



# Differences in groundwater and chloride residence times in saline groundwater: The Barwon River Catchment of Southeast Australia



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## ABSTRACT

The residence times of groundwater and chloride and the processes contributing to the development of saline (total dissolved solids (TDS) up to 45,379 mg/L) groundwater within the Barwon River Catchment of southeast Australia were investigated using major ion, stable isotope ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ , and  $\delta^{13}\text{C}$ ) and radioactive isotope ( $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ) geochemistry. The elevated groundwater salinity in the region is primarily due to evapotranspiration and recycling of solutes in saline lakes with minor contributions from weathering of halite, silicate and calcite minerals. Groundwater residence times estimated from  $^{14}\text{C}$  vary from modern to ~20 ka; for groundwater with lower  $^{14}\text{C}$  activities, the estimated residence times vary significantly depending on the assumed flow model and the  $^{14}\text{C}$  activity of recharge. Chloride residence times downgradient of Lake Murdeduke (a saline through-flow lake in the centre of the catchment) are greater than the corresponding groundwater residence times due to the recycling of Cl within the lake. Precise estimates of chloride residence time could not be determined using  $^{36}\text{Cl}$  due to  $R^{36}\text{Cl}$  in precipitation being lower than that of groundwater. This is most likely due to  $R^{36}\text{Cl}$  values in rainfall having been higher in the past than they are at present due to climate variability.  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ , and  $\delta^{13}\text{C}$  values also suggest that the region has experienced increasingly more evaporative conditions with time. The results of this study demonstrate that, while Cl is a useful tracer of hydrological processes, it must be applied carefully in arid and semi-arid regions of the world. In particular, recharge rates calculated using chloride mass balance may be underestimated where recycling of Cl has occurred.

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## 1. Introduction

Understanding groundwater systems requires being able to account for the behaviour of both the water and the solutes (Edmunds, 2009). Chloride is probably the most widely studied solute as it is one of the most abundant ions in groundwater and its concentration is readily measured. Because its concentration is not significantly impacted by biogeochemical reactions, ion exchange or decay, and because it forms minerals only at very high concentrations, chloride is commonly used to estimate groundwater recharge rates and residence times (e.g., Allison and Hughes, 1978; Wood and Sanford, 1995; Scanlon et al., 2006). Use of Cl in this way makes the explicit assumption that its residence time is equivalent to that of the groundwater in which it is contained. However, this assumption may not always hold true. For

example, in arid and semi-arid regions, Cl may be recycled over long timescales within saline lakes. Secondly, diffusion of old Cl from clays into adjacent aquifers may occur. Thirdly, if halite dissolution within an aquifer occurs, the halite represents a source of potentially very old Cl. Each of these scenarios results in Cl having a longer residence time than the water in which it is contained. If chloride residence times are significantly older than groundwater residence times, the use of Cl to estimate recharge rates or groundwater residence times will produce erroneous results. The implications of this are significant in terms of managing groundwater resources, protecting ecosystems, and assessing salinity impacts.

Chloride residence times can be estimated from chloride concentrations within the groundwater, knowledge of aquifer thickness and porosity, and an estimate of the amount of chloride delivered annually via rainfall. As an independent measure, chloride residence times can also be estimated using  $^{36}\text{Cl}$ . With a half-life of 301,000 years,  $^{36}\text{Cl}$  can be used to determine chloride residence times within the range of approximately 100 ka to 1 Ma (e.g. Bentley et al., 1986a; Phillips et al., 1986). Groundwater residence times up to approximately 35 ka are

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frequently estimated in regional aquifers using  $^{14}\text{C}$ . While  $^{14}\text{C}$  has been widely used as a tracer, most studies have not taken into account long-term variations in the  $^{14}\text{C}$  of the water that recharges the aquifer nor processes such as dispersion, which can impact calculated residence times.

In this study, we use  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ , and  $^3\text{H}$  in combination with major ion geochemistry and stable isotopes to understand the timescales and processes responsible for the development of saline groundwater within the Barwon River Catchment in southeast, Australia. In addition, we examine whether groundwater residence times and chloride residence times within the catchment are equivalent. While there have been a number of studies that have utilised both  $^{36}\text{Cl}$  and  $^{14}\text{C}$  (e.g. Bird et al., 1989; Love et al., 2000; Kulongoski et al., 2008; Plummer et al., 2012; Scheiber et al., 2015), this is the first application of these tracers that we know of that specifically addresses the potential differences between groundwater and chloride residence times. The outcomes of this study will help understand the timescales and processes by which chloride is stored and exported from similar catchments globally, and will better inform the use of Cl as a tracer in saline groundwater.

## 2. Setting

The Barwon River Catchment is located in southwestern Victoria, Australia. Comprising an area of approximately 3900 km<sup>2</sup> (DataSearch Victoria, 2015), the catchment is utilised primarily for grazing, cropping and forestry. Settlements within the catchment include the major population centres of Geelong and Ballarat, as well as numerous rural communities. This investigation focuses primarily on that portion of the catchment located in the vicinity of Winchelsea and Inverleigh (Fig. 1a).

The catchment has a temperate climate, with average annual rainfall ranging from approximately 430 mm near Inverleigh to approximately 1600 mm in the Otway Ranges (Department of Environment, Land, Water and Planning, Water Measurement Information System, WMIS, 2015). The majority of rainfall occurs during the austral winter months (July to September) and, during the summer months, potential evaporation exceeds precipitation (Bureau of Meteorology, BOM, 2016). The Barwon River is perennial (Department of Environment, Land, Water and Planning, Water Measurement Information System, WMIS, 2015) and flows northwards from the Otway Ranges, which reach a maximum elevation of approximately 650 m above sea level. There are a number of permanent and semi-permanent brackish to hyper-saline lakes within the study area (Tweed et al., 2011). The largest of these is Lake Murdeduke, which has an area of approximately 1,660 ha, a depth of approximately 5 m and a mineral ('salt') crust that periodically forms along its shores. From an analysis of regional groundwater flow paths, salt and water balances, and geochemistry, Coram (1996) concluded that Lake Murdeduke was a through-flow lake, with groundwater entering the lake along its west shore and discharging along its east shore.

The basement of the catchment comprises the early-Cretaceous Otway Group, which consists primarily of volcanogenic sandstone and mudstone with minor amounts of shale, siltstone, and coal (Tickell et al., 1991). The Otway Group is overlain by Tertiary sediments comprising (in ascending order) the Eastern View Formation, the Demons Bluff Formation, the Clifton Formation, the Gellibrand Marl and the Moorabool Viaduct Sand. The Tertiary sediments are in turn overlain by the Quaternary Newer Volcanics, which crop out over approximately 40% of the catchment. This study is based on groundwater sampled primarily from the Newer Volcanics and the Moorabool Viaduct Sand (Fig. 1a).

The Moorabool Viaduct Sand is a thin (generally less than 10 m thick), discontinuous unit of clayey sand that crops out at various locations across the catchment, including to the west of Lake Murdeduke and near Winchelsea and Inverleigh. Coram (1996) estimated that the

hydraulic conductivity of this unit was approximately 4.3 m/day. The Newer Volcanics have been broadly grouped into "older-" and "younger-phase" deposits. The older-phase Newer Volcanics, which are comprised mainly of weathered olivine basalt, are considered to be a poor aquifer, with groundwater generally only occurring within joints, vesicles, and poorly-connected interflow layers. Gill (1989) estimated that the older-phase Newer Volcanics have an average transmissivity of approximately 200 m<sup>2</sup>/day (which assuming an average thickness of 15 m equates to a hydraulic conductivity of 13.3 m/day). The younger-phase Newer Volcanics consist of basalt, scoria, undifferentiated pyroclastics, pyroclastic surge deposits and pyroclastic fall deposits (Tickell et al., 1991). They are less weathered and have a higher degree of fracturing than the older phase volcanics. Coram (1996) estimated that the younger-phase Newer Volcanics have an average hydraulic conductivity of 8.6 m/day. Together, the older- and younger-phase Newer Volcanics have an average thickness of approximately 30 m in the study area. Also present are Quaternary lunette deposits along the east shore of Lake Murdeduke and alluvium along the Barwon River (Fig. 1a).

Regional groundwater in the lower Tertiary units flows from recharge areas in the Otway Ranges to the north or northeast (Witebsky et al., 1995; Petrides and Cartwright, 2006). Flow direction within the Newer Volcanics and underlying Moorabool Viaduct Sand is more variable and is influenced by local topography. Recharge occurs across the basin and groundwater discharges into the Barwon River (Cartwright et al., 2013a). Shallow groundwater in the headwaters of the catchment generally has low (<500 mg/L) total dissolved solids (TDS) concentrations but in the centre of the catchment, near Lake Murdeduke, TDS concentrations in excess of 10,000 mg/L are common (Coram, 1996). TDS concentrations as high as 1200 mg/L have also been reported within the Barwon River (Cartwright et al., 2013a), which is interpreted to be the result of highly saline groundwater inflow (Roderick, 1988; Gill, 1989).

