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 years) groundwater from a semi-confined aquifer and younger groundwater (<100 years) 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 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; McCallum et al., 2010; 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 (Pinder and Sauer, 1971). In addition, bank waters may represent a source of nutrients or contaminants derived from the river that are gradually released following diminishing of the flood peak. The volume and duration of bank storage for a given river stretch will depend on the flood peak height and the flood duration (Cooper and Rorabaugh, 1963), as well as the hydraulic conductivity of the alluvial aquifer and the hydraulic gradient between the aquifer and river (Cartwright et al., 2014; Chen et al., 2006; McCallum et al., 2010). Whiting and Pomeranets (1997) showed that deeply-incised narrow rivers with wider floodplains and coarse alluvial material have greater bank storage potential. 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. 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).

The concentrations of solutes in river water are commonly lower than those in groundwater and mixing between infiltrating river water and groundwater may produce zones of lower solute concentrations in river banks. McCallum et al. (2010) showed that solute concentrations of bank water may take months to return to their original concentration. During that time period, the water that flows from the banks into the river is a mixture of regional groundwater and bank storage waters. This suggests that there may be a component of bank storage waters in river banks with a residence time of months to years. Recognising that bank storage waters may contribute to rivers over long timeframes is important for estimating groundwater discharge by chemical mass balance. If the bank storage waters are chemically similar to surface water rather than regional groundwater, using the composition of regional groundwater as an end member will result in underestimation of the groundwater flux (Cartwright et al., 2014; McCallum et al., 2010; Unland et al., 2013).

While the concept of bank storage is well understood, accurately quantifying the volume of water that infiltrates the banks and the duration of bank return flows remains difficult. Many studies have focused on using analytical and numerical solutions to understand bank storage from variations in the river hydrograph and groundwater heads. 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 is proposed to 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). These studies commonly 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. Therefore, there is a need to document the extent and timescales of bank storage in specific catchments.

Geochemical processes occurring within river banks, such as the bacterial degradation of organic matter or the weathering of minerals can influence the concentrations of DOC, O_2, NO_3, Na, K and other major ions in near-river groundwater (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 alluvial aquifers is important when developing groundwater extraction systems for water supply (Hiscock and Grischek, 2002).

It is important to carry out studies of bank storage in a range of environments as variations in climate and river form translate into variations in river regime (e.g., frequency and duration of floods) that may cause differences in bank infiltration. Field studies focussed on bank storage and the dating of bank water in Australian catchments has been limited. Lamontagne et al.

(2011) and Cendón et al. (2010) indicated the presence of relatively young (<50 years) groundwater in river banks, and Cartwright et al., (2010) showed that preferential floodplain recharge is likely to occur near rivers during flooding. In contrast, groundwater in upland catchments in Australia has been shown to have relatively long residence times (Atkinson et al., 2013). This study investigates bank storage processes in the Tambo River catchment, Victoria, Australia. The objectives of the study are to use the geochemistry of groundwater in the banks of the Tambo River at different discharges in order to: (1) define the major processes controlling the chemistry of water stored in river banks; (2) determine the age and likely sources water stored in river banks; and (3) identify the factors controlling bank storage and the distance over 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 will help in understanding bank storage processes in general.

1.1 Study area

Investigations took place on the middle catchment of the Tambo River in southeast Australia. 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). 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, the discharge of the Tambo River ranged from 10^{10} to 10^{11} m^3/sec (Victorian Water Resources Data Warehouse, 2013); however significant rainfall during August 2011 and March 2012 resulted in discharge events that peaked at greater than $5x10^{12}$ m^3/sec (Fig. 2).

The upper catchment of the Tambo River drains indurated Ordovician and Devonian turbidites and granites of the Eastern Victorian Uplands, while the lower and middle catchment is in the Gippsland Basin (Birch, 2003). The near-river sediments in the lower and middle catchment comprise coarse Quaternary alluvial gravels and sands. These recent alluvial sediments overly the Plio-Pleistocene Haunted Hill Gravels which represents the shallowest regional-scale aquifer in the Gippsland Basin. Clay layers throughout the Quaternary alluvium and Haunted Hill Gravels act as aquitards, separating a number of aquifer horizons that range from unconfined to fully confined (Hocking, 1976). Deeper aquifer systems in the lower Tambo catchment include the Late Miocene to Early Pliocene Boisdale Formation and the Ologocene to Pliocene Jemmys Point, Tambo River and Lake

Wellington Formations (Leonard, 1992; Birch, 2003; Hofmann and Cartwright, 2013). These deeper aquifer systems are separated from the near-surface sediments by clay layers that locally form aquitards. Regional groundwater flow in all aquifers is from the margins of the Gippsland Basin towards Lake King (Southern Rural Water, 2013). Overall, the lower and middle reaches of the Tambo River are gaining especially at low river discharge and hydraulic gradients at these times in the shallow alluvial sediments are towards the river (Unland et al., 2013). The regional groundwater from the deeper aquifers is artesian and head gradients around Lake King (Fig. 1) are upwards (Water Resources Data Warehouse, 2013; Southern Rural Water, 2013). The regional groundwater also has a high salinity (total dissolved solids up to 20,000 mg/L), is generally anoxic, and has a significantly higher temperature (up to 40 ^{o}C) than that of the shallow groundwater. Springs fed by this deeper groundwater are recorded around Lake King; however, these are rare elsewhere (although as discussed below, the regional groundwater may mix with the shallow groundwater and river water in the banks at Tambo Upper, Fig. 1). The majority of groundwater that discharges into the middle reaches of the Tambo River is most likely derived from the shallower aquifers (Southern Rural Water, 2013) and the flow is part of a local rather than regional system (c.f., Toth, 1963). This is consistent with the presence of clays in the Gippsland Basin sediments that produce a compartmentalised aquifer system.

Transects of groundwater monitoring bores were set up at three locations on the river banks of the middle Tambo River (Fig. 1, 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 depth, 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 installation of the shallower (<15 m deep) bores installation via auger drilling indicate that the alluvial aquifer at all transects is dominated by coarse sands with 10 to 20 cm thick clay layers dispersed throughout. Deeper bores were constructed via mud rotary drilling which tends to preferentially return coarser sediment fractions. While clay layers are harder to identify, the groundwater at >20m depth is artesian (see below) which suggests the presence of a clay-rich confining layer. All bores are screened in the alluvial sands/gravels and (except for the deeper bore at Tambo Upper) probably sample the local shallow groundwater rather than the deeper regional groundwater.

2 Methods

Bore and river elevations 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 bores 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 took place at 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 minutes with an impeller pump at a rate of 4 L/minute and then allowing groundwater heads to recover. Changes to groundwater levels were recorded using a Rugged TROLL 200 logger logging at 1 second intervals. Hydraulic conductivity was calculated using the Hvorslev method outlined by Fetter (1994). The anisotropy ratio of the sediments was not taken into account as it is not explicitly known and the aim was to provide a general characterisation of the hydraulic properties of the sediments. Commonly, the recovery time was <10 seconds and the estimated hydraulic conductivities are likely to be minimum values.

