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journal homepage: [www.elsevier.com/locate/jhydrol](http://www.elsevier.com/locate/jhydrol)Using groundwater geochemistry and environmental isotopes to assess the correction of  $^{14}\text{C}$  ages in a silicate-dominated aquifer system

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## summary

The use of  $^{14}\text{C}$  to constrain groundwater residence times requires careful correction of  $^{14}\text{C}$  activities ( $a^{14}\text{C}$ ) and an assessment of the degree of inter-aquifer mixing. In groundwater of the Campaspe Valley in the southern Murray Basin, Australia,  $\delta^{13}\text{C}$  values of dissolved inorganic carbon (DIC) range from 18‰ to +2‰. Using these  $\delta^{13}\text{C}$  values to correct  $^{14}\text{C}$  ages assuming that dissolution of or exchange with matrix calcite had occurred implies that locally >90% of the DIC is derived from carbonates. In turn, this suggests that low-salinity groundwater in the deeper confined Calivil–Renmark Formation up to 50–60 km from the basin margins in the Campaspe Valley has a component of modern recharge, which would require that widespread leakage from the overlying Shepparton Formation had occurred. However,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and major ion geochemistry of groundwater imply that negligible inter-aquifer mixing has

occurred and that calcite dissolution is a very minor process. The variable  $\delta^{13}\text{C}$  values are most probably due to methanogenesis via reduction of  $\text{CO}_2$  in the groundwater that results in the residual DIC being enriched in  $^{13}\text{C}$ . As methanogenesis by this mechanism has only a minor impact on  $a^{14}\text{C}$ , uncorrected  $^{14}\text{C}$  ages are a better estimate of groundwater residence times. Groundwater in the north of the Campaspe Valley has a residence time of 9–13 ka, which agrees with ages calculated from head gradients and hydraulic conductivities. Calivil–Renmark groundwater from the adjacent Pyramid Hill region, in an area where the aquifers contain lower hydraulic conductivity sediments, is substantially older (up to 20–25 ka). The age of groundwater from the Shepparton Formation increases irregularly with depth, with ages of in excess of 25 ka recorded at its base. This study illustrates the need to fully understand hydrogeological processes in order to correct  $^{14}\text{C}$  ages, especially in silicate-dominated aquifers where dissolution of carbonates may not be the major process controlling  $\delta^{13}\text{C}$  values.

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## Introduction

Accurate determinations of groundwater residence times are required to understand hydrogeological systems and to assess the sustainable use of groundwater. Because of its capacity to date groundwater that is up to 30,000 years old, and due to the ubiquitous presence of dissolved inorganic carbon (DIC) in groundwater,  $^{14}\text{C}$  is the most widely used radiogenic dating technique in regional aquifers (Edmunds, 2009). The use of  $^{14}\text{C}$  as a routine dating tool is increasing with the greater availability of accelerator mass spectrometers (AMS) that allow precise  $^{14}\text{C}$  determinations from DIC derived typically from 1 to 2 L of groundwater (Jull et al., 2004). However, the application of  $^{14}\text{C}$  dating is not without considerable problems. These include the anomalously high  $^{14}\text{C}$  activities ( $a^{14}\text{C}$ ) in groundwater recharged since the 1950s due to the atmospheric nuclear tests. Of more concern in most regional aquifers are the corrections required for the input of old  $^{14}\text{C}$ -free carbon derived

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Walraevens, 2009), and the application of geochemical mass transport models such as NETPATH (Plummer et al., 1991). While some of these schemes attempt to address a wide range of processes, many studies assume that DIC in groundwater is derived largely from dissolution of CO<sub>2</sub> from the soil zone under open-system conditions and that subsequent dissolution of (or exchange with) carbonates in the aquifer matrix is the main process that impacts DIC concentrations, δ<sup>13</sup>C values, and a<sup>14</sup>C along groundwater flow paths. However, ideally, all processes that can impact the DIC concentration of the groundwater should be accounted for (e.g., Buckau et al., 2000; Coetsiers and Walraevens, 2009), and independent geochemical tracers such as <sup>3</sup>H or <sup>4</sup>He contents (Buckau et al., 2000; Kulongoski et al., 2008) or <sup>87</sup>Sr/<sup>86</sup>Sr ratios (Bishop et al., 1994) should be used to verify ages or assess the origin and evolution of DIC. Additionally, the “reasonableness” of the estimated groundwater residence times can be assessed by the identification of palaeowaters that have distinctive δ<sup>18</sup>O values (Darling et al., 1997; Edmunds and Smedley, 2000; Chen et al., 2003; Zhu et al., 2007; Edmunds, 2009) or by comparison with estimates of groundwater flow rates based on physical models (Cronin et al., 2005). Groundwater mixing must also be accounted for; if significant mixing occurs, the <sup>14</sup>C ages will not reflect groundwater residence times.

This paper discusses groundwater residence times in the Campaspe region of the southeast Murray Basin, Australia based on new a<sup>14</sup>C data and a reinterpretation of the a<sup>14</sup>C data of Calf et al. (1986). The main aim of this study is to assess the correction of <sup>14</sup>C ages from a relatively simple flow system in aquifers that are dominated by silicate minerals where water–rock interaction is limited. This is the first time that such an assessment has been applied to southeast Murray Basin; previous studies (Calf et al., 1986; Cartwright and Weaver, 2005) have used correction schemes based on relatively simple models of calcite dissolution. The results of this study will help in the interpretation of <sup>14</sup>C data from other regional flow systems, which in turn will aid in the understanding and management of groundwater resources in those areas.

### Hydrogeology of the Southeast Murray Basin

The Murray Basin (Fig. 1a) occupies 300,000 km<sup>2</sup> of southeast Australia and contains a series of late Palaeocene to Recent sediments deposited on Proterozoic to Mesozoic basement. General descriptions of Murray Basin geology and hydrogeology are presented by, amongst others, Tickell (1978), Tickell and Humphries (1986), Lawrence (1988), Evans and Kellett (1989), Brown (1989), Stephenson and Brown (1989), Macumber (1991), Herczeg et al. (2001), and Cartwright et al. (2008). At its deepest, the basin is up to 600 m thick; however, the majority of the basin is <400 m thick. The basin is divided into three sub-basins or provinces (Riverine, Scotia, and Mallee–Limestone: Fig. 1a) that are separated by basement ridges. Except for a small region in the southwest that discharges to the Southern Ocean, the basin is closed and groundwater discharges to salt lakes near the basin centre. The River Murray and its tributaries is the only major surface water feature draining the basin.

The Riverine Province underlies the Riverine Plain of Victoria and New South Wales (Fig. 1a). It is separated from the Scotia Province by the Neckerboo Ridge, and from the Mallee–Limestone Province by a change in groundwater flow direction that coincides with the eastern edge of the Murray Group limestone aquifer and its over- and underlying low-permeability units (e.g., the Winnambool Formation, Geera Clay, and the Bookpurnong Beds: Lawrence, 1988). The Cainozoic sediments of the Riverine Province are dominantly terrestrial with a transition to marginal marine units in the west of the province. The stratigraphic sequence comprises three main units (Fig. 1b). The lowermost Renmark Group consists of Palaeocene to late Miocene fluvial sands, gravels, silts, and clays that form a confined aquifer system. In the west of the Riverine Province, these more permeable units are intercalated with lower permeability clays and marls of the Geera Clay and Winnambool Formation; however, in much of the Riverine Province such lower permeability units are absent. Overlying the Renmark Formation is the Pliocene Calivil Formation that comprises sands and gravels. In most of the Riverine Province, the Calivil Formation is in hydraulic continuity with the underlying Renmark Formation and these formations may be considered as a single aquifer (Lawrence, 1988; Macumber, 1991). The Calivil–Renmark sediments were deposited by, and are thickest in, ancestral drainage channels (“deep leads”) of present day rivers (e.g., the Campaspe, Loddon, Avoca, and Goulburn) that were established after the Middle Miocene marine regression (Macumber, 1991). The uppermost aquifer in the Riverine Province is the Shepparton Formation, which comprises a series of fluvio-lacustrine sediments. These sediments include clays, sands, and silts that are laterally discontinuous resulting in a highly heterogeneous aquifer system. The Shepparton Formation is unconfined and recharge potentially occurs across the Riverine Province. The heterogeneity of this unit may inhibit lateral flow, promoting downward flow towards the underlying Calivil–Renmark Formation. This is confirmed by the observation that <sup>14</sup>C ages of Shepparton groundwater commonly increase with depth (Calf et al., 1986; Cartwright et al., 2006). By contrast <sup>14</sup>C ages of groundwater from the Calivil–Renmark Formation generally increase away from the basin margins suggesting a greater component of lateral flow (Calf et al., 1986; Arad and Evans, 1987; Macumber, 1991; Cartwright and Weaver, 2005).

### Local hydrogeology of the Campaspe Valley and Pyramid Hill region

The Campaspe Valley is a deep lead aquifer system that occupies the palaeovalley of the Campaspe River. It extends northwards across the Riverine Plain from the Central Highlands basement of Palaeozoic granites and metamorphosed turbidite sediments that forms the southern boundary of the Murray Basin (Tickell, 1978; Tickell, 1982; Calf et al., 1986; Tickell and Humphries, 1986; Arad and Evans, 1987; Chiew et al., 1992). The basement to the south of the Campaspe Valley forms a range of low hills that rise to 350 m. The Riverine Plain north of the basement outcrop has subdued topography with ground elevations falling from 120 m in the south to 75 m in the north. The Campaspe Valley deep lead broadens northwards (Fig. 2a), and both the Shepparton and the Calivil–Renmark Formations thicken northwards to approximately 80 m and 95 m, respectively (Figs 2a and c). Within the Campaspe Valley, the Calivil–Renmark aquifer largely comprises coarse sands and gravels, with grain sizes fining northwards. The Shepparton Formation is a heterogeneous group of clays and silts with metre to tens-of-metre scale sand and gravel lenses that represent the deposits of past streams. The boundary between the Shepparton and Calivil Formations is commonly gradational with the Shepparton Formation sediments becoming coarser grained at the base of this unit. Horizontal hydraulic conductivities of the Calivil–Renmark Formation within the Campaspe Valley based on pump tests decrease northwards from 40 to 60 m/day, while the Calivil–Renmark Formation in the Pyramid Hill region to the west of the Campaspe Valley has lower hydraulic conductivities (Tickell, 1978; Tickell, 1982; Tickell and Humphries, 1986; Chiew et al., 1992). These studies reported that Shepparton Formation has horizontal hydraulic conductivities of 25–55 m/day and vertical hydraulic conductivities that are locally as low as 10<sup>−5</sup>–10<sup>−2</sup> m/day. Close to the southern margins of the basement, the Shepparton Formation sediments are coarser grained with a higher proportion of sands, and hydraulic conductivities are probably highest in this area.