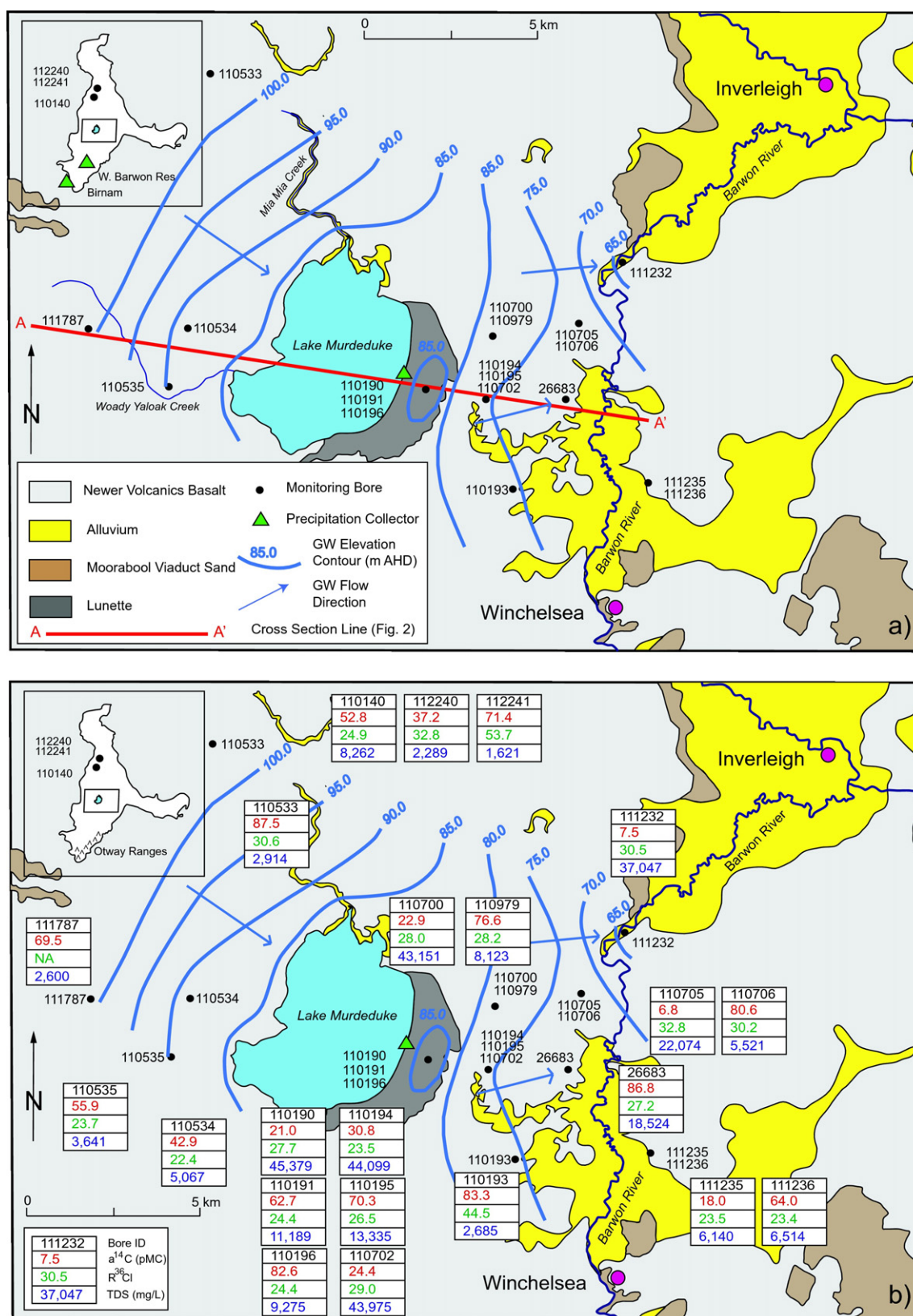
## 3. Methods

### 3.1. Sampling

Samples of precipitation, groundwater, Lake Murdeduke lake water and Lake Murdeduke salt crust were collected from the study area between September 2014 and November 2015. The EC, pH and temperature of the water samples were measured in the field using a calibrated, TPS® hand-held water quality meter and probes and alkalinity was determined using a Hach® digital titrator and reagents. Sampling locations are shown in Figs. 1a, 1b and 2.

Precipitation samples were collected using rainfall collectors located along the east shore of Lake Murdeduke, on the east side of the West Barwon Reservoir and at Birnam in the Otway Ranges (Fig. 1a). Precipitation collectors consisted of polyethylene storage containers equipped with funnels positioned approximately one-half metre above ground level. Water within the containers was periodically sampled, the containers rinsed with ultrapure water and then replaced. Precipitation samples were collected on six occasions at Birnam, on two occasions at the West Barwon Reservoir and on one occasion at Lake Murdeduke.

Groundwater samples were collected in March 2015 from 22 groundwater monitoring bores that comprise part of the Victorian State Observation Bore Network (SOBN). All but three of the bores are located within the vicinity of Lake Murdeduke; the remaining bores are located approximately 20 to 30 km to the north of the lake (Fig. 1a). The sampled bores are screened within the Newer Volcanics, the Moorabool Viaduct Sand or lunette deposits at depths ranging from approximately 8 to 65 m below ground level. At several locations, adjacent bores are screened at different depths within a single geologic unit and/or between units. Bore details are summarised in Table 1. Standing water levels were measured prior to sampling using an electronic water level tape. Groundwater

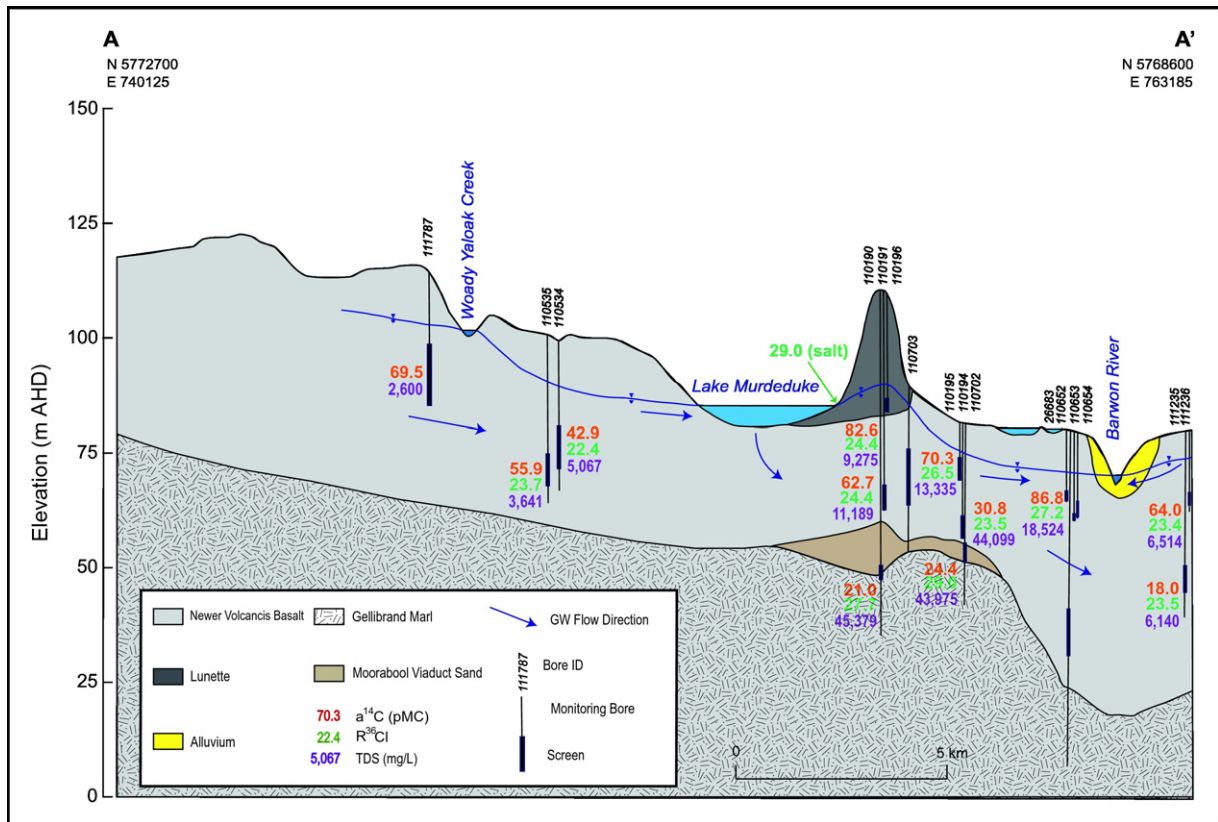


**Fig. 1.** Map of the Barwon River Catchment near Lake Murdeduke showing: a) lithology (DataSearch Victoria, 2015), groundwater flow and sampling locations, and b) groundwater a<sup>14</sup>C, R<sup>36</sup>Cl and TDS.

samples were collected using an impeller pump (shallow bores) or a piston pump (deep bores) set within the screened zone, with approximately three bore volumes of groundwater removed prior to sample collection.

Samples of Lake Murdeduke salt crust and lake water were collected along the east shore of the lake in March and June, 2015 respectively. The lake water sample was collected from approximately 0.5 m below the lake water surface.





**Fig. 2.** Geologic cross section through the study area showing lithology and  $a^{14}\text{C}$ ,  $R^{36}\text{Cl}$  and TDS in groundwater.

**Table 1**

Construction details and groundwater levels for monitoring bores sampled as part of this study. m = metres, bgl = below ground level, mp = measuring point, m AHD = metres Australian Height Datum, SWL = Standing Water Level, GW = Groundwater. SWL for 111787 provided by D. Banfield (pers. comm., 2015).

Bore ID	Geologic unit	Bore depth m bgl	Screen interval m bgl	Screen mid-point m bgl	mp m AHD	SWL m bmp	GW elevation m AHD
26683	Basalt	8.2	6–8	7	72.45	1.89	70.56
110140	Basalt	28.0	22–28	25	179.55	17.55	162.00
110190	M. Viaduct Sand	65.0	62–65	63.5	113.25	33.80	79.45
110191	Basalt	50.0	45–50	47.5	113.51	35.28	78.23
110193	Basalt	9.0	3–9	6	77.47	1.68	75.79
110194	Basalt/Clay	21.0	18–21	19.5	78.18	2.42	75.76
110195	Basalt	9.0	6–9	7.5	78.41	3.07	75.34
110196	Lunette	29.5	26–29.5	27.75	113.25	23.43	89.82
110533	Basalt	30.1	9–15	12	109.54	5.01	104.53
110534	Basalt	27.0	21–27	24	99.10	10.63	88.47
110535	Basalt	27.0	21–27	24	95.17	5.47	89.70
110700	Basalt	58.0	40–58	49	86.77	8.25	78.52
110702	M. Viaduct Sand	26.5	23–26.5	24.75	78.68	3.26	75.42
110705	Basalt	46.0	34–46	40	82.81	9.81	73.00
110706	Basalt	12.5	6–12.5	9.25	82.60	9.23	73.37
110979	Basalt	13.0	7–13	10	86.79	8.16	78.63
111232	Basalt	27.0	21–27	24	77.01	13.42	63.59
111235	Basalt/Clay	34.0	28–34	31	78.85	6.24	72.61
111236	Basalt	15.0	12–15	13.5	79.14	6.05	73.09
111787	Basalt	30.5	20.5–30.5	25.5	116.23	14.08	102.15
112240	M. Viaduct Sand	72.0	66–72	69	250.24	26.41	223.83
112241	Basalt	25.0	13–25	19	250.35	20.23	230.12

### 3.2. Analytical techniques

The groundwater samples were analysed for cations and anions,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$ ,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ , and  $^3\text{H}$  (select samples only). The precipitation and Lake Murdeduke salt crust samples were analysed for cations, anions and  $^{36}\text{Cl}$ . The salt crust sample was dissolved in ultrapure water prior to analysis. The Lake Murdeduke lake water sample was analysed for cations, anions,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ .

Cation analysis was conducted at Monash University using a ThermoFinnigan ICP-OES on samples that had first been filtered through 0.45  $\mu\text{m}$  cellulose nitrate filters and acidified to pH < 2 using double-distilled 16 M  $\text{HNO}_3$ . Anions were analysed at Monash University on filtered, un-acidified samples using a Metrohm ion chromatograph (IC). The precision of the cation and anion analyses, based upon replicate sample analysis, is  $\pm 2\%$  while the accuracy, based on analysis of certified water standards, is  $\pm 5\%$ . To assess quality control, duplicate samples were prepared and analysed at a rate of approximately one per every ten primary samples. Total dissolved solids (TDS) concentrations were determined by summing the concentrations of cations and anions.