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 hours of sample collection by titration using a Hach digital titrator and reagents with a precision of ±5%. Anion concentrations were determined on filtered (0.45µ cellulose nitrate filters) samples that using a Metrohm ion chromatograph at Monash University, Clayton, with a precision of ±2% estimated by replicate analysis. Cation concentrations were determined on samples that were filtered and acidified to pH <2 using twice distilled 16 M nitric acid by the Varian Vista ICP-AES at the Australian National University or the Thermo Finnigan X series II, quadrupole ICP-MS at Monash University. 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 hours in a ThermoFinnigan Gas Bench. δ^2H values of water were measured via reaction with Cr at 850°C using 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. The precision (1σ) of the analyses based on replicate analyses is $\delta^{18}O = \pm0.2$‰, $\delta^2H = \pm1$‰.

Samples for ^{14}C and ^3H analysis were collected during the April 2011 sampling period (Fig. 2). ^3H water samples were distilled and electrolytically enriched prior to analysis by liquid scintillation (Morgenstern and Taylor, 2009). The ^3H concentrations were expressed in tritium units (TU) with uncertainties ranging from ~25% at the quantification limit (0.13 TU) to <6% for ^3H 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 subsequently graphitised. The graphite targets were analysed using the STAR AMS at ANSTO following Fink et al. (2004). The activity of ^{14}C is expressed as percent 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 AHD in August 2011. There was less than 6 cm difference in elevations across the transect during any given sampling period. Groundwater elevations in B1 and B2 were within 3 cm of each other during all sampling periods, while elevations in B3 were 2 to 6 cm higher than in B1 and B2 (Fig. 3). Groundwater elevations at Bruthen were 3 to 4 cm higher than river elevations during all sampling periods except during March 2012 when groundwater levels were approximately 90 cm higher than the river elevation. Rising head slug tests at this transect indicate a hydraulic conductivity of ~8.5 x 10^{-3} m/s.

Groundwater elevation in the shallow bores at Tambo Upper ranged from 3.30 m AHD in April 2011 to 4.80 m AHD in August 2011. Groundwater elevations in TU5, TU2 and TU1 in individual campaigns were within 3 to 5 cm of each other. Groundwater elevations in TU4 were the lowest in the transect, averaging 3.92 m AHD 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 within the alluvial gravel that has higher heads than the surficial aquifer. During February and April 2011, groundwater elevations in this bore were 4.85 m and 4.69 m AHD, respectively, while in all other sampling periods the elevation exceeded that of the casing (5.04 m AHD). Groundwater elevations at Tambo Upper were higher than the river elevation during all periods except April 2011. Groundwater elevation closest to the river (TU1) was 32 cm higher than river elevation in February 2011, 5 cm lower then river water during April 2011, 3 cm higher than river elevation during August 2011 and 99 cm greater than river elevation during March 2012. Slug tests at this transect yielded hydraulic conductivities ranging from 5.1×10^{-4} to 8.6×10^{-5} m/s in the surficial aquifer, and 1.9×10^{-5} m/s in the semi-confined aquifer.

At Kelly Creek, groundwater levels in the shallower bores ranged from 3.07 m AHD in April 2011 to 3.68 m AHD 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 AHD in February 2011 to 4.33 m AHD in November 2011. Slug tests at this transect indicate hydraulic conductivities ranging from 2.4 to 3.4×10^{-5} m/s.

3.2 Electrical conductivity

Groundwater EC values at Bruthen ranged from 136 to 607 µS/cm. Groundwater at B3 was generally the most saline, ranging from 261 to 607 µS/cm, while that from B1 ranged from 136 to 293 µS/cm. Shallow groundwater at Tambo Upper was more saline than that from Bruthen, ranging from 717 µS/cm to 2,682 µS/cm. Shallow groundwater at Tambo Upper was also generally more saline closer to the river than further from the river, averaging 2,110 µS/cm at TU1 and TU2 over the study period, compared to 980 µS/cm at TU4 and TU5. Deeper groundwater at Tambo Upper was consistently the most saline in the transect, ranging from 2,490 µS/cm in April 2011 to 3,250 µS/cm in August 2011. Groundwater at Kelly Creek was generally more saline than Tambo Upper, with EC values ranging from 2,000 to 2,777 μS/cm over the study period. Groundwater EC values were less variable at Kelly Creek and did not generally increase or decrease with proximity to the Tambo River.

3.3 Stable isotopes

$\delta^{18}O$ and $\delta^{2}H$ values of groundwater and river water generally plot close to the both local (LMWL) and global meteoric water lines (GMWL); however river water at Kelly Creek from February 2011 plots to the right of the GMWL (Fig. 4). Groundwater and surface water samples from February 2011 define an array with a slightly shallower trend than the LMWL, while those from March 2012 define an array with a steeper trend than the LMWL. $\delta^{18}O$ 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 further from the river at B2 and B3 (average = -5.3±2.2 ‰). Stable isotope values were less variable at Tambo Upper with $\delta^{18}O$ values ranging from -5.3 to -6.3 ‰. Groundwater at TU3D, TU1 and TU2 has lower $\delta^{18}O$ values (average = -6.0±0.2 ‰) than at TU4 and TU5 (average = -5.6±0.2 ‰). Shallow groundwater at Kelly Creek showed little variability, with $\delta^{18}O$ values ranging from -5.3 to -5.8 ‰ during the study. The deeper groundwater at Kelly Creek had slightly lower $\delta^{18}O$ values (average = -5.9±0.5 ‰) than the shallow groundwater. River water had lower $\delta^{18}O$ values than groundwater during all sampling periods except February 2011. During this period, $\delta^{18}O$ values of river water increased form -5.7 ‰ at Bruthen to -3.4 ‰ at Kelly Creek. There was less variation in the river water at other times during the study, with $\delta^{18}O$ values ranging from -7.9 to -7.5 ‰.

3.4 ^{3}H and ^{14}C

^{3}H 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. ^{3}H activities were higher in groundwater further from the river at Tambo Upper at TU4 and TU5 (^{3}H activities 1.6 and 1.2 tritium units, respectively) compared to groundwater closer to the river at TU1 and TU2 (^{3}H activities 0.40 and 0.36 tritium units, respectively). ^{3}H activities in the deeper 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). ^{3}H 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 locations.

Groundwater from Bruthen is HCO_3-Ca-Na type (Fig. 5). NO_3, Br and Cl are the most variable anions over time, with relative standard deviations of 120, 91 and 82% of the mean concentrations, respectively. Na is the most variable cation at the site with relative standard deviations of 53% of the mean concentrations. 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 1,000 with increasing Cl concentrations (Fig. 6).

Groundwater from Tambo Upper is Cl-Na-Ca type (Fig. 5). NO_3 is the most temporally variable anion at Tambo Upper, with a relative standard deviation of 97% of the mean. In contrast, temporal variations in cations are relatively low at Tambo Upper, with relative standard deviations of between 15 and 21% of the mean values. 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, K concentrations below 0.2 mmol/L and Na concentrations below 7 mmol/L (Table 1). Deeper groundwater from Tambo Upper (TU3D) has Cl concentrations greater than 15 mmol/L, K concentrations greater than 0.8 mmol/L and Na concentrations greater than 16 mmol/L. Groundwater closer to the river at Tambo Upper (TU1 and TU2) has concentrations of Na, K, Mg and Ca that are intermediate between those of groundwater at TU3D and groundwater at TU4 and TU5.

