residence times at Kelly Creek increase from 96 yr at KC4 to 100 yr at KC2. The age of groundwater at KC1 is 99 yr and within the analytical uncertainty of groundwater at KC2. Based on these data, groundwater at Kelly Creek has a horizontal flow velocity of between 1.3 and 6.5 m yr^{-1} towards the river.

The ^3H and ^{14}C activities predicted by the mixing between groundwater from TU4 and deeper groundwater are shown in Fig. 10. While it is possible that groundwater from TU4 has already undergone some mixing with deeper groundwater (and C inputs from the aquifer are less than 10 % opposed to the 10–20 % indicated), this remains difficult to define. As such, mixing estimates at Tambo Upper will be conservative with respect to the input of deep groundwater. Groundwater from TU1, TU2 and TU5 plot below the mixing trend in Fig. 10. While there are uncertainties in these calculations it is possible that ^3H activities are lower than expected due to the decay of ^3H in shallow groundwater. Exponential piston flow modelling of water at TU1 and TU2 indicates that a residence time of ~ 20 yr would be required to cause the observed deviation in ^3H activities from the mixing trend shown in Fig. 10. This suggests a horizontal flow rate of 1.8 ± 0.6 m yr^{-1} towards the Tambo River at the Tambo Upper transect. This is consistent with shallow groundwater recharge on the floodplains of the Tambo River

HESSD
11, 1651–1691, 2014

and groundwater flow towards the river, which is somewhat expected given the gaining nature river section Unland et al. (2013).

4.4 Implications for groundwater – surface water interaction

The distribution of groundwater residence times does not support increased bank storage in the area immediately (within 10's of meters) neighbouring the Tambo River. If this was so, groundwater closer to the Tambo River would contain a higher proportion of younger water than groundwater further from the river and groundwater ages would decline towards the river. Instead, increasing groundwater age with proximity of the Tambo River was found at Kelly Creek and Tambo Upper, while groundwater a Bruthen was approximately the same age at 18 and 6 m distance from the Tambo River.

As the ^{3}H and ^{14}C activities were analysed for groundwater sampled in April 2011, these data can only be used to evaluate bank storage for the hydrological conditions leading up to sampling. This included a discharge event that increased river height by 0.5 m approximately 2 weeks prior to sampling. As such, these data indicate that an increase in river height of 0.5 m is not large enough to produce bank storage 5 to 10 m distance from of the river for a period greater than 2 weeks. Major ions and stable isotopes were analysed at several times, including after flood events which increased river height by ~5 m. Again there is little evidence of river water infiltrating into the river banks following these events. The curves expected for the mixing between shallow groundwater furthest from the river, deep groundwater, and river water at each transect with respect to Cl : Br, Na : Cl, and K : Cl ratios are shown in Fig. 11.

Data are shown for February 2011 and August 2011 to represent baseflow conditions when bank infiltration is likely to have the least impact on groundwater chemistry and post flood conditions, when bank infiltration is most likely to impact groundwater chemistry. The composition of groundwater from the two bores closest to the Tambo River at each transect are not consistent with the trends expected for mixing between river water and deep or shallow groundwater further form the river.

HESSD
11, 1651–1691, 2014

These observations indicate that either river water penetrates < 5 m into the banks during flooding, or that the hydrogeological processes outlined above including aquifer mixing, water rock interaction or the mobilisation and infiltration of Cl from the soil profile have a greater impact on the chemistry of water in the river banks than bank infiltration (Fig. 12). Similarly, δ^2H and δ^{18}O values of groundwater closer to the Tambo River do not decline after significant flooding, as would be expected for the infiltration of river water with the lower δ^2H and δ^{18}O values observed during flooding. Again, this suggests limited bank infiltration. The absence of significant bank infiltration is consistent with results from Vekerdy and Meijerink (1998) and Wett et al. (2002) who found bank infiltration to be minimal in confined and semi-confined aquifers, where pressure loading from the flood wave propagated rapidly into the neighbouring aquifers, limiting bank infiltration. While most bores near the Tambo River are screened in the alluvial aquifer which is unconfined, leakage of the underlying semi-confined aquifer into the alluvial aquifer does occur (Fig. 9). As such, it may be that pressure has propagated rapidly into the semi-confined aquifers of the area, and subsequently into the alluvial aquifer where confining layers are less prevalent – as is expected in river banks where erosive processes will actively diminish the formation of confining layers (Rinaldi and Darby, 2007).

It is however possible that bank storage is occurring, but that the gaining nature of the Tambo River near these transects is driving the return of bank water back into the river before sampling has taken place (Fig. 12). If this is the case, the storage period is significantly shorter than predicted by modelling (e.g. Cooper, 1963; Doble et al., 2012; McCallum et al., 2010; and Whiting and Pomeranets, 1997), with no discernible chemical change in bank water within ~ 1 week of a flood peak. In terms of groundwater age, it is possible that a higher proportion of recently infiltrated river water does remain in the river bank closer to the river, but horizontal groundwater flow velocities are slower than estimated. For example, if groundwater at Kelly Creek had a horizontal flow velocity half that of the 3.9 m yr^{-1} estimated (1.95 m yr^{-1}), groundwater closer to the river would have a mean residence time of 177 yr instead of the 99 yr modelled.