The Campaspe region is semi arid with average annual rainfall decreasing from 600 mm in the south to 400 mm in the north; rain is mainly in the Austral winter months, and potential evapotranspiration exceeds rainfall for much of the year (Bureau of Meteorology, 2009). Within the Campaspe Valley, groundwater from the Calivil–Renmark and the Shepparton Formations locally represent a viable water resource that is extensively used for stock watering, irrigation, and, increasingly, for town water supplies (for

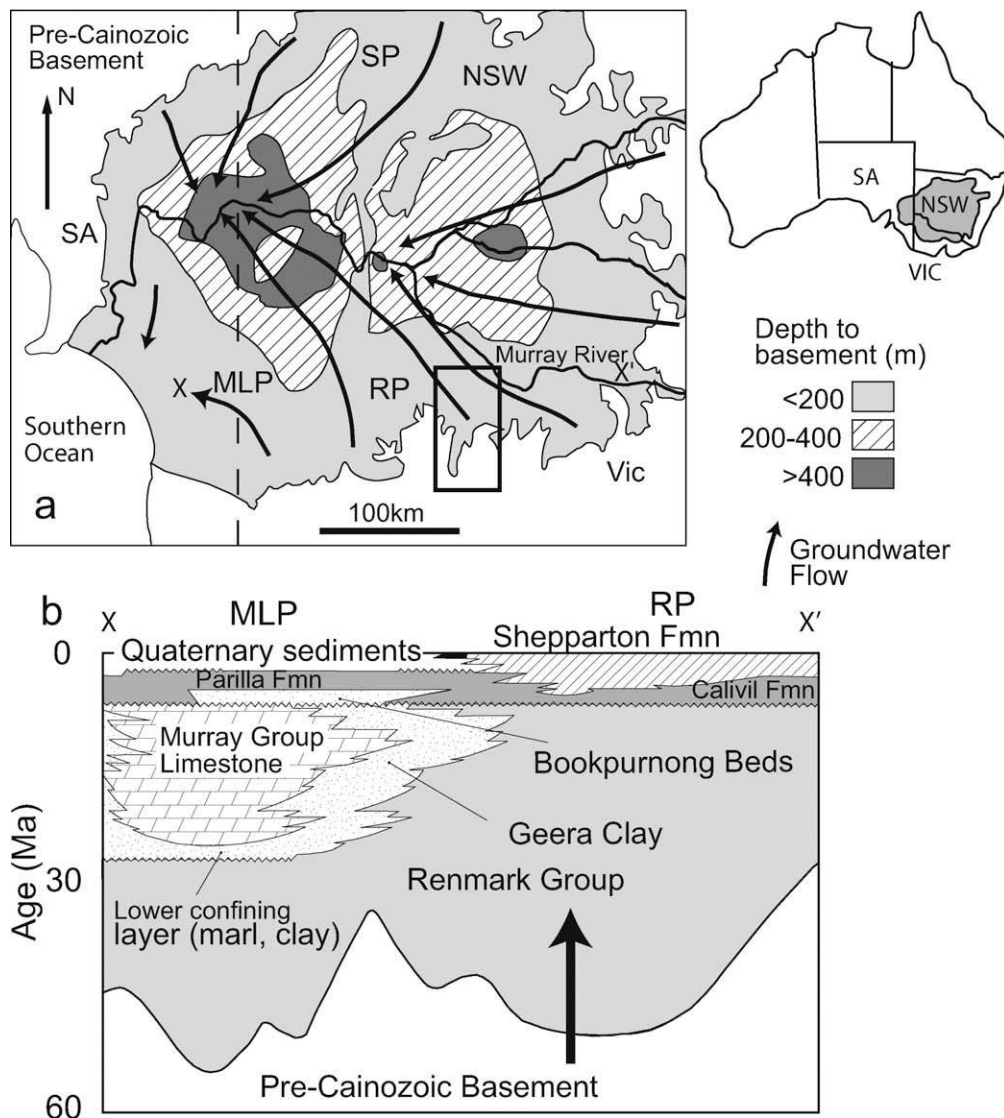


Fig. 1. (a) Map of the Murray Basin (after Evans and Kellett, 1989) showing depth to basement, groundwater flow paths, and major rivers. MLP = Mallee-Limestone Province, RP = Riverine Province, SP = Scotia Province. NSW = New South Wales, SA = South Australia, Vic = Victoria. Box shows location of Campaspe region (Fig. 2). Inset shows location of Murray Basin (shaded). (b) Generalised stratigraphic cross-section across the Mallee-Limestone and Riverine Provinces (after Evans and Kellett, 1989) along X–X' showing major units in the Murray Basin. Arrow indicates position of Campaspe Valley.

example, the town of Elmore, Fig. 2a, is supplied mainly by groundwater).

Groundwater flow is northwards (Fig. 2b). Present day lateral head gradients are  $10^{-4}$ – $10^{-3}$ , and vertical head gradients in the majority of the area are downwards between 0.05 and 0.1 (Fig. 2). The vertical distribution of hydraulic heads imply that groundwater flow in the Shepparton Formation has a downward component while that in the Calivil–Renmark Formation is mainly subhorizontal (Fig. 2c).  $\delta^{14}\text{C}$  of groundwater from the Campaspe Valley deep lead were initially reported by Calf et al. (1986). That study used a mass balance approach based on  $\delta^{13}\text{C}$  values to calculate groundwater ages and assumed that flow in the Calivil–Renmark aquifer was dominantly subhorizontal with little leakage from the overlying Shepparton Formation. However, the lack of a significant aquitard separating the Shepparton and the Calivil–Renmark Formations and the observation that hydraulic gradients are downward over much of the area makes it possible that leakage of groundwater from the Shepparton Formation into the Calivil–Renmark Formation occurs across the region. Since the Calivil–Renmark rocks do not crop out in the region, recharge of the Calivil–Renmark Formation through the Shepparton Formation must occur at least locally. Arad and Evans (1987) and Chiew et al. (1992) proposed that, due to the difference in hydraulic conductivities between the Shepparton and Calivil–Renmark Formations, inter-aquifer mixing was limited except for in the area south of Elmore (Fig. 2a) where the Shepparton Formation is thinnest and coarser grained. However, despite its importance, there have been few attempts to test the extent of inter-aquifer mixing.

#### Sampling and analytical techniques

Sampling and analytical techniques were described in detail by Cartwright and Weaver (2005) and Cartwright et al. (2006, 2007). Briefly, groundwater was sampled from groundwater monitoring bores using a polyethylene bailer or impeller pump (shallow bores) or a QED Micro Purge bladder pump (deeper bores). pH with an uncertainty of  $\pm 0.1$  was measured using an Orion 290 meter and Orion Ross electrodes. Alkalinity was determined using a Hach digital titrator and reagents with a precision of  $\pm 5\%$ . Cations were analysed using a Varian Vista ICP-AES at the Australian National University on samples that had been filtered through 0.45  $\mu\text{m}$  cel-

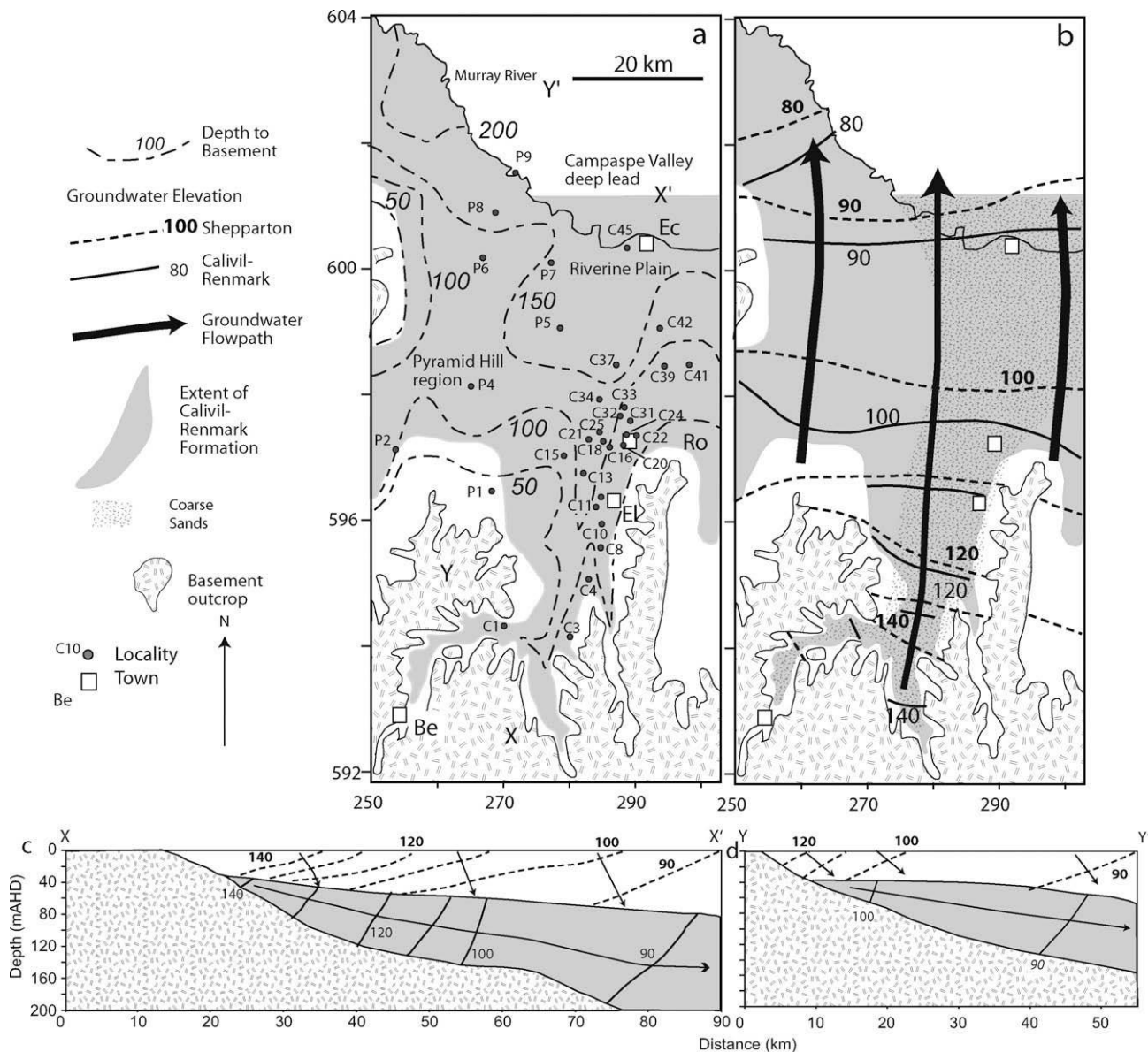


Fig. 2. (a) Generalised geological map of the Campaspe region showing the depth to basement and extent of the Calivil–Renmark aquifer. The deep lead of the Campaspe Valley is the area of coarse-grained sediments. Samples labelled C are within the Campaspe Valley, those labelled P are in the Pyramid Hill region. Towns are: Be – Bendigo, Ec – Echuca, El – Elmore, Ro – Rochester. Marginal numbers show Australian Map Grid references. (b) Hydraulic heads and groundwater flow paths in the Shepparton and Calivil–Renmark Formations. Heights are relative to the Australian Height Datum (AHD). (c) Cross section within the Campaspe Valley (line X–X' in Fig. 2a) showing hydraulic heads and groundwater flow. (d) Cross section within the Pyramid Hill region (line Y–Y' in Fig. 2a) showing hydraulic heads and groundwater flow. Data from [Arad and Evans \(1987\)](#), [Evans and Kellett \(1989\)](#), [Dimos et al. \(1994\)](#).

