
The evolution of groundwater in the Tyrrell catchment, south-central Murray Basin, Victoria, Australia

B. Petrides · I. Cartwright · T. R. Weaver

Abstract The Tyrrell catchment lies on the western margin of the Riverine Province in the south-central Murray Basin, one of Australia's most important groundwater resources. Groundwater from the shallow, unconfined Pliocene Sands aquifer and the underlying Renmark Group aquifer is saline (total dissolved solids up to 150,000 mg/L) and is Na-Cl-Mg type. There is no systematic change in salinity along hydraulic gradients implying that the aquifers are hydraulically connected and mixing during vertical flow is important. Stable isotopes ($^{18}\text{O}+^{2}\text{H}$) and Cl/Br ratios indicate that groundwater is entirely of meteoric origin and salts in this system have largely been derived by evapotranspiration of rainfall with only minor halite dissolution, rock weathering (mainly feldspar dissolution), and ion exchange between Na and Mg on clays. Similarity in chemistry of all groundwater in the catchment implies relative consistency in processes over time, independent of any climatic variation. Groundwater in both the Pliocene Sands and Renmark Group aquifers yield ages of up to 25 ka. The Tyrrell Catchment is arid to semi-arid and has low topography. This has resulted in relatively low recharge rates and hydraulic gradients that have resulted in long groundwater residence times.

Résumé Le Bassin Versant de Tyrrell se situe sur la bordure occidentale de la Province de Riverine, dans la zone centrale sud du Bassin de Murray, l'une des ressources en eau souterraines majeures en Australie. Les eaux souterraines de l'aquifère libre superficiel des Sables Pliocènes et de

l'aquifère sous-jacent du Renmark Group sont salées (solides dissous totaux atteignant 150,000 mg/L), et de faciès chloruré sodique et magnésien. La salinité ne varie pas selon les gradients hydrauliques, suggérant que les aquifères sont connectés hydrauliquement et que les mélanges sont importants au cours du trajet vertical. Les isotopes stables (^{18}O et ^2H) et les rapports Cl/Br indiquent que l'eau a une origine exclusivement météorique, et que les sels sont essentiellement issus de l'évaporation de l'eau de pluie dans ce système, avec quelques effets mineurs de la dissolution de halite, de l'altération des roches (majoritairement dissolution des feldspaths) et des échanges de bases entre Na et Mg dans les argiles. Les similarités chimiques entre toutes les eaux souterraines du bassin versant impliquent une relative continuité des processus dans le temps, indépendamment de tout changement climatique. Les âges des eaux souterraines des aquifères des Sables Pliocènes et du Renmark Group sont estimés à 25,000 ans au maximum. Le Bassin Versant de Tyrrell est aride à semi-aride, avec un relief bas. La recharge est par conséquent lente et les gradients hydrauliques peu marqués, générant des temps de résidence élevés.

Resumen La subcuenca de Tyrrell queda en el margen occidental de la Provincia de Riverine en la Cuenca de Murray sur-central, uno de las fuentes de agua subterránea más importantes de Australia. El agua subterránea del acuífero somero y libre de las Arenas del Plioceno, lo mismo del acuífero subyacente del Grupo Renmark es salina (Los Sólidos disueltos totales alcanzan hasta 150,000 mg/L) y es el tipo de Na-Cl-Mg. No hay ningún cambio sistemático en la salinidad a lo largo de los gradientes hidráulicos, implicando que los acuíferos se conectan hidráulicamente y que la mezcla durante el flujo vertical es importante. Los isótopos estables ($^{18}\text{O}+^{2}\text{H}$) y las proporciones de Cl/Br indican que el agua subterránea es completamente de origen meteórico y que las sales en este sistema se han derivado principalmente por evapotranspiración de lluvia, con una disolución menor de halita, meteorización de la roca (principalmente la disolución del feldespato), e intercambio iónico entre Na y Mg en las arcillas. La similitud en la química de toda el agua subterránea en la subcuenca, implica la consistencia relativa de los procesos con el tiempo, independiente de cualquier variación climática. El agua subterránea en los acuíferos de las Arenas del Plioceno y del Grupo Renmark

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tiene edades hasta 25,000 años. La Subcuenca de Tyrrell es árida a semiárida y tiene topografía baja. Esto ha producido proporciones de recarga y gradientes hidráulicos relativamente bajos, que a su vez han resultado en tiempos de residencia largos del agua subterránea.

Keywords Salinity · Tyrrell Catchment · Murray Basin · Isotopes · Groundwater age

Introduction

Nowhere in Australia is the problem of determining the origin of saline groundwater more important than in the Murray Basin, which contains some of the most productive agricultural land and delivers approximately 40% of Australia's income derived from agriculture and grazing. The basin has undergone substantial land use changes since European settlement 150–200 years ago, such as replacement of native vegetation by shallow-rooting crops (e.g. wheat and pasture) as well as extensive diversion of surface waters for irrigation. These activities have increased groundwater recharge, resulting in rising water tables that have contributed to the onset of dryland and irrigation salinity (Ghassemi et al. 1995). However, it is clear that groundwater in the basin was always saline. Bonython (1956) suggested that evaporation was the main process that caused this primary salinity. By contrast, Wopfner and Twidale (1967) and Johnson (1979) attributed the salts to seawater entrapped in the sediments at the time of their deposition, while Arad and Evans (1987), Chivas et al. (1991), Herczeg and Lyons (1991), Macumber (1991), and Cartwright and Weaver (2005) invoked a combination of marine aerosol accretion and rock weathering as the main source of salts in the basin. To effectively manage groundwater resources within this catchment, understanding the origin and migration of these salts is essential.

The total dissolved solids (TDS) in groundwater in the Murray Basin varies from <1,500 to >35,000 mg/L; however, as shown in Fig. 1, systematic variations in groundwater salinity are not evident. Saline groundwater exists from the basin margins to the discharge areas and across different climatic zones, which suggests that it is not simply a result of water–rock interaction or evaporation in arid areas. Most studies of Murray Basin hydrogeology have focused on the regions of fresher groundwater due to its importance in domestic and agricultural supply. However, areas dominated by saline groundwater (such as the Tyrrell Catchment; Fig. 1b) are more abundant, and understanding the processes that control the salinity in these areas is critical to our overall knowledge of basin hydrogeology. It is also important to determine if this saline groundwater is isolated from the adjacent fresh groundwater or whether it poses a risk to those resources. This study couples geochemical tracers with physical hydrogeology to examine vertical vs. horizontal flow, inter-connectivity between aquifers, groundwater residence times, and the origin and behaviour

of solutes in the Pliocene Sands and Renmark Group aquifers of the Tyrrell Catchment of the Murray Basin.

Geological and hydrogeological setting of the Murray Basin

The Murray Basin is a shallow, intracratonic, sedimentary basin with an areal extent of ~300,000 km². Detailed descriptions of Murray Basin geology and hydrogeology are presented by Tickell (1978), Tickell and Humphreys (1986), Arad and Evans (1987), Lawrence (1988), Brown (1989), Evans and Kellett (1989), Macumber (1991), Herczeg et al. (1992, 1993, 2001), and Cartwright and Weaver (2005). The Murray Basin contains a series of late Paleocene to Recent sediments that are up to 600 m thick and which overlie a Proterozoic to Mesozoic basement (Fig. 1c). The sediments show a transition from dominantly marine in the south-west and centre of the basin to marginal marine and terrestrial in the east and north of the basin (Lawrence 1975; Brown 1989; Evans and Kellett 1989; Macumber 1991; Fig. 1c). Except for a small region in the south-west of South Australia that discharges to the Southern Ocean (Macumber 1992; Herczeg et al. 1992), the Murray Basin is a closed groundwater system with the majority of groundwater discharging to numerous salt lakes in its centre. The Murray River is the sole conduit for the transport of groundwater and salts out of most of the basin (Evans and Kellett 1989). The basin is unconfined over much of its areal extent and there are few thick aquitard sequences that separate major aquifers. Thus, recharge may occur generally across the basin and flow paths may be complex.

There are three distinct provinces or sub-basins: Riverine, Scotia, and Mallee-Limestone (Fig. 1b). The Riverine Province, in which this study is based, underlies the Riverine Plain of Victoria and New South Wales. It is separated from the Scotia Province in the north-west by the Neckarboo Ridge and from the Mallee-Limestone Province in the south-west by a change in groundwater flow direction that coincides with the low-permeability Winnambool Formation, Geera Clay, and Bookpurnong Beds that envelop the eastern edge of the Murray Group Limestone aquifer (Lawrence 1988; Brown 1989; Evans and Kellett 1989). The Mallee-Limestone Province underlies the Wimmera and Mallee regions in western Victoria and eastern South Australia, and the Scotia Province occupies the most arid part of the basin east and south of the Barrier Range in South Australia and New South Wales (Evans and Kellett 1989).

The sediments of the Riverine Province are dominantly terrestrial with a transition to marginal marine units in the west. There are three main units. The basal Renmark Group aquifer is confined and virtually continuous over the entire province. It consists of Paleocene to late Miocene fluvial clays, silts, sands, and gravels. In the west of the province, these more permeable units are intercalated with lower permeability clays and marls of the Geera Clay and Winnambool Formation; however, in much of the Riverine Province, such low permeability

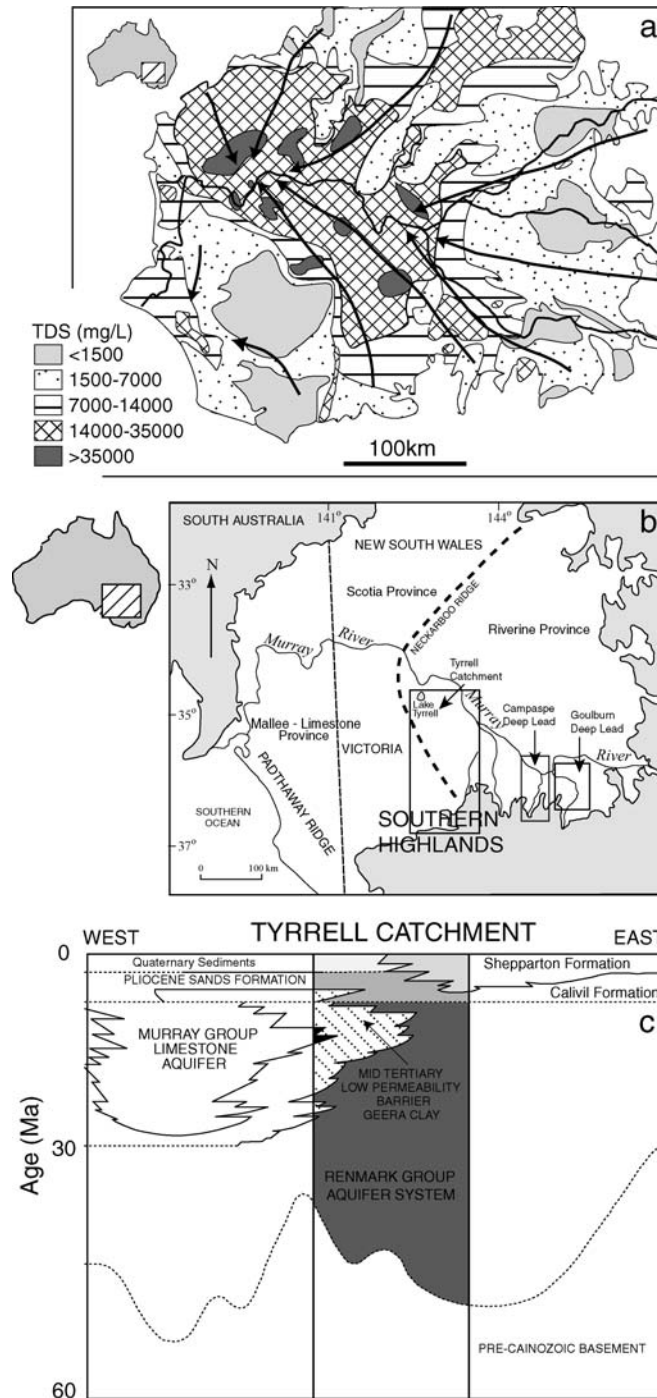


Fig. 1 a Salinity map of shallow groundwater in the Murray Basin (after Evans and Kellett 1989). Arrows indicate direction of regional groundwater flow. b Map of Murray Basin (after Evans and Kellett 1989) showing the three major provinces. Also shown