Shallow groundwater at Kelly Creek is Cl-Ca-Na type. SO_4 is the most variable anion at Kelly Creek, with relative standard deviations of between 108 and 206% of mean values at each bore. Na is the most variable cation at Kelly Creek, with relative standard deviations of between 22 and 43% of mean values. At Kelly Creek, shallow groundwater has Cl concentrations that range from 11.6 to 20.1 mmol/L and Ca concentrations that range from 3.1 to 8.5 mmol/L (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 ~1,000 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

Na:Cl ratios were higher in the groundwater at Bruthen and Kelly Creek during periods of lower rainfall compared to periods of higher rainfall (Figs 6 and 7). This suggests that the groundwater present in the banks during periods of low rainfall has longer residence times that facilitate water-rock interaction, specifically the dissolution of Na-bearing minerals such as plagioclase (Edmunds, 2009; Herczeg et al., 2001). The same trend is also apparent in the deeper groundwater at Tambo Upper (Fig. 8). Cl:Br ratios at Bruthen and Kelly Creek increase with increasing Cl concentrations (Figs 6 and 7). As evapotranspiration, which is the dominant process that controls groundwater salinity in southeast Australia (Herczeg et al., 2001; Cartwright et al., 2007, 2010), does not impact Cl:Br ratios, this implies the addition of Cl from an external source. Halite dissolution is a potential Cl source; however, there are no obvious stores of halite in the catchment. 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), which would be not be expected for a KCl source; however, K may be removed from waters recharging through the soils by vegetation (e.g., Schachtman and Schroder, 1994) or sorption onto clay minerals such as 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 the land surface and/or the soil profile into shallow groundwater (c.f., Panno et al., 2006).

Mixing between deeper groundwater (TU3D) and shallow groundwater (TU4) appears to dominate the chemical variability of groundwater throughout the rest of the transect at Tambo Upper (Fig. 8). The deeper groundwater has elevated Na:Cl and K:Cl ratios, likely to be attributed to greater residence times and Na and K mineral dissolution. Deeper groundwater is also relatively saline (17.11 to 27.03 mmol/L) compared to shallower groundwater at TU4 (3.94 to 6.24 mmol/L). Groundwater throughout the rest of the transect contain intermediate Cl concentrations and cation to chloride ratios, as is consistent with mixing between the two end members. It is also apparent that the relative proportion of the deeper groundwater end member in the bank waters at Tambo Upper increases the during wetter periods in August 2011 and March 2012, suggesting that hydraulic loading of the deeper, semi-confined aquifer is driving increased flow of deeper groundwater into the overlying alluvial aquifer at these times. As indicated in section 3.5, high variations in NO_3 concentrations were observed both temporally and spatially across the transects. These variations were not systematic with changing hydrological conditions or other major ions, suggesting that perhaps changing redox conditions have impacted the observed NO_3 concentrations. However, as redox conditions were not recorded and multi species analysis of N were not undertaken, these processes remain unresolved.

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, present-day ^{3}H activities are taken to be 3.2 tritium units which is the weighted average rainfall ^{3}H activity for July 2005 to June 2011 in the Melbourne area (Tadros et al., 2014), and we assume that pre-bomb pulse tritium activities were similar to these (Allison and Hughes (1977). For intervening years, the mean weighted average of ^{3}H concentration of precipitation in Melbourne was taken as that of local precipitation with the record extrapolated for years with no data (Cartwright et al., 2013). 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).

Lumped-parameter models are commonly used to describe groundwater flow in shallow unconfined and semi-confined aquifers (Małoszewski and Zuber, 1991; Małoszewski and Zuber, 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, exponential flow models assume a vertical stratification of groundwater ages in an aquifer and are 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 bores in unconfined to semi-confined aquifers screened below the water table that do not sample the shallowest groundwater that has very short residence times (Morgenstern, 2010; Cartwright and Morgenstern, 2012).

For the EPFM the activity of ^3H or ^{14}C at time t (C_t) is given by:

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

where C_i is the initial ^3H or ^{14}C activity, λ is the decay constant (5.63 x 10^{-3} yr^{-1} for ^3H , 1.21 x 10^{-4} yr^{-1} for ^{14}C), τ is the transit time, and g(τ) is the system response function. The system response function is given by:

$$g(\tau) = 0 \qquad \text{for } \tau < T(1\text{-}f) \qquad \text{and} \qquad (2a)$$

$$g(\tau) = (fT)^{-1}\, e^{(-\tau/(ft_t)+1/f-1)} \qquad \text{for } \tau > T(1\text{-}f) \qquad (2b)$$

where T is the mean residence time and *f* is the ratio of exponential flow to piston flow for the total flow volume (Zuber et al., 2005). *f* was estimated at 0.8 for shallow bores neighbouring the Tambo River on the basis of bore depth, screen length and aquifer lithology (c.f., Cartwright and Morgenstern, 2012; Cartwright et al., 2013).

While there are some differences in the estimated groundwater residence times between different types of flow models, the predicted variation in ^{14}C and ^3H activities are similar in all flow models that involve attenuation of the bomb-pulse peak of ^3H and ^{14}C during flow (e.g., as discussed by Cartwright et al., 2013). A similar covariance of ^{14}C and ^3H activities would be obtained using a dispersion model (Zuber et al., 2005) or the renewal rate model of

Le Gal La Salle et al. (2001; Fig. 9). The ^{14}C and ^{3}H activities also constrain mixing within the groundwater system (Le Gal La Salle et al., 2001; Cartwright et al., 2007, 2010, 2013). 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 that lowers $a^{14}C$ but which does not impact ^{3}H activities produces a similar displacement.

The co-variance between ^{3}H and ^{14}C for groundwater samples is shown in Fig. 9. Groundwater from Bruthen and Kelly Creek has ^{3}H and ^{14}C activities lie close to the predicted co-variance curves. Groundwater in aquifers dominated by siliclastic sediments typically undergo up to 20% closed system calcite dissolution (Vogel, 1970; Clark and Fritz, 1997) and if that is the case for this groundwater, it would explain the slightly lower than expected ^{14}C activities. Regardless, there can be very limited mixing between older and younger groundwater at these localities. By contrast, groundwater from TU1, TU2 and TU5 at Tambo Upper follow a trend consistent with the mixing between younger groundwater in the shallow aquifer (TU4) and older groundwater in the deeper semi-confined aquifer (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 years. Groundwater from Kelly Creek has longer residence times (96 to 100 years), 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 years. 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 years at Bruthen and <15 years at Kelly Creek. Uncertainties in groundwater age based on the uncertainty of ^{3}H activities were <1 year at Bruthen (based on an uncertainty of 0.14 tritium units) and <1.5 years at Kelly Creek (based on an uncertainty of 0.04 tritium units). As deeper groundwater from Tambo Upper site is ^{3}H 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) pg. 206) are ~17,200 years.

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 years at KC4 to 100 years at KC2. The age of groundwater at KC1 is 99 years 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/year towards the river.

The ^{3}H 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 deeper 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 ^{3}H activities are lower than expected due to the decay of ^{3}H in shallow groundwater. Exponential piston flow modelling of water at TU1 and TU2 indicates that a residence time of ~20 years would be required to cause the observed deviation in ^{3}H activities from the mixing trend shown in Fig. 10. This suggests a horizontal flow rate of 1.8±0.6 m/year towards the Tambo River at the Tambo Upper transect. This is consistent with shallow groundwater recharge on the floodplains of the Tambo River and groundwater flow towards the river, which is expected given the gaining nature of this section of the river (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, groundwater ages increase towards the Tambo River at Kelly Creek and Tambo

Upper, while groundwater a Bruthen was approximately the same age at 18 m 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 at and immediately prior 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, deeper 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 deeper or shallow groundwater further form the river. For example, during both February and August at Bruthen, Cl:Br, Na:Cl and K:Cl ratios from groundwater at B1 and B2 plot to the left the curves expected for mixing between river water and groundwater further from the river at B3 (Fig. 11a and b). This is partly due to the higher Cl concentrations in river water and groundwater from B3 (which range from 0.3 to 0.5 mmol L^{-1}) compared to groundwater from B1 and B2 (which range from 0.1 to 0.35 mmol L^{-1}). If mixing between river water and groundwater at B3 was occurring, Cl concentrations at B1 and B2 would be intermediate between those in the river and at B3.