lulose nitrate filters and acidified to pH 2. Anions were analysed on filtered unacidified samples using a Metrohm ion chromatograph at Monash University. Precision of anion and cation analyses based on replicate analyses is  $\pm 2\%$ . Percent modern carbon contents were determined by accelerator mass spectrometry (AMS) at the Rafter Labs, New Zealand, or the Australian National University, Australia. Stable isotope ratios were measured at Monash University.  $\text{CO}_2$  from dissolved inorganic carbon (DIC) was liberated by acidification using  $\text{H}_3\text{PO}_4$  in a He atmosphere and  $\delta^{13}\text{C}$  values were measured using continuous flow on a Finnigan MAT 252 mass spectrometer.  $\delta^{13}\text{C}$  values of calcite from aquifer sediments were analysed by a similar technique on mixed silicate-carbonate powders.  $\delta^{13}\text{C}$  values are expressed relative to PDB and the precision is  $\pm 0.2\%$ .  $\delta^{34}\text{S}$  values of sulfate were analysed on  $\text{BaSO}_4$  precipitated from filtered and acidified samples by the addition of  $\text{BaCl}_2$ . Analysis was via combustion using a Carlo Erba Flash Elemental Analyser and Thermo Finnigan DeltaPlus Advantage mass spectrometer.  $\delta^{34}\text{S}$  values are expressed relative to CDT and the precision is  $\pm 0.25\%$ . <sup>87</sup>Sr/<sup>86</sup>Sr ratios of groundwater were measured at the University of Adelaide using a Finnigan MAT 262 thermal ionisation mass spectrometer in static mode as outlined by [Cartwright et al. \(2007\)](#). <sup>88</sup>Sr/<sup>86</sup>Sr was normalized to 8.375209. Analyses of the standard SRM987 gave <sup>87</sup>Sr/<sup>86</sup>Sr ratios of  $0.710260 \pm 0.000009$  (1 $\sigma$ ). The Sr procedural blank was taken as 1 ng and not significant. Some of the Sr data formed part of the regional study of [Cartwright et al. \(2007\)](#).



## Groundwater chemistry

The general distribution of groundwater salinities is shown in Fig 3a and b. Unlike many regions of the Riverine Province, the Campaspe Valley contains relatively

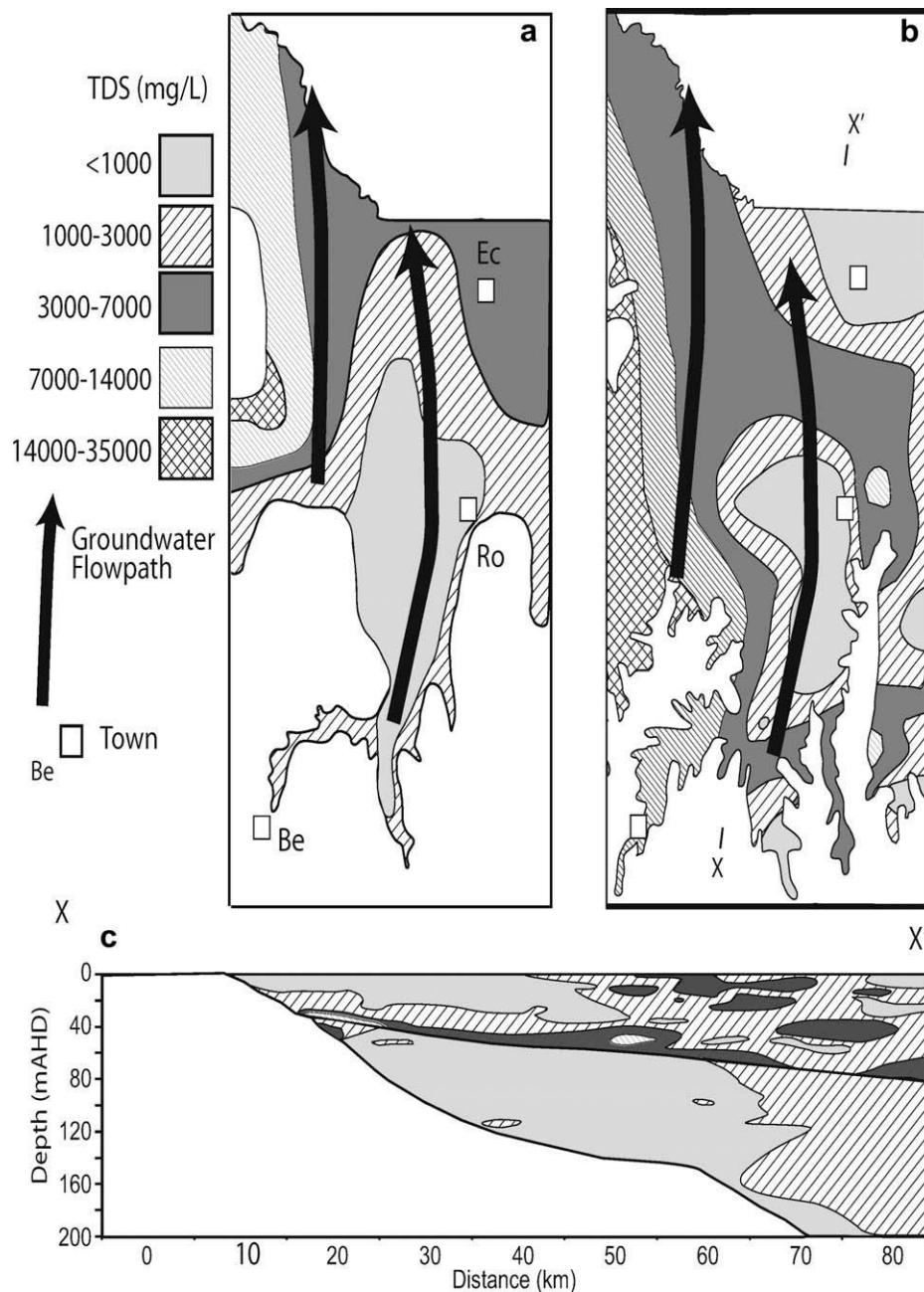


Fig. 3. Distribution of TDS contents in Calivil–Renmark groundwater (a) and Shepparton groundwater (b) in the Campaspe region. (c) Distribution of groundwater TDS contents along section X–X' (Fig. 2a). Data from Tickell (1982), Dimos et al. (1994) and the Victorian Water Resources Data Warehouse (<http://www.vicwaterdata.net/vicwaterdata/home.aspx>). These distributions represent broad averages and many local variations exist.

low-salinity groundwater, especially in Calivil–Renmark Formation where total dissolved solids (TDS) contents vary from <1000 mg/L in the south of the Campaspe Valley to 3000 mg/L in the north. As elsewhere in the Riverine Province (Cartwright et al., 2008), the Shepparton groundwater is generally more saline than the Calivil–Renmark groundwater, but TDS contents are still <7000 mg/L. Fig. 3c shows the distribution of groundwater salinities in cross-section along the Campaspe Valley. Especially in the Shepparton Formation, the salinity distribution in both this and in map view is a broad average as this formation is highly heterogeneous and groundwater salinity may vary widely on the scale of a few tens-of-metres (Tickell, 1978; Arad and Evans, 1987; Macumber, 1991). Groundwater salinities are broadly constant with depth within the Calivil–Renmark but are more variable within the Shepparton Formation. In the Pyramid Hill region, groundwater in both the Calivil–Renmark and Shepparton Formations is more saline with TDS contents locally >35,000 mg/L (Fig. 3a and b).

## Geochemical processes

Throughout the Mallee–Limestone and Riverine Provinces of the Murray Basin, including the Campaspe Valley and the Pyramid Hill region,  $d^{18}O$  and  $d^2H$  values of groundwater are similar to those of local rainfall, implying that, despite the high salinities and broadly seawater composition of the groundwater, there is

no connate water remaining in the basin (Herczeg et al., 2001; Cartwright et al., 2008). Additionally Cl/Br ratios that are close to those of the oceans show that halite dissolution is not important in generating the locally high groundwater salinities. Rather, major ion concentrations,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, and O, H, and S isotope data show that the dominant hydrochemical process is evapotranspiration of rainfall during recharge. The locally high evapotranspiration rates result from the subdued topography, low surface runoff rates, and the presence of water-efficient native vegetation that locally consumed >99% of available precipitation (Herczeg et al., 2001). Evapotranspiration resulted in the precipitation of calcite, gypsum, and clay minerals in the unsaturated zone during recharge (Arad and Evans, 1987; Macumber, 1991; Love et al., 1993; Herczeg et al., 2001; Dogramaci and Herczeg, 2002; Cartwright and Weaver, 2005; Cartwright et al., 2006, 2008). Many of the silicate-dominated aquifers in the southern Murray Basin are unreactive, and silicate weathering, carbonate dissolution and re-precipitation, ion exchange, and reactions between clay minerals are minor processes. Indeed, the groundwater probably achieves close to its final chemistry in the recharge zone (Herczeg et al., 2001). Differences in groundwater salinity across the southern Murray Basin are correlated with relative recharge rates (Herczeg et al., 2001; Cartwright et al., 2006). Areas dominated by high-hydraulic conductivity sediments (such as the Campaspe Valley) record higher rates of recharge and consequently contain lower salinity groundwater that has undergone lower degrees of evapotranspiration than the area between the deep leads (such as the Pyramid Hill region) that contain lower hydraulic conductivity sediments.

#### $\delta^{14}\text{C}$ and estimates of groundwater residence times

Fig. 4 shows the distribution of  $\delta^{14}\text{C}$  in the Calivil–Renmark and Shepparton groundwater.  $\delta^{14}\text{C}$  in the Calivil–Renmark groundwater within the Campaspe Valley decreases regularly from 95.1 pMC to as low as 19.6 pMC along the flow path, suggesting a system that is dominated by subhorizontal flow with recharge in the south of the Campaspe Valley. The Calivil–Renmark groundwater in the Pyramid Hill region has lower  $\delta^{14}\text{C}$  (6.4–44.2 pMC), consistent with lower hydraulic conductivities and lower groundwater fluxes in this region. The  $\delta^{14}\text{C}$  of Shepparton groundwater generally decreases with depth. Much of the Shepparton groundwater from <20 m has  $\delta^{14}\text{C}$  >100 pMC implying that it contains a component of modern water recharged during or since the atmospheric nuclear tests in the 1950s. Groundwater at the base of the Shepparton Formation locally has low  $\delta^{14}\text{C}$  (3–12 pMC), especially in the Pyramid Hill region, which is consistent with relatively low vertical flow rates in this aquifer (Calf et al., 1986; Cartwright et al., 2006). The heterogeneous distribution of  $\delta^{14}\text{C}$  in the Shepparton groundwater is consistent with the variable lithology and hydraulic conductivity of this unit.