are the Tyrrell Catchment and Goulburn and Campaspe deep leads. c Stratigraphy of the Murray Basin (after Evans and Kellett 1989). Shaded area displays the stratigraphy of the Tyrrell Catchment

units are absent (Cartwright and Weaver 2005). The Calivil Formation is in hydraulic continuity with the underlying Renmark Group and these formations may be considered as a single aquifer system (Lawrence 1988; Brown 1989; Evans and Kellett 1989; Macumber 1991; Cartwright and Weaver 2005). Calivil Formation sedi-

ments were deposited by the ancestral Murray River drainage system, which became established after the Middle Miocene regression (Macumber 1978). The Calivil-Renmark Group is thickest in these ancestral drainage channels (“deep leads”) of modern day rivers and contains coarse sands and gravels. These deep leads

are conduits for preferential groundwater flow and also tend to contain fresh groundwater (Macumber 1991).

The uppermost aquifers of the Riverine Province are the Shepparton Formation and Pliocene Sands. The Shepparton Formation directly overlies the Calivil Formation in the east of the Riverine Province and grades laterally into the Pliocene Sands in the west. The Shepparton Formation is a complex assemblage of fluvio-lacustrine sediments, comprising clay, silt and minor sand, while the Pliocene Sands consists of fluvio-lacustrine and beach barrier deposits and has a higher sand and quartz component. Recharge of groundwater into the Pliocene Sands and Shepparton Formation occurs across most of the Riverine Province. Downward leakage into the underlying Calivil-Renmark Group is promoted by heterogeneity within the formations.

The Tyrrell Catchment

The Tyrrell region shown in Fig. 2, lies at the western margin of the Riverine Province and encompasses ~30,000 km². The area slopes gently northwards from ~250 to ~50 m over 250 km from the basement outcrops in the south. The area is semi-arid with mean annual precipitation ranging from 350–400 mm/year in the north, to over 550–600 mm/year in the south and south-west (Bureau of Meteorology 2005). Rainfall is predominantly during the Australian winter, mainly between May and October, and annual evaporation ranges from approximately 1,700 to 1,900 mm/year, exceeding rainfall for most of the year (O’Rorke 1992; Dudding 1993).

Natural drainage is poor and there are several areas that were originally ephemeral swamps and wetlands (e.g. Kerang; Fig. 2b). However, significant modification of

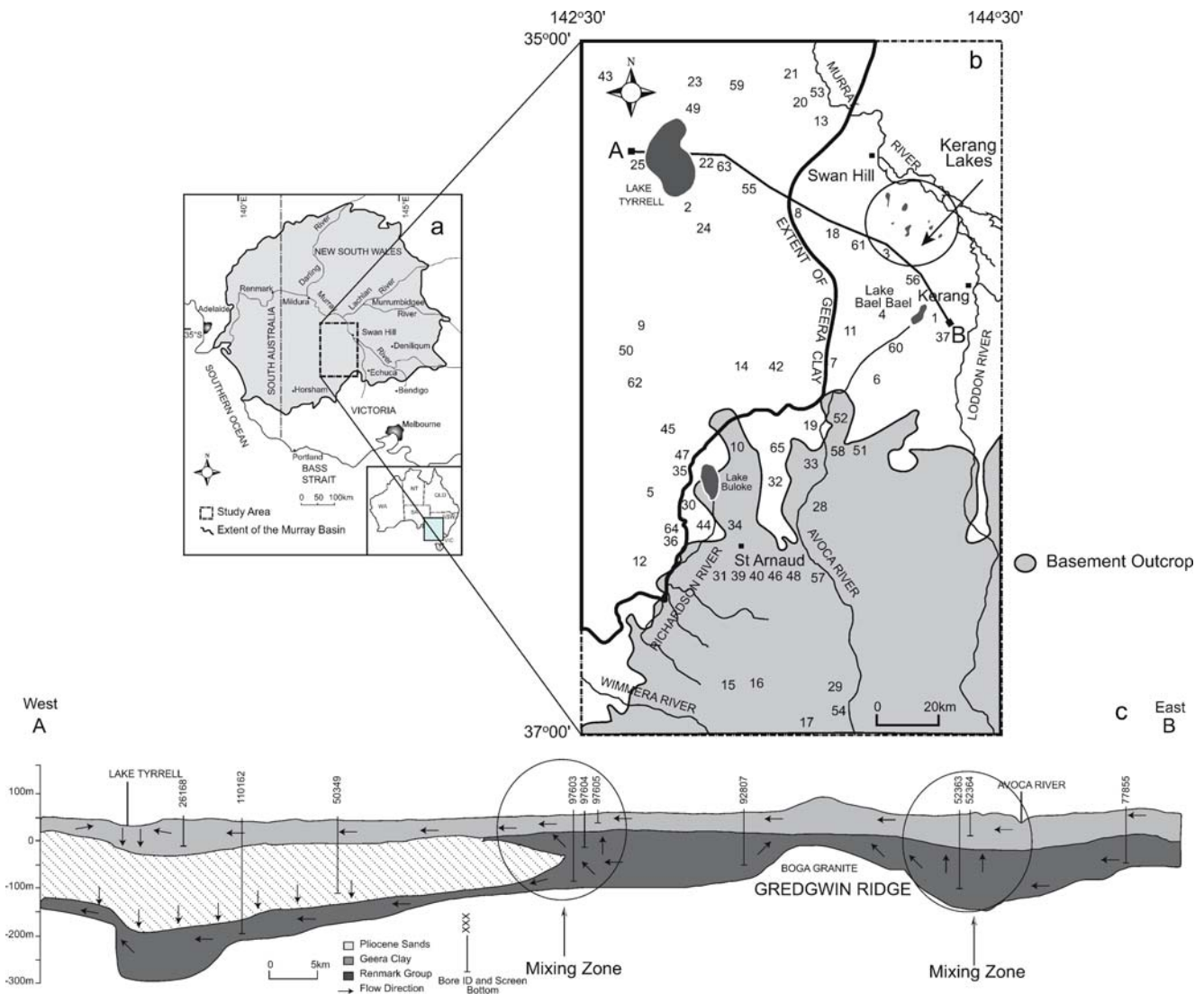


Fig. 2 a Map of the Murray Basin. b Map of the Tyrrell Catchment showing the major rivers, salt lakes, bore locations and major towns. Eastings and northings are from the Australian map grid. Numbers indicate location of bores sampled (bore locations shown on Table 1. c Stratigraphic cross-section of line A–B

showing major units of the Tyrrell Catchment. Groundwater flow direction, mixing zones and basement ridges are also displayed. Numbers indicate bore ID (which corresponds to bore locations given in b and Table 1)

drainage systems for agricultural development has occurred with the construction of irrigation channels and draining of swampy areas. Streams flowing northward across the Tyrrell Catchment do not reach the Murray River but flow into terminal lake systems. The Avoca River, the major surface water system in this catchment, terminates at Lake Bael Bael (Fig. 2b). Prior to 1850, the area was mostly covered by native Eucalyptus woodland, known locally as Mallee. These trees are extremely efficient users of water, returning more than 99% of precipitation to the atmosphere by evapotranspiration (Allison and Hughes 1983). Over the last 150 years ~80% of the study area has been cleared for dryland cropping and grazing which has resulted in increased recharge with the result that the water table is now generally within 5 m, and locally within 2 m, of the surface (Watkins et al. 1999). Allison and Hughes (1983), Leaney and Allison (1986), Calf et al. (1986), Cook et al. (1989), Cartwright and Weaver (2005), and Cartwright et al. (2004) suggest that recharge has increased from <1 mm/year to ~1–50 mm/year.

The main aquifer in the Tyrrell Catchment is the basal Renmark Group that is locally up to 300 m thick and which comprises predominantly quartz sand and gravels, with minor clay, carbonate minerals, calcite cements, and organic rich layers (Pratt 1988; Fig. 2c). Overlying this are the Calivil Formation and Pliocene Sands. The Calivil Formation has a higher proportion of gravel and coarse sand than the Pliocene Sands, which is comprised of medium to fine sands and silty sands. The Calivil Formation is less well defined in the Tyrrell Catchment; however, the formation has been recorded in the Avoca deep lead which underlies the Avoca River. The Shepparton Formation is only present near Kerang. Both the Renmark Group and Pliocene Sands overlie a basement of Palaeozoic rocks, and depth to the basement increases northwards up to 350 m (Tickell and Humphries 1986). TDS contents of groundwater in the Tyrrell Catchment range from <500 to >35,000 mg/L. The fresh groundwater in the Calivil Formation occurs where the Avoca River becomes a significantly losing stream. Groundwater salinity in this area increases with depth to >14,000 mg/L in the Renmark Group aquifer.

Sampling and analytical techniques

Groundwater was sampled from 102 groundwater monitoring bores from the Tyrrell Catchment (Fig. 2b). These were screened in the Pliocene Sands, Geera Clay and Renmark Formations. Groundwater samples were collected using a polyethylene bailer (shallow wells) or a QED Micro Purge bladder pump that was set, where possible, at the screened interval. Groundwater drawdown was minimized during pumping to ensure that water was extracted from the well screen.