HESSD
11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

It could be that this is this case, and that increased mixing between river water and groundwater closer to the river has resulted in the groundwater residence times that have been calculated. Under this scenario, it would require only a 10 % input of river water to increase the ^{3}H activity to the observed 0.40 TU (assuming river water has an atmospheric ^{3}H activity). While this would also cause an increase in the ^{14}C activities, a 10 % input of river water containing modern ^{14}C activities could be offset by an extra 2 % DIC input from carbonate dissolution, which is possible. In any case, these results suggest that if a higher proportion of infiltrated river water is present closer to the river, it does not chemically reflect a significant proportion groundwater compared to locally recharged groundwater. This shows that if bank storage processes are occurring, the impact of such processes on groundwater chemistry may be insignificant with respect to groundwater discharge studies, riparian ecology and river chemistry.

5 Conclusions

The mean groundwater residence times and horizontal flow velocities of groundwater neighbouring the Tambo River determined using ^{3}H and ^{14}C activities indicate that recharge of the alluvial aquifer is dominantly local (with 100's of meters of the Tambo River). The covariance between ^{3}H and ^{14}C activities show that mixing between relatively old groundwater from a deeper semi-confined aquifer, and younger groundwater from the unconfined alluvial aquifer is occurring in parts of the Tambo River bank. It is further shown that by coupling ^{3}H and ^{14}C to define a mixing trend, deviations in the activity of ^{3}H from the trend can be used to estimate the likely age of groundwater along its flow path. Na : Cl ratios > 1 in groundwater sampled during baseflow conditions and in older groundwater from the area indicate the dissolution of Na bearing minerals and is consistent with the weathering of silicic sands in the aquifer. Increasing Cl : Br ratios and increasing Cl concentrations during periods of increased rainfall indicate an input of Cl, as is consistent with the mobilisation of Cl accumulated in the soil profile through the use of fertilizers. Increasing groundwater age with proximity to

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

HESSD

11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

the Tambo River is consistent with the gaining nature of the Tambo River, but does not suggest that exchange between groundwater and surface water increases with increasing proximity to the river. Major ions, δ^2H and δ^{18}O values support this and do not show trends consistent with an increased input of river water to the groundwater closer to the river. These results suggest that either the strongly gaining nature of the Tambo River at the study locations is preventing significant lateral infiltration of river water into the bank, or that the rapid propagation of pressure into the underlying semi-confined aquifer, followed by leakage into the above unconfined aquifer is preventing significant bank infiltration. These results are indicative of the highly complex nature of groundwater and surface water processes that may be occurring within river banks and illustrates that while models can significantly help in conceptualising our understanding of groundwater-surface water interactions, field studies can offer complementary information that may otherwise be overlooked.

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HESSD
11, 1651–1691, 2014

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HESSD

11, 1651–1691, 2014

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Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

HESSD
11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

Table 1. Summary data for Bruthen transect. HCO_3 data in italics = calculated via charge balance. MGRT = mean groundwater residence time as calculated via exponential piston flow modelling (see Sect. 4.3).

Site	Date	EC	Level	Dist.	F	Cl	Br	NO_3	SO_4	HCO_3	Na	K	Ca	Mg	O	H	^3H	^{14}C	$\delta^{13}C$	MGRT
		$\mu S\,cm^{-1}$	m	m	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$\delta^{18}O$	δ^2H	TU	pMC	‰	yr
R	Feb 2011	121	7.84	0.00	0.08	9.63	0.03	0.24	1.94	*46.4*	7.65	1.38	7.77	3.95	−5.69	−39.1				
1	Feb 2011	146	7.87	5.56	0.04	9.60	0.05	0.04	6.05	*50.9*	12.1	1.65	8.33	3.05	−4.97	−33.6				
2	Feb 2011	191	7.88	17.6	0.06	5.61	0.02	0.05	23.5	*41.3*	7.16	3.00	10.4	5.14	−7.53	−47.9				
3	Feb 2011	261	7.90	18.3	0.12	13.3	0.07	0.02	11.5	*85.0*	19.2	2.52	10.3	7.33	−5.42	−36.5				
R	Apr 2011	109	7.61	0.00	0.05	3.63	0.01	0.11	0.90											
1	Apr 2011	200	7.66	5.56	0.04	6.75	0.10	0.37	5.83	67.1	16.9	2.03	12.2	4.09	−5.37	−34.7	2.65	98.04	−13.9	3.4
2	Apr 2011			17.6	0.15	10.3	0.17	0.30	11.4	183	27.3	2.68	8.47	7.31	−5.93	−37.4	2.84	99.33	−15.4	2.2
R	Aug 2011	145	8.81	0.00	0.04	17.6	0.02	2.17	5.02	*38.7*	11.7	1.68	6.44	4.85	−7.61	−46.6				
1	Aug 2011	179	8.84	5.56	0.06	5.66	0.03	0.20	5.36	*52.5*	2.52	2.44	11.3	4.91	−4.34	−24.7				
2	Aug 2011	173	8.84	17.6	0.12	12.7	0.08	0.03	36.2		BD	2.51	11.5	8.93	−5.38	−29.2				
3	Aug 2011	293	8.89	18.3	0.06	18.8	0.04	1.48	30.2		BD	5.28	10.4	6.35	−6.66	−36.5				
1	Nov 2011	229	7.91	5.56	0.07	11.1	0.05	0.00	6.07	*75.1*	15.2	2.10	10.4	5.37	−4.81	−31.6				
2	Nov 2011	215	7.88	17.6	0.08	14.6	0.05	2.72	10.1	*49.5*	13.7	3.91	8.20	4.58	−6.10	−34.6				
3	Nov 2011	607	7.94	18.3	0.05	78.2	0.21	0.08	12.1	*63.1*	33.1	3.32	15.8	14.4	−7.40	−44.4				
R	Mar 2012	156	7.47	0.00	0.09	17.5	0.03	0.77	4.12	*45.9*	11.1	1.53	8.17	5.08	−7.56	−46.2				
1	Mar 2012	293	8.36	5.56	0.05	17.8	0.06	0.03	16.5	*62.1*	9.41	1.72	17.8	6.38	−5.13	−28.7				
2	Mar 2012	136	8.36	17.6							6.87	2.43	4.91	2.27						
3	Mar 2012	287	8.38	18.3	0.16	23.4	0.07	0.00	22.0	*44.7*	19.1	1.66	8.43	6.87	−4.67	−22.2				