#### Correction of $^{14}\text{C}$ ages

Given the evidence for relatively little water–rock interaction in the aquifers, the absence of substantial carbonate units, and the relatively simple aquifer stratigraphy, it should be straightforward to determine groundwater residence times based on  $\delta^{14}\text{C}$ . However, despite the lack of carbonates,  $\delta^{13}\text{C}$  values of DIC are extremely variable. DIC from Calivil–Renmark groundwater in the Campaspe Valley has  $\delta^{13}\text{C}$  values ranging from 18‰ to 3‰ (Fig. 5a).  $\delta^{13}\text{C}$  values of DIC in the Calivil–Renmark Formation in the Pyramid Hill Region are mainly in the range 18‰ to 14‰, but are locally as high as +2‰ (Fig. 5b).  $\delta^{13}\text{C}$  values of DIC from Shepparton groundwater from both areas are mainly within the range (16‰ to 8‰), but are locally as high as 2‰. Minor calcite cements and veins do exist and the possible contribution of  $^{14}\text{C}$

C-free carbon from these sources needs to be assessed. Ca/Cl and DIC/Cl ratios do not increase along the flow path (Fig. 6), suggesting that progressive carbonate dissolution during groundwater flow has not occurred. In addition, Ca:Na ratios are 0.003–0.23, which are far lower than those from groundwater from aquifers where significant carbonate dissolution has occurred (generally >1: Mast et al., 1990; Leybourne et al., 2006). However, isotopic exchange between matrix calcite and DIC at conditions close to calcite saturation may change  $\delta^{13}\text{C}$  values without a change in major ion composition (Maloszewski and Zuber, 1991).

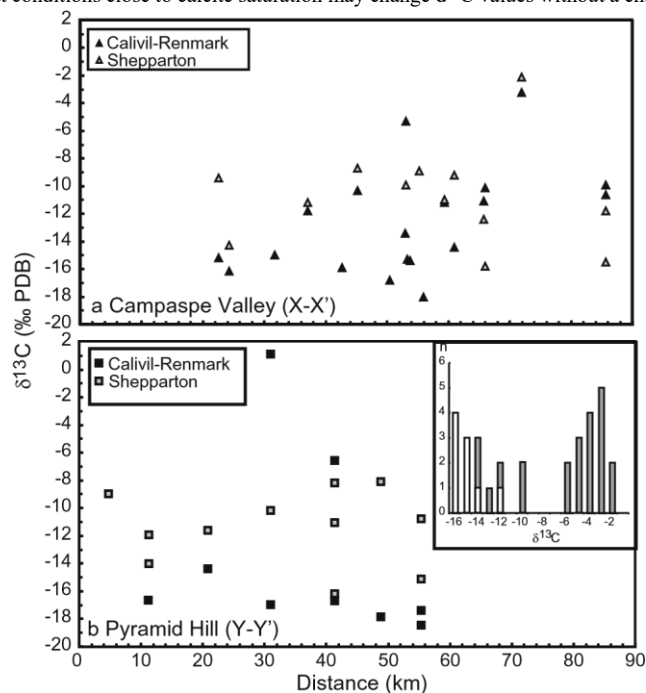


Fig. 5. Distribution of  $\delta^{13}\text{C}$  values with distance in the Campaspe Valley (a) and the Pyramid Hill region (b). Data from Table 1 and Calf et al. (1986). Inset shows frequency distribution of  $\delta^{13}\text{C}$  values of calcite from the regolith (open symbols) and the aquifer matrix (closed symbols).

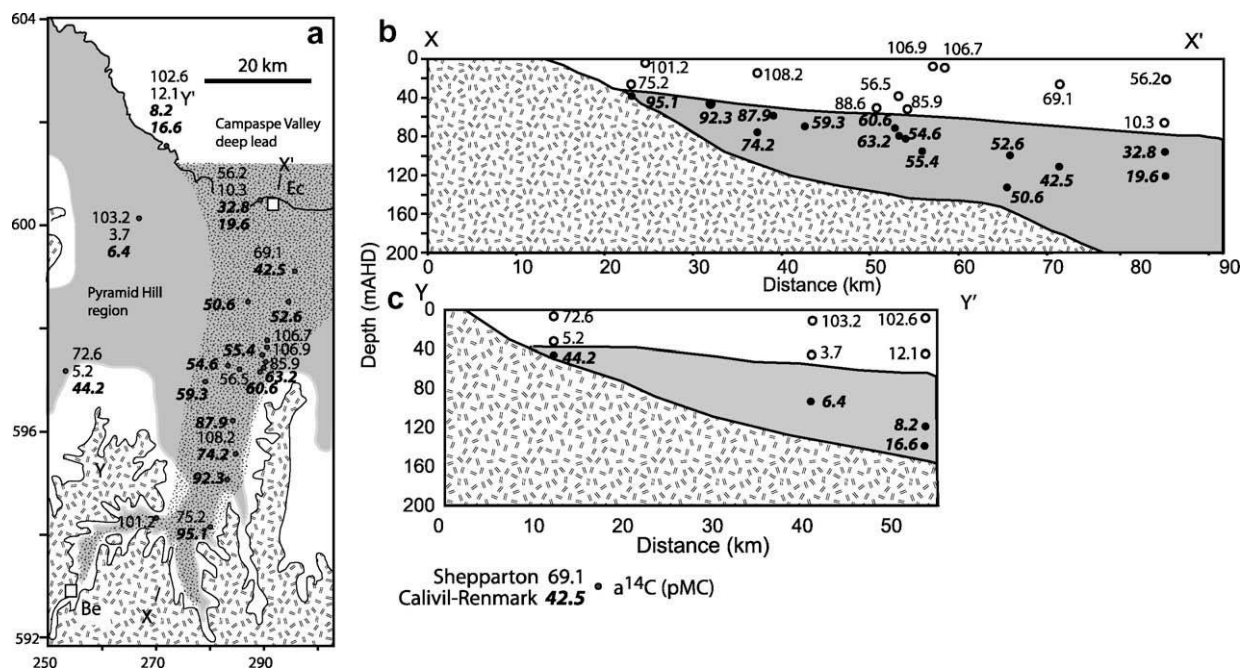


Fig. 4. (a) Distribution of  $^{14}\text{C}$  within the Campaspe Region, map symbols are as for Fig. 2. (b) Distribution of  $^{14}\text{C}$  within the Campaspe Valley along section X–X'. (c) Distribution of  $^{14}\text{C}$  within along section Y–Y' in the Pyramid Hill region. Data from this study and Calf et al. (1986) (Table 2).

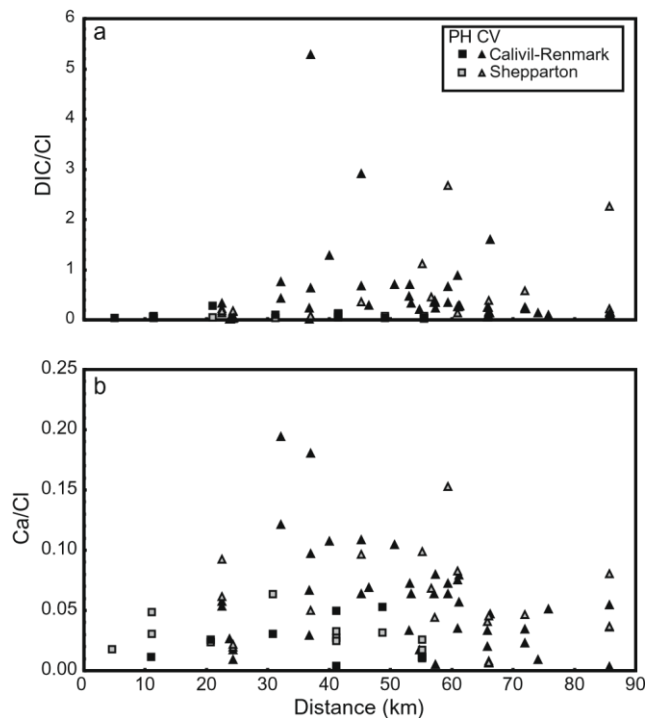


Fig. 6. Variation in dissolved inorganic carbon (DIC) concentrations (a) and Ca concentrations (b) with distance from the basin margins for groundwater from the Campaspe Valley (CV) and Pyramid Hill (PH). Data from Table 1 and Arad and Evans (1987). Concentrations are normalised to Cl concentrations to take into account differences in salinity.

Fig. 7 and Table 2 shows the corrected  $^{14}\text{C}$  ages that would result from using the  $\delta^{13}\text{C}$  values to correct for the input of  $^{14}\text{C}$ -free carbon by the aquifer matrix using mass balance (Clark and Fritz, 1997, p. 211), which is the type of correction most commonly applied to  $^{14}\text{C}$  ages. These calculations made the following assumptions. (1) DIC in the recharging groundwater had a  $\delta^{13}\text{C}$  value of 17.5‰ (appropriate for DIC resulting from dissolution of soil  $\text{CO}_2$  produced by the decay of C3 vegetation that is native to this region). (2) Calcite deposition due to evapotranspiration occurred in the unsaturated zone under open-system conditions and does not affect the  $\delta^{13}\text{C}$  of the recharging groundwater. (3) The  $\delta^{13}\text{C}$  value of the matrix calcite was 2‰ (i.e. the maximum  $\delta^{13}\text{C}$  value measured: Fig. 5). The resulting distribution of  $^{14}\text{C}$  ages in the Calivil–Renmark Formation within the Campaspe Valley is very irregular (Fig. 7a), and suggests that deep groundwater with a component of modern recharge (i.e. where  $A_0 > 100$  pMC) exists at considerable distances along the flow path. By contrast, Calivil–Renmark  $^{14}\text{C}$  ages from the Pyramid Hill region show a more regular increase along the flow path (Table 2 and Fig. 7c) that would imply less inter-aquifer mixing. Even increasing the assumed  $\delta^{13}\text{C}$  value of matrix calcite to +2‰ (which is significantly higher than any measured value) makes little difference to these conclusions. Applying these calculations to the Shepparton Formation implies that modern groundwater occurs within the Campaspe Valley at depths up to 30 m (Table 2 and Fig. 7b), while the Shepparton formation in the Pyramid Hill region contains older groundwater at similar depths (Table 2 and Fig. 7d). If this pattern of ages is correct, it implies groundwater flow in the Campaspe Valley is more complex than assumed (e.g., Calf et al., 1986; Arad and Evans, 1987; Chiew et al., 1992) with short-term leakage occurring through the Shepparton Formation throughout the flow system. In turn this suggests that the deeper groundwater is vulnerable to the leakage of shallow water from the Shepparton Formation that is locally saline and potentially contaminated by agricultural processes. Given the potential importance of these conclusions, it is clear that assessment of the  $^{14}\text{C}$  corrections are required; this is done below by providing independent constraints on calcite dissolution/exchange and on inter-aquifer mixing.