Stable isotopes were analysed at Monash University using Finnigan MAT 252 and ThermoFinnigan DeltaPlus Advantage mass spectrometers.  $\delta^{18}\text{O}$  values were determined via equilibration with  $\text{He-CO}_2$  at 32  $^\circ\text{C}$  for 24 to 48 h in a ThermoFinnigan Gas Bench.  $\delta^2\text{H}$  was measured by reaction with Cr at 850  $^\circ\text{C}$  using an automated Finnigan MAT H/Device.  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  were measured relative to internal standards calibrated using IAEA, SMOW, GISP and SLAP. Data were normalised following methods outlined by Coplen (1988) and are expressed relative to V-SMOW. Precision ( $1\sigma$ ), based on replicate analysis, is  $\pm 0.1\%$  for  $\delta^{18}\text{O}$  and  $\pm 1\%$  for  $\delta^2\text{H}$ .  $\text{CO}_2$  from dissolved inorganic carbon (DIC) was liberated by acidification using  $\text{H}_3\text{PO}_4$  in a He atmosphere in a ThermoFinnigan Gas Bench.  $\delta^{13}\text{C}$  values are expressed relative to PDB and the precision, based on replicate samples, is  $\pm 0.2\%$ .

$^{36}\text{Cl}$  analysis was conducted at the Australian National University (ANU) using accelerator mass spectrometry (AMS) and techniques described by Fifield (1999) and Fifield et al. (2013).  $^{36}\text{Cl}$  activities are expressed as  $R^{36}\text{Cl}$ , where  $R^{36}\text{Cl} = {}^{36}\text{Cl}/\text{Cl} \times 10^{-15}$ . Uncertainties in the  $R^{36}\text{Cl}$  values are derived from the counting statistics of the number of  $^{36}\text{Cl}$  counts combined in quadrature with a 3% reproducibility uncertainty. Uncertainties for the samples measured range between 5 and 6%.

$^{14}\text{C}$  analysis was performed at the Rafter Radiocarbon Laboratory of the Institute of Geological and Nuclear Sciences (GNS) in Lower Hutt, New Zealand. Analysis was conducted by first converting the DIC in the water samples to  $\text{CO}_2$  using  $\text{H}_3\text{PO}_4$ , re-combusting the  $\text{CO}_2$  with silver wire to remove sulphur, and converting the  $\text{CO}_2$  to graphite.  $^{14}\text{C}$  activities were then determined on the graphite using AMS.  $^{14}\text{C}$  activities ( $a^{14}\text{C}$ ) are expressed as pMC (percent modern carbon) where pMC = 100% corresponds to 95% of the  $^{14}\text{C}$  activity of the National Bureau of Standards (NBS) oxalic acid standard (Stuiver and Polach, 1977).

$^3\text{H}$  analysis was conducted at the GNS Water Dating Laboratory in Lower Hutt, New Zealand. The samples were distilled and electrolytically enriched prior to analysis by liquid scintillation counting, as described by Morgenstern and Taylor (2009).  $^3\text{H}$  activities are expressed in tritium units (TU) with a relative uncertainty and quantification limit of  $\pm 2\%$  and 0.02 TU, respectively.

### 3.3. Groundwater residence times

Groundwater residence times were estimated from the measured  $^{14}\text{C}$  activities of DIC via:

$$t = \frac{1}{\lambda} * \ln \left( \frac{q A_0}{A} \right) \quad (1)$$

(Clark and Fritz, 1997), where  $\lambda$  is the  $^{14}\text{C}$  decay constant ( $1.21 \times 10^{-4} \text{ yr}^{-1}$ ),  $A$  is the measured  $^{14}\text{C}$  activity,  $A_0$  is the initial  $^{14}\text{C}$  activity in the recharging water (assumed to be 100 pMC), and  $q$  is the proportion of DIC derived from the recharging water. Use of this approach assumes that  $q$  is known, or can be reasonably estimated, and that  $A_0$  has remained constant over time. It is also assumed that the sampled water has taken a direct flow path from the point of recharge to the sampling point with no mixing or dispersion (i.e., piston flow). These are simplifying assumptions; nevertheless, Eq. (1) is commonly used to estimate groundwater residence times.

Groundwater residence times were also estimated using TracerLPM (Jurgens et al., 2012), which is an Excel-based program that estimates mean residence times (MRTs) using lumped parameter models (LPMs). Use of this approach readily allows variation in  $A_0$  with time to be accounted for. In addition, it is not necessary to assume piston flow. However, LPMs are based upon simplified aquifer geometries, which may not always strictly apply to a given flow system. Furthermore, tracer input histories are in many cases incomplete and must therefore be interpolated. Nonetheless, the use of LPMs allows the impact of processes such as dispersion on  $^{14}\text{C}$  activities to be addressed.

### 3.4. Chloride residence times

Chloride residence times may be estimated using measured  $R^{36}\text{Cl}$  values in groundwater and:

$$t = -\frac{1}{\lambda} * \ln \frac{R - R_{se}}{R_0 - R_{se}} \quad (2)$$

(Bentley et al., 1986a), where  $\lambda$  is the  $^{36}\text{Cl}$  decay constant ( $2.3 \times 10^{-6} \text{ yr}^{-1}$ ),  $R$  is the measured  $R^{36}\text{Cl}$ ,  $R_0$  is the initial  $R^{36}\text{Cl}$  in recharge and  $R_{se}$  is the secular  $R^{36}\text{Cl}$  due to hypogene (subsurface) production. As with  $^{14}\text{C}$ , use of Eq. (2) assumes that  $R_0$  is both known and time invariant.  $R_{se}$ , which largely depends on the amount of uranium and thorium in the aquifer matrix, matrix porosity, and the Cl content

of groundwater, is difficult to determine but only becomes significant after about five half-lives (Clark and Fritz, 1997).

Chloride residence or accession times can also be estimated from:

$$t = \frac{Cl_{gw}}{m_{Cl}} * b * n \quad (3)$$

where  $Cl_{gw}$  is the chloride concentration in groundwater in  $\text{mg}/\text{m}^3$ ,  $m_{Cl}$  is the chloride deposition rate from precipitation in  $\text{mg}/\text{m}^2/\text{year}$ ,  $b$  is the saturated thickness of the aquifer in m, and  $n$  is aquifer porosity. Eq. (3) allows estimates of the time required for Cl in groundwater to accumulate using parameters that are commonly known, or which can easily be estimated. However, the Cl deposition rate is implicitly assumed to have remained constant with time, runoff is considered to be negligible and input by precipitation is assumed to be the only source of chloride within the aquifer.

## 4. Results

Groundwater elevations and the geochemistry of precipitation, groundwater, and Lake Murdeduke lake water and salt crust are summarised in Tables 1 and 2.

### 4.1. Groundwater elevations and head gradients

Groundwater elevations ranged from approximately 63.59 m AHD at bore 111232 to 230.12 m AHD at bore 112241. Shallow groundwater flow direction is generally to the east-southeast, except for an area of groundwater mounding immediately to the east of Lake Murdeduke (Figs. 1a, 1b and 2). Horizontal head gradients ranged from 0.002 to 0.008. Vertical head gradients ranged from 0.003 to 0.586 and were downward except at bore pairs 110190/110191 and 110194/110195, which are located between Lake Murdeduke and the Barwon River, where the gradients were upwards.

### 4.2. Major ion geochemistry

#### 4.2.1. Precipitation

The EC of precipitation ranged from 61.9 to 94.9  $\mu\text{S}/\text{cm}$  while TDS ranged from 25 to 43  $\text{mg}/\text{L}$ . Cl concentrations of the precipitation ranged from 8.5 to 15.7  $\text{mg}/\text{L}$ , which is higher than the mean concentrations reported by Blackburn and McLeod (1983) for Kybybolite (6.6  $\text{mg}/\text{L}$ ) in western Victoria and by Crosbie et al. (2012) for Melbourne (5.36  $\text{mg}/\text{L}$ ). The higher Cl concentrations in rainfall in the Barwon River Catchment may be due to evaporation within the collectors, aeolian transport of salt from Lake Murdeduke and/or addition of salts previously captured by overlying vegetation.

Molar Cl/Br ratios of precipitation ranged from 637 to 981 (Fig. 3a), which are slightly higher than the value of  $\sim 650$  which characterises seawater and coastal rainfall (Drever, 1997; Davis et al. 1998, 2001). Molar Na/Cl ratios (Fig. 3b) ranged from 0.55 to 0.93, which are similar to that of both seawater ( $\sim 0.86$ ) and rainfall in southeast Australia (0.6 to 1.1, Hutton and Leslie, 1958; Blackburn and McLeod, 1983; Crosbie et al., 2012).

#### 4.2.2. Lake Murdeduke water and salt crust

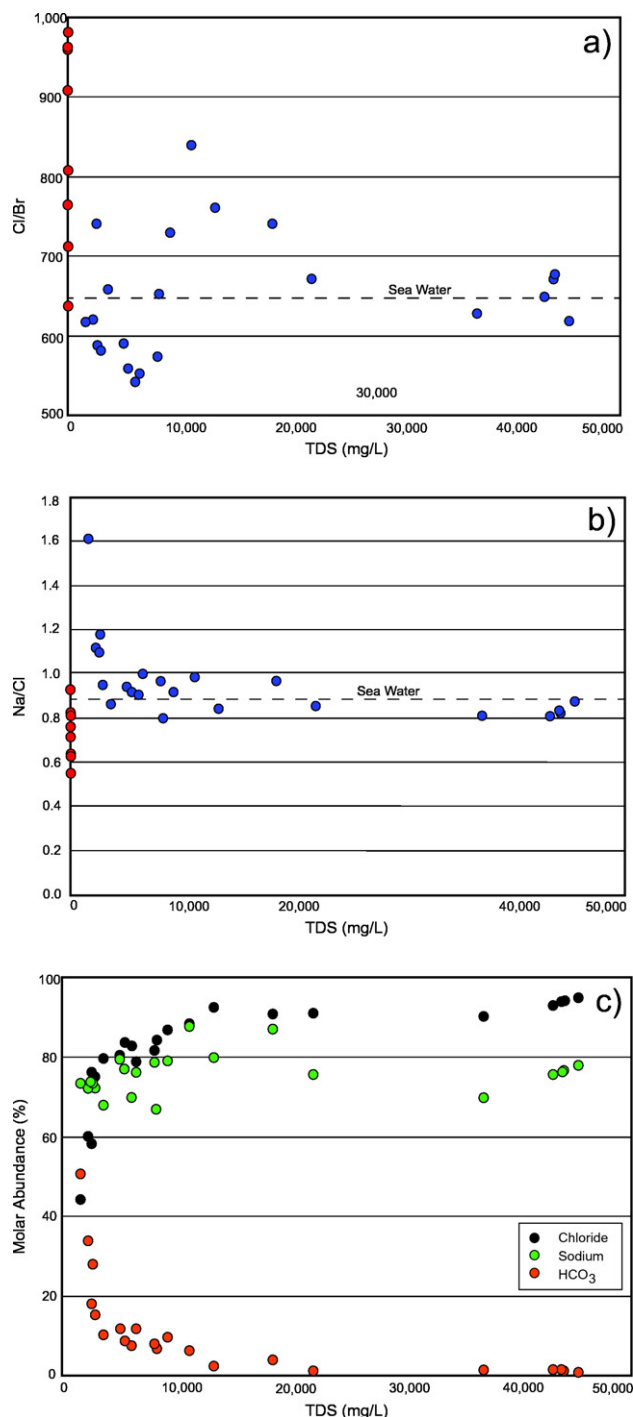
The water from Lake Murdeduke had an EC of 106,300  $\mu\text{S}/\text{cm}$ , a TDS concentration of 240,480  $\text{mg}/\text{L}$ , and a Cl concentration of 138,812  $\text{mg}/\text{L}$ . The TDS concentration is higher than that previously reported by Tweed et al. (2011) for the period 1965 to 2008. The molar Cl/Br ratio of the lake water was 786 while that of the salt crust was 4841.