HESSD
11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

Table 2. Summary data for Tambo Upper transect HCO_3 data in italics = calculated via charge balance. MGRT = mean groundwater residence time as calculated via exponential piston flow modelling (see Sect. 4.3). MGRT's at TU1, TU2 and TU5 have been given for the ^3H activities calculated by mixing and the measured ^3H activity, respectively.

Site	Date	EC	Level	Dist.	F	Cl	Br	NO_3	SO_4	HCO_3	Na	K	Ca	Mg	O	H	^3H	^{14}C	$\delta^{13}C$	MGRT
		$\mu S\,cm^{-1}$	m	m	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$\delta^{18}O$	δ^2H	TU	Pmc	‰	yr
R	Feb 2011	120	3.58	0.00	0.08	9.78	0.04	0.11	2.04	*48.1*	7.83	1.74	8.24	3.86	−5.63	−38.3				
1	Feb 2011	2395	3.90	8.82	0.14	572	1.88	0.33	25.2	*212*	279	23.0	99.6	30.3	−6.06	−38.4				
2	Feb 2011	2155	3.86	15.03	0.12	555	1.77	1.58	14.7	*157*	280	19.2	62.4	33.9	−5.97	−39.6				
3-D	Feb 2011	2656	4.85	22.34	0.36	607	1.98	2.54	22.8	*316*	374	35.4	64.6	29.8	−6.32	−39.1				
4	Feb 2011	764	3.78	23.73	0.12	176	0.52	0.07	21.3	*60.7*	72.8	4.65	33.9	17.7	−5.43	−37.3				
5	Feb 2011	1023	3.89	37.87											−5.69	−38.8				
R	Apr 2011	112	3.43	0.00	0.04		0.01	0.08	0.92		16.0	4.34	10.0	15.1	−7.88	−61.9				
1	Apr 2011	2210	3.38	8.82	0.14	460	1.43	0.22	36.8	291	280	26.9	111	40.7	−5.98	−37.0	0.40	38.0	−8.7	99/78
2	Apr 2011	2180	3.36	15.03	0.11	533	1.76	1.24	25.9	272	333	23.1	86.8	52.8	−5.98	−38.2	0.36	35.4	−7.2	100/80
3-D	Apr 2011	2488	4.69	22.34	0.34	534	1.72	0.33	10.9	439	468	33.8	71.8	41.2	−6.18	−38.3	< 0.03	10.6	−5.7	17 200
4	Apr 2011	717	3.30	23.73	0.11	140	0.42	0.47	15.9	100	98.1	4.42	37.1	21.2	−5.35	−34.9	1.55	94.5	−10	27
5	Apr 2011	1043	3.39	37.87	0.11	203	0.61	0.07	50.3	80.5	122	7.10	64.9	20.7	−5.74	−36.9	1.21	79.2	−9.3	68/52
R	Aug 2011	148	4.74	0.00	0.06	18.1	0.02	2.46	4.21	*36.5*	11.6	1.85	5.87	4.78	−7.66	−45.2				
1	Aug 2011	2682	4.77	8.82	0.11	599	1.63	0.53	12.6	*406*	339	27.3	105	38.2	−6.01	−32.9				
2	Aug 2011	2207	4.75	15.03	0.19	501	1.42	0.27	22.2	*279*	280	21.3	78.0	31.7	−5.92	−31.7				
3-D	Aug 2011	3250	5.04	22.34	0.26	753	2.09	0.11	34.2	*799*	600	48.4	80.9	45.2	−6.03	−33.4				
4	Aug 2011	774	4.70	23.73	0.08	207	0.41	0.12	5.59	*89.8*	98.3	3.44	32.6	17.6	−5.38	−27.7				
5	Aug 2011	1039	4.80	37.87	0.14	227	0.43	0.08	11.6	*118*	115	3.31	36.5	20.9	−5.34	−29.4				
1	Nov 2011	2018	3.74	8.82	0.30	439	1.42	0.56	49.7	*383*	303	15.5	79.4	26.5	−6.07	−35.0				
2	Nov 2011	2168	3.70	15.03	0.07	531	1.21	0.12	4.46	*294*	241	14.2	91.6	54.4	−5.93	−37.9				
3-D	Nov 2011	2938	> 5.04	22.34	0.19	639	2.28	0.21	46.8	*760*	554	41.2	63.1	38.7	−6.23	−39.1				
4	Nov 2011	864	3.61	23.73	0.18	178	0.56	0.21	1.24	*170*	98.8	4.00	36.0	20.1	−5.37	−35.2				
5	Nov 2011	1337	3.70	37.87	0.08	276	0.83	0.11	48.3	*207*	158	6.21	68.4	21.7	−5.84	−38.1				
R	Mar 2012	165	3.32	0.00	0.09	19.6	0.04	0.54	4.21	*48.5*	12.0	1.76	8.69	5.47	−7.64	−46.4				
1	Mar 2012	1350	4.30	8.82	0.07	385	0.93	0.13	33.5	*27.7*	141	19.4	68.5	24.2	−5.65	−28.3				
2	Mar 2012	1763	4.26	15.03	0.07	544	1.11	0.07	29.7	*BD*	190	11.7	70.4	35.7	−5.88	−26.6				
3-D	Mar 2012	3210	> 5.04	22.34	0.24	958	2.46	0.05	41.0	*BD*	484	35.2	58.7	33.3	−6.12	−40.8				
4	Mar 2012	881	4.22	23.73	0.10	221	0.53	0.09	1.45	*73.0*	88.7	4.48	38.0	19.7	n/a	−34.9				
5	Mar 2012	1320	4.32	37.87	0.09	344	0.76	0.30	40.4	*57.6*	148	6.38	63.3	21.2	−5.84	−26.7				