The same is true at Tambo Upper where Cl concentrations in groundwater at TU1 and TU2 are higher (~ 15 mmol L^{-1}) than in river water or groundwater further from the river at TU4 (<10 mmol L^{-1}) during both baseflow and flood conditions (Fig. 11c and d). The same is true for EC values which are lower in river water and at TU 4 (ranging from 120 to 881 µS cm^{-1} over the study) compared to EC values at TU1 and TU2 which ranged from 1,350 to 2,682 µS cm^{-1} over the study. Again, if mixing between river water and water at TU4 had a significant impact on groundwater chemistry at TU1 and TU2, Cl concentrations and EC values would be expected be intermediate between the river water and groundwater from TU4. Instead, groundwater in TU1 and TU2 has a geochemistry that is similar to that which would be expected for mixing between TU4 and TU3D (Fig. 11c and d). As asserted in section 4.1, such mixing is implied by the ^{3}H and ^{14}C data. Similarly, $\delta^{2}H$ and $\delta^{18}O$ values of groundwater close to the Tambo River do not decline after significant flooding, as would be expected for the infiltration of river water with the lower $\delta^{2}H$ and $\delta^{18}O$ values observed during flooding.

These observations indicate that river water penetrates <5 m into the banks during flooding suggesting limited bank infiltration. The absence of significant bank infiltration is consistent with results of 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). This upward leakage occurs close to the river where erosion has removed some of the confining layers (Rinaldi and Darby, 2007). It is 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 (~1 week after the flood peak) is significantly shorter than the several weeks to months predicted by modelling (e.g. Cooper, 1963; Doble et al., 2012; McCallum et al., 2010; Whiting and Pomeranets, 1997).

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 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, $\delta^{2}H$ and $\delta^{18}O$ 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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Site	Date	EC µS/cm	Level m	Dist. m	F mg/L	Cl mg/L	Br mg/L	NO_3 mg/L	SO_4 mg/L	HCO_3 mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	O $\delta^{18}O$	H $\delta^{2}H$	^{3}H TU	^{14}C pMC	$\delta^{13}C$ ‰	MGRT years
R	**Feb-11**	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-11**	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-11**	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-11**	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-11**	109	7.61	0.00	0.05	3.63	0.01	0.11	0.90											
1	**Apr-11**	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-11**			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-11**	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-11**	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-11**	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-11**	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-11**	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-11**	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-11**	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-12**	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-12**	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-12**	136	8.36	17.6							6.87	2.43	4.91	2.27						
3	**Mar-12**	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				

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 section 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**
		μS/cm	**m**	**m**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**$\delta^{18}O$**	**δ^2H**	**TU**	**pMC**	**‰**	**years**
R	**Feb-11**	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-11**	2,395	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-11**	2,155	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				
3D	**Feb-11**	2,656	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-11**	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-11**	1,023	3.89	37.87											-5.69	-38.8				
R	**Apr-11**	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-11**	2,210	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-11**	2,180	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
3D	**Apr-11**	2,488	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-11**	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-11**	1,043	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-11**	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-11**	2,682	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-11**	2,207	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				
3D	**Aug-11**	3,250	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-11**	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-11**	1,039	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-11**	2,018	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-11**	2,168	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				
3D	**Nov-11**	2,938	>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-11**	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-11**	1,337	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-12**	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-12**	1,350	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-12**	1,763	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				
3D	**Mar-12**	3,210	>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-12**	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-12**	1,320	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				

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 section 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
		µS/cm	m	m	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	$\delta^{18}O$	δ^2H	TU	pMC	‰	years
R	**Feb-11**	18,340	3.05	0	0.38	6,322	22.0	0.30	825	*899*	3,558	151	182.0	521	-3.38	-24.6				
1	**Feb-11**	2,004	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-11**	2,349	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				
3D	**Feb-11**		3.82	24.9							162	11.4	23.6	9.31	-5.81	-37.8				
4	**Feb-11**	2,364	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-11**	4,210		0	0.21	255	0.93	0.13	29.1	*8,690*	2683	153	403.7	116	-7.69	-45.5				
1	**Apr-11**	2,145	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-11**	2,455	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
3D	**Apr-11**	2,669	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-11**	2,099	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-11**	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-11**	2,568	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-11**	2,777	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				
3D	**Aug-11**	2,438	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-11**	2,717	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-11**	2,742		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-11**	2,542	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				
3D	**Nov-11**	2,738	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-11**	2,218	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-12**	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-12**	2,770		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-12**	2,495		17.9	0.41	605	1.53	0.10	1.11	*430*	219	3.72	237.8	32.8	-5.45	-32.8				
3D	**Mar-12**	2,345		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-12**	2,715		26.8	0.32	713	1.64	0.13	43.4	*24.3*	189	3.42	217.5	27.6	-5.62	-30.7				

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 section 4.3).