#### 4.2.3. Groundwater

The EC of the groundwater ranged from 2530 to 67,900  $\mu\text{S}/\text{cm}$  while TDS ranged from 1621 to 45,379  $\text{mg}/\text{L}$  (Fig. 2). Groundwater from four of the observation bores in close proximity to, and immediately

**Table 2**Geochemistry results of groundwater, precipitation and Lake Murdeduke lake water and salt crust. Saturation indices for calcite ( $SI_{\text{calcite}}$ ) calculated using PHREEQC. Results for 111787 provided by D. Banfield (pers. Comm., 2015).

Location	Sample date	Temp. °C	EC μS/cm	pH S.U.	TDS mg/L	HCO <sub>3</sub> mg/L	Cl mg/L	Br mg/L	SO <sub>4</sub> mg/L	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	δ <sup>13</sup> C ‰	δ <sup>18</sup> O ‰	δ <sup>2</sup> H ‰	d-excess ‰	R <sup>36</sup> Cl × 10 <sup>15</sup>	a <sup>14</sup> C pMC	<sup>3</sup> H TU	Cl/Br	Na/Cl	SI <sub>Calcite</sub>
Groundwater																							
26683	12/03/2015	15.0	32,000	7.81	18,524	771	10,074	30.7	729	6324	448	66.3	50.0	−13.2	−2.8	−24	−1.8	27.2	86.8	0.511	741	0.97	0.55
110140	11/03/2015	17.0	14,770	7.56	8262	590	4227	14.6	603	2193	534	24.2	52.4	−17.3	−5.2	−36	6.0	24.9	52.8	—	653	0.80	0.25
110190	10/03/2015	16.3	53,100	7.31	45,379	468	26,057	95.0	1532	14,820	2058	133.9	197	−12.7	−0.7	−16	−10.4	27.7	21.0	—	618	0.88	0.68
110191	10/03/2015	15.4	18,290	7.75	11,189	730	5892	15.8	472	3764	267	19.0	7.1	−10.8	−3.4	−28	−0.7	24.4	62.7	—	839	0.99	−0.30
110193	13/03/2015	14.0	4250	7.64	2685	712	861	3.3	214	658	103	8.9	28.7	−13.1	−4.9	−34	5.6	44.5	83.3	0.127	588	1.18	0.16
110194	10/03/2015	—	64,100	7.64	44,099	620	25,636	85.4	1676	13,677	2048	157.4	181	−12.9	−0.7	−16	−10.7	23.5	30.8	—	677	0.82	1.06
110195	10/03/2015	14.7	21,980	6.29	13,335	359	7618	22.6	531	4158	514	45.5	35.8	−14.4	−3.2	−26	0.1	26.5	70.3	—	761	0.84	−1.41
110196	10/03/2015	—	15,990	7.53	9275	922	4790	14.8	257	2846	356	6.1	68.2	−15.6	−3.3	−29	−2.0	24.4	82.6	0.010	729	0.92	0.55
110533	11/03/2015	—	5300	7.87	2914	444	1262	4.9	212	779	114	13.2	64.4	−16.6	−4.7	−31	6.3	30.6	87.5	1.399	581	0.95	0.59
110534	11/03/2015	14.7	8880	7.73	5067	612	2417	9.2	311	1473	176	1.8	40.6	−15.6	−4.9	−30	9.2	22.4	42.9	0.005	590	0.94	0.41
110535	11/03/2015	15.7	6470	8.00	3641	386	1709	5.9	284	956	191	18.4	70.0	−16.1	−5.0	−33	6.8	23.7	55.9	—	658	0.86	0.66
110700	12/03/2015	16.8	67,900	7.61	43,151	761	24,890	86.4	1935	13,056	2057	118.1	214	−13.2	−1.0	−16	−8.1	28.0	22.9	—	649	0.81	1.20
110702	10/03/2015	—	63,300	7.66	43,975	781	25,396	85.3	1616	13,620	2028	130.0	282	−12.7	−0.5	−16	−12.4	29.0	24.4	—	671	0.83	1.33
110705	12/03/2015	17.5	36,700	7.86	22,074	293	12,174	40.9	1395	6748	894	139.9	329	−15.8	−2.4	−24	−4.5	32.8	6.8	—	671	0.85	0.96
110706	12/03/2015	17.8	10,490	8.33	5521	503	2745	11.1	328	1633	231	18.6	34.8	−17.5	−3.8	−30	0.7	30.2	80.6	0.826	559	0.92	0.85
110979	12/03/2015	15.3	14,370	7.94	8123	664	3918	15.4	628	2457	316	28.4	39.5	−16.4	−4.0	−31	1.7	28.2	76.6	—	574	0.97	0.55
111232	13/03/2015	15.9	59,200	7.37	37,047	583	20,322	72.9	2530	10,695	2024	173.7	606	−15.4	−1.6	−20	−6.6	30.5	7.5	—	628	0.81	1.20
111235	12/03/2015	15.7	10,930	7.76	6140	464	2940	12.2	459	1720	213	52.4	269	−14.4	−5.3	−34	8.6	23.5	18.0	—	542	0.90	1.09
111236	12/03/2015	14.8	11,130	7.79	6514	749	2950	12.0	481	1911	222	31.3	139	−12.5	−5.3	−34	8.0	23.4	64.0	—	553	1.00	1.02
111787	20/01/2015	—	4345	7.81	2600	447	1093	3.3	108	776	120	17.5	31.0	−13.8	−5.2	−34	8.0	—	69.5	0.002	741	1.09	0.24
112240	11/03/2015	17.4	3820	7.56	2289	737	759	2.8	101	550	101.5	5.1	15.1	−16.0	−5.6	−35	9.4	32.8	37.2	—	620	1.12	−0.10
112241	11/03/2015	16.5	2530	7.92	1621	717	364	1.3	48	380	65.5	3.5	10.4	−14.9	−5.6	−36	8.7	53.7	71.4	0.073	618	1.61	0.12
Precipitation																							
Birnam	27/09/2014	22.1	80.3	6.49	25	5.7	8.5	0.02	1.5	5.1	0.7	2.6	0.8	—	−4.4	−22	14.0	13.7	—	2.446	962	0.93	—
Birnam	20/12/2014	—	—	—	—	—	—	—	—	—	—	—	—	—	−0.8	−10	−3.8	20.1	—	—	—	—	—
Birnam	9/05/2015	—	94.9	5.67	43	11.3	15.7	0.04	2.1	6.5	1.1	5.2	1.3	—	−4.5	−24	12.2	—	—	—	981	0.64	—
Birnam	18/05/2015	12.4	73.6	6.48	30	0.6	15.6	0.05	2.1	7.7	1.0	1.9	0.8	—	−5.4	−30	13.4	—	—	—	712	0.76	—
Birnam	18/07/2015	7.4	64.8	5.44	29	5.7	10.6	0.03	1.4	4.3	0.9	4.3	1.1	—	−5.8	−33	13.9	—	—	—	908	0.63	—
Birnam	5/11/2015	—	67.0	5.88	29	7.3	10.2	0.03	1.8	5.4	0.8	2.8	0.9	—	−3.4	−16	11.1	—	—	—	764	0.81	—
W. Barwon Res.	18/07/2015	8.8	61.9	4.34	25	0.0	14.1	0.04	1.6	5.0	0.8	1.8	0.9	—	−5.6	−30	15.4	19.1	—	—	808	0.55	—
W. Barwon Res.	5/11/2015	—	68.9	4.62	28	2.4	13.5	0.03	1.5	6.3	1.0	2.4	0.9	—	−3.5	−17	11.1	—	—	—	959	0.72	—
L. Murdeduke	18/05/2015	—	77.1	5.76	29	0.2	15.4	0.05	1.4	8.2	1.3	0.4	1.6	—	−3.7	−26	4.1	20.2	—	—	637	0.83	—
Lake Murdeduke																							
Lake Water	20/06/2015	8.2	106,300	8.47	240,480	615	123,658	355	6162	65,406	7656	434	98	—	−2.3	−25	−6.2	—	—	—	786	0.82	1.45
Salt Crust	10/03/2015	—	—	—	—	0.0	30.7	0.01	0.2	18.9	0.2	BDL	BDL	—	—	—	—	29.0	—	—	4841	0.95	—



**Fig. 3.** Geochemistry results showing: a) Cl/Br ratios and b) Na/Cl ratios in groundwater (blue circles) and in precipitation (red circles), and c) molar abundance of chloride, sodium and bicarbonate in groundwater.

downgradient of, Lake Murdeduke (110190, 110194, 110700 and 110702; Figs. 1b, 2) had TDS concentrations that exceed 40,000 mg/L. Two of these bores (110190 and 110702) are screened within the Moorabool Viaduct Sand while the remaining two (110194 and 110700) are screened within basalt. The lowest TDS concentrations were at bores 112240 and 112241, which are located approximately 30 km to the north of Lake Murdeduke. At locations where two or more bores are screened at different depths, TDS generally increases with depth below ground surface. The one exception to this is bore pair 111235/111236, where TDS varies little with depth.

Cl concentrations in groundwater range from 364 to 26,057 mg/L and the relative molar abundance of Cl increases from 44% of total anions at TDS = 1621 mg/L to more than 90% at TDS > 12,000 mg/L (Fig. 3c). In contrast,  $\text{HCO}_3$  decreases in relative abundance from approximately 50% at TDS = 1621 mg/L to <3% at TDS > 12,000 mg/L. Sulphate concentrations range from 48 to 2530 mg/L and  $\text{SO}_4$  constitutes <5.5% of total anions. Na is the dominant cation (67 to 88% on a molar basis) and its concentration is strongly correlated with TDS. Mg, Ca and K constitute 6 to 15%, <6.5% and <1.5% of total cations, respectively.

Molar Cl/Br ratios of the groundwater range from 542 to 839 and do not vary significantly with TDS (Fig. 3a). Cl/Br ratios scatter around the ratio of seawater and coastal rainfall and overlap with those of the local precipitation. Molar Na/Cl ratios range from 0.8 to 1.6 and are generally higher in groundwater with TDS < 3000 mg/L (Fig. 3b).