HESSD
11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀◀ ▶▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Table 3. Summary data for Kelly Creek transect. HCO_3 data in italics = calculated via charge balance. MGRT = mean groundwater residence time as calculated via exponential piston flow modelling (see Sect. 4.3).

Site	Date	EC	Level	Dist.	F	Cl	Br	NO_3	SO_4	HCO_3	Na	K	Ca	Mg	O	H	^3H	^{14}C	$\delta^{13}C$	MGRT
		$\mu S\,cm^{-1}$	m	m	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$\delta^{18}O$	δ^2H	TU	Pmc	‰	yr
R	Feb 2011	18 340	3.05	0	0.38	6322	22.0	0.30	825	*899*	3558	151	182.0	521	−3.38	−24.6				
1	Feb 2011	2004	3.14	7.02	0.3	518	1.54	0.35	0.43	*294*	178	3.82	178.0	33.6	−5.63	−37.0				
2	Feb 2011	2349	3.17	17.9	0.43	597	1.77	0.77	2.01	*374*	202	3.93	231.0	32.4	−5.61	−36.9				
3-D	Feb 2011		3.82	24.9							162	11.4	23.6	9.31	−5.81	−37.8				
4	Feb 2011	2364	3.2	26.8	0.38	637	1.92	0.56	1.14	*271*	197	2.59	229.0	29.6	−6.68	−41.1				
R	Apr 2011	4210		0	0.21	255	0.93	0.13	29.1	*8690*	2683	153	403.7	116	−7.69	−45.5				
1	Apr 2011	2145	3.15	7.02	0.3	474	1.36	0.27	0.28	446	204	3.29	206.9	43.6	−5.58	−35.5	0.40	80.4	−2.8	99
2	Apr 2011	2455	3.07	17.9	0.33	558	1.57	0.43	1.00	488	252	2.83	288.9	42.3	−5.63	−36.2	0.37	83.6	−2.9	100
3-D	Apr 2011	2669	3.95	24.9	0.39	413	1.30	0.68	68.9	445	372	17.8	123.3	48.7	−5.58	−36.3				
4	Apr 2011	2099	3.15	26.8	0.57	630	1.83	1.87	0.78	591	313	3.12	340.1	47.8	−6.17	−38.5	0.51	84.2	−3.7	96
R	Aug 2011	170		0	0.05	21.6	0.03	2.24	4.82	*39.0*	13.8	2.38	6.3	5.03	−7.48	−46.0				
1	Aug 2011	2568	3.63	7.02	0.24	590	1.40	0.84	0.38	*256*	146	4.27	218.9	42.8	−5.27	−29.5				
2	Aug 2011	2777	3.63	17.9	0.26	655	1.44	0.18	1.56	*355*	135	3.73	286.3	49.8	−5.28	−29.6				
3-D	Aug 2011	2438	4.30	24.9	0.23	608	1.30	2.12	61.4	*292*	218	12.1	185.7	51	−5.55	−29.2				
4	Aug 2011	2717	3.68	26.8	0.26	513	1.26	0.01	0.52	*291*	73.4	2.28	262.8	35.5	−5.42	−30.3				
1	Nov 2011	2742		7.02	0.45	533	1.70	2.70	0.68	*848*	286	6.14	249.3	48.7	−5.56	−35.5				
2	Nov 2011	2542	3.36	17.9	0.32	563	1.62	0.13	51.4	*711*	269	3.26	267.5	42.9	−5.69	−36.9				
3-D	Nov 2011	2738	4.33	24.9	0.41	436	1.44	0.04	0.57	*998*	338	11.0	192.0	50.7	−5.60	−36.3				
4	Nov 2011	2218	3.41	26.8	0.35	532	1.71	2.48	0.54	*552*	226	2.49	229.5	34.4	−5.48	−36.2				
R	Mar 2012	195		0	0.08	33.4	0.09	0.21	7.25	*465*	82.1	11.9	47.4	30.1	−7.58	−45.5				
1	Mar 2012	2770		7.02	0.3	598	1.48	0.04	2.44	*397*	218	4.39	215.2	37.9	−5.52	−33.1				
2	Mar 2012	2495		17.9	0.41	605	1.53	0.10	1.11	*430*	219	3.72	237.8	32.8	−5.45	−32.8				
3-D	Mar 2012	2345		24.9	0.37	560	1.45	0.16	0.46	*637*	292	8.75	199.4	41.6	−5.65	−34.2				
4	Mar 2012	2715		26.8	0.32	713	1.64	0.13	43.4	*24.3*	189	3.42	217.5	27.6	−5.62	−30.7				

