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Using ^{14}C and ^{3}H to understand groundwater flow and recharge in an aquifer window

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Abstract. Knowledge of groundwater residence times and recharge locations is vital to the sustainable management of groundwater resources. Here we investigate groundwater residence times and patterns of recharge in the Gellibrand Valley, southeast Australia, where outcropping aquifer sediments of the Eastern View Formation form an "aquifer window" that may receive diffuse recharge from rainfall and recharge from the Gellibrand River. To determine recharge patterns and groundwater flow paths, environmental isotopes (^{3}H, ^{14}C, δ^{13}C, δ^{18}O, δ^{2}H) are used in conjunction with groundwater geochemistry and continuous monitoring of groundwater elevation and electrical conductivity. The water table fluctuates by 0.9 to 3.7 m annually, implying recharge rates of 90 and 372 mm yr^{-1}. However, residence times of shallow (11 to 29 m) groundwater determined by ^{14}C are between 100 and 10 000 years, ^{3}H activities are negligible in most of the groundwater, and groundwater electrical conductivity remains constant over the period of study. Deeper groundwater with older ^{14}C ages has lower δ^{18}O values than younger, shallower groundwater, which is consistent with it being derived from greater altitudes. The combined geochemistry data indicate that local recharge from precipitation within the valley occurs through the aquifer window, however much of the groundwater in the Gellibrand Valley predominantly originates from the regional recharge zone, the Barongarook High. The Gellibrand Valley is a regional discharge zone with upward head gradients that limits local recharge to the upper 10 m of the aquifer. Additionally, the groundwater head gradients adjacent to the Gellibrand River are generally upwards, implying that it does not recharge the surrounding groundwater and has limited bank storage. ^{14}C ages and Cl concentrations are well correlated and Cl concentrations may be used to provide a first-order estimate of groundwater residence times. Progressively lower chloride concentrations from 10 000 years BP to the present day are interpreted to indicate an increase in recharge rates on the Barongarook High.

1 Introduction

Groundwater residence time can be defined as the period of time elapsed since the infiltration of a given volume of water (Campana and Simpson, 1984), or perhaps more accurately, the mean time that a mixture of waters of different ages have resided in an aquifer (Bethke and Johnson, 2008). The residence time of water within an aquifer is a key parameter in describing catchment storage and may be used to estimate historical recharge rates (Le Gal La Salle et al., 2001; Cook and Robinson, 2002; Cartwright and Morgenstern, 2012; Zhai et al., 2013), elucidate groundwater flow paths (Gardner et al., 2011; Smerdon et al., 2012), calibrate hydraulic models (Mazor and Nativ, 1992; Reilly et al., 1994; Post et al., 2013) and characterize the rate of contaminant

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spreading (Böhlke and Denver 1995; Tesoriero et al., 2005). From a water resource perspective, information on groundwater residence times is required for sustainable aquifer management by identifying the risk posed to groundwater reserves by over-exploitation (Foster and Chilton, 2003), climate change (Manning et al., 2012) and contamination (Böhlke, 2002).

Unconfined aquifers may be recharged over broad regions, leading to young groundwater at shallow depths over broad areas (Cendón et al., 2014). On the other hand, the residence time of groundwater in confined aquifers generally increases away from discrete recharge areas. The geology of catchments is often complex and heterogeneous, and outcrops of aquifers in more than one location may provide "windows" for groundwater recharge (Meredith et al., 2012). It is important to document groundwater flow from such aquifer windows. If they act as recharge areas, changes in land-use such as agricultural development may introduce contaminants to the deeper regional groundwater systems. By contrast, if they are local discharge areas, use of regional groundwater from these areas may impact rivers, lakes or wetlands that are receiving groundwater.

Rivers may also recharge shallow groundwater if the hydraulic gradient between the river and the groundwater is reversed during high flows (Doble et al., 2012). Episodic recharge of aquifers by large over-bank floods is also locally important (Moench and Barlow, 2000; Cendón et al., 2010; Doble et al., 2012), particularly in arid areas (Shentsis and Rosenthal, 2003); however, the potential for over-bank events to recharge aquifers in temperate areas is still poorly understood. Additionally, during high flow, water from rivers is likely stored temporarily in the banks (McCallum et al., 2010; Unland et al., 2014); however, the depth and lateral extent to which bank exchange water infiltrates the aquifer is not well documented. Lastly, knowledge of residence times of groundwater in close proximity to the river can provide important information on groundwater–river interactions (Gardner et al., 2011). Local groundwater flow paths in connection with rivers are often underlain by deeper regional flow paths (Tóth, 1963), but the role these flow paths play in contributing to river baseflow remains unclear (Sklash and Farvolden, 1979; McDonnell et al., 2010; Frisbee et al., 2013; Goderniaux et al., 2013). This may be elucidated from understanding residence times of near-river groundwater (Smerdon et al., 2012).

Radioactive environmental isotopes, in particular ^{14}C and ^{3}H, have proved useful tools for determining groundwater residence times (Vogel et al., 1974; Wigley, 1975). Produced in the atmosphere via the interaction of N_2 with cosmic rays, ^{14}C has a half life of 5730 years and can be used to trace groundwater with residence times up to 30 ka. The use of ^{14}C in dating groundwater was first discussed by Muennich (1957), and has subsequently been widely used due to the ubiquitous presence of dissolved inorganic carbon (DIC) in groundwater (Cartwright et al., 2012; Samborska et al., 2012; Stewart, 2012). The calculation of ^{14}C ages may be complicated if groundwater DIC is derived from a mixture of sources (Clark and Fritz, 1997). Where a large proportion of DIC is derived from the dissolution of ^{14}C-free carbonate minerals in the aquifer matrix, the ^{14}C originating from the atmosphere or soil zone will be significantly diluted. Additional sources of ^{14}C free DIC include old geogenic carbon from igneous degassing (Bertrand et al., 2013; Frederico et al., 2002) or CO_2 produced together with methane from old organic carbon in the aquifer matrix (Aravena et al., 1995). Groundwaters recharged post-1950 may have anomalously high ^{14}C activities (a^{14}C) due to the ^{14}C produced during atmospheric nuclear tests. Objective ^{14}C dating requires recognition and quantification of these processes. A number of models based on both major ion and stable C isotope geochemistry have been proposed to correct apparent ^{14}C ages (Han and Plummer, 2013)

With a significantly shorter half-life (12.33 years), ^{3}H can be used to date groundwater with residence times of up to 100 years (Vogel et al., 1974).With the decay of the 1960s ^{3}H bomb-pulse peak in the Southern Hemisphere to near background levels, unique ages may now be determined from single ^{3}H measurements (Morgenstern et al., 2010). As ^{3}H is part of the water molecule, there is negligible change to ^{3}H activities other than decay, and ^{3}H is an excellent tracer for the movement of water through hydrological systems (Michel, 2004). Used in conjunction with ^{14}C data, ^{3}H may also be used to study mixing in shallow aquifers (Le Gal La Salle, 2001; Cartwright and Morgenstern, 2012).