#### 4.3. Stable isotopes ( $\delta^2\text{H}$ , $\delta^{18}\text{O}$ , $\delta^{13}\text{C}$ )

$\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of groundwater and Lake Murdeduke lake water are illustrated in Figure 4a along with the Melbourne Meteoric Water Line (MMWL) and the Global Meteoric Water Line (GMWL), which are defined as  $\delta^2\text{H} = 7.43 * \delta^{18}\text{O} + 8.6$  (Hughes and Crawford, 2012) and  $\delta^2\text{H} = 8.0 * \delta^{18}\text{O} + 10$  (Craig, 1961), respectively. The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of groundwater define an array with a slope of 3.9 to the right of the MMWL, indicating that evaporation occurred during or prior to recharge (Clark and Fritz, 1997). The array intercepts the MMWL at approximately  $\delta^2\text{H} = -38\text{‰}$  and  $\delta^{18}\text{O} = -6.5\text{‰}$ , which are lower than the weighted average  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of modern rainfall in Melbourne located 100 km to the east ( $\delta^2\text{H} = -28.4\text{‰}$ ,  $\delta^{18}\text{O} = -4.98\text{‰}$ ; Hughes and Crawford, 2012). The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of Lake Murdeduke water lie close to the same trend line as the groundwater samples. Deviation from the GMWL can be expressed as deuterium excess ( $d$ ), where  $d = \delta^2\text{H} - 8 * \delta^{18}\text{O}$  (Dansgaard, 1964) and there is a strong correlation between TDS and deuterium excess (Fig. 4b).

The  $\delta^{13}\text{C}$  values of DIC in groundwater range from  $-17.5\text{‰}$  to  $-10.8\text{‰}$ , with an average value of  $-14.6\text{‰}$ . There is no correlation between  $\delta^{13}\text{C}$  values and  $\text{HCO}_3$ , Ca or Mg concentrations, depth below ground surface, or TDS. However, the four samples (bores 110190, 110194, 110700 and 110702) having the highest TDS concentrations (>43,000 mg/L) have relatively similar  $\delta^{13}\text{C}$  values ( $-13.2$  to  $-12.7\text{‰}$ ).

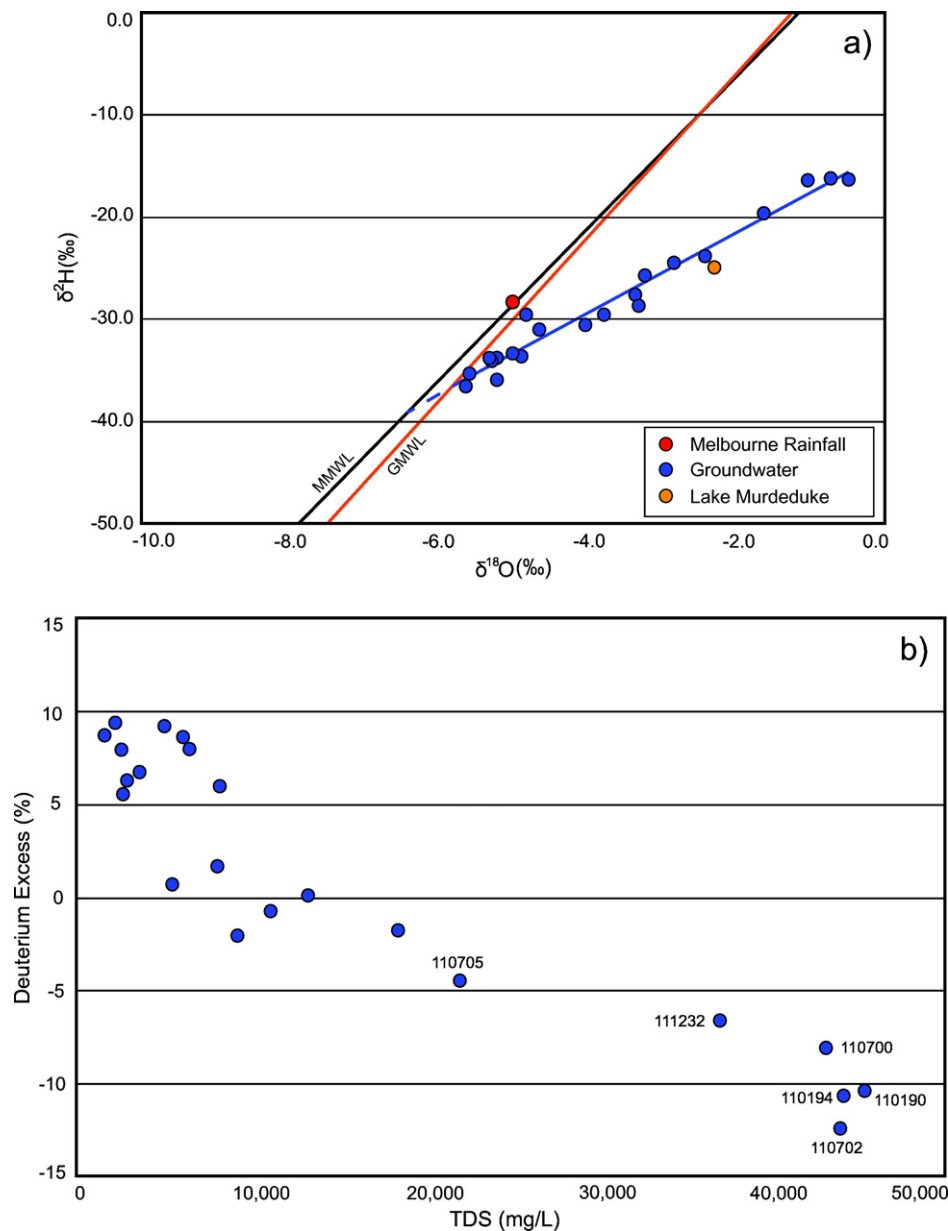
#### 4.4. Radioisotopes ( $^{14}\text{C}$ , $^3\text{H}$ , $^{36}\text{Cl}$ )

$^{14}\text{C}$  and  $^{36}\text{Cl}$  activities of the groundwater are illustrated in Figs. 1b and 2 and summarised in Table 2.  $^{14}\text{C}$  of groundwater range from 6.8 pMC at bore 110705 to 87.5 pMC at bore 110533. West of Lake Murdeduke, there is a decrease in  $^{14}\text{C}$  in groundwater eastwards in the direction of flow. Groundwater  $^{14}\text{C}$  to the east of, and downgradient of, Lake Murdeduke are higher than those immediately upgradient of the lake;  $^{14}\text{C}$  also decrease in the direction of groundwater flow. At locations where two or more bores are screened at different depth intervals,  $^{14}\text{C}$  are lower in the deeper bore (Fig. 2).

There is generally no correlation between  $\delta^{13}\text{C}$  values and  $^{14}\text{C}$ . However, in groundwater with  $^{14}\text{C} < 31$  pMC (bores 110190, 110194, 110700, 110702, 110705, 111232 and 111235) there is a trend of decreasing  $\delta^{13}\text{C}$  values with decreasing  $^{14}\text{C}$  (Fig. 5a). There is also no correlation between  $^{14}\text{C}$  and TDS; however, the four samples with the highest TDS concentrations (>43,000 mg/L) have relatively similar  $^{14}\text{C}$  (21 to 31 pMC).

Aside from one outlier (bore 111235), groundwater may be divided into two populations using deuterium excess and  $^{14}\text{C}$  (Fig. 5b). The first population is characterised by  $^{14}\text{C} < 31$  pMC and d-excess values  $< -4.5\text{‰}$ . This groundwater is from bores 110190, 110194, 110700, 110702, 110705 and 111232, which also have the highest TDS concentrations (Fig. 4b). The second population is characterised by  $^{14}\text{C} > 37$  pMC and d-excess values  $> -2\text{‰}$ . Both populations demonstrate





**Fig. 4.** Stable isotope results showing: a)  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  for groundwater and Lake Murdeduke water relative to the Melbourne Meteoric Water Line (MMWL), the Global Meteoric Water Line (GMWL) and Melbourne rainfall, and b) deuterium excess as a function of TDS for groundwater.

increasingly negative d-excess values with increasing  $\delta^{14}\text{C}$  and, although the data are scattered, the trends have similar slopes.

$^3\text{H}$  activities of groundwater ranged from below detection at bores 110196, 110534 and 111787 to 1.399 TU at bore 1110533. Bore 1110533 is located approximately 7 km to the northwest of Lake Murdeduke and groundwater from this bore also had the highest  $\delta^{14}\text{C}$  (87.53 ‰). In general, measurable  $^3\text{H}$  activities were only present in shallow (<15 m below ground level) groundwater with  $\delta^{14}\text{C}$  > 80 ‰ (Fig. 6).

$R^{36}\text{Cl}$  values of precipitation ranged from  $13.7$  to  $20.2 \times 10^{-15}$ . Three of the four samples have  $R^{36}\text{Cl}$  values of approximately  $20 \times 10^{-15}$ , which are similar to the predicted  $R^{36}\text{Cl}$  value of rainfall of  $\sim 20 \times 10^{-15}$  for this region (Davie et al., 1989).  $R^{36}\text{Cl}$  values of groundwater (Figs. 1b and 2) ranged from  $22.4$  to  $53.7 \times 10^{-15}$ , with the highest values being recorded in the groundwater from bores 112241 ( $53.7 \times 10^{-15}$ ) and 110193 ( $44.5 \times 10^{-15}$ ). Bore 112241 is located approximately 30 km to the north of Lake Murdeduke while bore 110193

is located approximately 5 km to the southeast of the lake. Excluding these two samples, the  $R^{36}\text{Cl}$  of the groundwater clusters between  $22$  and  $33 \times 10^{-15}$  with an average value of  $27.0 \times 10^{-15}$ . This average value is similar to that of the Lake Murdeduke salt crust sample ( $29.0 \times 10^{-15}$ ) but is higher than that of the precipitation samples.  $R^{36}\text{Cl}$  values do not correlate with  $\delta^{14}\text{C}$  (Fig. 7) or with Cl concentration (Fig. 8).

## 5. Discussion

The major ion and isotope geochemistry of the precipitation, groundwater, Lake Murdeduke water and salt crust samples, in combination with groundwater elevations, allow a comprehensive understanding of hydrogeologic and geochemical processes, groundwater and chloride residence times, and the climatic controls relating to the development of saline groundwater in the Barwon River Catchment.