HESSD
11, 1651–1691, 2014

HESSD
11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

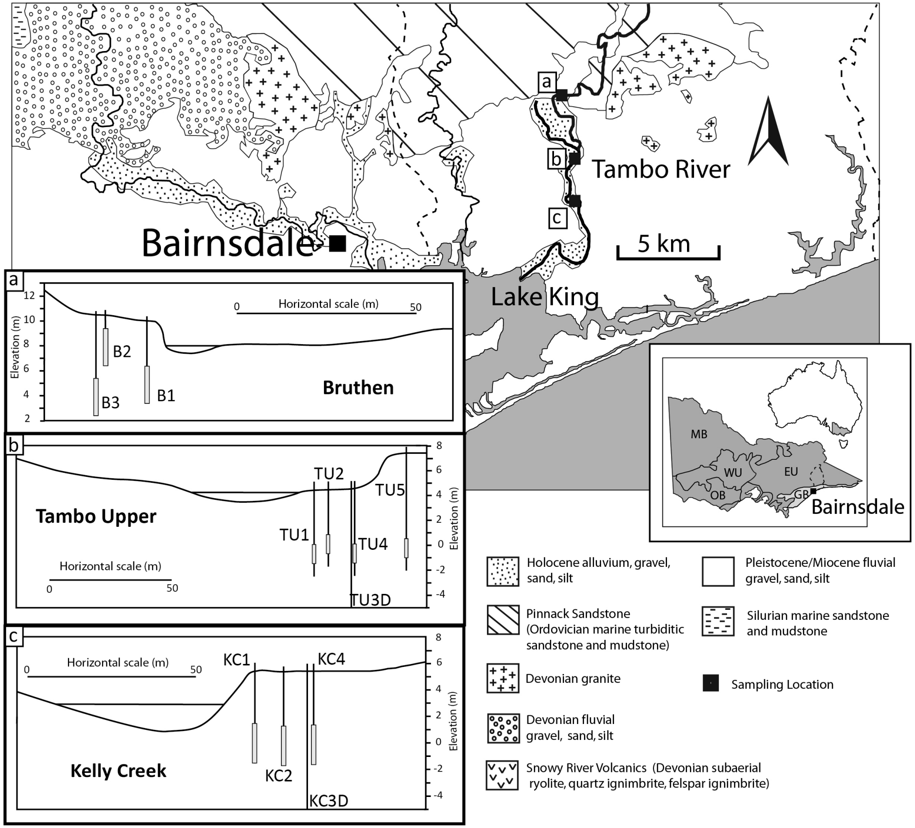

Fig. 1. Location of field area and schematic cross sections of bore transects at Bruthen **(a)**, Tambo Upper **(b)** and Kelly Creek **(c)**. Screened sections indicated by open boxes. Dashed line = Tambo River basin boundary (transects orientated facing upstream).

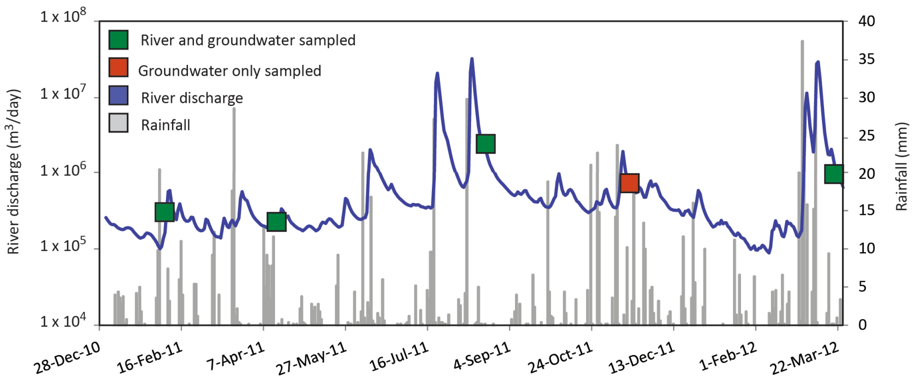

Fig. 2. Surface and groundwater sampling frequency superimposed on Tambo River hydrograph (Battens Landing, station 223209) and rainfall (Bairnsdale Airport, station 85279).