#### Constraints on calcite dissolution/exchange

Using the  $\delta^{13}\text{C}$  values to correct for calcite dissolution/exchange implies that up to 90% of the DIC in some samples is derived from the aquifer matrix. However, silicate minerals dominate the aquifers and even in karst systems the contribution from matrix calcite is rarely  $>50\%$  (Vogel, 1971). Sr isotopes provide a valuable independent assessment of carbonate dissolution or exchange because, firstly, aquifer minerals have a wide and predictable range of  $^{87}\text{Sr}/^{86}\text{Sr}$

$\text{Sr}/\text{Sr}$  ratios controlled by their initial  $\text{Sr}/\text{Sr}$  ratios,  $\text{Rb}/\text{Sr}$  ratios, and age (Faure, 1991; Katz and Bullen, 1996). In general, silicate minerals, especially potassic silicates such as biotite and Kfeldspar that are more than a few million years old have high  $^{87}\text{Sr}/^{86}\text{Sr}$

$\text{Sr}/\text{Sr}$  ratios. By contrast, Ca-rich minerals such as calcite or gypsum have low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios that remain little changed over time. Secondly, unlike C isotopes, mineral precipitation and dissolution does not fractionate  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Finally, the very long half-life of  $^{87}\text{Rb}$  compared with typical groundwater residence times of  $<1$  Ma means that there is essentially no change in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios due to the decay of  $^{87}\text{Rb}$  in groundwater.

Carbonate from the Renmark Group sediments in the Campaspe Valley has  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7110–0.7140 (Cartwright et al., 2007), which is significantly below those of the groundwater (0.7159–0.7165). The relatively high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the groundwater (Table 1) is due to the Sr isotope ratios being controlled by weathering or exchange with silicate minerals during recharge (Cartwright et al., 2007). An increase in  $\delta^{13}\text{C}$  values of DIC resulting from dissolution of or isotopic exchange between groundwater and calcite would thus be accompanied by a reduction in  $^{87}\text{Sr}/^{86}\text{Sr}$  ra-



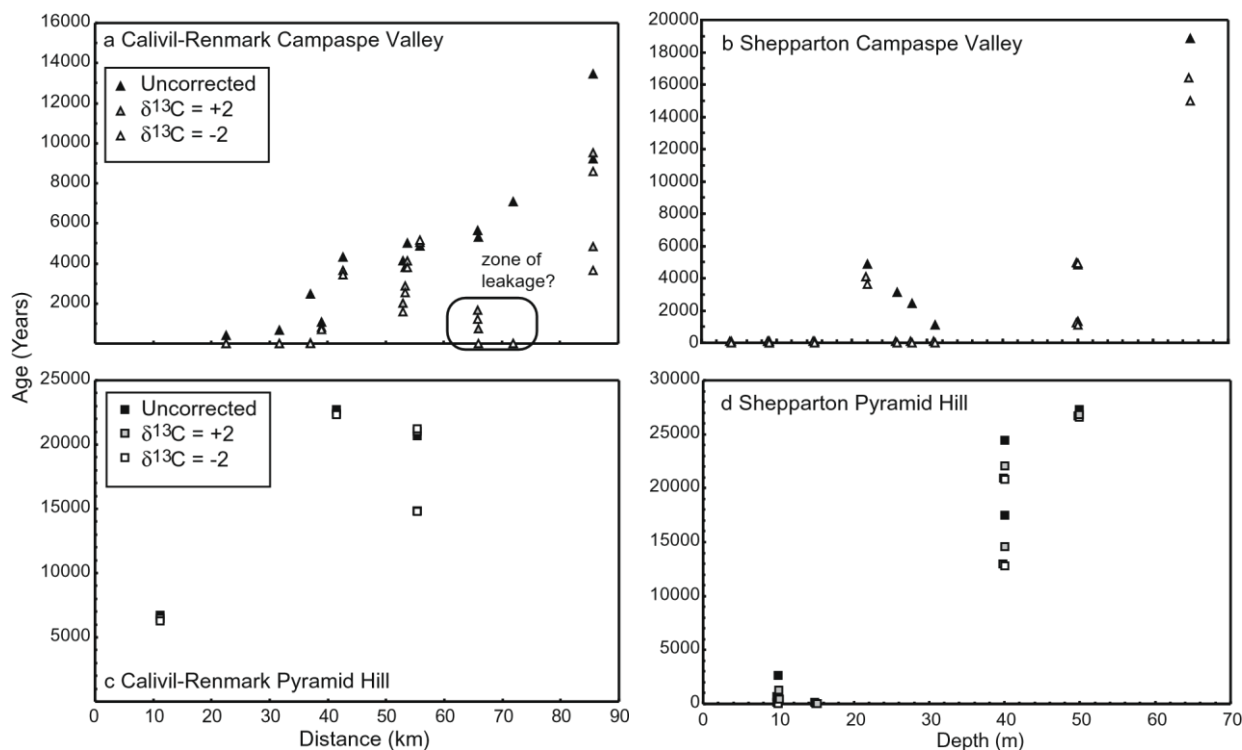


Fig. 7. Variation in  $^{14}\text{C}$  ages from the Campaspe Valley groundwater (a, b) and the Pyramid Hill groundwater (c, d). Data from Table 2. Calivil–Renmark ages are relative to distance from the basin margins along X–X<sup>0</sup> and Y–Y<sup>0</sup> (Fig. 2). Shepparton ages are relative to depth below surface. Corrected ages used a mass balance approach based on the dissolution of calcite with  $\delta^{13}\text{C} = 2\text{‰}$  and  $\delta^{13}\text{C} = +2\text{‰}$ , as discussed in text.

tios in the groundwater. Fig. 8 shows the trends in  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{13}\text{C}$  values for dissolution of calcite calculated from:

$$R_f = \frac{xR_A + (1-x)R_B}{x + (1-x)} \quad \delta^{13}\text{C}_f = x\delta^{13}\text{C}_A + (1-x)\delta^{13}\text{C}_B$$

(Faure, 1991), where  $x$  is the proportion of component A in the mixed sample,  $C$  is the elemental concentration, and  $R$  is the isotopic ratio. Molar Sr/Ca ratios of calcite in the Murray Basin are  $5 \times 10^3$  (Dogramaci and Herczeg, 2002), which results in a concentration of Sr of  $5 \times 10^2$  mol/kg. C concentrations in calcite are 10 mol/kg. Groundwater generally contains between  $1 \times 10^6$  and  $1 \times 10^5$  mol/kg Sr and  $1 \times 10^3$  and  $1 \times 10^2$  mol/kg C (Table 1).

The following isotopic ratios are used for the calculations: Calivil–Renmark groundwater  $^{87}\text{Sr}/^{86}\text{Sr} = 0.71625$ ,  $\delta^{13}\text{C} = 17.5\text{‰}$ ; Shepparton groundwater  $^{87}\text{Sr}/^{86}\text{Sr} = 0.71450$ ,  $\delta^{13}\text{C} = 15\text{‰}$  and; calcite  $^{87}\text{Sr}/^{86}\text{Sr} = 0.71125$ ,  $\delta^{13}\text{C} = 2\text{‰}$ .

For this range of values, a change of a few permil in  $\delta^{13}\text{C}$  values by calcite dissolution would be accompanied by a noticeable change in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Exchange of C and Sr between the groundwater and the calcite would result in similar trends. That the  $\delta^{13}\text{C}$  values and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the groundwater from this catchment show no significant correlations (Fig. 8) implies that they are controlled by different processes. As discussed by Cartwright et al. (2007), Sr in the groundwater from the southeast Murray Basin as a whole is derived primarily from silicate minerals or clays derived from those minerals with little input from carbonate dissolution.

#### Constraints on mixing

The implication from the corrected  $^{14}\text{C}$  ages that significant leakage of groundwater from the Shepparton into the Calivil–Renmark Formation has occurred throughout the Campaspe Valley does not agree with other aspects of the groundwater geochemistry. Firstly, the vertical distribution of groundwater salinity (Fig. 3c) is difficult to reconcile with significant vertical mixing. At any one location, the salinity of the Calivil–Renmark groundwater is relatively constant throughout the aquifer. If significant leakage of higher salinity water from the Shepparton Formation had occurred, it would result in higher salinities at the top of the aquifer that decrease with depth. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the groundwater (Fig. 9) also imply that there is little vertical leakage.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the Calivil–Renmark groundwater within the Campaspe Valley are 0.7159–0.7165 while, except for Loc. C45, those of the Shepparton groundwater are 0.7141–0.7148 (Fig. 9a). Average Sr concentrations in Calivil–Renmark groundwater are 0.75 of those in the Shepparton groundwater (Table 1); hence, significant leakage of groundwater from the Shepparton Formation would lower the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the Calivil–Renmark groundwater. Fig. 9e shows the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of mixed samples calculated using Eq. (1) using the measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and a range of relative Sr concentrations. If inter-aquifer leakage were widespread,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the Calivil–Renmark groundwater should decrease along the flow path, which is not observed. The higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the Shepparton groundwater at Loc. C45 are probably primary as hydraulic gradients in this region are downwards precluding upwards mixing from the Calivil–Renmark Formation. A similar difference between  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the Calivil–Renmark groundwater and that in the Shepparton Formation is observed in the Pyramid Hill region (Fig. 9c and d), which also precludes inter-aquifer mixing in that region.

This interpretation of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios assumes that Sr is behaving conservatively and that no resetting of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios occurs due to mineral reactions or isotopic exchange between Sr in groundwater and the minerals in the aquifers. Comparison of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and major ion geochemistry implies that  $^{87}\text{Sr}/^{86}\text{Sr}$

Table 1

Bore locations, major ion concentrations,  $\delta^{13}\text{C}$  values, and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of groundwater from the Campaspe region.

