



## 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

from: (1) dissolution of carbonate minerals or organic material from the aquifer matrix; (2) the input of deep-seated geogenic  $\text{CO}_2$  from volcanic activity or metamorphism of limestone; or (3) methanogenesis of organic material in the aquifer matrix (e.g., Clark and Fritz, 1997; Kalin, 2000). In addition, diffusion of C from low porosity layers can also impact  $a^{14}\text{C}$  (Sudicky and Frind, 1981).

There are numerous schemes for correcting  $^{14}\text{C}$  ages that are based on  $\delta^{13}\text{C}$  values of DIC (e.g., Fontes and Garnier, 1979; Salem et al., 1980; Clark and Fritz, 1997; Gallagher et al., 2000; Kalin, 2000; Coetsiers and Walraevens, 2009), major ion geochemistry (Tamers, 1975; Celle-Jeanton et al., 2009; Coetsiers and 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  $\text{CO}_2$  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,  $\delta^{13}\text{C}$  values, and  $a^{14}\text{C}$  along groundwater flow paths. However, ideally, all processes that can impact the DIC con-

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centration of the groundwater should be accounted for (e.g., Buckau et al., 2000; Coetsiers and Walraevens, 2009), and independent geochemical tracers such as  $^3\text{H}$  or  $^4\text{He}$  contents (Buckau et al., 2000; Kulongoski et al., 2008) or  $^{87}\text{Sr}/^{86}\text{Sr}$  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  $\delta^{18}\text{O}$  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  $^{14}\text{C}$  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  $^{14}\text{C}$  data and a reinterpretation of the  $^{14}\text{C}$  data of Calf et al. (1986). The main aim of this study is to assess the correction of  $^{14}\text{C}$  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  $^{14}\text{C}$  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  $\sim 300,000$  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 low-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 hydro-

lic 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, Lodden, 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  $^{14}\text{C}$  ages of Shepparton groundwater commonly increase with depth (Calf et al., 1986; Cartwright et al., 2006). By contrast  $^{14}\text{C}$  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  $\sim 350$  m. The Riverine Plain north of the basement outcrop has subdued topography with ground elevations falling from  $\sim 120$  m in the south to  $\sim 75$  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 heterogenous 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  $10^{-5}$ – $10^{-2}$  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  $\sim 600$  mm in the south to  $\sim 400$  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

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