HESSD

11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

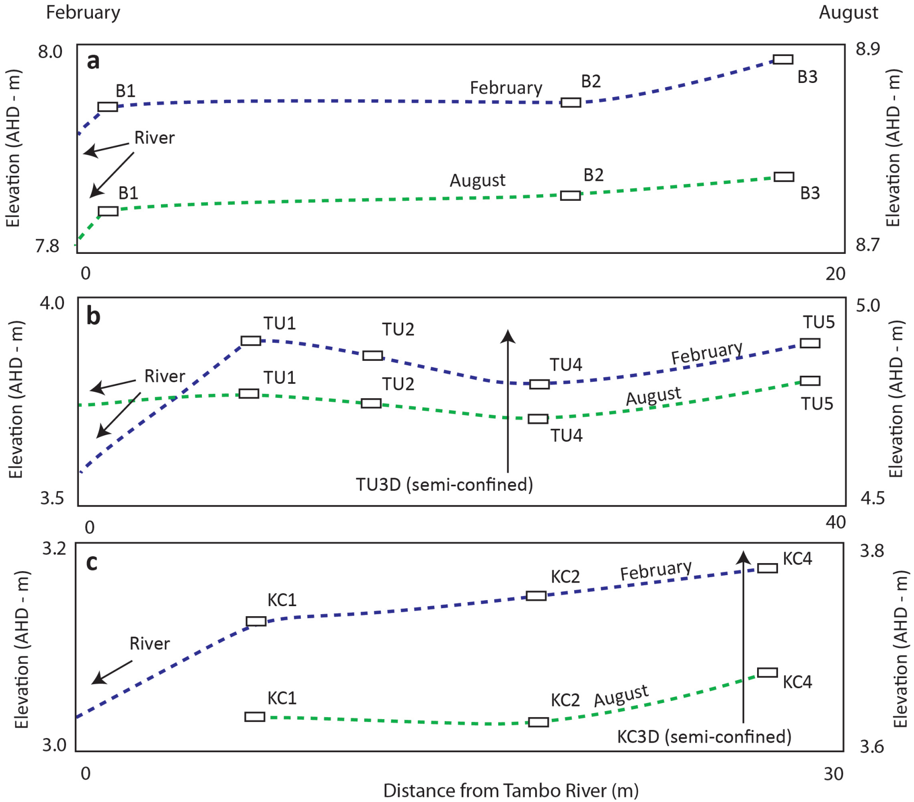

Fig. 3. Groundwater elevations during February 2011 and August 2011 at Bruthen **(a)**, Tambo Upper **(b)** and Kelly Creek **(c)**. White rectangles = measured elevation, dashed lines = interpolated elevations.

HESSD
11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀︎ ▶︎
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

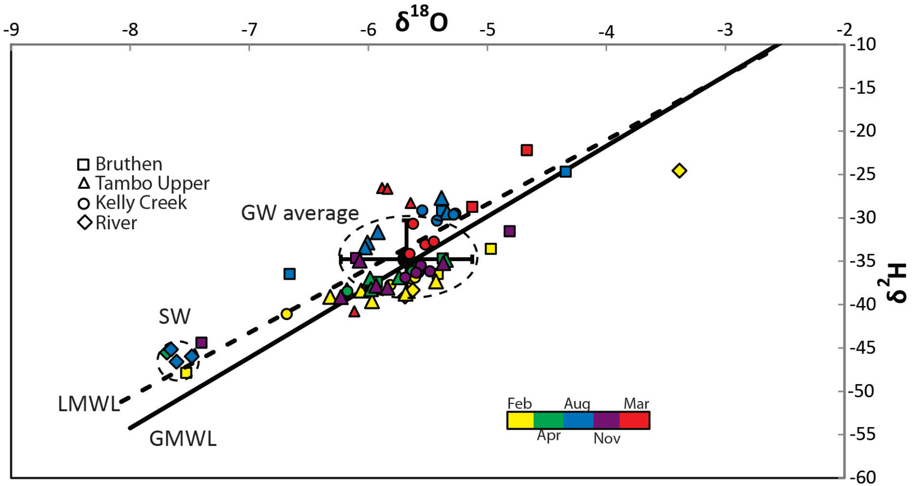

Fig. 4. δ^{18}O and δ^{2}H values of bank water and river water from the Tambo River. LMWL defined by Melbourne meteoric water line in Hughes et al. (2012).

HESSD
11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

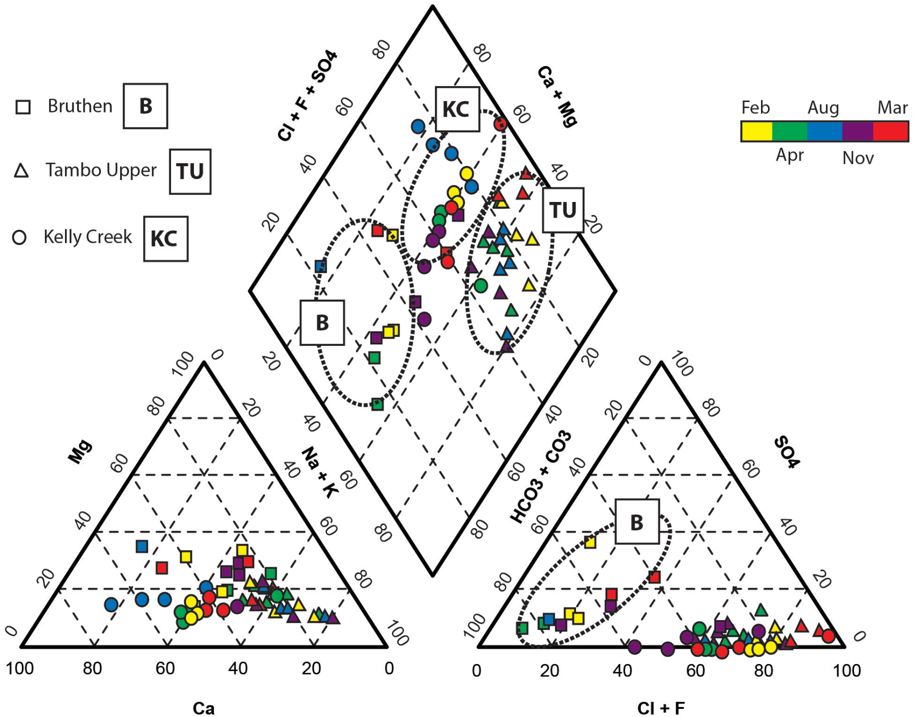

Fig. 5. Piper plot of bank water from the Tambo River. Black markers = HCO_3 measured, grey and white markers = HCO_3 calculated via charge balance.