Loc (Fig. 2)	Bore	Ea	Nb	Dist <sup>b</sup> (km)	Depth <sup>c</sup> (m)	pH	TDS (mg/L)	DO (mg/L)	CO <sub>2</sub> (mg/L)	HCO <sub>3</sub> (mg/L)	CO <sub>3</sub> (mg/L)	Cl (mg/L)	NO <sub>3</sub> (mg/L)	SO <sub>4</sub> (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Sr (mg/L)	$\delta^{13}\text{C}$ (‰PDB)	$\delta^{34}\text{S}$ (‰CDT)	$^{87}\text{Sr}/^{86}\text{Sr}$
C1	65873	270100	5943300	24.3	30	6.44	13,600	1	214	248		7070	15.5	1720	3670	72.8	543	43.2	3.83	16.2	19.5	0.71600
C3	65875	280000	5941500	22.5	46	7.03	792	3	82	95		368	1.2	2.7	187	22.2	30.9	2.20	0.16	15.2	19.4	0.71599
C8	62589	284299	5956000	37.0	75	6.65	504	2	212	151		49	3.76	9.85	52.2	10.0	14.3	1.91	0.19	11.8		0.71651
C11	60131	284900	5964200	45.2	90	7.21	486	1	124	181		70.5	0.04	0.87	80.9	8.68	14.6	2.37	0.14	10.3	31.1	0.71593
C16	60136	285850	5972050	53.1	85	6.99	554	2	56	98		219	0.36	0.32	138	8.28	28.6	3.99	0.29	5.3	30.8	0.71643
C33	89576	288440	5978350	59.4	86	6.7	1330	bd	166	151		336	1.16	364	212	27.6	51.1	6.13	0.35	11.2	18.9	0.71631
C34	60138	284700	5979900	60.9	85	7.53	809	tr	16	321		226	1.54	37.6	155	8.90	17.7	24.7	0.71	14.4		0.71640
C37	47253	287100	5984800	65.8	131	10.07	1140	tr	bd	120	180	533	0.95	29.8	229	20.0	22.9	6.30	0.25	11.1		0.71613
C39	47247	294199	5985001	66.0	97	10.52	1090	1	bd	35	169	512	1.45	1.7	338	4.56	13.5	9.39	0.08	10.1	33.7	0.71622
C42	79327	296050	5990900	71.9	110	7.21	848	bd	38	112		441	1.25	11.9	202	11.6	20.8	5.84	0.25	3.2	38.4	0.71640
C45	102828	289200	6004650	85.7	95	6.61	2530	bd	120	135		1160	0.6	145	835	72.0	56.0	5.00	1.16	10.6		
C45	102827	289200	6004650	85.7	120	6.78	2470	bd	122	76		1280	2	14.1	884	4.61	71.9	13.7	1.15	9.9	22.1	0.71625
C1	65874	270100	5943300	24.3	5	7.21	3230	5	110	322		1630	0.3	185	751	36	168	9.48	0.95	14.3	19.2	0.71438
C3	65876	280000	5941500	22.5	28	6.64	1340	2	58	63		586	22	166	321	40.9	74.6	2.41	0.61	9.4	19.7	0.71455
C8	62600	284299	5956000	37.0	15	6.72	9242	2	230	277		4180	10	1550	2410	237	346	5.19	3.14	11.2		0.71482
C11	60182	284900	5964200	45.2	14	6.73	766	5	85	77		319	4.44	47.1	154	34.9	28	3.80	0.30	8.7	28.2	0.71448
C24	60129	284850	5974200	55.2	35	7.24	455	2	62	106		100	2.94	50.4	103	11.2	15.7	3.46	0.16	8.9		
C33	89594	288440	5978350	59.4	8.5	7.03	2500	4	432	584		257	7.5	636	474	44.5	51.3	6.33	0.58	11.0		0.71419
C34	60184	284700	5979900	60.9	9	6.22	4180	bd	280	76		1870	2.1	588	962	175	178	6.75	1.98	9.2		0.71412
C37	47254	287100	5984800	65.8	26	8.59	8930	1	78	311		4080	2.6	1320	2530	187	412	3.56	0.67	12.4		
C39	47249	294199	5985001	66.0	11	10.48	2560	1	bd	207	158	1090	2.25	188	870	8.81	20.3	11.7	1.80	15.8		
C42	79328	296050	5990900	71.9	26	7.15	614	1	1080	39		207	0.48	0.91	209	10.9	14.7	12.0	0.15	2.1	47.2	0.71467

C45	102830	289200	6004650	85.7	22	6.44	305	tr	326	80	33	0.03	74.1	74.7	2.97	5.52	0.89	0.48	15.5	18.5	0.71601
C45	102829	289200	6004650	85.7	65	6.91	2420	bd	2430	34	965	2.4	336	694	40.4	94.5	13.7	0.72	11.8	0.71623	
P2	60441	253800	5971200	11.2	65	8.33	4680	1	30	189	2580	0.4	231	1430	33.0	119	69.0	0.67	16.7	0.71649	
P4	100503	264800	5980900	20.9	60	7.18	13,800	2	168	242	6770	bd	1520	4480	199	394	27.6	4.71	14.5		
P5	97119	278500	5991100	31.1	86	7.45	2340	1	18	38	1380	1.2	3.2	778	48.0	52.6	15.6	0.95	+1.1	0.71577	
P6	97150	277300	6001400	41.4	75.8	7.31	1380	tr	17	28	735	10.9	3.6	521	3.45	46.2	10.2	0.30	6.6		
P7	95040	266700	6001400	41.4	95	7.65	6970	1	174	320	2710	2.0	1300	2100	151	196	15.3	2.33	16.7	0.71597	
P8	97152	268800	6008950	49.0	120	7.76	6200	tr	94	217	3140	0.4	547	1870	188	138	10.3	2.79	17.9		
P9	87807	271900	6015400	55.4	110	9.02	4574	bd	4	21	2700	2.8	98.1	1560	30.8	115	11.5	0.69	18.5	0.71586	
P9	87806	271900	6015400	55.4	130	8.20	4695	bd	87	173	2750	0.1	114	1420	35.1	110	12.1	0.80	17.4		
P1	68963	268000	5964900	4.9	28	7.66	3750	6	4.3	107	2000	5.5	362	1130	40.1	88.4	11.5	0.90	9.02		
P2	60443	253800	5971300	11.3	10	7.06	23,200	4	158	597	14,200	18	214	6490	493	963	59.0	4.01	11.98	0.71442	
P2	60442	253800	5971300	11.3	40	7.85	9900	1	236	357	5310	3.0	884	2260	290	509	37.7	8.53	14.02	0.71450	
P4	100504	264800	5980900	20.9	10	7.73	1970	tr	62	279	784	1.7	150	638	21.1	26.1	9.22	0.31	11.67		
P5	97120	278500	5991100	31.1	26	7.54	10,600	tr	398	348	5550	6.0	74.0	2880	395	918	47.6	4.65	10.2	0.71427	
P7	95042	266700	6001400	41.4	15	8.53	5010	9	96	320	2380	5.7	499	1500	72.8	121	15.1	1.56	11.1	0.71487	
P7	95041	266700	6001400	41.4	50	7.58	9330	1	270	150	5080	6.4	443	3020	142	201	15.6	3.04	16.2	0.71540	
P8	97151	277300	6001400	41.4	22.5	7.65	7310	tr	270	320	3370	7.8	692	2280	125	223	15.8	1.93	8.2		
P8	97153	268800	6008950	49.0	5	8.11	22,700	bd	364	246	13,400	15.5	203	7070	479	874	28.1	10.3	8.11		
P9	87809	271900	6015400	55.4	10	7.07	40,500	tr	528	303	23,500	bd	2130	11,900	685	1460	27.5	9.91	16.82		
P9	87808	271900	6015400	55.4	40	6.91	19,800	bd	210	155	10,700	bd	1920	6040	207	588	16.0	13.0	15.12	0.71447	

tr = trace.

bd = below detection.

<sup>a</sup> Eastings from Australian Map Grid (AMG Zone 55).

<sup>b</sup> Northings from Australian Map Grid (AMG Zone 55).

<sup>c</sup>



Distance along flowpath.  
d Depth of middle of screen.

Table 2 a<sup>14</sup>C and calculated ages of groundwater from the Campaspe region.

Loc (Fig. 2)	Bore <sup>a</sup>	Dist <sup>b</sup> km	d <sub>13</sub> C	a <sup>14</sup> C pMC	Age <sup>c</sup> (years)	Age <sup>d</sup> (years)	Age <sup>e</sup> (years)
Campaspe Valley: Calivil–Renmark Formation							
C3	65875	22.5	15.2	95.1	415	Mf	M
C4	62627	31.6	15.0	92.3	662	M	M
C8	62589	37.0	11.9	74.2	2470	M	M
C10	60245	39.0	15.9	59.3	4320	3420	3610
C13	“McEwan”	42.7	16.8	87.9	1070	684	764
C15	60250	52.9	13.4	60.6	4140	1600	2190
C20	89657	53.3	15.3	63.2	3790	2530	2800
C21	89643	53.7	15.4	54.6	5000	3800	4060
C25	60259	55.9	18.0	55.4	4880	4880	4880
C37	47253	65.8	11.1	50.6	5630	1230	2345
C39	47247	66.0	10.1	52.6	5310	M	1336
C42	79327	71.9	3.2	42.5	7070	M	M
C45	102827	85.7	9.9	32.8	9230	3660	5145
C45	102828	85.7	10.6	19.6	13,500	8600	9860
Campaspe Valley; Shepparton Formation							
C1	65874	22.5	14.3	102.1	M	M	M
C3	65876	24.3	9.4	75.2	2360	M	M
C8	62600	37.0	11.2	108.2	M	M	M
C18	60270	53.2	17.9	56.5	4720	4720	4720
C22	89606	54.5	17.2	85.9	1260	1100	1130
C15	60196	50.7	14.5	88.6	1000	M	M
C31	5688	57.4	14.0	106.9	M	M	M
C32	“Block 56”	58.5	13.4	106.7	M	M	M
C42	79328	71.9	2.1	69.1	3050	M	M
C45	102830	85.7	15.5	56.2	4760	3620	387
C45	102829	85.7	11.8	10.3	18,800	15,000	1590
Pyramid Hill: Calivil–Renmark Formation							
P2	60441	11.2	16.7	44.2	6750	6290	6390
P7	95040	41.4	16.7	6.4	22,800	22,300	22,400
P9	87807	55.4	18.5	8.2	20,700	20,700	20,700
P9	87806	55.4	17.4	16.6	14,900	14,800	14,800
Pyramid Hill: Shepparton Formation							
P2	60443	11.3	14.0	72.6	2650	545	1020
P2	60442	11.3	12.0	5.2	24,400	20,800	21,700
P7	95042	41.4	11.1	103.2	M	M	M
P7	95041	41.4	16.2	3.7	27,255	26,500	26,700
P9	87809	55.4	15.1	102.6	M	M	M
P9	87808	55.4	10.8	12.1	17,460	12,800	14,000

<sup>a</sup> Bore details in Table 1, data in italics from Calf et al. (1986).

<sup>b</sup> Distance along flow path.

<sup>c</sup> Uncorrected age.

<sup>d</sup> Age corrected for dissolution of matrix calcite with  $dC = 2\text{‰}$  (cf., Clark and Fritz, 1997).

<sup>e</sup> Age corrected for dissolution of matrix calcite with  $dC = 2\text{‰}$  (cf., Clark and Fritz, 1997).

<sup>f</sup> Modern (containing component of post 1950s recharge).