Depth to water, pH, EC, alkalinity, dissolved CO₂, dissolved O₂, and temperature were measured in the field. pH was measured using an Orion 290 meter and Orion

Ross electrodes that were calibrated against standard solutions at each location. EC and temperature were measured using an Orion 240 conductivity meter and probe. Alkalinity and dissolved CO₂ were determined using a Hach digital titrator and reagents. Dissolved O₂ was determined using a Hach drop titrator and reagents. Samples for major ion analysis were collected in HDPE bottles filled to overflowing and stored at ~4°C until analysis. Cations were analysed using a Varian Vista ICP-AES at the Australian National University on samples that had been filtered through 0.45-µm cellulose nitrate filters and acidified to pH 2 using 16N ultrapure HNO₃ immediately after collection. Anions were analysed on filtered unacidified samples using a Metrohm ion chromatograph at Monash University. Field parameters and chemical analyses are presented in Tables 1 and 2.

¹⁴C activities shown in Table 3 were determined by Accelerated Mass Spectrometry on the 14UD tandem electrostatic accelerator at the Australian National University. Stable isotope ratios presented in Table 4 were measured at Monash University using a Finnigan MAT 252 mass spectrometer. δ¹⁸O values of water were measured via equilibration with He-CO₂ at 32°C for 24–48 h in a Finnigan MAT Gas Bench and analysed using continuous flow. δ²H values of water were measured via reaction with Cr at 850°C using an automated Finnigan MAT H/Device. δ¹⁸O and δ²H values were measured relative to internal standards that were calibrated using IAEA SMOW, GISP, and SLAP standards (Coplen 1988). Data were normalised following Coplen (1988) and are expressed relative to Vienna Standard Mean Ocean Water (VSMOW) where δ¹⁸O and δ²H values of SLAP are –55.5 and –428‰, respectively. CO₂ from dissolved inorganic carbon (DIC) was liberated by acidification using H₃PO₄ in a He atmosphere and analysed by continuous flow. δ¹³C values are expressed relative to PDB (*Belemnitella Americana* from the Cretaceous Pee Dee Formation, South Carolina). Many samples were analysed twice and the precision based on replicate analyses is: δ¹⁸O=±0.1, δ²H=±1, δ¹³C=±0.1‰. The organic component of the aquifer sediments were combusted using a Carlo Erba 1112 Series 3 Flash Elemental Analyser and δ¹³C values were determined by continuous flow (Table 2).

The mineralogy of sediments was determined by X-ray diffraction (XRD) on a Philips PW 1010, 36 kW, 28 mA X-ray diffractometer at Amdel Laboratories, South Australia and setup in θ-θ configuration. The X-ray source was a tube with a cobalt target. The detector was engaged to sweep over an angle from 5 to 55° which captures d-spacings from 20 to 1.9 Å. Whole-rock compositions were determined using a Spectro Analytical Instrument XLAB2000 energy dispersive polarizing XRF spectrometer at Macquarie University, New South Wales. Major elements were measured on a sample fused with lithium borate flux in a ratio of approximately 1–6. Trace elements were measured on approximately 5 g of pressed powder. Deconvolution of the spectra used proprietary software developed by the manufacturers. Calibration of the

Table 1 Bore locations, depths, and groundwater elevations for the Tyrrell Catchment

Bore location (Fig. 2b)	Bore ID	Top of screen (m b.g.l.)	Bottom of screen (m b.g.l.)	Groundwater elevation (mAHD) ^a	ΔH (m/m) ^b
	Pliocene Sands				
15	5233	29	31	213.6	
16	5241	63	69	210.3	
17	5364	9	11	296.6	
18	6097	31	31.5	63.4	
19	370	16	18	95.1	
20	26160	27.49	27.99	54.1	
21	26167	24.9	25.4	51.5	
22	26168	23.61	24.11	50.6	
23	40650	10.5	13.5	46.3	
24	40653	12.5	13	49.0	
25	49987	52	60	46.5	
1	50315	58	68	70.5	0.003 ^P
1	50316	27	32	70.6	0.025 ^{P-R}
2	51350	20	21	43.6	0.016 ^{P-R}
3	52364	55	58	74.1	0.003 ^{P-R}
26	53978	23	72	ND	
27	53981	4.8	38	ND	
28	56747	18.3	30.5	144.5	
4	58524	18	21	71.1	0.030 ^P
4	58525	6	8	70.7	0.064 ^{P-R}
29	60050	18	20	250.9	
30	60061	15.5	17.5	116.0	
31	60068	18	20	139.8	
32	60074	14	16.5	121.2	
33	60215	35	36	153.4	
34	60522	51	57	116.9	
35	60523	45	51	110.7	
5	61851	18	24	100.7	-0.004 ^{P-R}
36	73981	34	60	115.7	
6	77306	55	61	78.1	0.016 ^P
6	77307	32	35	77.7	
37	77855	20	22.5	75.4	
7	85933	30	36	95.0	-0.026 ^{P-R}
38	89310	15	21	ND	
39	92684	36	42	137.6	
8	97605	24	30	53.0	0.129 ^{P-R}
40	103875	24	30	142.3	
9	110128	40	46	60.4	0.068 ^{P-R}
10	110182	25	28	94.4	0.078 ^P
10	110183	35	41	94.4	0.010 ^{P-R}
41	110186	50	56	95.3	
42	110871	40	46	69.5	0.029 ^{P-R}
10	110874	48	51	72.6	
12	113122	48	54	154.5	0.005 ^P
12	113123	5	11	154.3	
43	115390	1.5	20	44.3	
44	116573	44	50	127.7	
45	116639	30	36	80.7	
46	116699	39	45	139.3	
47	116741	29	31	99.8	
48	116746	21	27	145.7	
49	116765	24	30	54.0	
50	116771	30	36	66.6	
51	119378	8.5	10.5	121.0	
52	119380	9.5	11.5	100.0	
53	119384	23	25	59.5	
13	119386	17	19	61.1	0.030 ^P
13	119387	7	9	60.8	
54	325497	16.5	25.3	213.6	
65	Salt lake	ND	ND	ND	
	Geera Clay				
55	50349	80	86	56.3	
	Renmark Group				
56	46916	207	210	71.4	
1	50314	120	123	72.1	
2	51346	170	190	46.2	
3	52363	126	129	74.3	

Table 1 (continued)

Bore location (Fig. 2b)	Bore ID	Top of screen (m b.g.l.)	Bottom of screen (m b.g.l.)	Groundwater elevation (mAHD) ^a	ΔH (m/m) ^b
11	52367	189	199.5	73.6	
11	52368	135	139	72.8	
57	58326	48	59	154.6	
4	58523	64	86	74.6	
5	61850	110	122	100.3	
58	65270	86	92	102.2	
7	85932	83.5	89.5	93.6	
59	88000	303	309	Artesian	
60	89309	83	86	75.9	
61	92807	106	109	71.2	
8	97603	157	160	70.0	
8	97604	85	95	57.8	
62	103893	143	146	76.1	
63	110162	246	249	68.3	
9	110163	153.94	157	68.1	
14	110179	86	92	73.1	0.192 ^{R-R}
14	110180	114	116	78.1	
10	110181	95	98	95.0	
64	116591	86	92	115.4	

^aDensity corrected relative to the Australian Height Datum (mAHD)

^bVertical head gradients (ΔH). Those denoted ^P are within the Pliocene Sands, ^{P-R} are between the Pliocene Sands and Renmark Group Formations. Negative values are downward, while positive values are upwards. *ND* not determined; *m b.g.l.* metres below ground level

instrument was made against a wide range of natural rock standards and synthetic materials.

Tyrrell groundwater flow

A combination of groundwater elevations, hydraulic conductivity and radiogenic isotopes allow both current and historic flow systems to be defined (cf. Edmunds et al. 1982; Weaver and Bahr 1991; Herczeg et al. 1992; Kimblin 1995; Weaver et al. 1995; Elliot et al. 1999; Herczeg and Edmunds 2000; Edmunds and Smedley 2000; Cartwright and Weaver 2005). As shown in Fig. 3a, recharge to the unconfined Pliocene Sands occurs over much of the Riverine Province. The Renmark Group does not crop out and, therefore, can only be recharged through the Pliocene Sands. This is most likely to occur in the south of the region where depth to the Renmark Group is locally only 20 m and the Pliocene Sands and Shepparton Formations contain a higher component of sands than clays.

Groundwater in the shallowest aquifer flows away from the southern highlands towards the low-lying flood plains of the Loddon, Avoca, Avon-Richardson, and Wimmera Rivers. Groundwater flow converges on Lake Tyrrell implying that it is a discharge lake (Fig. 3a). The direction of groundwater flow in the Renmark Formation is also similar (Fig. 3b); however, flow does not tend to converge around Lake Tyrrell due to the presence of the Geera Clay aquitard. The Gredgwin Ridge and Lake Boga Granite in the centre of the catchment (Fig. 2c) divert regional groundwater flow. Local recharge may also occur near these basement highs. Groundwater flows underneath the

River Murray and its major tributaries indicating that they are not fully penetrating rivers.

Horizontal potentiometric gradients along flow line A-A' (Fig. 3a,b) are $\sim 4 \times 10^{-4}$ m/m in the Pliocene Sands and $\sim 3 \times 10^{-4}$ m/m in the Renmark Group aquifers. Slightly greater horizontal hydraulic gradients exist in the southern highlands (7×10^{-4} – 1×10^{-3} m/m; Fig. 3b). The regional Pliocene Sands aquifer has a horizontal hydraulic conductivity of ~ 1 – 2 m/day (Lawrence 1975). For a porosity of 0.2, regional groundwater flow rates calculated from Darcy's Law are only ~ 0.002 – 0.004 m/year.