2 Study site

The Otway Basin is located in southwest Victoria, covering an area of 150 000 km^2. The basin was formed during the Cretaceous rifting of Australia and Antarctica (Briguglio et al., 2013) and is infilled with Upper Cretaceous and Cenozoic siliciclastic and calcareous sediments that form several aquifers and aquitards. The basin is divided into a number of sub-basins with regional groundwater flow paths originating at topographic highs. The Gellibrand River Catchment is one of these sub-basins. This study focuses on a 250 km^2 upland area of the Gellibrand River Catchment (known as the Gellibrand Valley), which lies at the foothills of the Otway Ranges, directly south of the Barongarook High (Fig. 1).

Cretaceous Otway Group sediments of the Eumeralla Formation form the basement of the catchment and crop out in areas of higher relief. The Eumeralla Formation consists of thickly bedded siltstone, mudstone and volcanolithic sandstone. It has a low primary porosity and hydraulic conductivity and acts as a poor aquifer (Leonard et al., 1981). Cenozoic sediments of the Wangerrip group overlie the bedrock and form major aquifers in the region to which flow is constrained (Van den Berg, 2009). The primary aquifer in the study area is the Eastern View Formation or the equiva-

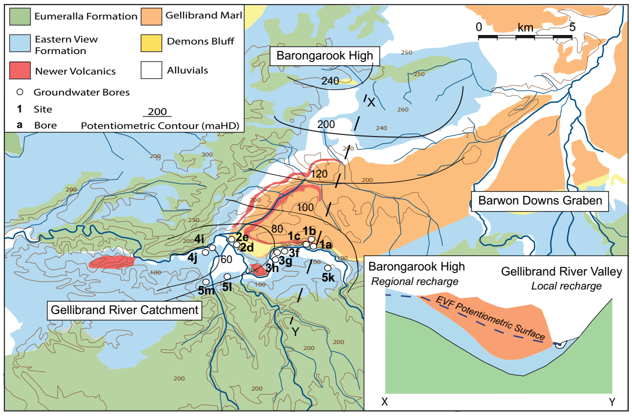

Figure 1. Geology, groundwater flow and cross-sectional view of the upper part of the Gellibrand River Catchment (the Gellibrand Valley). Potentiometric contours for the Eastern View Formation are created from groundwater data (Water Resources Data Warehouse, 2013) and are expressed in metres above Australian Height Datum (mAHD). Sampled groundwater bores are also shown. Letters refer to bores in Table 1.

lent Dilwyn Formation (Van den Berg, 2009; Petrides and Cartwright, 2006; Atkinson et al., 2013) that is composed of gravel, fine to coarse grained sand, and major clay layers. The Eastern View Formation comprises predominantly quartz, feldspars, and carbonates ($< 2\,\%$) and has hydraulic conductivities of 10^{-2} to $10^{2}\,\mathrm{m\,d^{-1}}$ (Hortle et al., 2011). It is underlain by another productive aquifer, the Pebble Point Formation; however, this is much thinner and is separated from the above layers by the Pember Mudstone. To the north, the Eastern View Formation is confined by the Gellibrand Marl, which is a regional aquitard that comprises 100 to 200 m of clay, and the Demons Bluff formation, which comprises fine-grained silts. Basaltic intrusions of the Quaternary Newer Volcanics are also present. The floodplain is covered with recent alluvial deposits of sand and clay. Regional groundwater recharge occurs on the Barongarook High where the Eastern View Formation crops out. Groundwater flows southwest along the Gellibrand River Catchment from the Barongarook High as well as eastwards into the Barwon Downs Graben. However, there is also potential for localized recharge within the Gellibrand Valley, where outcropping sediments of the Eastern View Formation potentially act as an aquifer window (Fig. 1).

The Gellibrand Valley contains a mixture of cool temperate rainforest on the valley sides and cleared agricultural pasture through which the Gellibrand River flows. Rainfall across the catchment averages $\sim 1000\,\mathrm{mm\,yr^{-1}}$, with most of the rainfall occurring in the Australian winter between June and September (Bureau of Meteorology, 2013). The Gellibrand River is gaining and groundwater contributes between 10 and 50 % to total river flow dependent on flow conditions (Atkinson et al., 2013). River flows are between $5 \times 10^{4}\,\mathrm{m^{3}\,day^{-1}}$ and $2 \times 10^{6}\,\mathrm{m^{3}\,day^{-1}}$ (Fig. 2c), with low flows during summer months (December to March) and high flows and flooding during winter (June to August) (Victorian Water Resources Data Warehouse, 2013). During flooding there is the potential for aquifer recharge from over-bank flow.

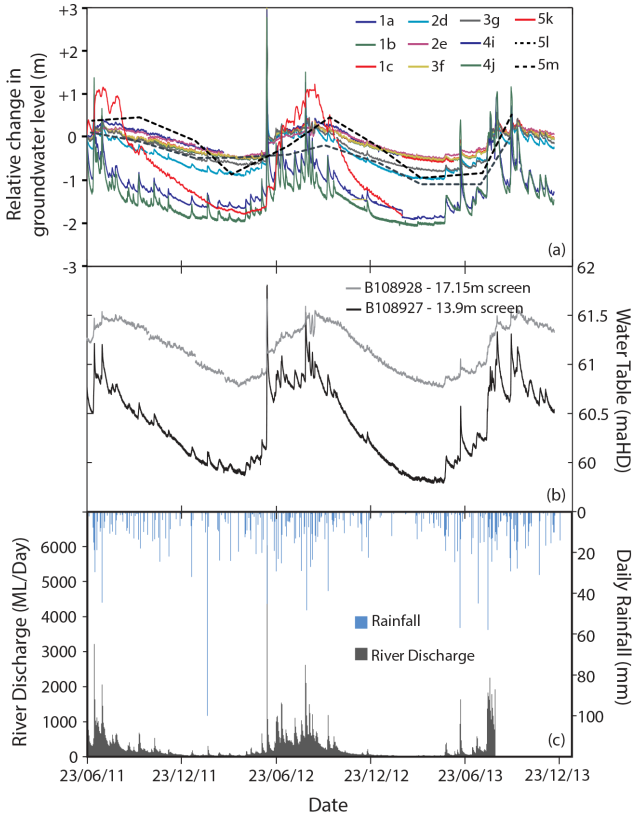

Figure 2. (a) Groundwater elevations in bores display clear annual cycles. **(b)** Groundwater head-gradients in the Gellibrand Valley are upwards, implying a discharge zone (Victorian Water Resources Data Warehouse, 2013). **(c)** Flow in the Gellibrand River. Baseflow conditions during summer months transition into high flows in winter following winter rainfall (Bureau of Meteorology, 2013).