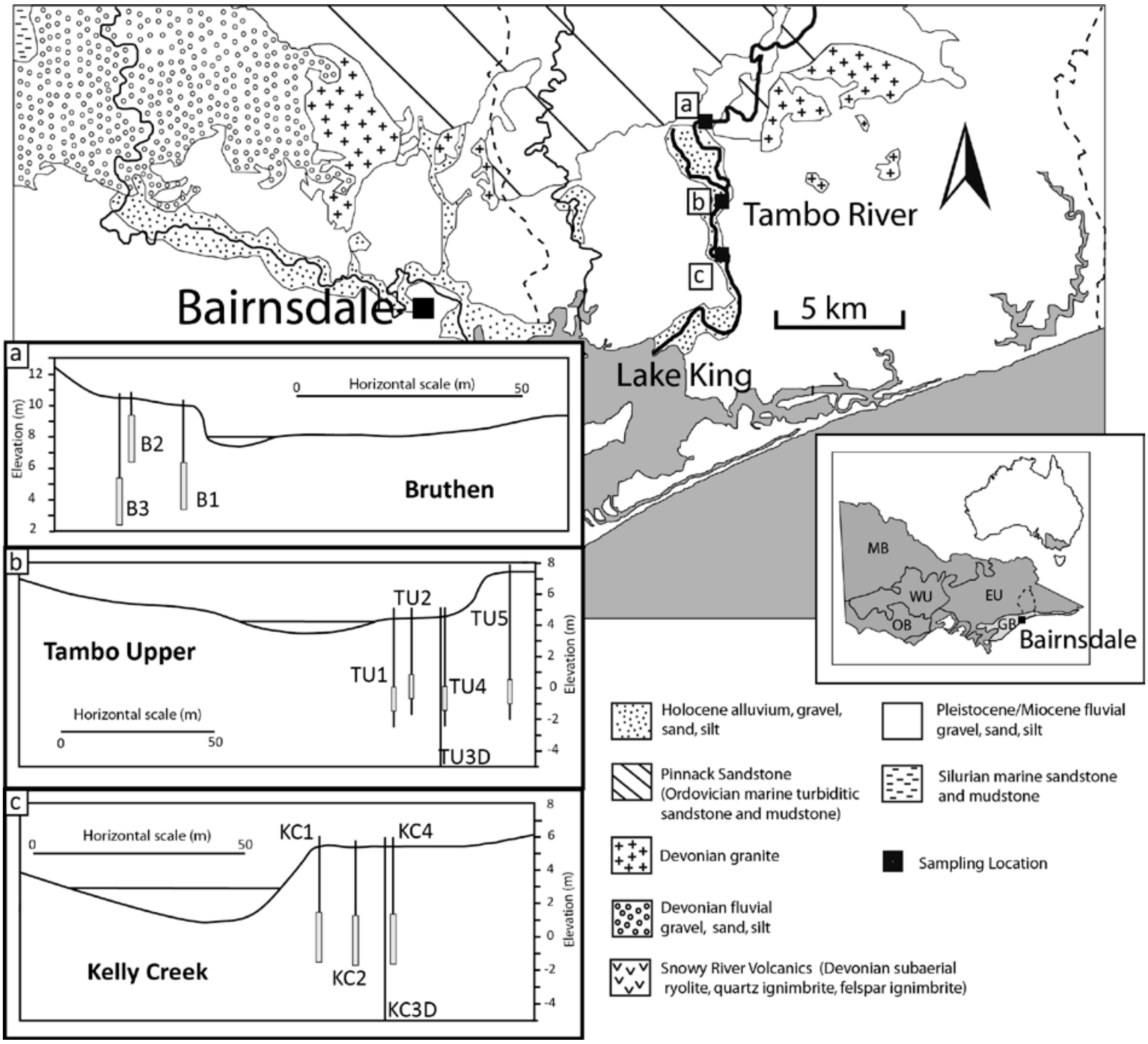

Figure 1. Location of field area and schematic cross sections of bore transects at Bruthen (a), Tambo Upper (b) and Kelly Creek (c). Screened sections indicated by open boxes. Dashed line = Tambo River basin boundary (transects orientated facing upstream).

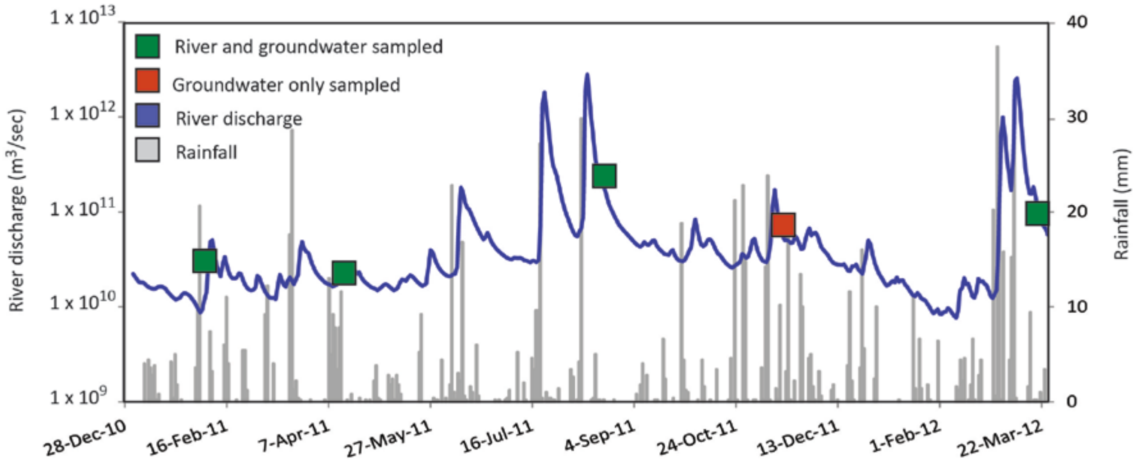

Figure 2. Surface and groundwater sampling frequency superimposed on Tambo River hydrograph (Battens Landing, station 223209 – Water Resources Data Warehouse, 2013) and rainfall (Bairnsdale Airport, station 85279 – Bureau of Meteorology, 2013).

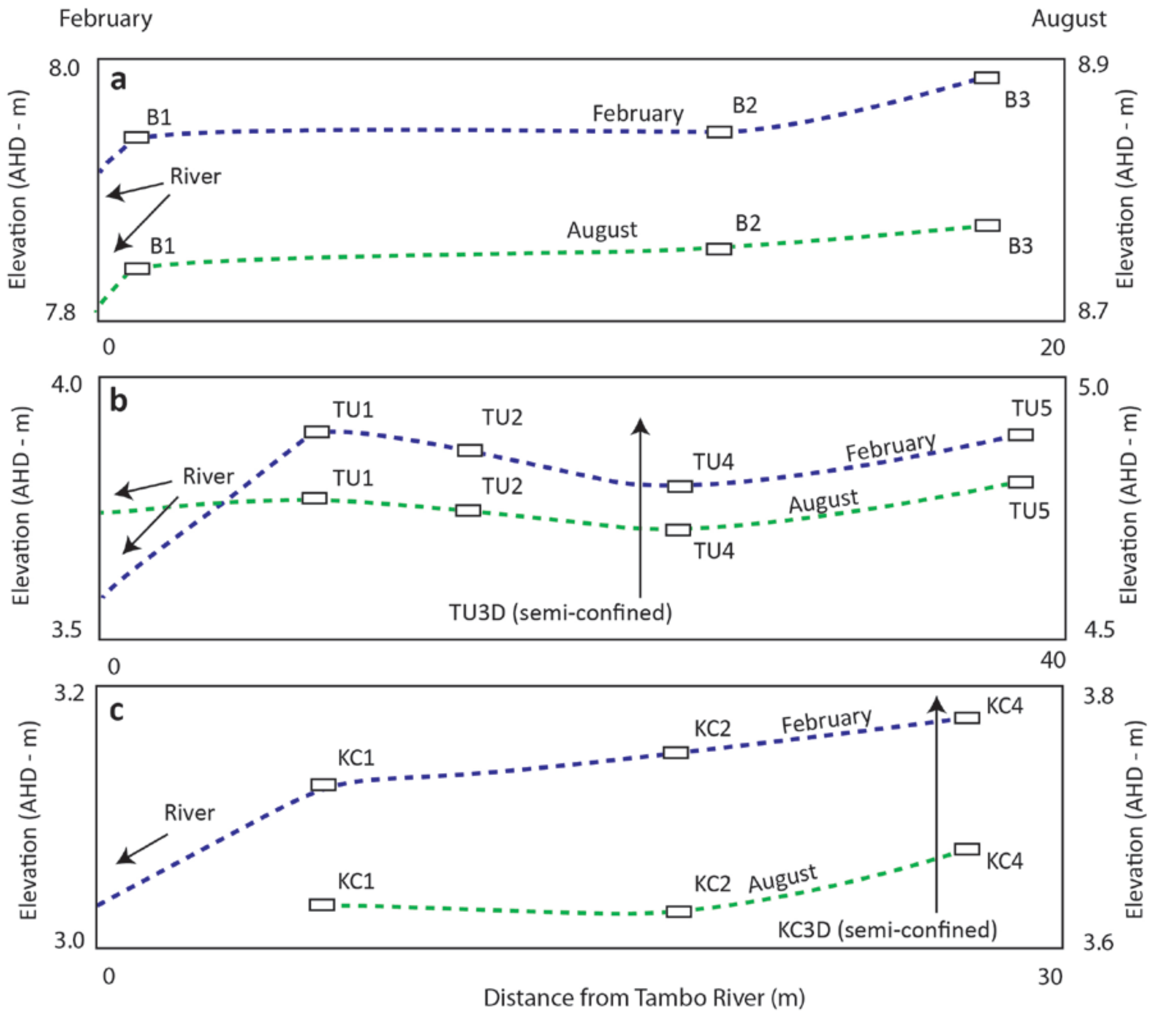

Figure 3. Groundwater elevations during February 2011 and August 2011 at Bruthen (a), Tambo Upper (b) and Kelly Creek (c). White rectangles = measured elevation, dashed lines = interpolated elevations.