Vertical hydraulic gradients within the Pliocene Sands and between the Pliocene Sands and the Renmark Formation estimated from localities with nested bores are generally upwards with magnitudes of up to 0.13 m/m (Table 1); however, at most localities, gradients are < 0.1 m/m (Fig. 3c). The magnitude of the vertical hydraulic gradient broadly decreases to the north and north-west, implying greater vertical connection between these two aquifer systems in that area. In the south of the area, hydraulic gradients are downwards, indicating a potential for downward leakage. Vertical hydraulic gradients within the Renmark Group are generally lower than those within the Pliocene Sands (Table 1). At several localities (i.e. Lake Tyrrell and Swan Hill; Fig. 3c), hydraulic gradients within the Pliocene Sands are upwards, whilst those between the Pliocene Sands and Renmark Group are downward, probably due to perching of water tables in the heterogeneous Pliocene Sands. Also, recent increases in recharge that have caused the water table to rise have left the system in hydraulic disequilibrium. Lateral groundwater flow is impeded in the Kerang-Swan Hill region where the Pliocene Sands grades

Table 2 Major chemistry of Tyrrell groundwater

Bore ID	pH	EC mS/cm	TDS mg/L	O ₂ mg/L	CO ₂ mg/L	HCO ₃ mg/L	Cl mg/L	Br mg/L	NO ₃ mg/L	SO ₄ mg/L	Na mg/L
Pliocene Sands											
5233	6.99	12.8	8,704	1	376	443	3,820	14.8	2.8	715	2,030
5241	7.27	4.9	3,332	4	168	270	1,250	4.6	1.8	240	643
5364	6.83	3.6	2,448	3	221	176	950	3.2	5.7	120	513
6097	6.81	53.5	36,380	6	292	317	19,500	64.0	3.0	4,550	10,600
6370	6.34	28.1	19,108	2	220	132	9,800	40.0	4.0	2,390	4,200
26160	4.95	52.1	35,428	1	240	5	19,000	55.0	bd	4,100	10,600
26167	5.34	68.4	46,512	1	204	55	25,500	72.0	150.0	6,310	10,200
26168	5	69.7	47,396	0	260	12	24,250	68.0	BD	5,070	11,300
40650	3.97	64.9	44,132	3	300	0	23,170	66.0	18.0	1,940	9,750
40653	4.25	35.8	24,344	2	160	0	14,480	48.0	2.0	3,390	6,500
49987	3.28	118.1	80,308	2	190	0	51,110	156.0	8.0	5,780	23,200
50315	7.61	62.3	42,364	2	302	381	22,740	72.0	4.0	4,280	8,570
50316	7.36	65.0	44,200	3	234	285	23,280	71.0	7.0	4,840	9,370
51350	8.85	>150	10,2000	0	180	12	11,7150	336.0	36.0	20,140	60,700
52364	7.96	35.2	23,936	5	204	616	11,750	42.0	1.0	3,150	5,970
53978	7.38	28.8	19,584	2	112	61	10,520	42.5	1.0	2,420	4,380
53981	7.06	31.2	21,216	3	60	46	10,920	43.5	3.5	2,390	5,080
56747	5.57	19.3	13,124	0	160	0	7,860	25.2	0.4	600	1,740
58524	7.363	65.9	44,812	1	226	100	23,730	76.0	16.0	4,820	10,500
58525	7.091	48.4	32,912	2	190	427	16,850	54.0	11.0	3,620	98,00
60050	7.24	13.5	9,180	2	221	298	4,200	12.8	BD	710	2,010
60061	6.74	31.8	21,624	1	10	46	11,060	44.0	11.5	2,670	58,20
60068	7.23	13.5	9,180	2	186	226	4,370	16.4	6.4	790	2,130
60074	6.63	28.1	19,108	3	32	51	9,480	41.0	BD	3,860	5,020
60215	7.14	23.9	16,252	4	424	625	7,800	30.5	BD	2,860	4,000
60522	7.69	13.3	9,044	3	144	190	4,500	16.2	BD	950	2,090
60523	7.06	39.2	26,656	3	382	277	13,030	55.0	1.5	3,100	6,360
61851	6.83	31.5	21,420	3	140	70	12,280	53.0	1.5	3,230	5,510
73981	7.61	32.4	22,032	2	240	265	11,480	46.5	12.0	2,790	5,880
77306	7.99	1.8	1,224	0	2	159	460	1.7	1.3	90	280
77307	7.62	28.2	19,176	6	120	395	8,910	31.5	3.5	1,850	4,030
77855	7.72	17.9	12,172	8	186	388	5,460	18.4	1.2	1,610	3,000
85933	7.06	2.2	1,496	7	150	235	500	1.7	3.1	90	376
89310	8.27	2.4	1632	2	104	300	560	2.0	7.9	140	366
92684	7.12	14.8	10,064	2	160	293	5230	15.8	BD	1,210	2,350
97605	6.79	34.8	23,664	4	140	434	11,380	38.0	13.0	2,160	6,540
103875	7.71	2.9	1,972	2	138	98	840	3.1	11.3	210	462
110128	6.87	36.8	25,024	0	116	338	13,260	45.0	BD	3,890	6,790
110182	8.49	5.1	3,468	2	154	187	1,530	5.1	7.8	410	798
110183	6.95	13.2	8,976	3	100	73	4,660	18.2	BD	910	1,930
110186	7.51	17.7	12,036	8	228	587	5,300	18.8	3.6	1,250	3,160
110871	7.07	1.5	1,000	7	14	93	340	1.2	1.9	40	227
110874	7.26	10.4	7,072	1	82	188	3,700	13.0	1.4	670	1,470
113122	6.83	5.2	3,536	4	160	439	1,670	6.4	BD	320	746
113123	7.08	8.4	5,712	6	201	447	2,510	7.8	20.0	660	1,410
115390	2.77	63.0	42,840	2	0	0	22,620	65.0	11.0	4,230	9,590
116573	8.53	15.9	10,812	2	106	52	5,580	22.2	1.6	1,220	2,470
116639	7.35	24.4	16,592	4	160	298	8,320	30.5	BD	1,830	4,250
116699	7.8	28.2	19,176	1	180	163	9,920	38.5	4.5	2,450	4,800
116741	8.26	14.5	9860	2	110	304	5,130	17.2	16.4	1,230	2,590
116746	7.91	20.1	13,668	4	150	195	7,640	23.6	8.4	1,580	3,270
116765	7.66	149.0	101,320	2	536	272	67,590	160.0	64.0	11,660	35,200
116771	6.73	40.2	27,336	4	156	37	13,980	47.0	1.0	3,440	7,740
119378	7.14	10.3	7,004	1	310	357	3,740	13.2	3.0	720	1,520
119380	7.45	13.0	8,840	1	180	189	4,590	18.2	37.6	930	2,130
119384	5.53	57.8	39,304	1	282	122	21,610	62.0	BD	4,430	9,270
119386	6.83	0.9	626	6	160	281	210	0.7	8.6	40	106
119387	3.91	57.4	39,032	2	372	0	21,950	60.0	BD	4,000	8,760
325497	8.52	2.9	1,972	3	46	92	840	3.6	12.5	150	407
Salt lake	3.6	95.9	65,212	4	30	0	38,820	82.0	2.0	7,590	17,900
Geera Clay											
50349	7.12	32.8	22,304	3	102	28	11,420	40	1	2,103	5,590
Renmark Group											
46916	6.65	12.5	8480	4	2	2	4,180	14.8	BD	6	2,100
50314	5.97	51.0	34,680	0	52	12	18,880	59.0	5.0	2,116	9,160
51346	8.44	115.7	78,676	0	220	146	47,660	132.0	28.0	2,592	21,700
52363	6.42	21.9	14,892	4	280	354	7,170	25.0	BD	1,200	3,270

Table 2 (continued)

K mg/L	Ca mg/L	Mg mg/L	Sr mg/L	Si mg/L	SI Cc	SI D	SI G	SI Q	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	$\delta^{13}\text{C}$ ‰
90	75	288	1.40	7.21	-0.45	-0.01	-1.41	-1.15	-4.5	-32	-5.2
38	42	128	0.75	16.6	-0.46	-0.14	-1.83	-0.80	-4.8	-33	-7.0
31	25	97	0.36	23.5	-1.25	-1.61	-2.25	-0.65	-5.7	-35	-6.4
231	846	2,560	12.4	28.0	-0.09	0.61	-0.19	-0.46	-3.3	-28	-5.4
226	336	983	11.1	46.5	-1.16	-1.53	-0.59	-0.31	-4.2	-33	-4.6
207	570	2,360	10.4	33.4	0.06	0.80	-0.16	-0.86	-3.5	-29	-1.6
146	870	3,740	16.1	22.8	-3.80	-6.65	-0.40	-0.41	-3.4	-28	-1.1
222	485	3,140	12.2	38.3	-2.32	-3.69	-0.12	-0.54	-3.4	-29	0.4
222	132	1,730	4.14	42.9	-3.51	-5.88	-0.44	-0.33	-3.6	-32	-2.8
59	271	855	5.91	29.7	-3.04	-4.97	-0.13	-0.78	-1.6	-21	ND
453	387	3,610	5.67	9.79	-0.42	-0.06	-0.45	-0.54	-1.8	-21	ND
87	1110	2,740	21.0	8.94	ND	ND	-1.27	-0.28	-3.1	-29	-9.1
69	1270	2,780	23.4	4.35	ND	ND	-0.60	-0.47	-3.3	-30	-6.4
1170	807	11,400	12.9	3.36	ND	ND	-0.53	-0.78	0.9	-11	0.7
132	552	1,520	8.59	15.3	0.59	1.85	0.03	-1.28	-3.8	-31	-5.5
98	405	688	8.81	8.40	-1.13	-0.70	0.20	-0.91	-4.3	-31	-4.2
118	339	790	7.48	BD	1.23	3.22	-0.39	-0.79	-3.7	-30	-0.5
36	128	321	2.80	BD	-0.92	-1.19	-0.57	0.00	-4.8	-34	ND
86	932	3,150	21.8	4.80	0.00	0.00	-1.53	0.00	-3.5	-29	-4.8
106	592	1,090	12.6	28.7	-0.08	0.66	-0.16	-1.20	-2.8	-25	-4.7
96	136	397	1.10	18.8	0.21	0.95	-0.31	-0.46	-4.2	-27	-2.8
127	442	670	9.10	32.2	-0.12	0.53	-1.20	-0.74	-3.6	-28	-2.6
53	193	303	3.16	6.02	-1.10	-1.69	-0.43	-0.47	3.4	9	-5.3
113	458	680	10.6	19.9	-0.10	0.29	-0.99	-1.23	-3.1	-23	-1.8
250	234	677	4.40	16.1	-1.17	-1.87	-0.26	-0.68	-3.9	-31	-7.9
77	149	335	4.96	6.15	0.16	1.09	-0.62	-0.78	-5.0	-36	ND
294	371	833	11.6	7.51	0.15	0.96	-1.04	-1.22	-3.2	-31	-4.4
152	598	827	12.5	17.9	-0.10	0.49	-0.50	-1.10	-3.1	-28	-5.6
178	463	818	11.5	15.4	-0.76	-1.09	-0.25	-0.70	-2.4	-22	-0.3
13	49	30	0.39	8.80	0.55	1.69	-0.43	-0.81	1.5	0	ND
116	449	801	8.25	25.4	0.21	0.48	-1.92	-1.07	-2.8	-25	-5.4
39	248	532	4.50	10.7	0.71	1.97	-0.54	-0.57	-0.3	-9	-4.8
16	23	22	0.31	17.9	0.61	1.85	-0.72	-0.97	-5.4	-37	-11.9
7	77	47	0.80	5.69	-0.88	-1.48	-2.24	-0.77	3.4	12	ND
111	188	410	6.21	5.43	0.89	1.83	-1.65	-1.27	-4.8	-35	-6.1
128	490	804	8.09	9.32	-0.18	0.26	-0.89	-1.26	-3.4	-30	-12.0
17	39	63	0.76	11.3	-0.09	0.30	-0.50	-0.98	-5.3	-35	-4.7
113	427	866	7.94	8.25	-0.47	-0.48	-1.81	-0.95	-2.5	-24	-8.1
45	94	80	1.62	7.59	-0.17	0.28	0.37	-1.06	0.4	-8	-5.9
61	266	309	6.05	6.73	0.87	1.96	-1.29	-1.16	-4.1	-33	-4.1
57	178	409	3.39	11.5	-0.74	-1.11	-0.81	-1.18	-4.2	-31	-7.3
4	27	23	0.27	1.41	0.44	1.51	-0.93	-0.92	-1.9	-18	-9.9
87	245	257	4.15	4.07	-1.17	-2.15	-2.50	-1.85	-3.5	-29	-3.5
46	54	185	1.41	17.0	-0.02	0.28	-0.91	-1.40	-4.1	-29	-6.0
35	55	202	1.51	21.8	-0.67	-0.55	-1.68	-0.76	-4.2	-29	-6.4
138	358	2,390	8.12	34.4	-0.48	-0.14	-1.46	-0.65	-3.3	-26	ND
64	241	403	5.45	6.52	ND	ND	-0.58	-0.37	-2.2	-8	-1.7
90	203	471	7.54	6.59	0.52	1.56	-0.80	-1.21	-0.5	-13	ND
150	438	805	11.9	11.4	0.03	0.73	-0.81	-1.17	-3.7	-26	-1.4
51	85	268	3.48	11.4	0.49	1.55	-0.47	-0.93	-1.2	-15	-1.8
118	203	630	4.78	18.0	0.62	2.03	-1.19	-0.96	-3.1	-25	-1.6
440	711	5470	10.7	2.87	0.38	1.54	-0.86	-0.73	1.6	-7	-4.7
145	593	977	10.9	13.9	0.55	2.35	-0.08	-1.25	-3.3	-28	-7.4
82	234	241	3.10	25.2	-1.16	-1.79	-0.29	-0.81	-4.6	-33	-1.9
22	252	256	4.72	27.0	0.11	0.54	-0.90	-0.61	-4.9	-33	-5.9
119	731	2,540	15.6	26.4	0.14	0.59	-0.82	-0.58	-3.3	-28	-4.4
6	34	23	0.30	49.3	-1.82	-2.78	-0.26	-0.50	-5.2	-27	-2.6
114	477	2,600	16.5	52.2	ND	ND	ND	ND	-3.0	-28	ND
14	33	75	0.70	17.5	ND	ND	-0.49	-0.20	-5.2	-36	-4.5
363	1,330	3,060	18.4	2.14	0.24	1.13	-2.02	-0.80	-1.0	-15	ND
93.1	418	1,180	3.92	0.32	-1.03	-1.33	-0.59	-2.44	-4.1	-31	-5.3
24	144	44	2.68	BD	-1.94	-3.66	-0.13	-2.75	-2.7	-22	ND
195	1820	1380	16.8	0.15	0.30	2.20	-1.27	ND	-3.2	-26	-9.0
420	145	2880	2.22	BD	-0.46	-0.41	-0.69	-1.24	-0.2	-6	-7.5
76	416	609	5.93	5.92	-1.24	-1.84	-2.32	-1.91	-4.5	-31	-6.1