Although groundwater residence times in the Otway Basin have been explored in the Gambier Embayment (Love et al., 1994) and nearby Barwon River Graben (Petrides and Cartwright, 2006), little is known of the residence times of groundwater in the Gellibrand River Catchment. This is despite the groundwater in Eastern View Formation being a potentially valuable water resource (Petrides and Cartwright, 2006). Here we evaluate groundwater residence times in the Gellibrand Valley where the Eastern View Formation is exposed, forming an aquifer window, and regular episodic river floods occur, to understand the origins of groundwater within the valley and to identify whether groundwater recharge via rainfall and/or the river occurs in this part of the groundwater system. This is important in understanding the potential impacts of land-use change and pollution in the catchment as well as the dynamics of recharge in catchments where aquifer material is exposed in more than one location. It is also important to fully understand groundwater systems such as this that have the potential to be developed as significant water resources. Radioactive tracers ^{14}C and ^{3}H are used to determine residence times and define groundwater flow paths, while major ion chemistry is employed to determine dominant geochemical processes. Water table fluctuations and groundwater electrical conductivities are also continuously monitored. These easily measurable, robust parameters can be used to observe changes in storage and infer sources of aquifer recharge (Vogt et al., 2010) and allow for comparison with radioisotopes in understanding the dynamics of groundwater systems. Together, isotopic and physico-chemical approaches provide insight on both short-term (electrical conductivity, water levels) and long-term recharge processes (^{3}H and ^{14}C).

3 Methods

A number of groundwater monitoring bores that form part of the Victorian State Observation Bore network are present in the Gellibrand Valley (Victorian Water Resources Data Warehouse, 2013). These are screened in the Eastern View Formation, with depths of between 0 and 42 m. Bores located within 25 m of the Gellibrand River generally have screen depths between 11 and 15 m, while bores located on the floodplain have depths between 21 and 42 m. Groundwater from the Eastern View Formation was sampled from 13 bores. Ten of these are located within 25 m of the river in a 14 km^{2} area of the catchment (sites 1 to 4 in Fig. 1), with three further samples taken from bores situated further back on the floodplain between 1 and 2 km from the river (site 5 in Fig. 1). Groundwater was sampled using an impeller pump set in the screen, with two to three bore volumes purged before sampling. Groundwater samples were collected in 1 L, 0.25 L and 0.125 L HDPE bottles and stored at $\sim 4\,^{\circ}$C until analysis. In the field, samples for anion analysis were filtered through 0.45 µm cellulose nitrate filters, while samples for cation analysis were filtered and acidified with high-purity 16 N HNO_3 to pH < 2. Additionally, electrical conductivity (EC) and pH of groundwater were measured in the field using a calibrated TPS WP-81 conductivity/pH meter and probes. To assess transient changes in groundwater levels and EC, Aqua TROLL 200 (in situ) data loggers were deployed in June 2011. A significant drop in EC in near-river groundwater is shown in some bores following flooding in June 2012 when bores were overtopped. However, immediately upon pumping in October 2012 (bores 3g, 4i) and April 2013 (bore 1b), the EC of the groundwater returned to pre-flood EC values. We interpret this as floodwater that infiltrated down the bore and was not displaced by groundwater prior to pumping, and these data have been omitted. Rainfall samples were also collected in the catchment throughout the study period for chemical analysis.

Cations were analysed on filtered, acidified samples using a Thermo Finnigan X Series II Quadrupole ICP-MS. Anions were measured on filtered unacidified samples using a Metrohm ion chromatograph. The precision of major ion concentrations based on replicate analyses is ±2 %. Charge balances are within ±5 %. Stable isotope ratios were measured using Finnigan MAT 252 and Thermo Finnigan Delta-Plus Advantage mass spectrometers. δ^{18}O values were measured via equilibration with He-CO_2 at 32 °C for 24 to 48 h in a Finnigan MAT Gas Bench while δ^{2}H values were measured by the reaction of water samples with Cr at 850^{o}C using a Finnigan MAT H/Device. Both δ^{18}O and δ^{2}H were measured against an internal standard that has been calibrated using the IAEA, SMOW, GISP and SLAP standards. Data were normalized following methods outlined by Coplen (1988) and are expressed relative to V-SMOW where δ^{18}O and δ^{2}H values of SLAP are -55.5 and -428 ‰ respectively. Precision is ±1 ‰ for δ^{2}H and ±0.2 ‰ for δ^{18}O.

^{14}C and ^{3}H samples of groundwater were measured at the Australian Nuclear Science and Technology Organisation (ANSTO) and the Tritium and Water Dating Laboratory, Institute of Geological and Nuclear Sciences (GNS), (New Zealand). For ^{14}C analysis performed at ANSTO, CO_2 was extracted from water samples in a vacuum line using orthophosphoric acid and converted to graphite through reduction with excess H_2 gas in the presence of an iron catalyst at 600 °C. ^{14}C concentrations were measured using a 10 kV tandem accelerator mass spectrometer. δ^{13}C values for these samples are derived from the graphite fraction used for radiocarbon via elemental analysis–isotope ratio mass spectrometry (EA-IRMS).

For ^{14}C samples measured at GNS, CO_2 was extracted from groundwater samples through addition of orthophosphoric acid. CO_2 was made into a graphite target and analysed by accelerator mass spectrometry (AMS). An aliquot of the extracted CO_2 was used for δ^{13}C analysis. ^{14}C activities are expressed as pMC (percent modern carbon) where pMC = 100 % corresponds to 95 % of the ^{14}C concentration of National Bureau of Standards (NBS) oxalic acid standard (Stuiver and Polach, 1977), with a precision of ^{14}C/^{12}C ratios of ±0.5 (Fink et al., 2004). At both ANSTO and GNS, samples for ^{3}H were distilled and electrolytically enriched prior to being analysed by liquid scintillation counting as described by Neklapilova et al. (2008a, b) and Morgenstern and Taylor (2009). ^{3}H activities are expressed in tritium units (TU) with a relative uncertainty of ±5 % and a quantification limit of 0.13 to 0.14 TU at ANSTO and 0.02 TU and a relative uncertainty of 2 % at GNS.

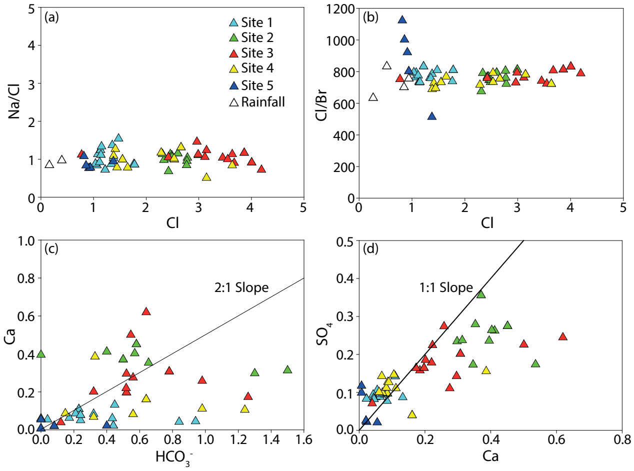

Figure 3. Geochemical characteristics of groundwater in the Eastern View Formation: **(a)** mCl / Br vs. mCl; **(b)** mNa / Cl vs. mCl; **(c)** mCa vs. mHCO$_3$; **(d)** mSO$_4$ vs. mCa. Rainfall samples are also plotted where measured. Data are from Table 1 with repeat measurements over the sampling period included.