HESSD
11, 1651–1691, 2014

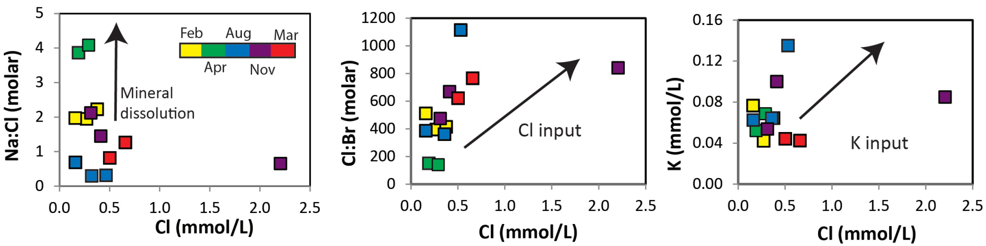

Fig. 6. Trends in major ion chemistry at Bruthen indicating mineral dissolution, the input of Cl into groundwater and the input of K into groundwater.

HESSD
11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.

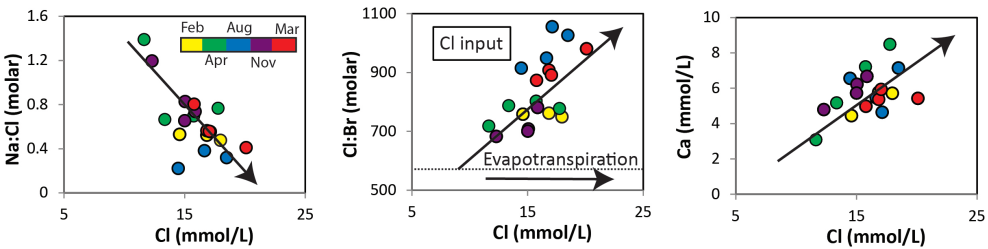

Fig. 7. Trends in major ion chemistry at Kelly Creek indicating Cl inputs during increased rainfall.

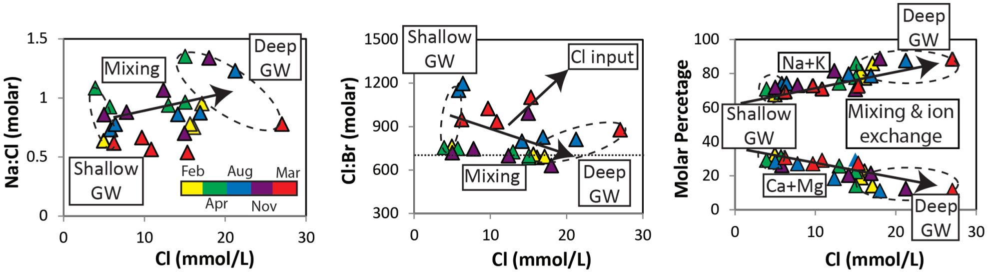

Fig. 8. Trends in major ion chemistry at Tambo Upper indicating mixing between groundwater in the shallow, unconfined aquifer and groundwater from the deeper, semi-confined aquifer.

HESSD
11, 1651–1691, 2014

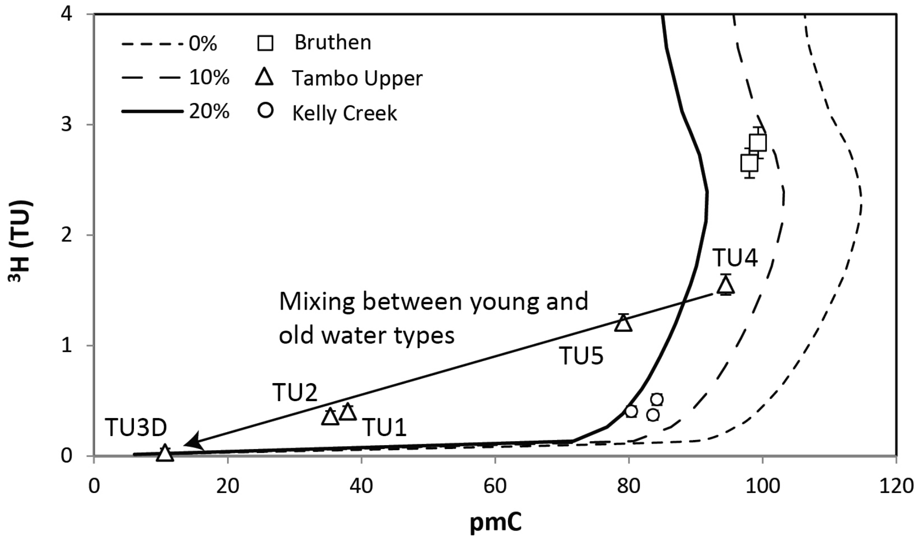

Fig. 9. Co-variance of ^{3}H and ^{14}C in groundwater and that predicted by Eq. (1) for 0, 10 and 20 % DIC input from closed systems calcite dissolution.