Table 2 (continued)

Bore ID	pH	EC mS/cm	TDS mg/L	O ₂ mg/L	CO ₂ mg/L	HCO ₃ mg/L	Cl mg/L	Br mg/L	NO ₃ mg/L	SO ₄ mg/L	Na mg/L
52367	6.19	23.6	16,048	5	64	146	8,100	27.5	11.0	40	4,120
52368	7.87	12.5	8,500	4	102	340	3,730	13.6	0.4	575	1,970
58326	7.11	7.9	5,372	3	211	154	2,920	16.0	1.2	341	1,120
58523	7.181	75.6	51,408	2	322	512	28,550	90.0	14.0	5,632	12,200
61850	6.82	30.6	20,808	2	180	183	10,800	44.0	3.5	2,622	5,170
65270	7.51	6.0	4,080	3	241	317	1,850	6.6	BD	389	996
85932	10.23	1.6	1,088	2	0	105	370	1.2	0.8	142	308
88000	9.78	4.6	3,101	2	10	458	1,310	4.9	0.2	6	790
89309	7.25	22.8	15,504	4	302	403	7,070	24.5	1.0	1,788	3,400
92807	7.87	31.0	21,080	4	86	439	10,280	37.0	1.0	1,853	5,660
97603	7.78	35.0	23,800	5	176	39	11,910	39.0	5.0	1,168	5,970
97604	7.23	32.5	22,100	3	230	366	10,900	40.0	11.0	1,713	5,420
103893	8.43	14.2	9,656	2	0	66	4,170	15.2	BD	654	2,460
110162	6.16	148.3	10,0844	0	806	124	79,740	196.0	32.0	13,592	33,100
110163	7.47	34.0	23,120	1	65	32	10,860	41.0	BD	2,191	6,950
110179	7.78	18.4	12,512	6	80	356	5,330	17.6	1.2	1,077	3,120
110180	7.9	22.3	15,164	2	374	795	6,700	22.0	5.0	1,270	3,910
110181	7.06	7.0	4,760	1	150	305	2,160	6.7	0.9	749	1,170
116591	7.46	33.2	22,576	1	80	357	12,620	56.0	BD	2,957	6,010

BD below detection; ND not determined

Log saturation indices (SI) of calcite (Cc), dolomite (D), gypsum (G), amorphous silica (Q)

laterally into the clay-rich Shepparton Formation, which causes discharge in this area. By contrast, the lower and more consistent vertical head gradients within the Renmark Group suggest that it is dominated by lateral flow and that the aquifer is relatively homogeneous.

The Geera Clay has horizontal hydraulic conductivity of $\sim 4 \times 10^{-4}$ m/day and a vertical hydraulic conductivity of $\sim 2 \times 10^{-5}$ m/day (Lawrence 1975), and pinches out in the western margin of the study area (Fig. 2c). Downward vertical gradients exist between the overlying Pliocene Sands and the Geera Clay, suggesting that the saline groundwater from the Pliocene Sands recharges the Geera Clay. Downward gradients also exist between the Geera Clay and the underlying Renmark Group, suggesting that flow of saline groundwater from the Geera Clay into the Renmark Group also occurs.

Radiocarbon and groundwater ages

The activity of ^{14}C ($a^{14}\text{C}$) in dissolved inorganic carbon (DIC) shown in Table 3 supports many of the assertions made above and allow further constraints to be made on the flow systems. $a^{14}\text{C}$ values range from 84.7 to 10.3 pmc in the Pliocene Sands and from 83.6 to 11.5 pmc in the Renmark Group. Groundwater from the Geera Clay has the lowest pmc (5.2 pmc), which is consistent with it being a low hydraulic conductivity unit.

Groundwater residence times were calculated from the $a^{14}\text{C}$ values using a statistical approach, an alkalinity correction, and a $\delta^{13}\text{C}$ correction (Clarke and Fritz 1997). Each model attempts to correct for the volume of “dead” carbon derived from the aquifer matrix. Firstly, in keeping with the general lithology of the rocks, only a small percentage of the carbon is likely to be derived from carbonate sources such as calcite cements. Following

Vogel (1970), a value of 15% was used based on the lithology of the sediments. This simple correction makes no attempt to correct the age of individual samples that may have experienced different water-rock interaction histories. The second model uses the measured $\delta^{13}\text{C}$ and pH values (Tables 1 and 2) to calculate the percentage of calcite dissolution, assuming soil CO₂ has a $\delta^{13}\text{C}$ of -23‰ and calcite has a $\delta^{13}\text{C}$ of 0‰ (Clarke and Fritz 1997). This method also has several drawbacks. For example, the pH measured in the groundwater may not be identical to the pH in the recharge zone, and the $\delta^{13}\text{C}$ of the soils that were present during recharge and the $\delta^{13}\text{C}$ values of any carbonate cements are unknown. This is especially the case as the sediments are dominantly terrestrial and the $\delta^{13}\text{C}$ of terrestrial carbonates is much more variable than that of marine carbonates (Clarke and Fritz 1997). The alkalinity correction (Clarke and Fritz 1997) is based on major ion chemistry but does not take into account Ca produced or lost by ion-exchange or derived from silicate weathering. Additionally, none of the models take into account changes in major ion chemistry or $\delta^{13}\text{C}$ values resulting from carbonate precipitation. Despite these problems, the models yield similar ages ranging from Modern to 26 ka. A modern age suggests some component of recharge following atmospheric nuclear tests in the 1950s and 1960s.

$a^{14}\text{C}$ values in groundwater from the Pliocene Sands aquifer gradually decrease both along the hydraulic gradient and with depth (Fig. 3a,d), suggesting both lateral and vertical flow in this aquifer. One exception to this is sample 50316 (Fig. 3a,d) that is screened from 27–32 m and which has an $a^{14}\text{C}$ of 10.3 pmc. This bore is located near the Kerang Lakes discharge complex (Fig. 2b) where the Pliocene Sands contain a higher component of clays. Older ages may be the result of slow

Table 2 (continued)

K mg/L	Ca mg/L	Mg mg/L	Sr mg/L	Si mg/L	SI Cc	SI D	SI G	SI Q	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	$\delta^{13}\text{C}$ ‰
85	259	517	3.36	1.26	0.81	2.06	-0.99	-1.21	-4.4	-32	ND
38	271	405	3.89	6.03	-0.73	-0.60	-1.65	-0.92	0.2	-9	-6.7
77	73.8	273	1.80	12.4	0.47	1.84	-0.14	-0.80	-4.7	-33	-6.4
118	964	3,920	20.7	11.4	-0.38	-0.26	-0.36	-0.89	-3.2	-28	-5.3
173	541	861	12.0	11.9	-0.05	0.43	-1.54	-0.95	-3.1	-29	-2.9
68	60.4	104	1.33	11.8	1.04	1.73	-2.23	-1.07	-3.4	-28	-8.0
4	15.2	4	0.16	23.0	1.21	3.39	-4.06	-3.08	-4.8	-29	-19.6
36	10.9	48	0.44	0.16	0.28	1.00	-0.51	-1.16	-6.0	-39	15.8
79	416	679	6.93	6.00	1.08	2.49	-0.43	-1.02	-4.3	-33	-8.9
112	618	731	8.06	8.44	-0.05	0.28	-0.61	-2.36	-3.8	-31	-15.6
117	663	897	9.59	0.38	0.51	1.34	-0.38	-1.26	-4.9	-34	-21.3
106	811	883	12.9	5.01	0.44	0.88	-1.10	-2.70	-4.4	-33	-17.5
36	150	75	1.87	0.21	-1.21	-1.28	0.11	ND	-2.2	-17	-3.1
433	877	6,110	11.4	BD	-1.05	-0.99	-1.08	-2.09	-0.1	-15	ND
138	123	697	2.10	0.83	0.49	1.68	-1.00	-1.28	-3.8	-25	-17.1
61	180	506	4.02	4.96	1.24	2.94	-0.69	-1.17	-3.7	-30	-10.6
71	387	593	5.32	6.36	-0.42	-0.46	-1.18	-1.02	-4.9	-36	-15.1
54	83.3	100	1.76	10.0	0.53	1.68	-0.39	-0.90	-0.1	-11	-5.4
152	506	954	13.3	12.1	0.92	2.79	-0.27	-1.09	-3.0	-26	-5.8

infiltration rates and longer residence times. Unlike the Pliocene Sands aquifer, $a^{14}\text{C}$ values from groundwater in the Renmark Group do not correlate with depth (Fig. 3b,d). Along the eastern margin of the region, $a^{14}\text{C}$ values decrease along flow paths from south to north consistent with northward flowing groundwater, suggesting that groundwater increases in age. However, along the western

margin of the area, $a^{14}\text{C}$ values increase from south to north contrary to the groundwater flow paths. The irregular distribution of the $a^{14}\text{C}$ values is most probably the result of combined lateral and vertical flow.