4 Results

4.1 Groundwater elevations

Groundwater elevations decrease from 230 m relative to the Australian Height Datum (AHD) on the Barongarook High to < 60 mAHD within the Gellibrand Valley (Fig. 1), with groundwater flowing from the Barongarook High towards the Gellibrand Valley and then westwards. Groundwater elevations from all depths and positions within the Gellibrand Valley are in phase and fluctuate between 1 and 3 m annually (Fig. 2a). The water table rises between June and August following winter rainfall (Fig. 2c) and head gradients at nested sites are upwards (Fig. 2b). The Gellibrand River has high water levels that result in flooding during winter months (June to August) and low flows in summer (December to March) (Fig. 2c).

4.2 Groundwater geochemistry

The chemistry of groundwater in the Gellibrand Valley is summarized in Table 1. Groundwater is oxic, with electrical conductivities between 140 and 600 µS cm^{-1} and pH values ranging from 4.8 to 6.0. Groundwater from close proximity to the river (sites 1 to 4) generally has higher EC values (144 to 545 µS cm^{-1}) than groundwater further back on the floodplain at site 5 (149 to 220 µS cm^{-1}). Despite the range of salinity, the relative proportions of the major ions in groundwater are similar across the catchment. The groundwater is NaCl type. Cl constitutes between 68 and 92 % of total anions on a molar basis, with HCO$_3$ accounting for 0 to 25 %. Increases in Cl concentrations are associated with a decrease in HCO$_3$. Na comprises between 60 and 85 % of total cations

Table 1. Screen depth, Cl, ^{18}O, ^{2}H, ^{13}C, a^{14}C and ^{3}H activities of groundwater samples. [a]Refers to bore name on the Victorian Water Resources Data Warehouse. [b] Measured as depth to the middle of the well screen. [c]^{3}H activities that are below detection.

Sample	Screen	EC	Cl	Br	Na	Ca	Mg	K	HCO$_3^-$	SO$_4^{2-}$	δ^{18}O	δ^{2}H	δ^{13}C$_{DIC}$	a^{14}C		^{3}H	
No.	Depth (m)	(µS cm^{-1})	(mg L^{-1})								(‰ VSMOW)		(‰ PDB)	pMC	1σ	TU	1σ
1a (108899)[a]	29[b]	282	60	0.18	35.1	4.8	2.9	2.2	0.23	0.14	−5.6	−32.7	−21.4	81	0.34	bd[c]	–
1b (108916)	14.5	197	38.6	0.12	29.3	3.4	4.1	1/9	0.24	0.09	−5.3	−30.4	−22.1	83.3	0.28	bd	–
1c (108917)	14.5	238	44	0.08	20.3	1.0	2.6	0.7	0.44	0.08	−5.3	−31.1	−21.5	77.8	0.29	bd	–
2d (108927)	14	430	86	0.07	69.1	16.3	9.9	7.4	0.5	0.36	−5.6	−32	−20	39.5	0.2	bd	–
2e (108928)	17	446	96	0.08	76.3	19.9	11	8.6	0.58	0.27	−5.5	−33.6	−19.8	40.9	0.21	bd	–
3f (108933)	11.2	491	121	0.1	84	8.6	5.3	9.1	0.52	0.16	−5.6	−34.1	−20.1	33.8	0.20	bd	–
3g (108934)	11.5	545	125	0.06	103.8	13.5	8.5	10.5	0.78	0.2	−5.8	−32.4	−20.4	29	0.16	bd	–
3h (108935)	11.5	144	27	0.04	19.9	1.7	2.7	0.7	0.12	0.07	−4.8	−31.2	−21.3	88.6	0.17	bd	–
4i (108940)	11.5	243	53	9.02	35.4	3.6	3.21	2.2	0.56	0.11	−5.8	−34	−22.3	64	0.24	bd	–
4j (108941)	11.5	414	89	0.03	80.3	7.1	3.9	11.5	0.64	0.03	−5.7	−34.3	−21.5	49	0.21	bd	–
5k (110737)	42	149	31	0.02	16.9	0.9	2.3	0.7	0.08	0.03	−5.1	−29.4	−22.4	100	0.3	1.24	0.06
5l (80732)	21	200	48	0.1	30	0.33	4.2	0.5	0	0.1	−4.5	−29.7	−24.2	101.5	0.17	1.02	0.03
5m (80735)	21	217	30	0.03	16.5	0.32	10.5	3.6	0	0.11	−4.2	−29.1	−25.3	100.7	0.17	1.47	0.04

with Ca constituting 1 to 10 %, Mg constituting 0 to 10 % and K constituting 0 to 10 %. Increased Na concentrations are associated with decreases in both Ca and Mg concentrations. Molar Cl / Br ratios are between 400 and 600 and do not increase with increasing Cl (Fig. 3b); molar Na / Cl ratios are 0.7 to 1.3 and also remain stable with increasing Cl concentrations (Fig. 3a). Na / Cl ratios of groundwater samples are similar to those measured in rainfall in southeast Australia (Blackburn and Mcleod, 1983) and the Cl / Br ratios are also similar to those expected for local rainfall (Cartwright et al., 2006). There is a weak correlation between Ca and HCO_3 (Fig. 3c) and between Ca and SO_4 (Fig. 3d).

4.3 ^{13}C, a^{14}C and ^{3}H concentrations

The a^{14}C of groundwater ranges from 29 to 101.5 pMC. ^{3}H activities are below detection for the majority of groundwater samples (Table 1), with the exception of bores 5k, 5l and 5m, which have activities of 1.02, 1.47 and 1.24 TU, respectively. Groundwater from these bores has a^{14}C > 90 pMC. The distribution of a^{14}C and ^{3}H values across the catchment is heterogeneous with no relationship to depth or along lateral groundwater flow paths. A strong inverse correlation ($R^2 = 0.87$) is observed between a^{14}C and Cl concentrations (Table 1). A similar correlation is observed for Na ($R^2 = 0.855$), K ($R^2 = 0.82$), Ca ($R^2 = 0.6$) and Mg ($R^2 = 0.54$).

4.4 Stable Isotopes (δ^2H, δ^{18}O, δ^{13}C)

δ^{18}O and δ^2H values of groundwater define a narrow field ($\delta^{18}\mathrm{O} = -4$ to -6 ‰ and $\delta^2\mathrm{H} = -28$ to -40 ‰) that is close to both the global and local meteoric water lines (Fig. 4a). The Gellibrand Valley is located between Melbourne and Adelaide, with groundwater generally plotting between the average isotopic compositions of meteoric waters located in those areas. Groundwater samples from site 5 are enriched in both δ^{18}O (+0.7 ‰) and δ^2H (+3.5 ‰) relative to groundwater from sites 1 to 4 and have ^{3}H activities > 1 TU (Fig. 4a). Additionally samples that are enriched in δ^{18}O have a^{14}C > 100 pMC (Fig. 4b). δ^{13}C values of DIC from groundwater range from -19.8 to -25 ‰, with an average of 21.7 ‰ (Table 1).

4.5 Continuous electrical conductivity

Continuous groundwater EC records for a number of near-river bores and 5k, which is situated on the floodplain, are shown in conjunction with changes in river height for the study period (Fig. 5). Groundwater EC values in all bores for most of the data set show little or no response to changes in river height, although minor dilution of groundwater EC occurs during high flow events in August and September 2013. Minor changes in EC correlate to sampling events in which groundwater bores were pumped.