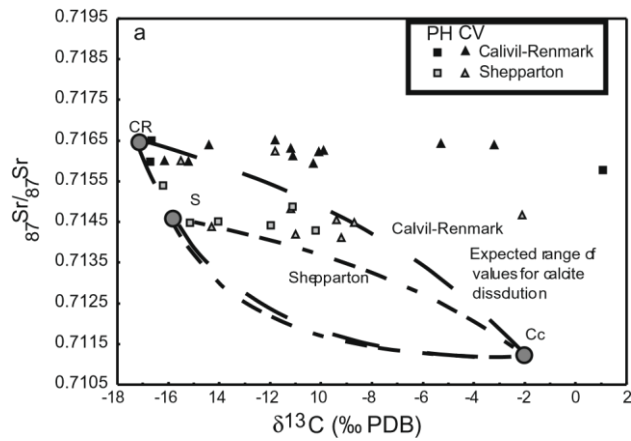


Fig. 8.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios vs.  $\delta^{13}\text{C}$  of groundwater from the Campaspe Valley. Lines show predicted trends for calcite (Cc) dissolution by Shepparton (S) and Calivil–Renmark (CR) groundwater calculated using Eq. (1). Fields encompass range of Sr and DIC concentrations discussed in text.

ratios in the southern Murray Basin are unaffected by mineral dissolution within the aquifers (Cartwright et al., 2007). That study also showed that isotopic exchange of Sr only occurs in the more clay-rich regions of the Murray Basin (and specifically does not occur in the Campaspe Valley). The observation that  $^{87}\text{Sr}/^{86}\text{Sr}$

Sr/ Sr ratios in the Calivil–Renmark Formation do not change with depth (Fig. 9b and d) is also consistent with a lack of leakage from the overlying Shepparton Formation. Overall, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the groundwater in the Campaspe catchment implies that the proposal of Calf et al. (1986), Arad and Evans (1987), and Chiew et al. (1992) that recharge of the Calivil–Renmark Formation through the Shepparton Formation largely occurs in the area south of Elmore are correct. Minor leakage of Shepparton groundwater into the very top of the Calivil–Renmark aquifer may occur elsewhere in the region, but this does not significantly mix with groundwater in the bulk of the aquifer (Arad and Evans, 1987). The leakage of groundwater between the two aquifers is probably limited by the substantially lower hydraulic conductivity of the Shepparton Formation compared with the Calivil–Renmark Formation.

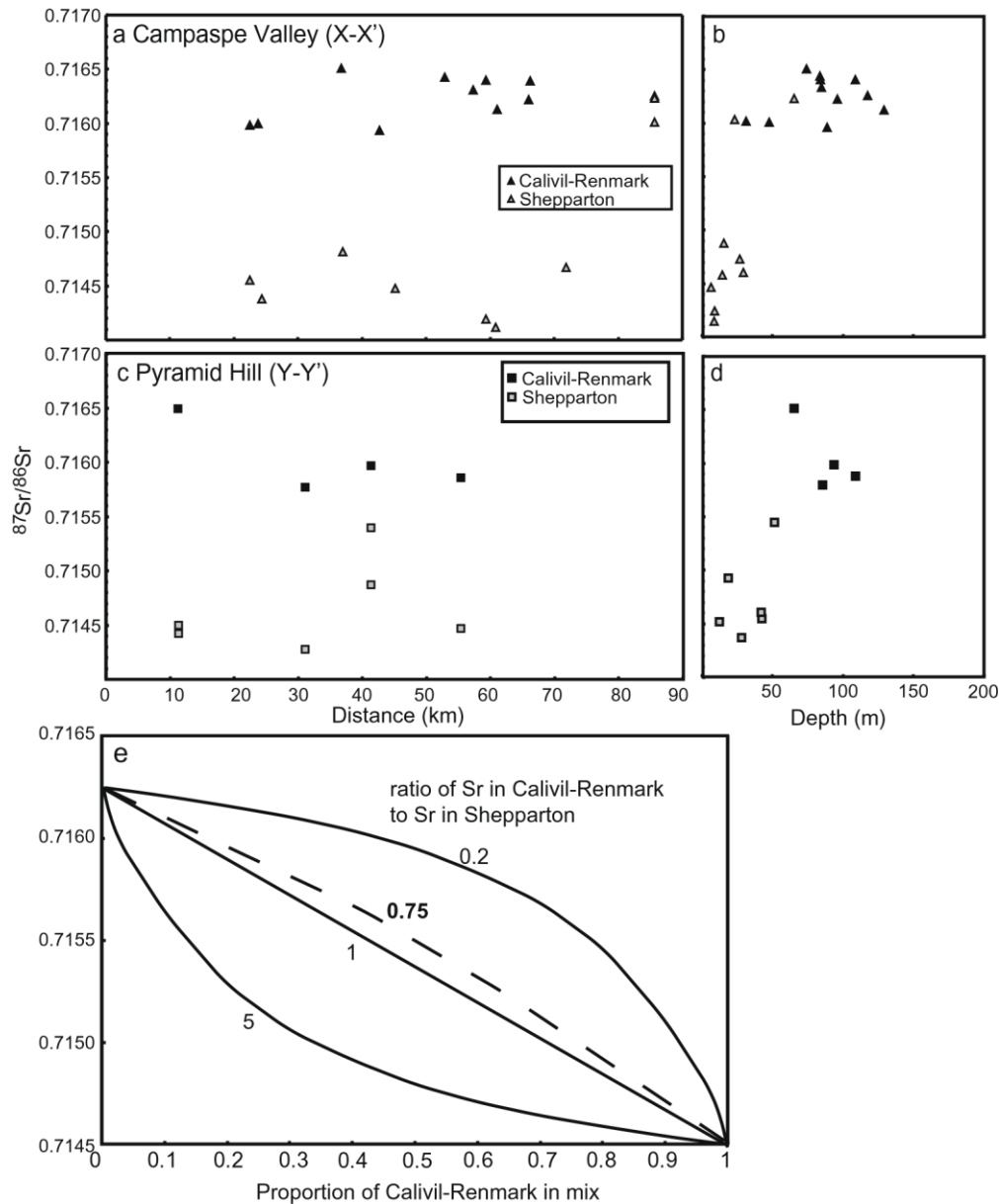


Fig. 9. Variation in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of groundwater from the Campaspe Valley with distance (a) and depth (b) and the Pyramid Hill region with distance (c) and depth (d). (e) Variation in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of Calivil–Renmark groundwater due to mixing with water from the Shepparton Formation contoured for different relative ratios of Sr concentration calculated using Eq. (1). Dashed line is for Sr concentration in the Calivil–Renmark groundwater being 0.75 that of the Shepparton Formation (which is the measured ratio). Data from Table 1.

## Discussion

While carbonate dissolution within the aquifers in the Campaspe area seems unlikely, understanding the variation of the  $\delta^{13}\text{C}$  values is critical to interpreting the  $^{14}\text{C}$  ages. There are several processes which can impact both  $\delta^{13}\text{C}$  and  $\delta^{14}\text{C}$  values but not affect the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios that need to be considered.

## Incorporation of mantle $\text{CO}_2$

Mineral springs in the Daylesford area in the headwaters of the Campaspe River (40 km to the south of the region depicted in Fig. 2) contain up to several g/L of mantle-derived DIC with  $\delta^{13}\text{C}$  values of 6‰ to 0‰ (Cartwright et al., 2002; Weaver et al., 2006). The input of mantle  $\text{CO}_2$  into the aquifers of the Campaspe region would raise the  $\delta^{13}\text{C}$  values of the groundwater and reduce  $\delta^{14}\text{C}$  as the mantle-derived  $\text{CO}_2$  will be  $^{14}\text{C}$  free. However, this scenario is unlikely because: (a) the mineral springs occupy a restricted area around Daylesford with few known from elsewhere in Victoria; (b) the groundwater in the south of the Campaspe region closest to the mineral springs has relatively low  $\delta^{13}\text{C}$  values (Fig. 5c) the geochemistry of the mineral water is significantly different from that of groundwater from the Campaspe region, specifically the mineral waters have very high DIC/cation ratios (Weaver et al., 2006).



## Dissolution of organic carbon

The Renmark sediments locally contain centimetre-thick coal seams that may be oxidised by the groundwater. However, this organic matter is rare and would yield DIC with low  $\delta^{13}\text{C}$  values. In general the content of organic matter in the soils, regolith, and aquifers of the Riverine Province are low (Lawrence, 1988), and this is unlikely to be a source of DIC.

## Methanogenesis

In the absence of free  $\text{O}_2$ ,  $\text{NO}_3$ , and  $\text{SO}_4$ , bacteria may consume carbon to produce  $\text{CH}_4$  and  $\text{CO}_2$ . Abiogenic and thermocatalytic methanogenesis are also possible, but these processes are unlikely to occur at the relatively low temperatures recorded in the Campaspe groundwater (Sherwood-Lollar et al., 1989). There are two main biogenic methanogenesis processes: (a) the breakdown of long chain organic molecules via a variety of pathways that leads eventually to acetate fermentation and which has a net reaction of the form:



and (b) the direct reduction of dissolved  $\text{CO}_2$  in the groundwater via:



(Clark and Fritz, 1997; Valentine et al., 2004; Leybourne et al., 2006). Studies carried out at a variety of temperatures and pH conditions summarised by Clark and Fritz (1997) and Valentine et al. (2004) suggest that  $^{13}\text{C}$  fractionations between  $\text{CO}_2$  and  $\text{CH}_4$  are 60–80‰ for  $\text{CO}_2$  reduction and 20–50‰ for acetate fermentation. Thus, both processes can produce DIC that is enriched in  $^{13}\text{C}$ . If acetate fermentation occurs, the enrichment is due to the subsequent dissolution of  $^{13}\text{C}$ -enriched  $\text{CO}_2$  produced by Eq. (2), while if direct reduction occurs the enrichment is due to the removal of  $\text{CH}_4$  with low  $\delta^{13}\text{C}$  values. As discussed above, Calivil–Renmark and Shepparton sediments have low organic contents and, if methanogenesis occurs, it most probably involves  $\text{CO}_2$  reduction. The lack of a correlation between DIC concentrations and  $\delta^{13}\text{C}$  values (Fig. 10a) also implies that acetate fermentation (which increases DIC concentrations) is unlikely. There are a number of observations that support the  $\text{CO}_2$  reduction methanogenesis model. Firstly, the groundwater has low DO concentrations and is locally anoxic (Table 1). Secondly, there is evidence of bacterial reduction of  $\text{SO}_4$  and  $\text{NO}_3$ . Overall the groundwater contains  $<22$  mmol/L  $\text{SO}_4$  and  $<0.36$  mmol/L  $\text{NO}_3$ . The locally low  $\text{SO}_4$  and  $\text{NO}_3$  concentrations suggest that bacteriological reduction of these solutes has occurred (cf., Coetsiers and Walraevens, 2009). In support of this assertion, samples with  $\delta^{13}\text{C}$  values  $>8$ ‰ have the lowest  $\text{SO}_4$  and DIC concentrations (Fig. 10b) and locally dissolved sulfate has high  $\delta^{34}\text{S}$  values (Fig. 10c).  $\delta^{34}\text{S}$  values of atmospheric deposition and gypsum deposits in the southern Murray Basin are 15–23‰ (Dogramaci et al., 2001). Much of the groundwater from the Campaspe Valley has  $\delta^{34}\text{S}$  values in this range (Fig. 10c) implying that the sulfate is largely derived from those sources. Groundwater with the elevated  $\delta^{34}\text{S}$  values also has high  $\delta^{13}\text{C}$  values and low  $\text{SO}_4$  concentrations, which is consistent with bacteriological reduction taking place (e.g., Dogramaci et al., 2001; Petrides et al., 2004, 2006). Finally, reaction (3) results in an increase in pH. Locally high pH values exist in groundwater in this region (Table 1) and elsewhere in the southern Murray Basin (up to 11: Cartwright et al., 2008) that maybe the result of methanogenesis.