Old and young groundwater is present in both the south of the area and the northern discharge zones. The oldest groundwater ($a^{14}\text{C}=11.4$ pmc) in the Renmark

Table 3 Activity of ^{14}C values and calculated ages from Tyrrell groundwater

Bore ID	TDS (mg/L)	$a^{14}\text{C}^a$ (pmc)	^{14}C age ^b uncorrection (years)	$\delta^{13}\text{C}^c$ correction (years)	Alk ^d correction (years)	qSTAT ^e correction (years)
Pliocene Sands						
50315	42,364	31.21±0.18	9,301±0.45	5,223	7,149	8,282
50316	44,200	10.28±0.1	18,219±80	11,407	16,175	17,463
61851	21,420	84.52±0.37	1,299±35	Modern	232	46
85933	1,496	73.67±0.33	2,402±35	117	Modern	1,183
97605	23,664	71.13±0.32	2,684±35	713	Modern	1,476
110128	25,024	73.55±0.33	2,415±35	1,134	Modern	1,196
110182	3,468	84.68±0.43	1,283±40	Modern	Modern	31
110186	12,036	60.3±0.27	4,011±35	1,681	965	2,838
Geera Clay						
50349	22,304	5.16±0.08	23,750±130	26,128	23,192	23,161
Renmark Group						
52367	16,048	26.15±0.15	10,723±45	7,709	7,794	9,745
52368	850	72.53±0.32	2,527±35	333	Modern	1,312
61850	20,808	11.45±0.14	17,359±100	15,372	15,515	16,572
85932	1,088	74.71±0.34	2,290±35	5,190	Modern	1,067
97603	23,800	53.72±0.41	4,938±60	6,824	4,409	3,793
97604	22,100	37.87±0.21	7,748±45	8,495	5,272	6,683
110162	100,844	79.37±0.45	1,803±45	Modern	1,444	567
110163	23,120	72.54±0.34	2,526±35	324	786	1,310
110181	4,760	83.62±0.38	1,385±35	Modern	Modern	135

^aActivity of ^{14}C

^bAge calculated assuming no dilution by matrix carbon

^cCorrected using $\delta^{13}\text{C}$ values (see text)

^dCorrected using alkalinity model (Clarke and Fritz 1997)

^eCorrected using qSTAT model (Vogel 1970)

Table 4 Mineralogical and relevant elemental compositions of aquifer material from the Tyrrell Catchment

Sample	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MgO (%)	CaO (%)	NaO (%)	K ₂ O (%)	Sr (mg/L)	Rb (mg/L)	Mineralogy	Minor	Trace
Bore ID (core depth m)										Dominant	Sub-dominant	
Basement												
Granite/basement	64.77	15.55	5.37	2.27	3.71	3.54	2.83	266	118	Q/I	AL/B	KF
61850 (125–126 m)	51.14	28.84	2.3	1.47	0.06	0.38	6.53	58	306	MU/I	KA	–
85932 (94.5–95 m)	60.52	19.88	7.66	0.1	0.05	0.08	0.32	17	25	KA	Q	MU/SM
52367 (203–206 m)	69.24	16.01	3.51	0.63	0.05	0.42	5.25	53	335	ND	ND	ND
Renmark Group												
50349 (78–81 m)	51.29	10.95	9.03	0.94	4.56	0.39	0.85	313	52	ND	ND	ND
50349 (102.5–106 m)	55.45	4.91	5.27	1.08	14.83	0.44	0.96	697	37	ND	ND	ND
52367 (120–123 m)	58.36	12.06	6.13	0.71	0.56	0.53	1.13	71	63	Q/KA	MU/I	KA/SM
52367 (195–198 m)	98.13	0.61	0.24	0.02	0.03	0.08	0.05	8	4	ND	ND	ND
61850 (65–68 m)	69.02	9.34	6.60	0.82	0.50	0.49	1.13	78	50	ND	ND	ND
61850 (113–116 m)	69.49	8.05	2.09	0.59	0.28	0.44	1.52	61	80	Q/I	SM	KA/GY
88000 (253–256 m)	55.29	11.32	8.87	1.05	1.43	0.76	1.08	115	55	Q/KA	SM	SI/GY/PY
88000 (304–320 m)	88.26	2.14	2.59	0.19	0.40	0.05	0.20	48	11	ND	ND	ND
Geera Clay												
50349 (81–84 m)	23.48	4.26	4.41	1.32	33.73	0.14	0.35	764	19	CA/KA	Q/SM	AR/PY
Pliocene Sands												
50349 (12.5–15.5 m)	94.86	1.65	1.86	0.06	0.06	0.04	0.12	12	6	Q/KA	I	MU/KA
50349 (49.5–52 m)	69.16	9.22	7.19	0.68	0.33	0.29	1.06	56	48	ND	ND	ND
52367 (21–24 m)	65.37	14.81	5.47	1.03	0.11	0.63	2.27	69	114	Q/I	MU	–
52367 (78–81 m)	63.74	9.94	10.01	0.67	0.37	0.34	1.38	63	70	ND	ND	ND
52367 (108–111 m)	20.38	3.37	3.55	0.92	0.76	0.96	0.34	116	22	ND	ND	ND
61850 (21–24 m)	97.06	0.77	0.75	0.02	0.03	0.10	0.08	17	4	ND	ND	ND
61850 (33–36 m)	48.86	4.52	21.8	0.74	0.77	0.14	0.39	46	19	Q/KA	I/SM	B/GY
88000 (21–24 m)	95.96	0.53	0.36	0.02	0.58	0.07	0.08	73	4	Q/KA	I	MU/GY
88000 (55–57 m)	74.13	4.07	6.83	0.02	0.58	0.07	0.08	385	24	ND	ND	ND

ND not determined; AL albite, B biotite, CA calcite, GY gypsum, I illite, KA kaolinite, KF k-feldspar, MU muscovite, PY pyrite, Q quartz, SI siderite, SM smectite

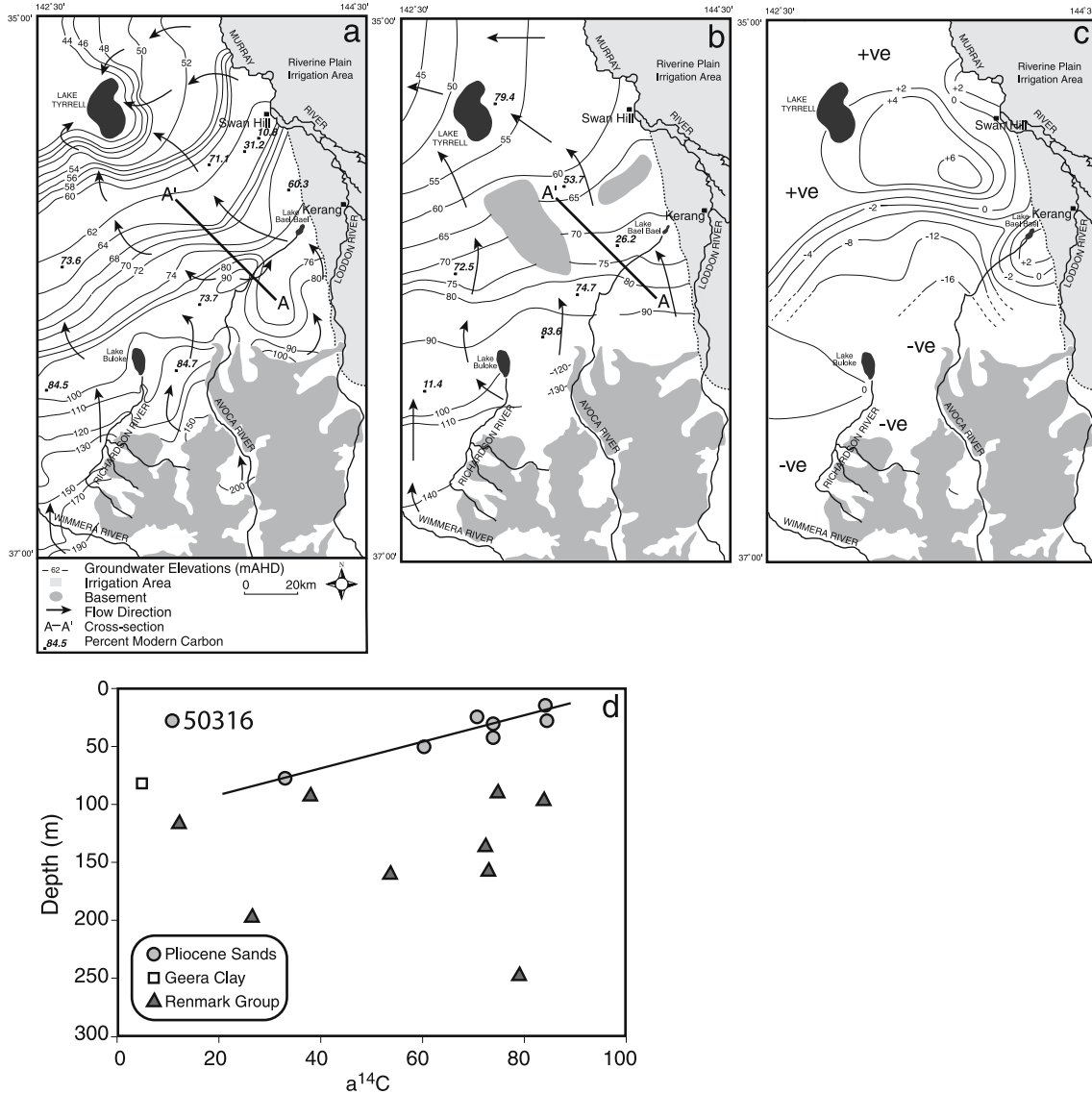


Fig. 3 a Groundwater elevations (mAHd) of the Pliocene Sands aquifer. Groundwater elevations corrected for density following Pratt 1988. Groundwater flows from the southern highlands towards Lake Tyrrell. $a^{14}C$ values are in *bold italics*. b Groundwater elevations (mAHd) of the Renmark Group aquifer. Groundwater does not converge around Lake Tyrrell. $a^{14}C$ values are in *bold*

italics. c Equivalent fresh water head difference in metres between the shallowest and deepest aquifers. A positive value indicates a potential for upward flow. d Variation in $a^{14}C$ contents with depth, indicating vertical flow. Data for Bore 50316 shows deviation from the trend

Group is from 116 m in the south of the area where the Renmark Group is overlain by 20 m of Geera Clay. Groundwater in the uppermost Pliocene Sands in this region is young ($a^{14}C=84.5$ pmc). The old groundwater could reflect the time taken for groundwater to infiltrate through the Geera Clay into the Renmark Group or groundwater may be trapped in an isolated pocket near a basement ridge where groundwater flow is negligible.