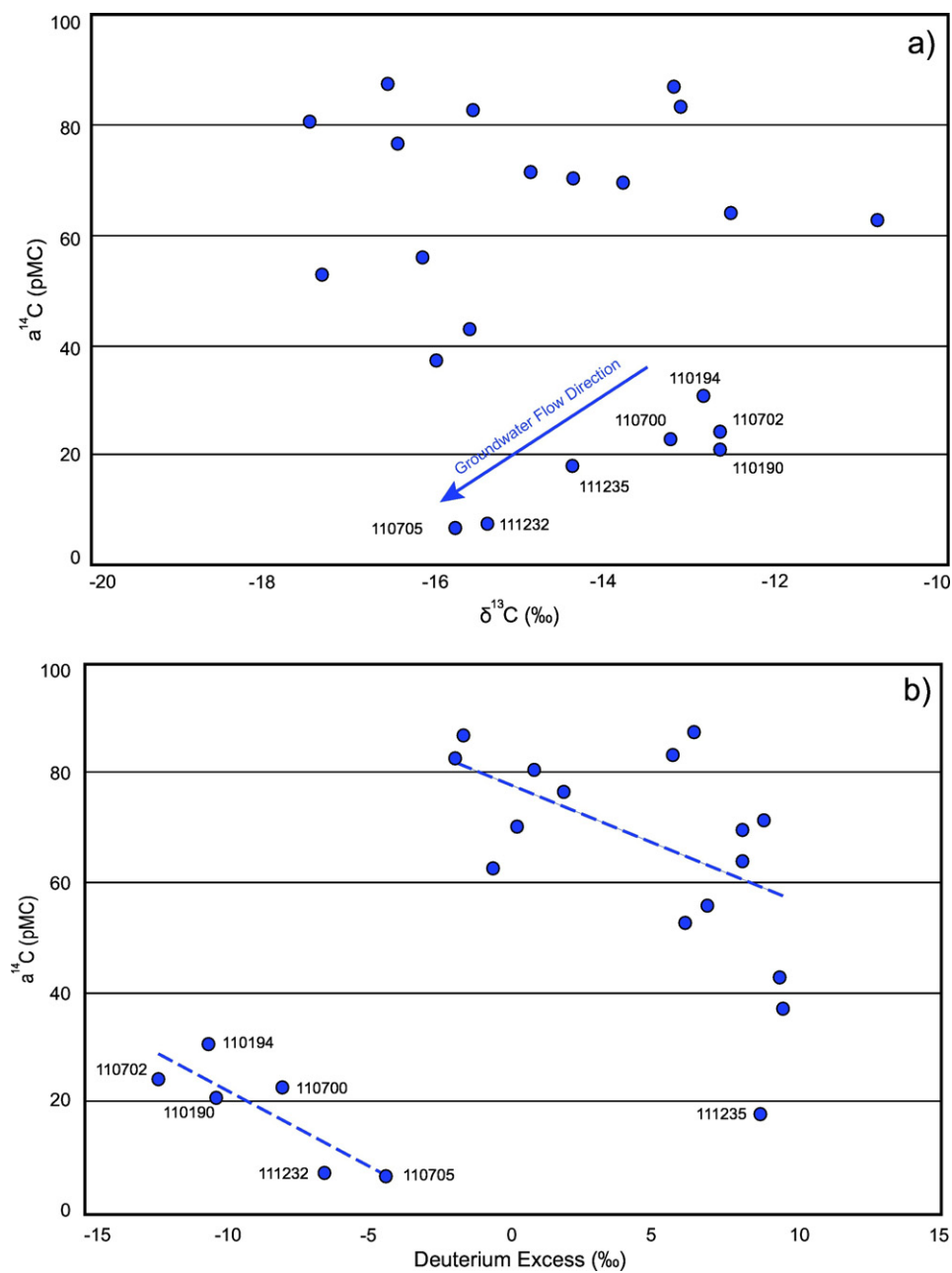


Fig. 5.  $a^{14}\text{C}$  in groundwater as a function of: a)  $\delta^{13}\text{C}$ , and b) deuterium excess.

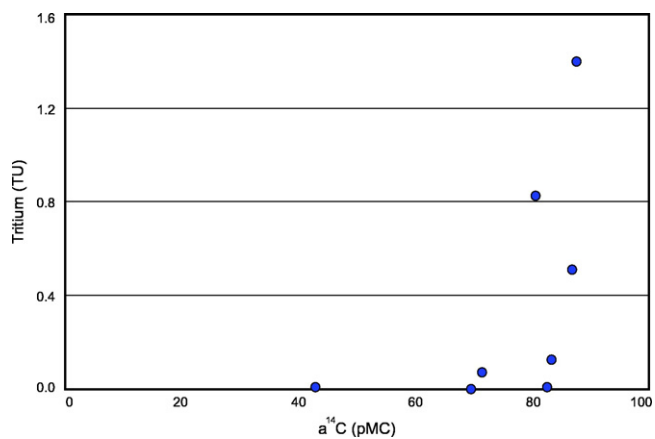


Fig. 6. Tritium activity as a function of  $a^{14}\text{C}$  in groundwater.

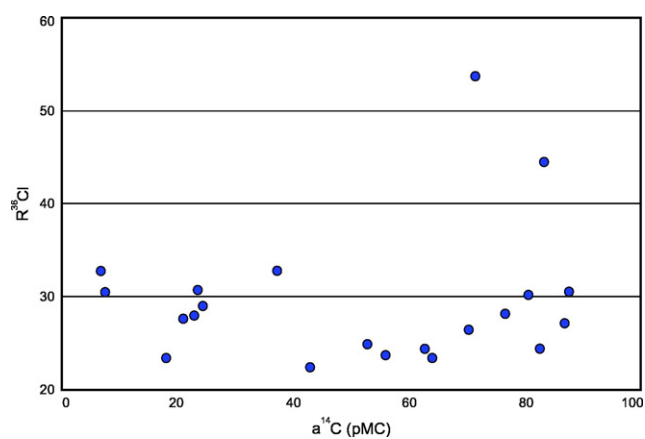


Fig. 7.  $R^{36}\text{Cl}$  as a function of  $a^{14}\text{C}$  in groundwater.

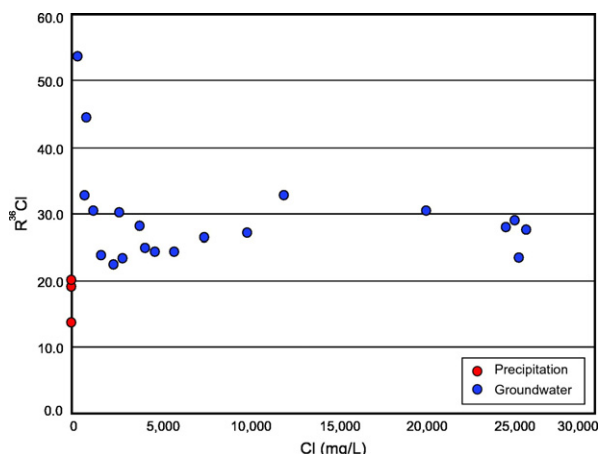


Fig. 8.  $R^{36}\text{Cl}$  in groundwater and in precipitation as a function of Cl concentration.

### 5.1. Groundwater flow

The distribution of hydraulic heads and a general decline in  $a^{14}\text{C}$  implies that the groundwater flows from northwest to southeast across the study area. The area to the northwest of Lake Murdeduke is interpreted to be a regional recharge area, while the upward head gradients to the southeast of the lake imply that there is groundwater discharge close to and into the Barwon River. TDS concentrations of groundwater increase from  $\leq 6000$  mg/L northwest of Lake Murdeduke to  $> 20,000$  mg/L southeast of the lake (Fig. 1b).  $^{14}\text{C}$  activities are also higher in groundwater to the southeast of the lake than to the northwest (Figs. 1b, 2). This implies that Lake Murdeduke is a through-flow lake, as proposed by Coram (1996), and that shallow groundwater to the east of the lake is recharged by highly saline lake water.

The Moorabool Viaduct Sand appears to play an important role in the distribution of groundwater salinity within the catchment. The highest TDS concentrations occur either within (bores 110190 and 110702) or immediately above (bores 110194, 110700, 110705 and 112232) this unit. As discussed above, this saline groundwater reflects saline through-flow from Lake Murdeduke. The full aerial extent of the unit is not known; however, it may occur below or in close proximity to the lake.

### 5.2. Geochemical processes

The observations that Cl/Br ratios of groundwater range from 542 to 839, do not vary appreciably with increasing TDS, and are similar to those of both seawater and local precipitation (Fig. 3a) indicates that, in common with the majority of groundwater in southeast Australia (Cartwright et al., 2004; Bennetts et al., 2006), halite dissolution is not a significant contributor to groundwater salinity. Because Cl/Br ratios in halite generally exceed  $10^4$  (McCaffrey et al., 1987; Herczeg and Edmunds, 2000), substantial halite dissolution would be expected to result in much higher Cl/Br ratios than those observed. In addition, other than salt crusts that periodically form along the shores of Lake Murdeduke, there are no known deposits of halite within the study area. The salt crust from Lake Murdeduke had a Cl/Br ratio of approximately 4,800, which is much higher than that of groundwater. While dissolution of salt crust most likely occurs periodically, the lack of elevated Cl/Br ratios implies that this salt is not a major contributor to groundwater salinity.

Molar Na/Cl ratios of groundwater are generally similar to those of both seawater and precipitation and do not vary markedly with increasing TDS (Fig. 3b). Only in low TDS groundwater are more elevated Na/Cl ratios (up to 1.6) evident, which suggests that only minor weathering of silicate minerals occurs. In addition, there is no correlation between

$\delta^{13}\text{C}$  values and  $\text{HCO}_3^-$ , Ca or Mg concentrations, implying that calcite and/or dolomite dissolution are not significant processes. This is consistent with there being no major carbonate deposits in the study area, although calcite minerals may be present as cements, veins or evaporite minerals within the Lake Murdeduke (Tweed et al., 2011). Groundwater  $\delta^{13}\text{C}$  values are variable ( $-17.5$  to  $-10.8$ ‰), which is likely the result of minor dissolution of calcite, in combination with a variable  $\delta^{13}\text{C}$  signature of through-flow from Lake Murdeduke.

Decreasing molar abundance of bicarbonate with increasing TDS (Fig. 3c) suggests that precipitation of calcite minerals occurs as a result of evapotranspiration. This hypothesis is supported by the observation that, with but three exceptions (bores 110191, 110195 and 112241), the groundwater is oversaturated with respect to calcite (Table 2, saturation indices calculated using PHREEQC: Parkhurst and Appelo, 2013).

### 5.3. Climatic controls

Both  $\delta^{13}\text{C}$  values and  $a^{14}\text{C}$  of groundwater southeast (down gradient) of Lake Murdeduke decrease in the direction of groundwater flow (Fig. 5a). In addition, the deuterium excess increases and TDS decreases in the flow direction (Fig. 4b), implying that the groundwater close to Lake Murdeduke is more evaporated than water further down the flow path. The decrease in  $a^{14}\text{C}$  is due to radioactive decay as groundwater moves away from Lake Murdeduke. There are no processes, however, that can decrease the TDS of groundwater along a flow path. Likewise, in the absence of high-temperature water-rock interaction, there are no processes that increase d-excess (Clark and Fritz, 1997). These trends, therefore, most likely represent a progressive increase in evaporation at Lake Murdeduke over time. Similarly, as there are few processes that decrease the  $\delta^{13}\text{C}$  values of DIC in groundwater (Clark and Fritz, 1997), it is also likely that the variation in groundwater  $\delta^{13}\text{C}$  values also reflect changes to the  $\delta^{13}\text{C}$  values of Lake Murdeduke water over time as a result of evaporation. Although enrichment of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in evaporating water is well documented, comparatively little is known about the effect of evaporation on  $\delta^{13}\text{C}$  values. However, in a series of laboratory experiments, Horton et al. (2015) demonstrated that evaporation of lake water can lead to enrichment in  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) due to equilibrium exchange with atmospheric carbon dioxide. The data from this study may represent the first field scale evidence of variable  $\delta^{13}\text{C}$  enrichment due to changes in the degree of evaporation of lake water.