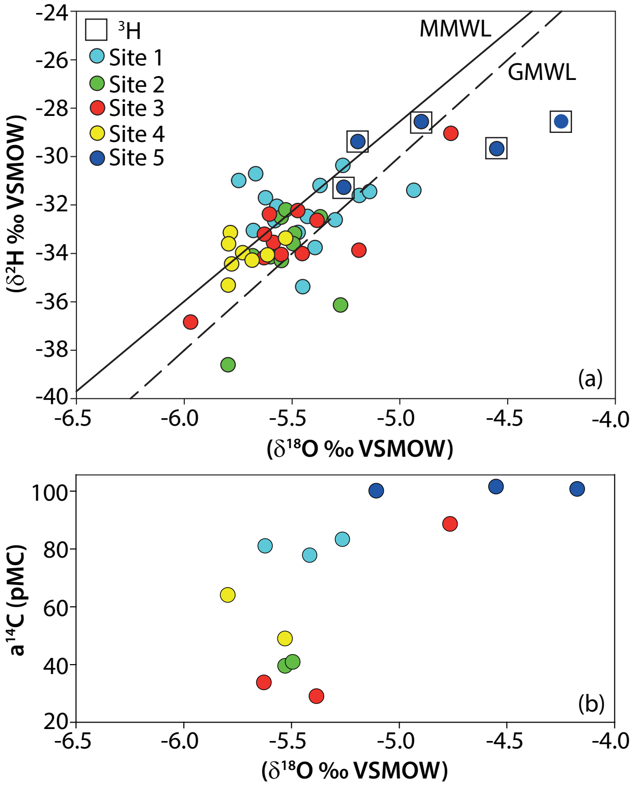

Figure 4. (a) ^{2}H vs. ^{18}O values of the Gellibrand River and surrounding groundwater sampled over March 2011–August 2013 and the weighted average for rainfall from Adelaide and Melbourne. MMWL = Melbourne Meteoric Water Line (Hughes and Crawford, 2012). GMWL = Global Meteoric Water Line (Clarke and Fritz, 1997). Groundwater with ^{3}H activities > 1 TU is also highlighted. Data are from Table 1 with repeat measurements over the sampling period included. **(b)** a^{14}C vs. ^{18}O of groundwater samples.

5 Discussion

5.1 Groundwater chemistry

Understanding geochemical processes in groundwater is required for correction of ^{14}C ages and in documenting groundwater flow and recharge. Processes that govern the evolution of groundwater geochemistry and sources of solutes in the Eastern View Formation can be determined from the major ion geochemistry. The observation that Cl / Br ratios are between 500 and 1000, which is similar to those expected in rainfall, and do not increase with increased TDS implies that evapotranspiration rather than halite dissolution is the major process controlling groundwater salinity (Herczeg et al., 2001; Cartwright et al., 2006). This conclusion is also consistent with an absence of halite in the aquifer lithologies. The δ^{18}O and δ^2H values of groundwater generally lie close to the meteoric water line and do not define evaporation trends, implying that transpiration in the soil zone or upper parts of the aquifer is likely to be dominant over evaporation. Na / Cl ra-

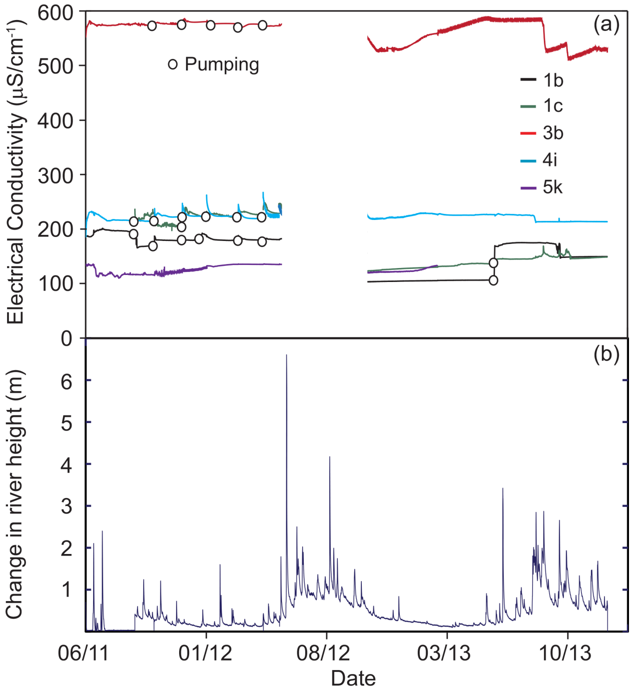

Figure 5. (a) Continuous electrical conductivity monitoring of near-river groundwater. **(b)** Changes in river height over the study period. Groundwater EC and river level data from deployed Aqua TROLL 200 (in situ) data loggers.

tios in groundwater are also similar to those in local rainfall (∼ 1), implying that silicate weathering is limited (e.g. Edmunds et al., 2002), while the increase in Na concentrations at the expense of Ca may indicate ion exchange reactions on the surface of clay minerals (e.g. Herczeg et al., 2001). That Ca and $mHCO_3$ are poorly correlated suggests that negligible dissolution of calcite has occurred. A handful of groundwater samples have a 1 : 1 Ca : SO_4 ratio, indicating some minor gypsum dissolution may take place. Together, the major ion geochemistry suggests that water–rock interaction is limited with minimal silicate weathering, negligible dissolution of halite and carbonate minerals and some minor dissolution of gypsum. As is the case elsewhere in southeast Australia, including within the Otway basin, the primary geochemical process is evapotranspiration promoted by the moderate rainfall and water-efficient native vegetation, and groundwater salinity is largely controlled by the degree of evapotranspiration during recharge (Herczeg et al., 2001; Bennetts et al., 2006; Petrides and Cartwright, 2006).

Groundwater from the near-river sites 1 to 4 has lower δ^{18}O and δ^{2}H values relative to that from the floodplain away from the river at site 5. In a catchment of $< 250\,\text{km}^2$ with a^{14}C varying between 29.1 and 101.5 pMC, climatic influences and the altitude effect are the most likely drivers in variability between groundwater samples (e.g. Dansgaard, 1964). As there is potential for groundwater recharge on the elevated Barongarook High and within the Gellibrand Valley, the depleted stable isotope signature of groundwater at sites 1 to 4 relative to groundwater samples from site 5 may reflect altitudinal differences of groundwater recharged at these locations. Assuming typical altitudinal gradients in rainfall of −0.15 to −0.5 ‰ per 100 m for δ^{18}O (Clark and Fritz, 1997) and an elevation difference of ∼ 150 m between the Gellibrand Valley and the Barongarook High, groundwater recharged on the Barongarook High is expected to be depleted in ^{18}O by −0.25 to −0.75 ‰ relative to that which is locally recharged in the valley. δ^{18}O values of groundwater from sites 1 to 4 are ∼ −0.7 ‰ lower than groundwater from site 5. Thus, the stable isotopes indicate that water in the near-river environment may have been recharged from the Barongarook High, while water from the floodplain is recharged locally within the valley. This is supported by the negligible ^{3}H activities at sites 1 to 4, which indicate old water, and elevated activities at site 5 indicating recently recharged water. It is possible that the differences in stable isotopes between the sites are driven by climatic factors rather than altitude.