The youngest groundwater ($a^{14}C=79.4$ pmc in Fig. 3b) from the Renmark Group is from Bore 110162 (bore location 63 in Fig. 2b) on the eastern margin of Lake Tyrrell. Bore 110162 is screened in the deeper part of the Renmark Group (247.5 m) where the sediments are more

coarsely grained than the upper parts of the Renmark Group. This groundwater also contains high nitrate concentrations (32 mg/L) suggesting that leakage of recent water from the surface may be occurring.

Given the complexity in the groundwater flow system and the variation in radiocarbon data, hydraulic conductivity values can not be determined using ^{14}C data. However, as recharge to the unconfined Pliocene Sands aquifer occurs across the province and vertical flow dominates, recharge rates can be calculated using radiocarbon data. For a velocity of 0.0056 m/year (determined from ^{14}C data), a porosity of 0.1–0.2, and an average annual rainfall for the Tyrrell Catchment of between 350–

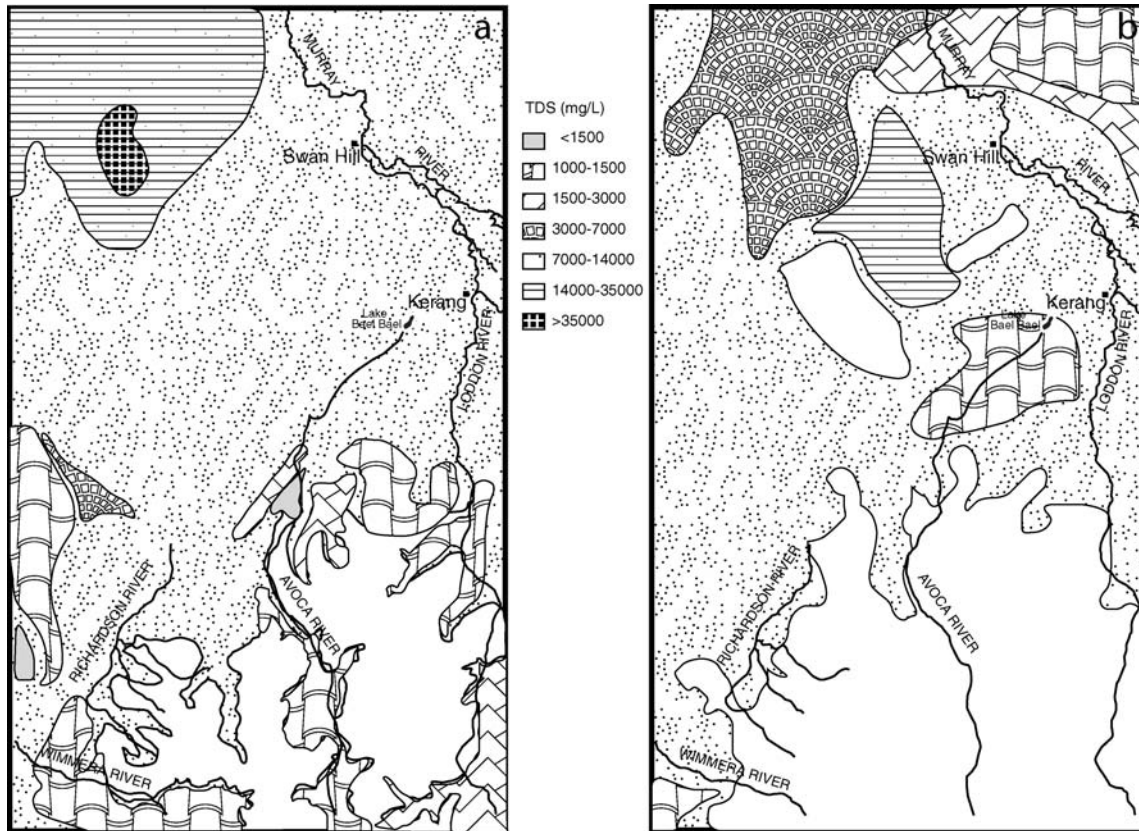


Fig. 4 Distribution of TDS contents in **a** the Pliocene Sands and **b** the Renmark Group groundwater. Data from Table 2. These values represent broad averages and many local variations exist

550 mm/year, this equates to a maximum “historical” recharge rate of 1 mm/year or approximately 0.20.3% of total rainfall.

Major ion chemistry

The major ion chemistry of groundwater is a powerful tool for determining solute sources and for describing groundwater evolution (e.g. Edmunds et al. 1982; Arad and Evans 1987; Weaver and Bahr 1991; Macumber 1991, 1992; Herczeg et al. 1992, 1993; Acworth and Jankowski 1993; Kimblin 1995, Jankowski and Acworth 1993; Weaver et al. 1995; Elliot et al. 1999; Herczeg and Edmunds 2000; Edmunds and Smedley 2000; Cartwright and Weaver 2005; Cartwright et al. 2004; Petrides and Cartwright 2005).

General patterns

TDS contents of the groundwater in this study range from 626 to >100,000 mg/L (Table 2). In general, the groundwater from the Tyrrell Catchment, especially in the Pliocene Sands Formation, is more saline than that in the adjacent Campaspe and Goulburn deep leads (Fig. 1b). For example, TDS up to 13,000 and 16,700 mg/L, respectively, occur in the Calivil Formation (Arad and

Evans 1987, Cartwright and Weaver 2005). As shown in Fig. 4, unlike many groundwater flow systems that show increasing TDS along flow paths (e.g. Arad and Evans 1987; Macumber 1991; Elliot et al. 1999; Edmunds and Smedley 2000), the Tyrrell Catchment groundwater does not show a regular spatial variation in TDS contents. In the south of the area, groundwater from the Pliocene Sands has a lower TDS content than that from the deeper Renmark Formation where most samples have TDS contents >6,000 mg/L. This fresh groundwater is due to the Avoca River recharging the groundwater system (O’Rorke 1992). In the north of the region, where hydraulic gradients change from downwards to upwards, the Pliocene Sands is more saline than the underlying Renmark Group. The lack of systematic variation in groundwater salinity along flow paths, and the irregular distribution in ^{14}C ages implies a flow system where both lateral and vertical flow and groundwater mixing occurs. Given the complexity of the flow system, chemistry will be discussed relative to salinity.

As shown in Fig. 5, groundwater from the Renmark Group and Pliocene Sands show a similar change in chemistry with increasing Cl concentration. In the more saline groundwater (Cl >500 mmol/L), Cl is the dominant anion (up to 99% of total anions), while HCO_3^- has a high relative abundance in the fresher groundwater samples. In the Pliocene Sands groundwater, SO_4 comprises up to

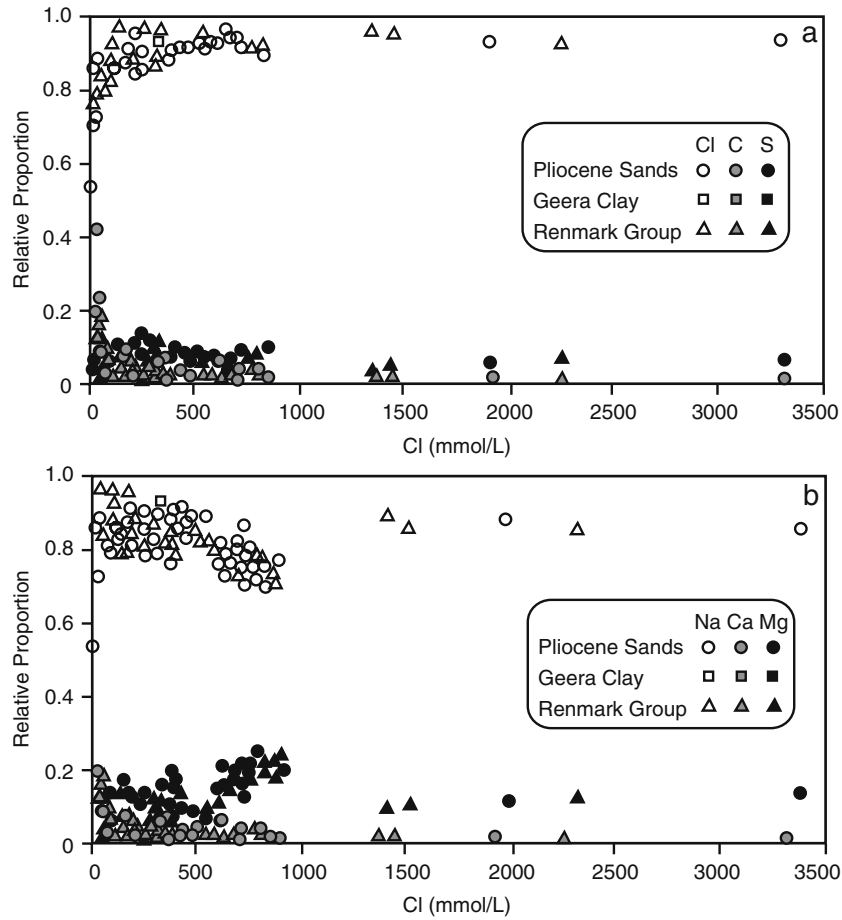


Fig. 5 Relative proportion of major **a** anions and **b** cations in Tyrrell Catchment groundwater. Data from Table 2

16% of total anions and does not vary in relative abundance as salinity increases. In the Renmark Group groundwater, SO_4 comprises <8% of total anions and declines in relative abundance as salinity increases. NO_3 and F comprise <1% of total anions and do not vary in relative abundance with salinity. With increasing salinity, there is a noticeable decline in the relative abundance of Na to ~70% of total cations with a proportionate increase in the relative abundance of Mg and to a lesser extent Ca. While there are minor differences, overall the groundwater chemistry from the two aquifers is similar as would be expected if there was substantial interformational flow.