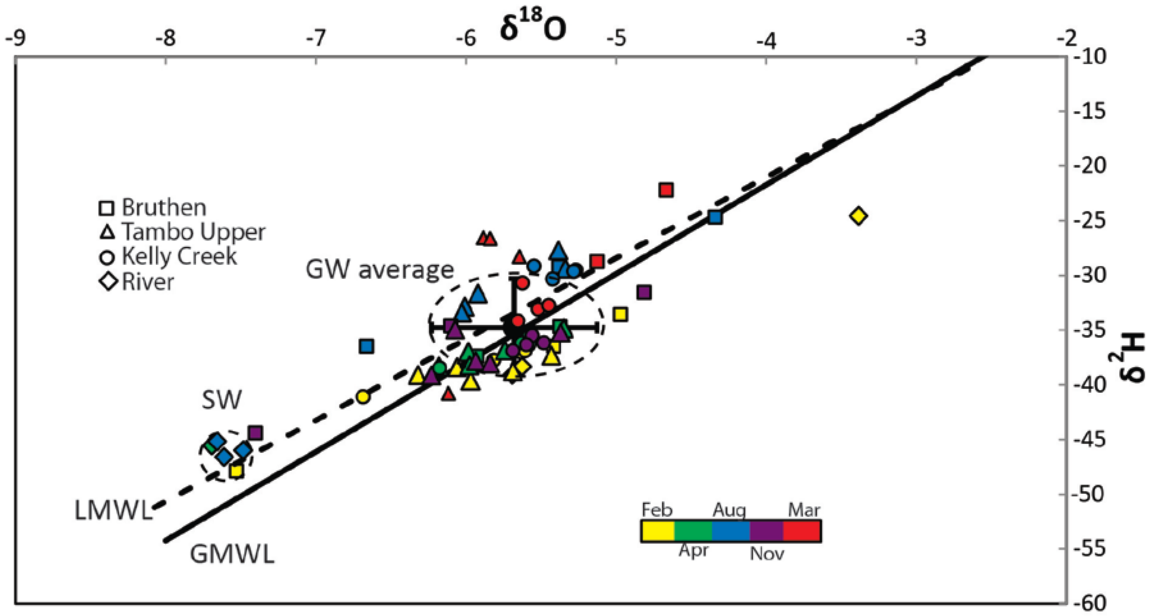

Figure 4. $\delta^{18}O$ and $\delta^{2}H$ values of bank water and river water from the Tambo River. LMWL defined by Melbourne meteoric water line in Hughes et al., 2012. Dashed lines indicate typical river water and bank water values.

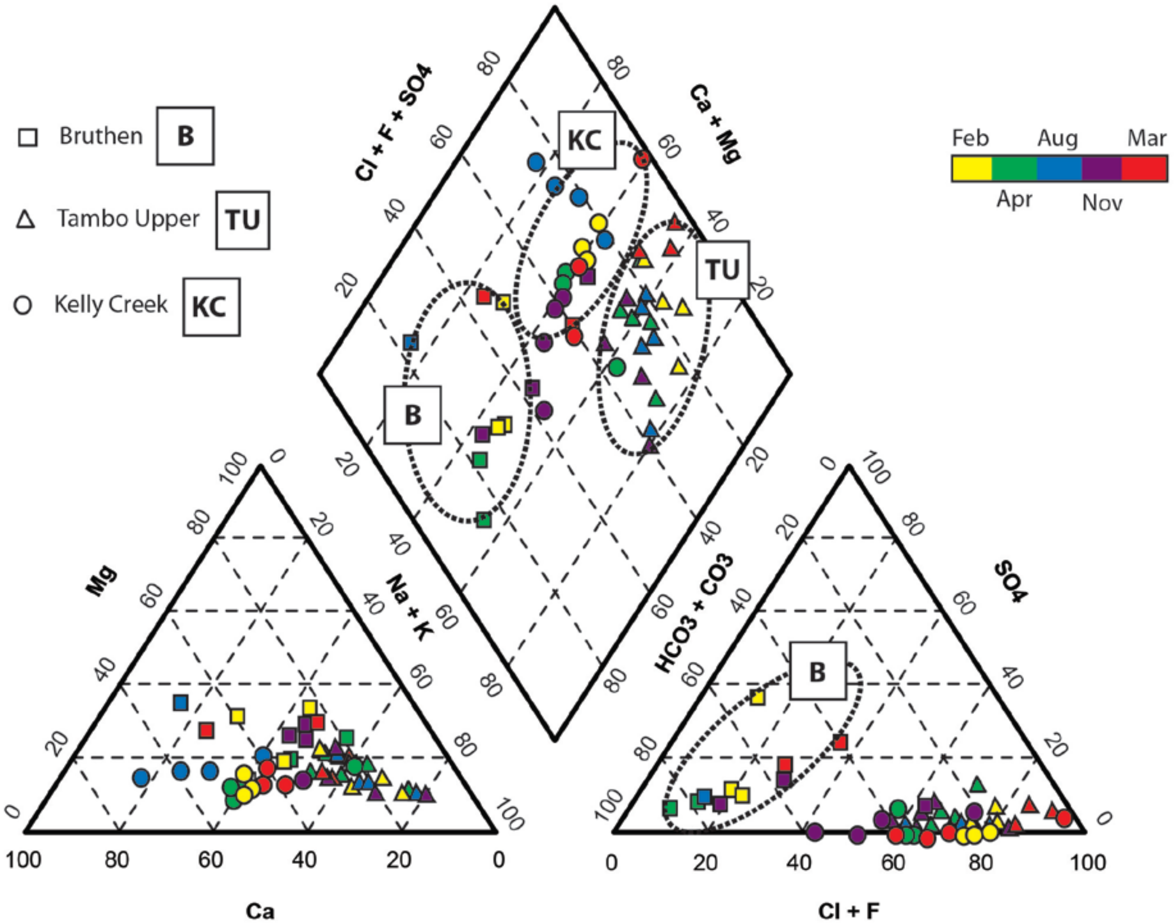

Figure 5. Piper plot of bank water from the Tambo River. Black markers = HCO_3 measured, grey and white markers = HCO_3 calculated via charge balance.