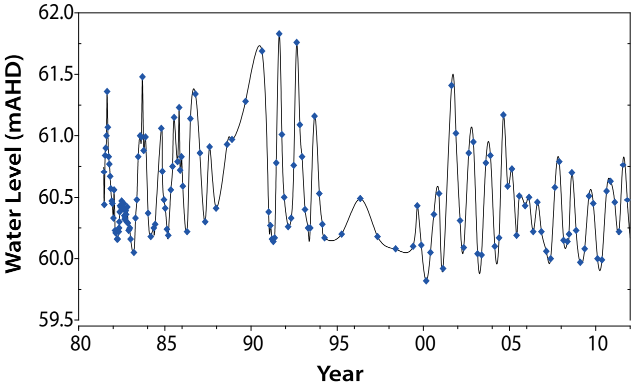

Figure 6. Historical water table fluctuations 1988–2011 for bore 108927 (Victorian Water Resources Data Warehouse, 2013). The magnitude of annual recharge cycles is coherent with those recorded in data loggers over the study period (2011 to 2013).

It is also possible that the variations in δ^{18}O values represent variation in the climate during recharge. While this has been proposed elsewhere in the Otway Basin (Love et al., 1994), in this part of the Otway Basin climatic variation has not been recorded in groundwater δ^{18}O values (Petrides and Cartwright, 2006). The lack of a systematic variation in δ^{18}O values with a^{14}C in groundwater from sites 1 to 4 also indicates that a climatic influence on δ^{18}O values is unlikely.

5.2 Water table fluctuations

Annual cycles of groundwater elevations are present in all groundwater bores, which are screened 11 to 40 m below the ground surface. The fluctuations in groundwater levels across the Gellibrand Valley are likely a pressure response to

Table 2. Radiocarbon ages of groundwater in the Gellibrand Catchment corrected for calcite dissolution. Uncertainties are calculated varying q by ± 0.1 plus the analytical uncertainty of a^{14}C from Table 1.

Sample	q	Radiocarbon age (years)	Uncertainty
1a	0.93	1150	+630/ − 980
1b	0.96	1190	+360/ − 940
1c	0.93	1520	+590/ − 970
2d	0.86	6530	+940/ − 1050
2e	0.86	6170	+950/ − 1060
3f	0.87	7870	+950/ − 1050
3g	0.89	9260	+930/ − 1040
3h	0.93	380	+630/ − 380
4i	0.97	3440	+290/ − 930
4j	0.93	5310	+630/ − 980

recharge on the flood plain following rainfall events via hydraulic loading (Cartwright et al., 2006; Brodie et al., 2008; Unland et al., 2014). The magnitude of annual water table fluctuations recorded in data loggers is similar to those over the previous 30 years (Fig. 6). Recharge was estimated for years 2012 and 2013 using the water-table fluctuation method Eq. (1):

$$R = S_y * \Delta h / \Delta t \tag{1}$$

(Scanlon et al., 2002), where S_y is specific yield, Δh is the change in water table height between the hydrograph recession and hydrograph peak and Δt is time. The water table rise is estimated as the difference between peak groundwater levels and the extrapolated antecedent recession. The estimate of recharge from this method is sensitive to the estimate of the specific yield. S_y is assumed to be 0.1, which is close to the measured effective porosity of the Eastern View Formation (Love et al., 1993), and takes account of the presence of finer sized sediments such as silt and clay in the aquifer. Annual water table fluctuations are between 0.9 and 3.7 m across all bores, which for S_y values of 0.1 imply that $R = 130$ to $372\,\mathrm{mm\,yr^{-1}}$ in 2012 (mean of $200\,\mathrm{mm\,yr^{-1}}$) and 90 to $300\,\mathrm{mm\,yr^{-1}}$ in 2013 (mean of $164\,\mathrm{mm\,yr^{-1}}$). This equates to between 11 and 32 % of rainfall in 2012 and 12 and 28 % of rainfall in 2013. The bores are screened 11.2 to 42 m below the ground surface and thus these recharge estimates will be minima due to the attenuation of pressure variations with depth (Scanlon et al., 2002). Recharge estimates are also susceptible to the value of specific yield, particularly where the aquifer is composed of finer sized sediments such as silt and clay. Regardless, estimates using bore hydrographs indicate that significant groundwater recharge to the unconfined Eastern View aquifer in the valley occurs via direct infiltration of precipitation.

5.3 ^{14}C ages

As groundwater in the Eastern View Formation contains dissolved oxygen and nitrate (Victorian Water Resources Data Warehouse, 2013), δ^{13}C values are low, and there are no reported occurrences of methane or coal seams within the Gellibrand River Catchment, methanogenesis is unlikely to be a source of DIC. Likewise there are no obvious sources of geogenic CO_2 in this area. Based on the major ion geochemistry, only minor calcite dissolution occurs in the Eastern View Formation, which is to be expected as the Cenozoic aquifers are siliceous and contain only minor carbonate minerals. While only minor carbonate dissolution is likely, determination of groundwater residence times requires this to be taken into account. If it is assumed that closed system dissolution of calcite in the aquifers is the major process, the fraction of C derived from the soil zone (q) may be derived from the δ^{13}C values of DIC ($\delta^{13}\mathrm{C_{DIC}}$), carbonate ($\delta^{13}\mathrm{C_{cc}}$) and recharging water ($\delta^{13}\mathrm{C_r}$) via:

$$q = \frac{\delta^{13}\mathrm{C_{DIC}} - \delta^{13}\mathrm{C_{cc}}}{\delta^{13}\mathrm{C_r} - \delta^{13}\mathrm{C_{cc}}} \tag{2}$$

(Clark and Fritz, 1997). The calcite is assumed to have a δ^{13}C of ~ 0 ‰ (Love et al., 1994; Petrides and Cartwright, 2006) as is appropriate for marine sediments. $\delta^{13}\mathrm{C_r}$ is calculated from the δ^{13}C of the soil carbon in the recharge zone. Pre-land clearing vegetation in southeast Australia was dominated by eucalypts that have δ^{13}C values of -30 to -27 ‰ (Quade et al., 1995). Assuming a ~ 4 ‰ ^{13}C fractionation during outgassing (Cerling et al., 1991), δ^{13}C values of soil CO_2 would be -26 to -23 ‰ (average of -24.5 ‰). At 20 °C and pH 6.5, $\delta^{13}\mathrm{C_r}$ calculated from the fractionation data of Vogel et al. (1970) and Mook et al. (1974) is ~ -20 ‰. Although the calculated $\delta^{13}\mathrm{C_r}$ values require the pH and temperature of recharge and the δ^{13}C of the soil zone CO_2 to be estimated, they are similar to those from other studies in southeast Australia and consistent with the predicted δ^{13}C values of DIC in equilibrium with calcite in the regolith (Quade et al., 1995; Cartwright, 2010). Calculated q values are between 0.85 and 0.97 (Table 2), implying that only 10 to 15 % of DIC in groundwater from the Eastern View formation is derived from calcite in the aquifer; this is similar to the expected contribution of calcite dissolution in siliceous aquifers (Vogel et al., 1970) and similar to other estimates from the Otway Basin (Love et al., 1994; Petrides and Cartwright, 2006).