### 5.4. Groundwater residence times

Determination of groundwater residence times using Eq. (1) requires an estimate of  $q$ , the proportion of DIC derived from the recharging water. While there are no limestones in the Barwon River Catchment, minor dissolution of calcite from veins, cements, and the soil zone is still possible. Since the  $\delta^{13}\text{C}$  of such calcite is unknown and can potentially be variable (Quade et al., 1995; Quade and Cerling, 2013), it is not possible to estimate the proportion of DIC contributed from calcite dissolution using isotope mass balance (e.g. Ingersoll and Pearson, 1964; Tamers, 1967; Fontes and Garnier, 1979). Additionally, such calculations assume predominantly closed system dissolution of calcite whereas open-system calcite dissolution in the unsaturated zone may also occur and may increase  $\delta^{13}\text{C}$  values without significantly impacting  $a^{14}\text{C}$  (Clark & Fritz, 1997; Cartwright et al., 2013b). Similarly, if calcite precipitation has occurred, the major ion geochemistry does not allow the proportion of DIC derived from carbonate dissolution to be estimated.

The highest recorded  $a^{14}\text{C}$  of 87.53 pMC is from bore 110533, which is in the recharge area northwest of Lake Murdeduke. This groundwater has a  $^3\text{H}$  activity of  $\sim 1.4$  TU, which suggests that the groundwater was recently recharged. Assuming that the  $^{14}\text{C}$  in this groundwater is modern, this implies that there has been a contribution of  $\sim 12\%$  old carbon from the aquifer matrix. Estimates of between 0 and 17% contribution

**Table 3**

Groundwater and chloride residence times. PFM = Piston Flow Model, DM = Dispersion Model.

Bore ID	<sup>3</sup> H	<sup>14</sup> C	<sup>14</sup> C age, Eq. 1		PFM		DM				Cl <sup>-</sup> accession time
			q = 0.85	q = 0.95	q = 0.85	q = 0.95	q = 0.85 D p = 0.05	D p = 0.5	q = 0.95 D p = 0.05	D p = 0.5	
	TU	pMC	Years	Years	Years	Years	Years	Years	Years	Years	Years
26683	0.511	86.84	Modern	742	Modern	720	Modern	202	716	762	6296
110140	–	52.78	3939	4859	4179	5478	4297	5110	5439	6692	2642
110190	–	20.97	11,570	12,489	13,165	13,964	13,968	21,946	15,256	24,535	16,285
110191	–	62.68	2518	3438	2419	3540	2533	2937	3667	4304	3682
110193	0.127	83.27	Modern	1089	Modern	990	Modern	305	1000	1132	538
110194	–	30.76	8403	9322	9075	10,255	9746	13,945	10,928	16,123	16,023
110195	–	70.28	1572	2491	1410	2415	1468	1697	2501	2900	4761
110196	0.010	82.55	242	1161	240	1025	258	337	1063	1211	1996
110533	1.399	87.53	Modern	677	Modern	662	Modern	Modern	664	693	789
110534	0.005	42.88	5656	6576	6340	7100	6407	8167	7511	9986	1511
110535	–	55.92	3461	4381	3559	4888	3704	4350	4857	5864	1068
110700	–	22.88	10,849	11,769	12,482	13,225	12,979	20,013	14,251	22,509	15,556
110702	–	24.36	10,331	11,250	11,403	12,755	12,266	18,643	13,523	21,071	15,872
110705	–	6.75	20,940	21,860	24,270	25,165	27,193	53,719	28,499	57,510	7609
110706	0.826	80.57	442	1362	405	1293	475	467	1256	1445	1716
110979	–	76.57	863	1783	750	1619	806	883	1689	1957	2449
111232	–	7.52	20,047	20,967	23,385	24,379	26,042	50,475	27,348	54,164	12,701
111235	–	18.02	12,823	13,742	14,389	16,554	15,756	25,566	17,059	28,321	1837
111236	–	63.97	2350	3269	2230	3420	2331	2702	3454	4041	1844
111787	0.002	69.50	1664	2584	1475	2550	1566	1813	2615	3034	683
112240	–	37.19	6833	7753	7530	8390	7823	10,520	8945	12,495	474
112241	0.073	71.41	1440	2360	1349	2290	1337	1542	2349	2723	227

by calcite dissolution to DIC in groundwater (i.e.  $q$  values of 0.83 to 1.0) from non-carbonate aquifers in southeast Australia were made by Love et al. (1994), Cartwright et al. (2010, 2012), Atkinson et al. (2014) and Raiber et al. (2015). In keeping with those studies,  $q$  values of between 0.85 and 0.95 are adopted here. A  $q$  value of 0.85 is frequently cited as typical for non-carbonate aquifers (e.g., Clark and Fritz, 1997) and the groundwater chemistry data indicate that at least some calcite dissolution is occurring, implying that  $q$  is less than 1.0. For these  $q$  values, groundwater residence times calculated using Eq. (1) vary from modern at bores 26683, 110193 and 110533 to 21,860 years at bore 110705 (Table 3).

The mean residence time (MRT) of groundwater was also estimated using the Piston Flow Model (PFM) and the Dispersion Model (DM) within TracerLPM. The PFM, which assumes that no hydrodynamic dispersion occurs between the recharge area and the sampling point, is similar to the use of Eq. (1) except that  $A_0$  can be varied with time. In contrast, the DM allows for variable degrees of dispersion through use of the dispersion parameter  $D_p$ . The dispersion parameter represents the ratio of dispersion to advection and, as its value approaches zero, advection becomes the dominant process controlling tracer transport. The DM can apply to a variety of aquifer configurations and is considered to best represent the flow system within the study area. In this study, two values of the dispersion parameter were employed, 0.05 and 0.5, as the range defined by these values applies to most flow systems of this scale (Zuber and Maloszewski, 2001; Gelhar et al., 1992). The  $^{14}\text{C}$  record for the southern hemisphere in Jurgens et al. (2012) was used for  $A_0$ . As with the calculations above, it was assumed that there was a contribution of between 5 and 15%  $^{14}\text{C}$ -free carbon to the DIC.

MRTs estimated using the PFM varied from modern at bores 26683, 110193 and 110533 to 25,165 years at bore 110705 (Table 3, Fig. 9). At most locations, MRTs calculated using the PFM exceeded those determined using Eq. (1) by less than 10%, with the relative difference increasing as residence time increased. For groundwater with  $a^{14}\text{C} > 70$  pMC, MRTs calculated using the PFM were shorter than those determined using Eq. (1). This is due to the fact that atmospheric  $a^{14}\text{C}$  ( $A_0$ ) within the southern hemisphere has often been below 100 pMC, which Eq. (1) does not account for. MRTs estimated using the DM varied from modern at bores 26683, 110193 and 110533 to 57,510 years at bore 110705 (Table 3, Fig. 9). MRTs calculated using the DM were typically longer, but not significantly so, than those determined using Eq. (1) or the PFM when  $D_p$  was set equal to 0.05. Significant differences between MRT estimates only become apparent when  $D_p$  was set equal to 0.5, leading to relative differences in MRTs as high as 90% (in groundwater with  $a^{14}\text{C} < 10$  pMC). The variability in groundwater residence

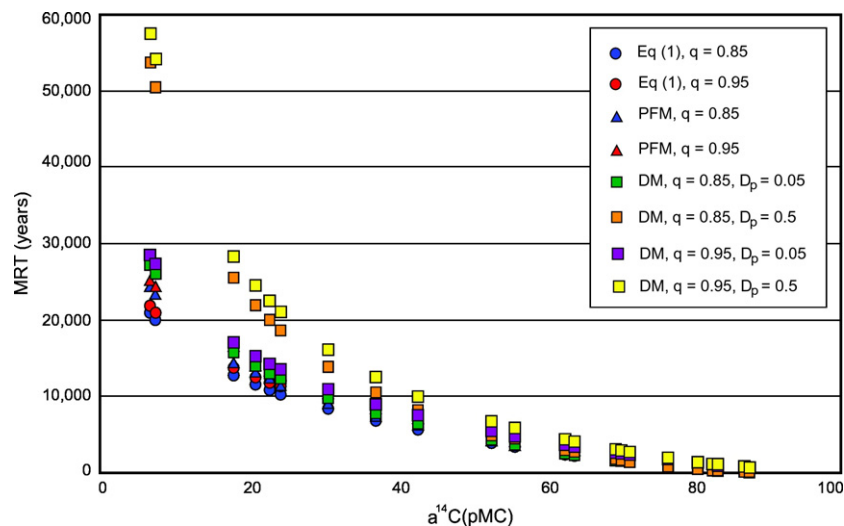
**Table 4**

Hydraulic conductivity estimates for the Newer Volcanic basalt based upon groundwater elevations and distances between bore pairs and groundwater residence times determined using  $a^{14}\text{C}$  and Equation 1.  $K_x$  = horizontal hydraulic conductivity,  $K_z$  = vertical hydraulic conductivity.

Bore pair	Distance (m)	GW elevation (m AHD)	Hydraulic gradient	Residence time (Years)	$K_x$ (m/day)	$K_z$ (m/day)
111787 110534	2860	102.15 88.47	0.005	1664 5656	$2 \times 10^{-2}$	–
111787 110535	2850	102.15 89.70	0.004	1664 3461	$5 \times 10^{-2}$	–
110191 110194	1760	78.23 75.76	0.001	2518 8403	$3 \times 10^{-2}$	–
110700 110705	2530	78.52 73.00	0.002	10,849 20,940	$2 \times 10^{-2}$	–
110979 110700	39	78.63 78.52	0.003	863 10,849	–	$2 \times 10^{-4}$
110706 110705	31	73.37 73.00	0.012	442 20,940	–	$2 \times 10^{-5}$

times determined using the three methods demonstrates the uncertainties in using radioactive tracers to determine groundwater residence times.