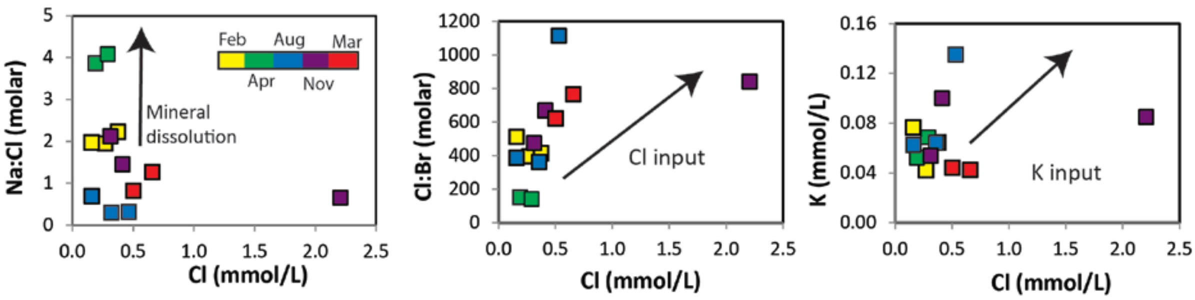

Figure 6. Trends in major ion chemistry at Bruthen indicating mineral dissolution, the input of Cl into groundwater and the input of K into groundwater.

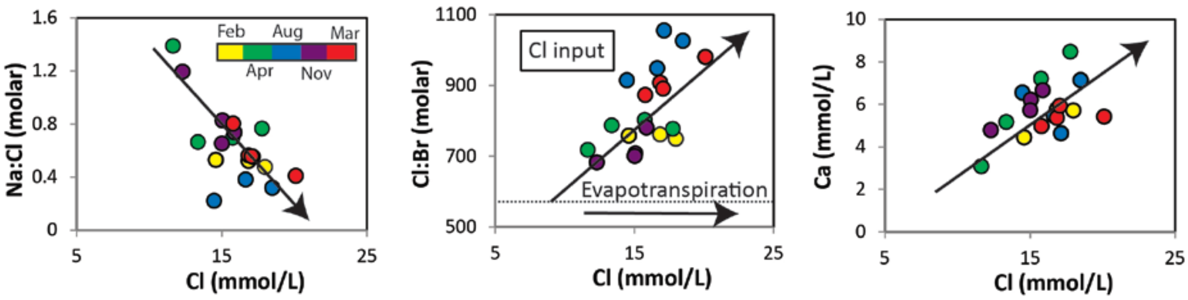

Figure 7. Trends in major ion chemistry at Kelly Creek indicating Cl inputs during increased rainfall.

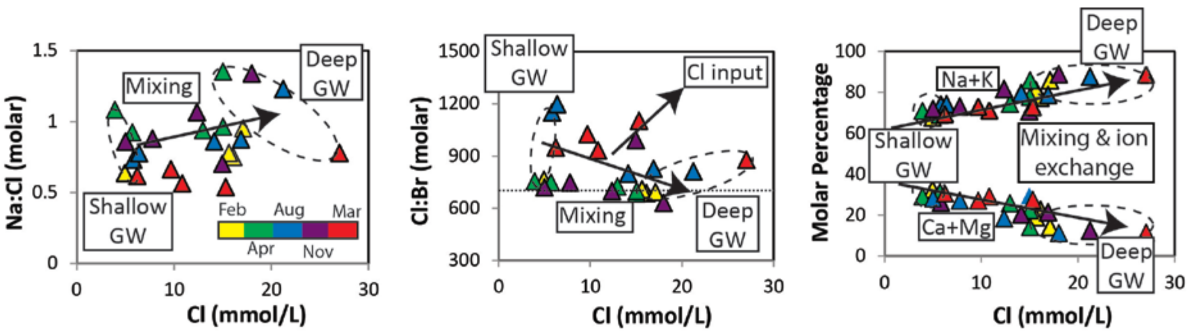

Figure 8. Trends in major ion chemistry at Tambo Upper indicating mixing between groundwater in the shallow, unconfined aquifer and groundwater from the deeper, semi-confined aquifer.

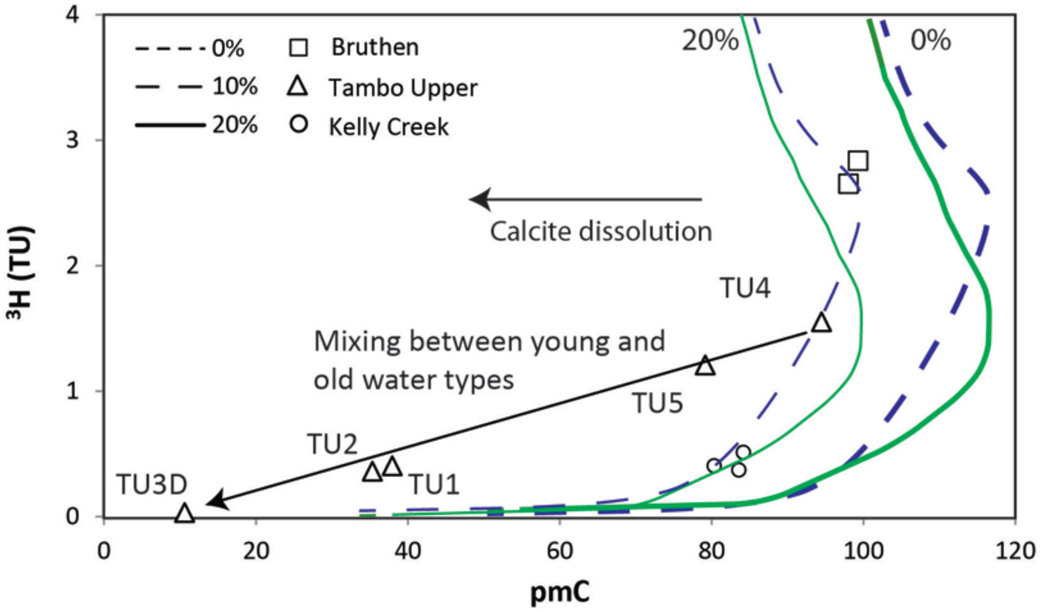

Figure 9. Co-variance of ^{3}H and ^{14}C in groundwater and that predicted by Eq. (1) (Solid lines) for 0% and 20% DIC input from closed system calcite dissolution. Dashed lines are the predicted of co-variance of ^{3}H and ^{14}C from the renewal rate model of Le Gal La Salle et al. (2001).

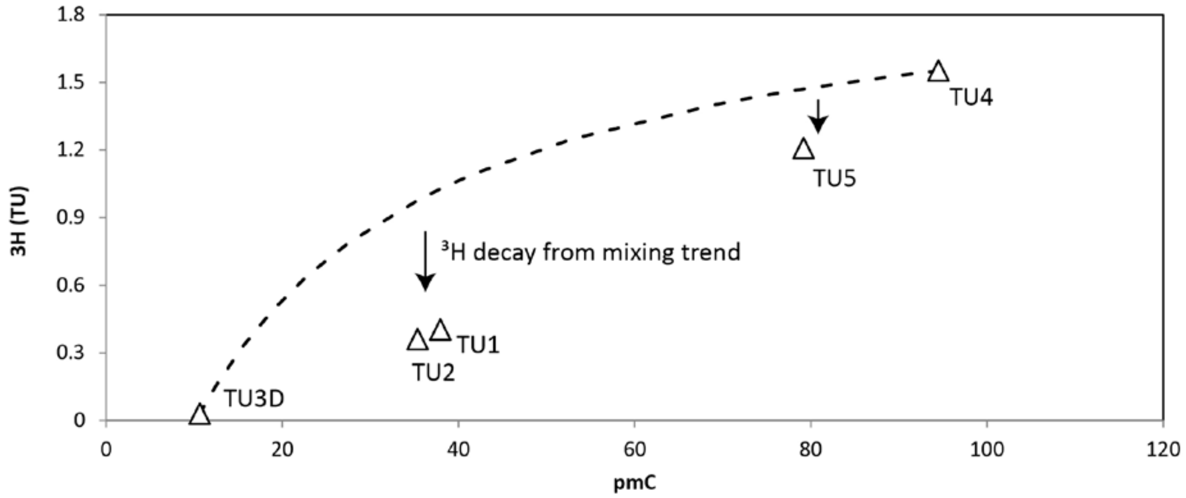

Figure 10. ^{3}H and ^{14}C activities of groundwater at Tambo Upper and predicted trend for mixing between deeper groundwater (TU3D) and shallow groundwater (TU4). Curve based on DIC, ^{3}H and ^{14}C activities from Table 2.