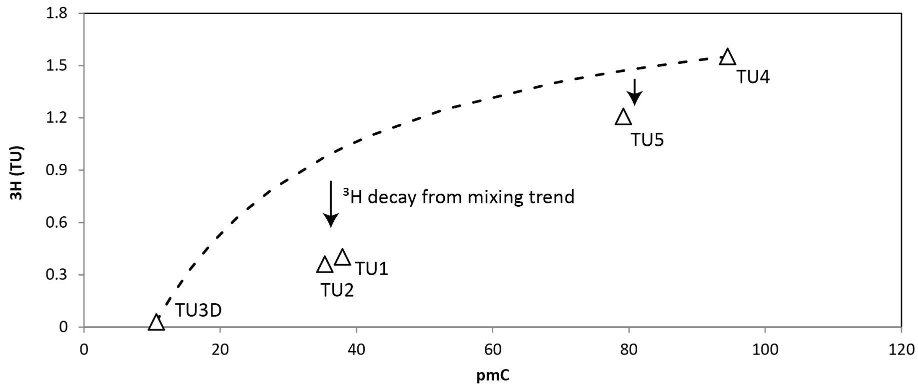

Fig. 10. ^{3}H and ^{14}C activities of groundwater at Tambo Upper and predicted trend for mixing between deep groundwater (TU3D) and shallow groundwater (TU4). Curve based on DIC, ^{3}H and ^{14}C activities from Table 2.

HESSD
11, 1651–1691, 2014

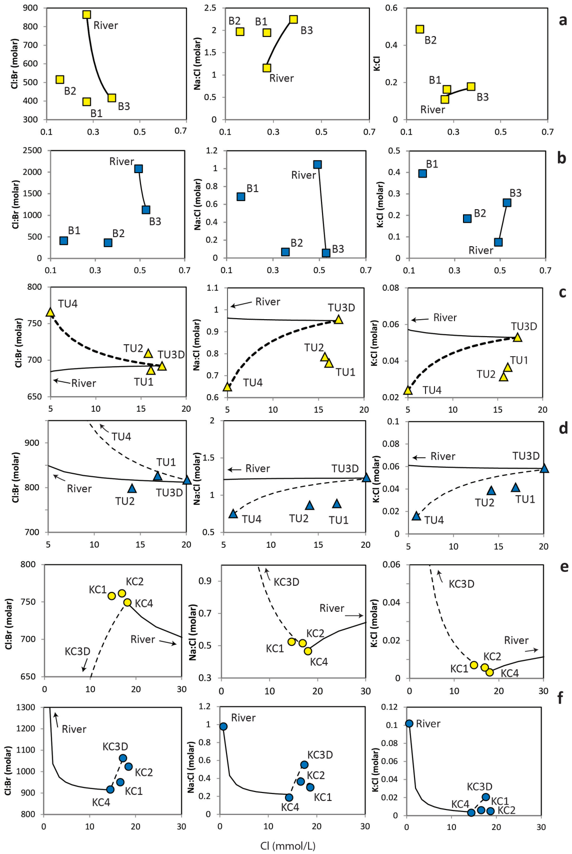

Fig. 11. Predicted mixing curves between river water and groundwater at Bruthen **(a, b)**, Tambo Upper **(c, d)** and Kelly Creek **(e, f)**. Yellow data points = February 2011, blue data points = August 2011.

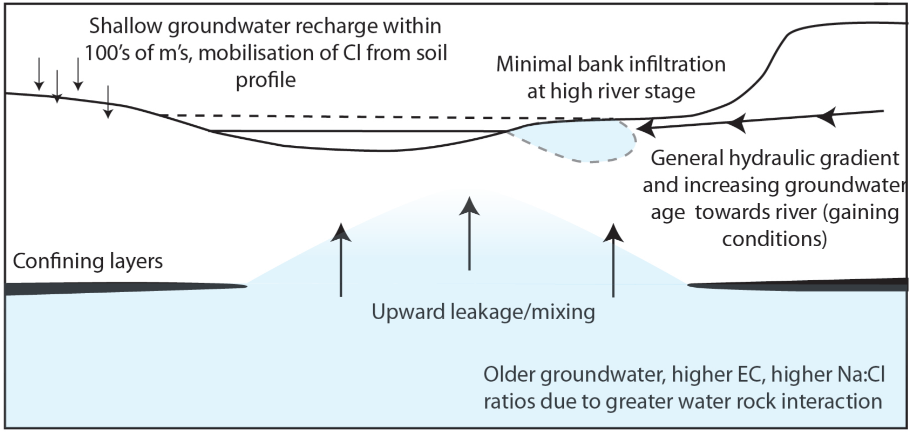

Fig. 12. Schematic representation of the Tambo River and major hydrogeochemical processes in the presence of discontinuous semi-confining layer at baseflow (solid line) and high flow (dashed line) conditions.

HESSD
11, 1651–1691, 2014

Residence times and mixing of water in river banks

N. P. Unland et al.