Using the q values from Table 2, ^{14}C ages (t) corrected for closed-system calcite dissolution are calculated from Eq. (3), where a^{14}C is the activity of ^{14}C in groundwater DIC, and $\mathrm{a_o^{14}C}$ is the activity during recharge (assumed to be 100 pMC).

$$t = -8376 \ln\left(\frac{\mathrm{a^{14}C}}{\mathrm{q.a_o^{14}C}}\right) \tag{3}$$

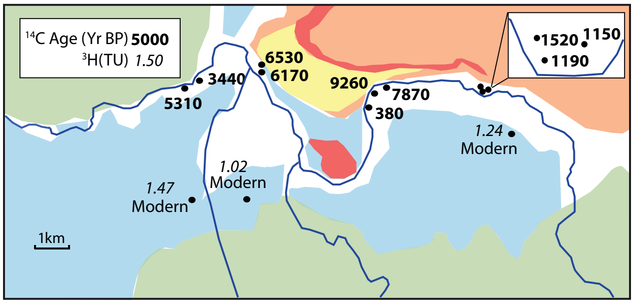

Figure 7. Groundwater residence times within the Gellibrand Valley. Residence times up to 9260 years are found in close proximity to the river. Modern local groundwaters with a^{14}C > 100 pMC are situated back on the floodplain. Data from Tables 1 and 2.

Radiocarbon ages for groundwater in the Eastern View Formation range from 380 to 9260 years (Table 2) with the exception of bores 5k, 5l and 5m, which have a ^{14}C > 100 pMC and represent groundwater that has a component of water recharged during or after the atmospheric nuclear tests in the 1950s to 1960s. The majority of ^{14}C ages, however, suggest that groundwater in the valley, especially in the near-river environment, has long residence times (Fig. 7).

5.4 ^{3}H activities and recharge rates

With a shorter half-life, ^{3}H activities can infer the presence of modern groundwater. The water table fluctuations imply that the Gellibrand Valley receives considerable recharge (90 to 370 mm yr^{-1}), and although head gradients at nested sites are upwards, implying that the valley is a groundwater discharge zone (Fig. 2b), these may be reversed during periods of high rainfall. If local recharge is significant in recharging the groundwater system across the valley, it would be expected that the groundwater would have relatively high ^{3}H activities. Recently recharged groundwater in other Victorian catchments has ^{3}H activities up to 3.6 TU (Cartwright and Morgenstern, 2012).

^{3}H activities across most of the groundwater from the Gellibrand Valley are negligible, and with ^{14}C ages of 380 to 9260 years, much of the groundwater is regional, originating from the Barongarook High. The exception to this is groundwater from the southern edge of the valley (site 5), where the Eastern View Formation overlies the basement rock (Eumeralla Formation) and ^{3}H activities and ^{14}C activities are substantially higher than for groundwater from sites 1 to 4. The mean residence times of water samples from the southern margin of the valley (site 5) were evaluated from ^{3}H activities using the TracerLPM Excel workbook (Jurgens et al., 2012). As the aquifer is unconfined throughout the valley, and bore screens sample only part of the aquifer, the partial exponential model (PEM) is applied, with the PEM ratio calculated for bores 5k, 5l and 5k as the ratio of the unsampled thickness of the aquifer to the sampled thickness (Jurgens et al., 2012). A value of 2.7 TU was used to represent modern and pre-bomb pulse rainfall based on the ^{3}H activity of rainfall measured at Monash University and expected ^{3}H values in Southern Victoria (Tadros et al., 2014). For intervening years, the mean weighted average of ^{3}H activities in precipitation in Melbourne was extracted from the International Atomic Energy Agency Melbourne record (International Atomic Energy Association, 2014). Calculated groundwater ages of 65 years (5k), 73 years (5l) and 59 years (5m) indicate that groundwater away from the river is modern and likely recharged from direct infiltration of precipitation. This supports δ^{18}O and δ^{2}H data, which suggests that sites 1 to 4 sample old, regional groundwater recharged on the Barongarook High, while site 5 samples locally recharged groundwater within the valley. Although groundwater levels across sites 1 to 5 demonstrate annual recharge cycles, in the near-river environment (sites 1 to 4) much of the regional groundwater is from within 5 to 10 m of the water table, suggesting that any local recharge penetrates only to a limited depth, and does not mix with the bulk of the water in the Eastern View Formation. Conversely the high ^{3}H activities and ^{14}C activities at site 5, which occur in groundwater from depths of 21–42 m, imply that recharge to the deeper parts of the aquifer locally occurs at the southern edge of the floodplain.

The Gellibrand River has the potential to recharge regional groundwater during high river stages and episodic floods. Aquifer recharge from surface water can be assessed by combining data from groundwater EC values and ^{3}H activities. The EC of river water varies between 120 and 200 µS cm^{-1} and is lower than that of groundwater in the catchment throughout the year. ^{3}H activities of river water are between 1.24 and 2.0 TU during baseflow conditions (Atkinson et al., 2013), and may be higher during high flow events as local modern rainfall (with ^{3}H activities of 2.4 to 3.2 TU: Tadros et al., 2014) and relatively "young" water draining the upper catchment likely comprise a significant component of river flow at those times. Significant amounts of aquifer recharge through over-bank events or bank exchange should result in groundwater with low EC values, and high ^{3}H activities near the river. Except for in June 2012 when the bores were overtopped and a limited response to high river flow events (June to July 2013), groundwater EC remains relatively constant throughout the study period and there is only a minor inverse relationship with river height (Fig. 6). This indicates that there is little exchange of river water to the depth of the aquifer sampled by the bores. Additionally the activities of ^{3}H in near-river bores are negligible, again suggesting that recharge from the river does not penetrate more than a few metres into the adjacent aquifer. Thus, flow through the river bank or river flooding does not appear to be a significant mechanism of recharge in the Gellibrand Valley. Instead, with upward head gradients and evidence for limited recharge in the near-river environment, the river likely acts as a groundwater discharge zone for most of the year, supplied

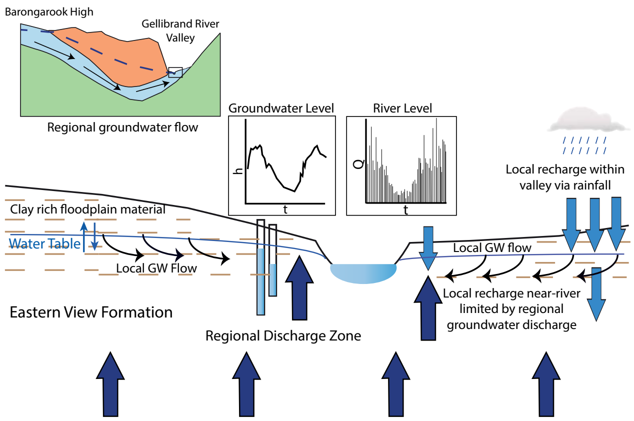

Figure 8. Groundwater flow conceptualization in the Gellibrand Valley. Though appreciable amounts of recharge are estimated from bore hydrographs and high river flows, the depth to which recharging waters infiltrate into the Eastern View Formation (downward leakage) is limited by strong upward head gradients, and a floodplain that consists of appreciable amounts of silt and clay.