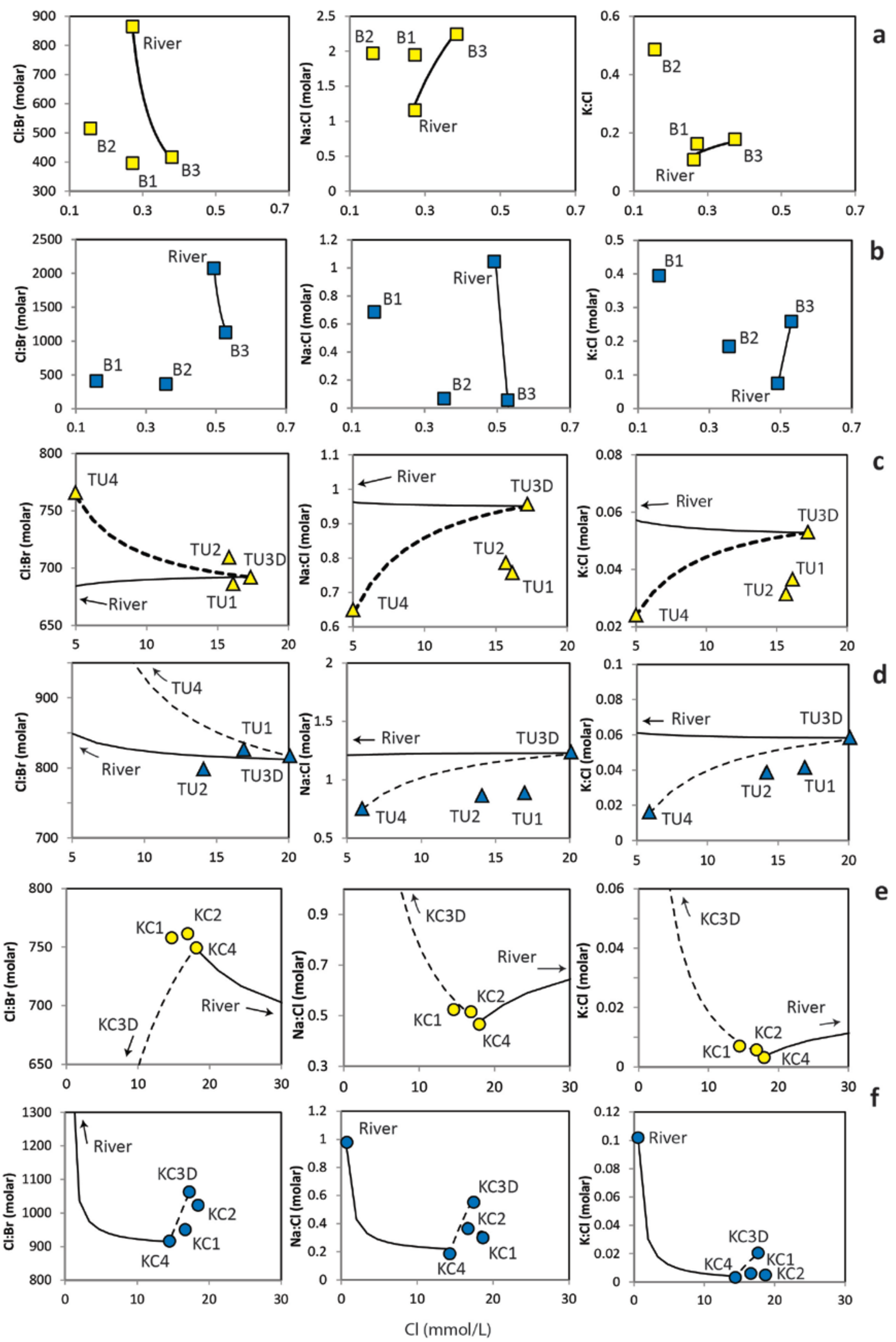

Figure 11. Predicted mixing curves between river water and groundwater at Bruthen (a,b), Tambo Upper (c,d) and Kelly Creek (e,f) constructed using the end-member compositions from Tables 1 to 3. Yellow data points = February 2011, blue data points = August 2011.

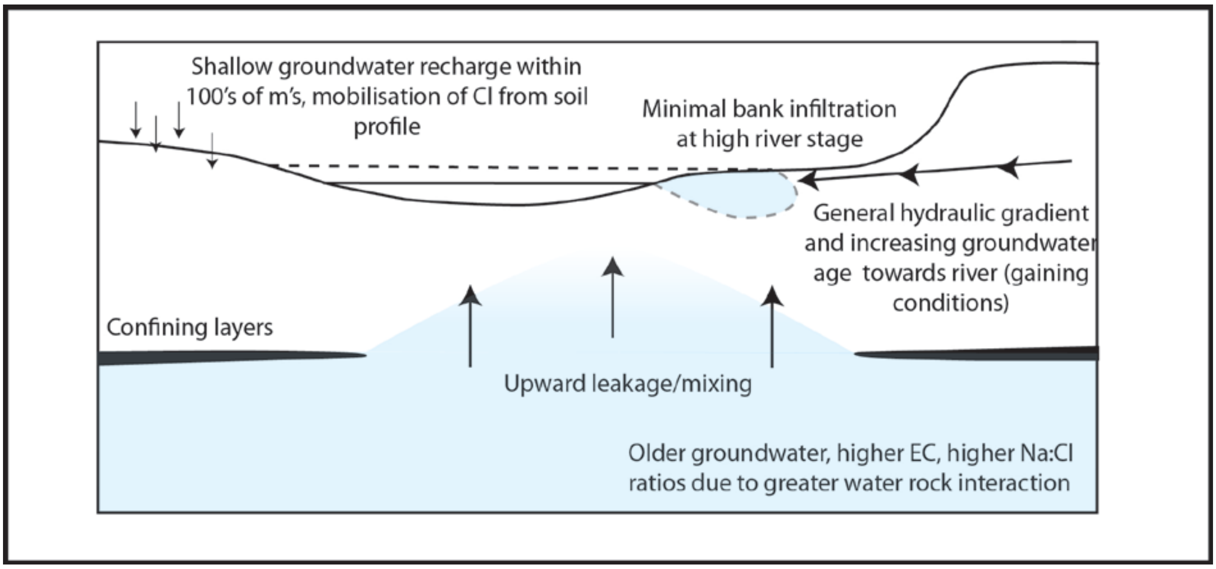

Figure 12. Schematic representation of the Tambo River and major hydrogeochemical processes at baseflow (solid line) and high flow (dashed line) conditions. The deeper groundwater is from 15 to 20 m below ground surface within the alluvial aquifer and is confined beneath the clay layer.