For  $^{13}\text{C}$  fractionations between DIC and  $\text{CH}_4$  of 60–80‰, the production of a small amount of methane will produce a significant increase in  $\delta^{13}\text{C}$  of the residual DIC by either batch or continuous (Rayleigh) generation (Fig. 11). Saliege and Fontes (1984) estimated that the mass-dependant fractionation of  $^{14}\text{C}$  relative to  $^{12}\text{C}$  is 2.3 times that of  $^{13}\text{C}$ . Thus, an increase in  $\delta^{13}\text{C}$  of 10‰ should result in an increase in  $\delta^{14}\text{C}$  of 2.3‰. This is a relatively minor change that does not produce a significant correction of the  $^{14}\text{C}$  ages. If methanogenesis were the only process affecting the DIC in this the aquifers post recharge, then uncorrected ages may be most appropriate.

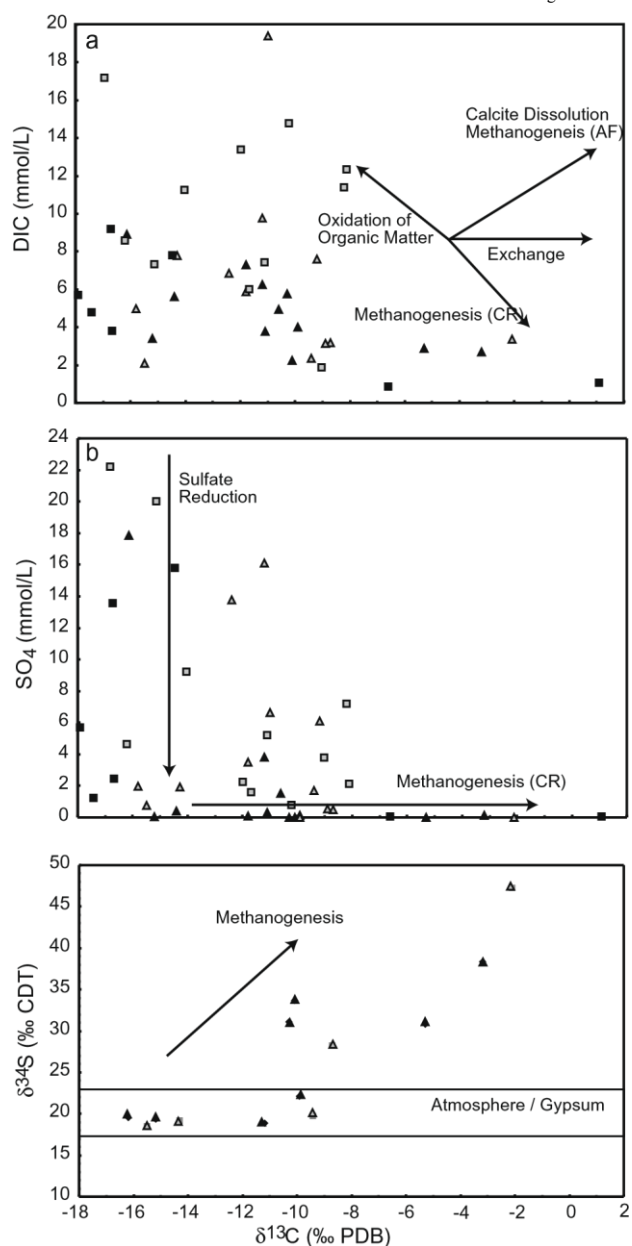


Fig. 10. (a) DIC concentrations vs.  $\delta^{13}\text{C}$  values. Arrowed lines show expected trends for a variety of processes (Coetsiers and Walraevens, 2009). AF = acetate fermentation; CR = carbon reduction. (b)  $\text{SO}_4$  concentrations vs.  $\delta^{13}\text{C}$  values. Arrowed lines show expected trends for sulfate and carbon reduction (Coetsiers and Walraevens, 2009). (c)  $\delta^{34}\text{S}$  vs.  $\delta^{13}\text{C}$  values; box shows range of  $\delta^{34}\text{S}$  values in atmospheric deposition and gypsum deposits from the southern Murray Basin. Data from Table 1.

The uncorrected ages of the Calivil–Renmark groundwater in the north of the Campaspe Valley near Echuca are 9–13 ka (Fig. 7a). Calivil–Renmark groundwater in the Pyramid Hill region is substantially older at any given distance along the flow path with ages of 20–25 ka recorded in the north of the area (Fig. 7c). The age of groundwater from the Shepparton Formation across the area increases irregularly with depth, with ages of in excess of 25 ka recorded at its base (Fig. 7b and d).

#### Comparison with hydrodynamic ages

In the Riverine Province, there are no correlations between  $\delta^{18}\text{O}$  values and position in the flow system (Cartwright et al., 2008) and

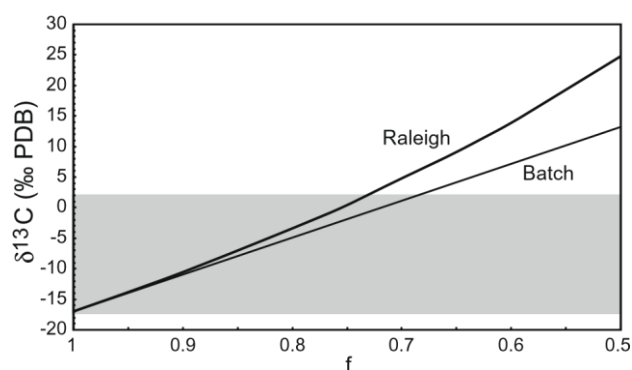


Fig. 11. Changes to  $\delta^{13}\text{C}$  values of residual DIC resulting from carbon reduction with a fractionation of 60‰ (Valentine et al., 2004) by batch and Raleigh fractionation (cf., Clark and Fritz, 1997).  $f$  is the fraction of the original carbon remaining and the shaded area shows the range of  $\delta^{13}\text{C}$  values in the Campaspe region.

stable isotopes cannot be used to provide a check on groundwater age (cf., Darling et al., 1997; Edmunds and Smedley, 2000; Herczeg et al., 2001; Chen et al., 2003; Zhu et al., 2007; Edmunds, 2009). However, comparison of the  $^{14}\text{C}$  ages with those calculated from physical hydrogeology may provide a test of reasonableness. Lateral hydraulic gradients in the Calivil–Renmark Formation in the Campaspe Valley are  $4 \times 10^{-4}$  (Fig. 2) and hydraulic conductivities are 40–200 m/day, with an average for the whole Campaspe Valley of 80–100 m/day (Tickell, 1978, 1982; Arad and Evans, 1987; Chiew et al., 1992). While shallow groundwater elevations have changed over the last 200 years following land clearing, those in confined deeper aquifers are less impacted. The Campaspe Valley broadens and deepens from the recharge area south of Elmore northwards with an 8-fold increase along the flow path. Horizontal groundwater fluxes will thus decrease northwards, which is consistent with the hydraulic gradients declining northwards (Fig. 2) even though hydraulic conductivities also decline in that direction (Tickell, 1978; Tickell, 1982; Chiew et al., 1992). Using these parameters and a porosity of 0.2 yields hydrodynamic ages calculated using Darcy's Law of 7.5–9.5 ka for the groundwater around Echuca. While this calculation is subject to a number of uncertainties, it does yield ages that are in broad agreement with those calculated above assuming no dilution by matrix carbon.

## Conclusions

Even in a relative simple catchment such as the Campaspe Valley, the interpretation of groundwater flow and groundwater residence times is not straightforward. The use of  $\delta^{13}\text{C}$  values to correct the  $^{14}\text{C}$  ages assuming carbonate dissolution or exchange produces age estimates that are at odds with the general understanding of the flow system, the aquifer mineralogy, and the groundwater geochemistry. The use of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and other aspects of groundwater geochemistry was invaluable in understanding the behaviour of DIC in this system. The results of this study allows for better management of water resources in the Campaspe area. The conclusion that groundwater from the Shepparton Formation is not leaking into the deeper Renmark Formation throughout the Campaspe Valley implies that the risk from surface contamination is low. However, the observation that the age of the Renmark groundwater in the Campaspe Valley is up to 13 ka illustrates that this is a finite resource.

Methanogenesis by reduction of DIC may be an important process in other aquifers, which if not accounted for may affect the correction of  $^{14}\text{C}$  ages. In the Campaspe Valley, the existence of groundwater with high  $\delta^{13}\text{C}$  values drew attention to this process occurring. The same process may occur in other aquifer systems; however, it may not be obvious that is the case if  $\delta^{13}\text{C}$  values are not as high as they are in the Campaspe region. In the Murray Basin, especially in regions away from the major limestone aquifers, relatively little water–rock interaction occurs aside from cation exchange, and there is negligible dissolution of carbonate in most of the silicate-dominated aquifers. In such cases attributing increases in  $\delta^{13}\text{C}$  values to calcite dissolution would produce plausible, if ultimately incorrect, corrections to  $^{14}\text{C}$  ages. Possible examples in the Murray Basin, include the Renmark Group groundwater from the Goulburn Valley or the Wimmera region where age corrections by Cartwright and Weaver (2005) and Leaney et al. (2003) considered only calcite dissolution despite the groundwater in these deeper aquifers being anoxic and, in the case of the Wimmera region, bacteriological sulfate reduction occurring (Dogramaci et al., 2001). The conclusions of Coetsiers and Walraevens (2009) that methanogenesis in the Neogene aquifers in Belgium was via acetate fermentation required that the organic matter being reduced was modern ( $\delta^{14}\text{C}$  100), which in turn required that this process occurred in the recharge zone. While that study tried to constrain a range of processes that impacted  $^{14}\text{C}$  ages, methanogenesis via DIC reduction may overcome this issue. This study demonstrates the need to apply a multi-tracer approach to the correction of  $^{14}\text{C}$  ages.

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