The residence times of groundwater, in combination with groundwater elevations and distances between the bores, allow the horizontal and vertical hydraulic conductivities of the Newer Volcanics basalt to be estimated using Darcy's Law. In these calculations, an effective porosity of 5% was assumed, which is at the upper end of the range (1–5%) suggested by Finegan (1996) for the Newer Volcanics basalt near Melbourne. Hydraulic conductivity values were calculated using groundwater ages derived from Eq. (1). However, these estimates do not change appreciably if MRTs from the Piston Flow Model or Dispersion Model are utilised instead. Horizontal hydraulic conductivities for the basalt range from  $2 \times 10^{-2}$  to  $5 \times 10^{-2}$  m/day while vertical horizontal conductivities are between  $2 \times 10^{-5}$  and  $2 \times 10^{-4}$  m/day (Table 4). An inherent assumption in these calculations is that the hydraulic gradient has not changed appreciably with time. The calculated horizontal hydraulic conductivity values are more than two orders of magnitude lower than that (8.6 m/day) estimated by Coram (1996) for the younger-phase basalts. However, those estimates were based on slug tests, which typically examine a very small area around a bore, whereas the estimates from this study are regional in scale. In addition, it is possible that the bores were screened across fractures to ensure groundwater entry or that drilling may have disturbed the adjacent basalt. Lastly, lack of detailed geologic mapping in the area does not allow



**Fig. 9.** Mean residence times (MRTs) for groundwater calculated using Eq. 1, the Piston Flow Model (PFM) and the Dispersion Model (DM) for  $q = 0.85$  and  $0.95$  and  $D_p = 0.05$  and  $0.5$ .



us to distinguish whether these values are representative of the younger or older-phase Newer Volcanic basalts. Due to a lack of bores, hydraulic conductivities could not be calculated for the Moorabool Viaduct Sand or lunette deposits.

### 5.5. $R^{36}\text{Cl}$ and chloride residence times

$R^{36}\text{Cl}$  values of groundwater in the Barwon catchment ( $22.4$  to  $53.7 \times 10^{-15}$ ) are greater than those of both local modern precipitation ( $13.7$  to  $20.2 \times 10^{-15}$ ) and the predicted rainfall  $R^{36}\text{Cl}$  value of  $\sim 20 \times 10^{-15}$  (Davie et al., 1989). Consequently, it is not possible to determine chloride residence times using Eq. (2). Possible reasons for the  $R^{36}\text{Cl}$  values in groundwater being higher than those of modern precipitation are: 1) input of bomb-pulse  $^{36}\text{Cl}$  into groundwater during the 1950s and 1960s (Bentley et al. 1982); 2)  $R^{36}\text{Cl}$  values in rainfall in the past have been higher than at present; 3) deep, subsurface (hypogene) production of  $^{36}\text{Cl}$  through nuclear reactions involving uranium, thorium and/or their daughter products (Andrews et al., 1986); and/or 4) shallow, near-surface (epigene) production of  $^{36}\text{Cl}$  as a result of cosmic ray spallation of potassium and calcium and/or neutron capture by  $^{35}\text{Cl}$  (Phillips et al., 1983). Each of these possibilities is discussed briefly below.

The elevated  $R^{36}\text{Cl}$  values at bores 112241 ( $53.7 \times 10^{-15}$ ) and 110193 ( $44.5 \times 10^{-15}$ ) likely reflect the input of bomb-pulse  $^{36}\text{Cl}$ . Both waters have measurable tritium, as well as  $^{14}\text{C}$  activities that are close to the maximum observed, which suggests that some fraction of the water is derived from recharge 50 to 60 years ago during the nuclear testing era.

A strong indication that  $R^{36}\text{Cl}$  values of rainfall during the past were different than they are presently is provided by the salt crust sample collected from Lake Murdeduke. Its  $R^{36}\text{Cl}$  of  $29 \times 10^{-15}$  is significantly higher than the value of  $\sim 20 \times 10^{-15}$  measured in present day rainfall. As the  $R^{36}\text{Cl}$  value is a function of both  $^{36}\text{Cl}$  fallout and Cl deposition, a change in either of the two parameters will cause the ratio to vary. Chloride deposition is sensitive to distance from the coast (Bentley et al., 1986b; Keywood et al., 1997, 1998), especially in areas relatively close to the coast such as the present study location. During the last glacial maximum, the coast line would have been much further away; thus, chloride deposition would have been lower, resulting in higher  $R^{36}\text{Cl}$  values in rainfall. Since the chloride in Lake Murdeduke must represent at least tens of thousands of years of accumulation, its  $R^{36}\text{Cl}$  value will represent an average over a period of time during which the coastline has moved substantially. Hence, it is not surprising that the salt crust sample's  $R^{36}\text{Cl}$  value is nearly 50% higher than that of modern rainfall.

Deep, hypogene production of  $^{36}\text{Cl}$  by nuclear reactions only becomes significant after 1 ma or more. As discussed below, it is unlikely that the residence time of Cl in the catchment is that long. Similarly, significant epigene production of  $^{36}\text{Cl}$  requires long exposure at or close to the surface and again is unlikely to make an important contribution.

While it is not possible to determine precise residence times from the  $R^{36}\text{Cl}$  values, some broad constraints may be made. Excluding bores 112241 and 110193, where bomb pulse input is suspected, the  $R^{36}\text{Cl}$  values of the groundwater are relatively similar and do not decrease along the groundwater flow paths or with depth. In addition, there are no correlations between  $R^{36}\text{Cl}$  values and  $\delta^{14}\text{C}$  or Cl concentrations. These observations suggest that limited decay of  $^{36}\text{Cl}$  has occurred. In turn, this implies that the residence time of Cl in the Barwon catchment may be a few thousand to tens-of thousand years old but not hundreds of thousands of years.

### 5.6. Chloride accession times

Chloride accession times for the Newer Volcanics basalt, Moorabool Viaduct Sand and lunette deposits were estimated using Eq. (3), measured chloride concentrations in groundwater (Table 2), estimates of average aquifer thicknesses and porosity, and a Cl deposition rate of 2400 mg/year. The Cl deposition rate is based upon an average chloride

concentration in rainfall of 6 mg/L, derived from Blackburn and McLeod (1983) and Crosbie et al. (2012), and an average annual rainfall of 400 mm/year, which is approximately that of Inverleigh. The porosities of the Newer Volcanics basalt, the Moorabool Viaduct Sand and lunette deposits are unknown but, for the purposes of these calculations, are assumed to be 5%, 15% and 10%, respectively. Likewise, the average saturated thickness of these units is assumed to be 30 m, 10 m and 10 m, respectively. Chloride accession times range from approximately 225 years at bore 112241 to approximately 16,000 years at bores 110190 and 110194 (Table 3). The accession times listed in Table 3 are conservative estimates, as increases in either porosity or aquifer thickness would increase the accession times. Likewise, in keeping with the interpretation of the  $R^{36}\text{Cl}$ , if this region was further inland in the past Cl deposition rates would likely be lower (based on modern distribution of Cl concentrations in rainfall (Blackburn and McLeod, 1983)), which would also increase the estimated accession times. At around half of the localities, the chloride accession time exceeds the groundwater residence time calculated using  $\delta^{14}\text{C}$ . In general, chloride accession times in groundwater immediately downgradient of Lake Murdeduke are greater than the groundwater residence times calculated using  $^{14}\text{C}$ , while groundwater upgradient or far from the lake have similar (or lower) Cl accession and residence times. Chloride residence times calculated in this manner are at best broad estimates; nonetheless, these results suggest that chloride is being recycled within the study area and is locally older than the groundwater in which it is contained. This in turn suggests that any estimate of aquifer recharge based upon groundwater Cl concentrations would be underestimated.

A key assumption in estimating recharge via the chloride mass balance method, as well as determining chloride accession times, is that runoff is negligible so that all chloride delivered via rainfall enters the subsurface. If significant runoff occurs, some of the chloride delivered by rainfall is diverted away from the recharge area, which in turn results in lower chloride concentrations in groundwater. To test the assumption of negligible runoff, the annual volume of water exported by Mia Mia Creek (Fig. 1) was compared to that of average annual rainfall. Except for flood events in 2001, 2003 and 2005, average flow within Mia Mia Creek during the period 1997 to 2009 was approximately  $3.3 \times 10^5 \text{ m}^3/\text{year}$  (Department of Environment, Land, Water and Planning, Water Measurement Information System, WMIS, 2015). In comparison, based upon a catchment area of  $1.1 \times 10^8 \text{ m}^2$  (Milne, 2008) and an average annual rainfall of 0.4 m (Bureau of Meteorology, BOM, 2016), approximately  $4.4 \times 10^7 \text{ m}^3$  of rainfall is delivered to the catchment each year. The volume of water exported by Mia Mia Creek is thus less than 1% of that delivered by rainfall. In addition, much of the water in the rivers in the Barwon River Catchment is derived from groundwater inflows rather than from direct runoff (Cartwright et al., 2013b). Overall, these observations suggest that export of Cl via runoff is minimal.

## 6. Conclusions

Elevated groundwater salinity in the Barwon River Catchment is primarily the result of the inflow of highly saline water from Lake Murdeduke, a through flow lake located in the centre portion of the catchment. Highly saline lake water enters the shallow groundwater system, is transported eastward through the Moorabool Viaduct Sand and the Newer Volcanics basalt, and then discharges into the Barwon River. Groundwater residence times estimated from  $\delta^{14}\text{C}$  are up to  $\sim 20$  ka. Significant differences in estimated residence times in groundwater with low  $\delta^{14}\text{C}$  result from adoption of different flow models and the use of different input functions for  $^{14}\text{C}$  in rainfall. While studies of  $^{14}\text{C}$  in groundwater commonly consider corrections for  $^{14}\text{C}$ -free carbon inputs, there have been few studies that have looked at the impacts of adopting different flow models or varying  $^{14}\text{C}$  in recharge. This study shows that, especially in groundwater with long residence times, varying these conditions can produce significantly different results.

Even using conservative assumptions, chloride accession times downgradient of Lake Murdeduke are greater than the residence times of the groundwater in which it is contained. This study is one of only a few to attempt to estimate the residence time of solutes and groundwater and while it was not possible to calculate Cl residence times using  $^{36}\text{Cl}$ , the lack of significant  $^{36}\text{Cl}$  decay implies that the residence time of Cl is on the order of tens of thousands of years not longer. Based upon a  $^{14}\text{C}$  in groundwater, the horizontal hydraulic conductivity of the Newer Volcanics basalt is approximately  $10^{-2}$  m/day while vertical horizontal conductivities range from approximately  $10^{-5}$  to  $10^{-4}$  m/day.

Other saline lakes elsewhere in this and adjacent catchments operate in a similar way and produce high salinity groundwater throughout the Newer Volcanics Province (Bennetts et al., 2006). In these and other semi-arid catchments globally, similar decoupling of solutes and water is likely and this must be taken into account in using Cl to understand hydrological processes. Specifically, Cl concentrations will underestimate recharge rates calculated using chloride mass balance. This study also illustrates the utility of isotope tracers in assessing environmental change. While the use of oxygen and hydrogen isotopes in this regard is well established, the variation in  $\text{R}^{36}\text{Cl}$  and  $\delta^{13}\text{C}$  values in the Barwon River groundwater also reflect environmental change. The observation that  $\text{R}^{36}\text{C}$  values in rainfall were likely higher in the past than they are at present is most probably related to sea level changes and consequently the distance of this area from the coast. The increase in  $\delta^{13}\text{C}$  values in groundwater downgradient of the Lake Murdeduke suggest that the region has experienced increasingly more evaporative conditions with time.

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