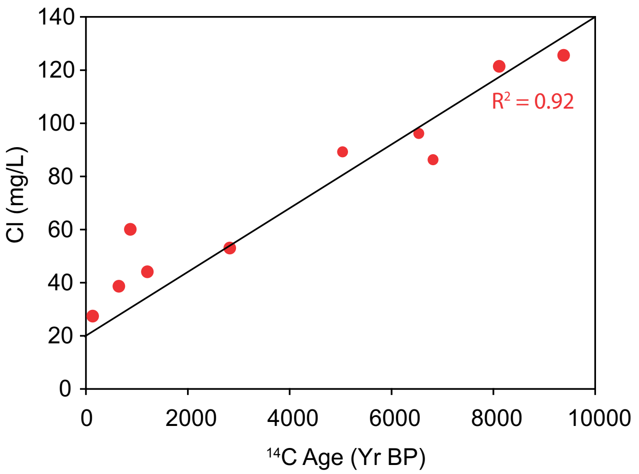

Figure 9. ^{14}C age vs. Cl. ^{14}C ages are taken from the calcite corrected ages in Table 1.

by a combination of regional groundwater from the Barongarook High and local groundwater recharged within the valley.

5.5 Groundwater flow paths and conceptual model

Radiocarbon ages are up to 10 ka, implying that the groundwater in the Gellibrand Valley has a long residence time; in turn this implies that the area is a regional discharge zone. Most of the groundwater originates on the Barongarook High, and this region potentially provides a substantial proportion of baseflow to the Gellibrand River. The large range of ^{14}C ages in the Gellibrand Valley is a likely result of heterogeneous geology, where the presence of low hydraulic conductivity sediments such as silt and clays in the Eastern View Formation leads to variable velocities along groundwater flow paths. Groundwater travel times may also be determined using the present day hydraulic gradients. From Darcy's law and assuming a porosity of 0.1 (Love et al., 1994) and a hydraulic conductivity of 0.2 to 2 m day^{-1} (Love et al., 1993) calculated travel times are between 1000 and 10 000 years, which are similar to those implied by the ^{14}C ages. This and the depleted stable isotope signature of groundwater samples from sites 1 to 4 support the idea that groundwater in the valley is predominantly regional groundwater derived by recharge on the Barongarook High. The high ^{3}H activities in groundwater bores from site 5 situated away from the river imply that local recharge via precipitation recharges the aquifer to depths of 21 to 42 m at the southern edge of the floodplain. However, for the most part, shallow groundwater in the Gellibrand Valley, including in the near-river environment, is predominantly regional groundwater. Though groundwater elevations display clear annual cycles and winter months are punctuated by high river flow, localized recharge from both of these processes combined is stored in the upper 10 m of the aquifer. The infiltration of precipitation within the Gellibrand Valley is likely limited by the presence of silts and clays on the floodplain and riverbanks. This is coupled with strong upward hydraulic gradients in the Eastern View Formation, driven by regional groundwater flow from the Barongarook High, which ensure that recharge in the near-river environment does not penetrate deep within the aquifer (Fig. 8).

5.6 ^{14}C ages & Cl

The good correlation of a^{14}C with chloride implies that chloride concentrations correspond to groundwater age (Fig. 9). Correlations between ^{14}C and Cl have also been documented in groundwater from the Eastern View Formation in other regions of the Otway Basin (Love et al., 1994). In assessing this relationship, chloride sources must be considered. That the Cl / Br ratios in the groundwater are similar to those of rainfall precludes significant halite dissolution by the groundwater from the Eastern View Formation, and there are no extensive occurrences of halite in the aquifer matrix.

We propose three possible explanations of this trend. Firstly, the relationship between a^{14}C and Cl may be explained by mixing of low-salinity groundwater that is locally recharged within the valley (site 5) and high-salinity regional groundwater from the Barongarook High (sites 1 to 4). However, groundwater samples from site 5 that have high a^{14}C and low Cl also have high ^{3}H activities (0.99 to 1.47 TU) suggesting that if mixing has occurred it must have been at a very slow rate, otherwise the resultant groundwater (sites 1 to 4) would be expected to contain measurable ^{3}H. This implies that mixing between the shallow groundwater system and the deeper groundwater is limited.

It is possible that the Cl concentrations in groundwater preserve a record of climate variability. In the Otway Basin, Love et al. (1994) report a decrease in Cl concentrations in groundwater recharged between 18 and 10 ka, followed by an increase in Cl concentrations in groundwater recharged from 10 ka to the present day, which they attribute to increased evapotranspiration rates during a warming Holocene climate. However, in this study decreasing Cl concentrations with increasing a^{14}C would imply that recharge rates on the Barongarook high increased from 10 000 years BP to the present, which is not likely given the warming trend over that period.

It is more likely that the correlation between a^{14}C and Cl concentrations reflects spatially variable recharge on the Barongarook High due to the heterogeneous sediments within the Eastern View Formation. Evapotranspiration during recharge is commonly the dominant process in determining the salinity of groundwater in SE Australia (Herczeg et al., 2001). Low recharge rates result in higher degrees of evapotranspiration and higher salinity groundwater, and the resultant correlation between Cl concentrations and ^{14}C ages has been noted in other catchments (Leaney et al., 2003; Cartwright et al., 2006). Variable recharge rates could result in a wide range of recharge ages in the Gellibrand Valley, with the high Cl–low a^{14}C groundwater being derived from regions with locally low recharge rates. Regardless of which model is correct, the chloride measurements provide a useful first-order estimate of groundwater residence times.

6 Conclusions

Though widely available water-table measurements offer an insight into recharge, the dynamics of groundwater flow systems and recharge patterns can only be fully understood when combined with geochemical data, in particular radiogenic tracers such as ^{3}H and ^{14}C. These can be used to assess the importance of recharge and discharge in aquifer windows, which in turn define groundwater pathways and allow the potential fate of pollutants to be assessed. Here shallow (11 to 42 m) groundwater bores indicate that a significant level of recharge occurs in the Gellibrand River Valley (90 to 370 mm yr^{-1}). However, the groundwater at 5 to 10 m below the water table has ^{14}C ages between 350 and 10 000 years, and below-detection ^{3}H activities. Furthermore, there is no indication of water from the river penetrating more than $\sim$10 m following flood events. In the Gellibrand River Valley, outcropping aquifer sediments act as a regional discharge zone. Upward head gradients are maintained for long periods of time and aided by the presence of silts and clays on the floodplain; this limits the depth to which diffuse and localized recharge (via over-bank events and bank exchange) penetrates the aquifer.

There is most likely a shallow local flow system within the Gellibrand River Valley that has limited connectivity with the deeper groundwater, particularly in the near-river environment. This potentially limits the spread of pollutants such as nitrate and pesticides that may derive from the agricultural activities into the regional groundwater. Future land-use, climate change or groundwater exploitation that occurs on the Barongarook High or in the Gellibrand River Catchment is likely to affect both the chemistry of groundwater and groundwater fluxes to the Gellibrand River, highlighting the importance of protecting regional recharge zones.

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