Correlation coefficients

A cluster analysis shown in Fig. 6 (e.g. Davis 1973) performed on groundwater chemistry from the Pliocene Sands and Renmark Group aquifers defines four main groupings: (1) Na, Cl, Br concentrations have strong mutual correlations (>0.95) and Mg is also correlated with this group (0.88); (2) Ca, K, Li concentrations are mutually correlated (>0.69), Fe, Mn, Ba are also mutually correlated (>0.68) and correlated to Ca, K, Li (0.66); and (3) C, F, N concentrations are mutually correlated (0.81)

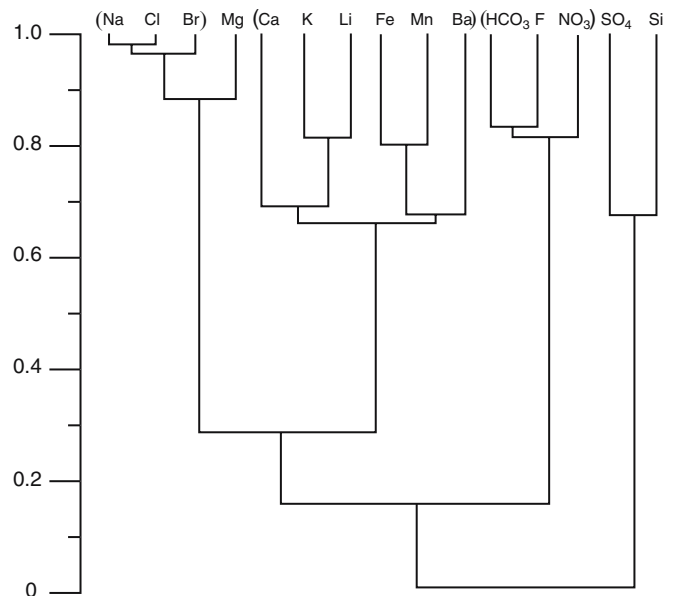


Fig. 6 Diagram showing correlation coefficients between the major and selected minor ions in the Tyrrell Catchment groundwater constructed using methods outlined in Davis (1973). Brackets show groupings of ions discussed in the text

but show weak correlation to the other groups of ions; and (4) Si and S have a mutual correlation of (0.68) but are weakly correlated with the other groups of ions. These clusters form the basis for discussing the sources of the solutes in the Tyrrell Catchment groundwater.

Na, Cl, Br

The relationships between Na, Cl and Br shown in Fig. 7 may be used to constrain the origins of solutes in the groundwater. Molar Cl/Br ratios of Tyrrell groundwater (Fig. 7a) show a general increase from as low as 411 up to 916 with increasing salinity. The lowest Cl/Br ratios are lower than those of the oceans (575–600; Davis et al. 1998) and probably reflect the climatic conditions when these waters were recharged. Coastal rainfall commonly

has a similar Cl/Br ratio to the oceans (Davis et al. 1998; Petrides and Cartwright 2005); however, Cl/Br ratios in inland regions, especially in arid or semi-arid climates may be lower. For example, low salinity (Cl <100 mmol/L) groundwater from the Riverine Province has Cl/Br ratios locally as low as 50 (Arad and Evans 1987; Watkins et al. 1999; Cartwright et al. 2004; Cartwright and Weaver 2005). Also, Davis et al. (1998) showed that fresh groundwater in the USA is characterized by decreasing Cl/Br ratios from ~400 near the coast to <150 in the continental interior. Similarly, groundwater from the Great Artesian Basin in north-east Australia has Cl/Br ratios as low as 280–300 (Herczeg et al. 1991).

Molar Cl/Br ratios of halite of 8,000–16,000 have been recorded in the Riverine Province by Cartwright et al. (2004). Similarly, Smith (1991) recorded Cl/Br ratios of halite of ~14,000–30,000 in eastern Saudi Arabia. The increase in Cl/Br ratios in the Tyrrell Catchment with increasing salinity implies that some halite dissolution has occurred. However, if halite dissolution were the main process in increasing salinity, Cl/Br ratios would be far greater than those recorded. From simple mass balance, if the water that recharges this system has a similar Cl concentration (~0.3 mmol/L) and Cl/Br ratio (350) to that of the freshest groundwater, then dissolution of only 1 mmol of halite would raise Cl/Br ratios to >1,400 (higher than any of the groundwater in this study). Therefore, evapotranspiration is almost certainly the dominant process in increasing salinity. The one sample from the Geera Clay, the major confining unit in the area, has a Cl/Br ratio of 643 suggesting that it too has undergone evapotranspiration not halite dissolution.

In the Tyrrell Catchment, Cl/Br ratios show some systematic variation with position. In the Pliocene Sands, groundwater with high Cl/Br ratios (>700) exist in the south (the regional recharge area) and north (the local discharge area). The Renmark Group groundwater also has high Cl/Br ratios (>700) in the local discharge area in the north. These data imply that minor halite dissolution has mainly occurred in those areas. These samples tend to be the most saline, therefore higher degrees of evaporation has led to salt accumulating in the unsaturated zone which can be dissolved by subsequent infiltrating or discharging water. In the centre of the catchment, Cl/Br ratios are 400–650 in both aquifers, implying less halite dissolution. Throughout the catchment, groundwater from the Pliocene Sands and Renmark Group Formations at the same localities generally has similar Cl/Br ratios suggesting that vertical flow is important.

Cl/Br ratios show a distinct variation with depth (Fig. 7b). The majority of groundwater from >30 m has uniform Cl/Br ratios between 500 and 800 while groundwater from <30 m has heterogeneous Cl/Br ratios. The trend of Cl/Br ratios becoming less variable at depth is seen elsewhere in the Riverine Province (Cartwright et al. 2004; Cartwright and Weaver 2005) and probably reflects mixing of groundwater with initially heterogeneous Cl/Br ratios during vertical groundwater flow. Some deeper groundwater samples with higher Cl/Br ratios may reflect

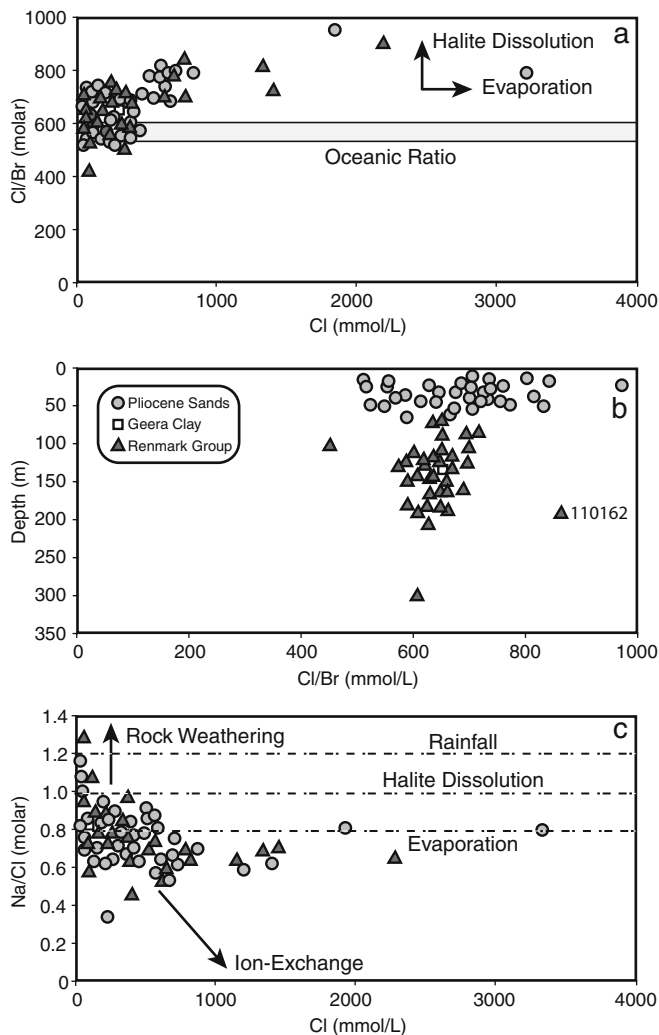
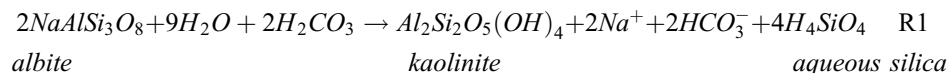


Fig. 7 Variations in Cl/Br and Na/Cl ratios of Tyrrell groundwater. **a** Cl/Br ratios vs. total Cl concentrations. Arrows point in the general direction of halite dissolution and evaporation. **b** Cl/Br ratios vs. depth. Cl/Br ratios from the Pliocene Sands tend to be more variable than those from the Renmark Group. **c** Na/Cl ratios vs. total Cl concentrations. Data indicate ion exchange reactions with clays

vertical recharge of modern day surface waters that have dissolved minor volumes of halite. Groundwater from bore 110162 located near Lake Tyrrell (location 63 in Fig. 2b) at a depth of 247.5 m has a Cl/Br ratio of 900, an $a^{14}\text{C}$ of 79.3 pmc, and a high nitrate concentration (32 mg/L). All these observations suggest that it has received a component of recent recharge from the surface. In this location, there is ~100 m of Geera Clay, suggesting that it is leaky due to fractures.



This reaction produces aqueous silica and kaolinite, which is also common in the weathered rocks as shown in Table 4. Much higher Na/Cl ratios of up 19.4 have been recorded in the least saline groundwater from the Goulburn Valley (Cartwright and Weaver 2005). Therefore, the relative contribution of feldspar weathering to the solute load of the Tyrrell groundwater is minor. This is also consistent with the low saturation indices of aqueous silica (SI = -3.08 to -0.41; Table 2).

With increasing salinity, the relative proportion of Na to other cations decreases (Fig. 5b) and groundwater with Cl concentrations >50 mmol typically has lower Na/Cl ratios than those of local modern rainfall (~1.2–1.4; Blackburn and McLeod 1983; Fig. 7c). The observation that the Na/Cl ratio in the most saline samples are lower than local rainfall is probably due to ion-exchange of Na for divalent cations such as Mg on clays coupled with the

Na/Cl ratios (molar) of most groundwater from both the Pliocene Sands and Renmark Group Formations lie between 0.65–0.9 (Fig. 7c). Only the least saline groundwater (<50 mmol/L Cl) has significantly higher molar Na/Cl ratios (up to 1.28). The higher Na/Cl ratios are probably due to Na derived from weathering of albitic feldspar, which is common in the clastic sediments in the Murray Basin (Lawrence 1988; Brown 1989; Evans and Kellett 1989; Macumber 1991) via a reaction such as:

minor halite dissolution that was inferred from the Cl/Br ratios.

Other major ions (K, Mg, Ca, S)

These major ions have a number of potential sources including silicate minerals (e.g. plagioclase feldspar, chlorite or biotite), dolomite or calcite, and gypsum. Trends of K/Cl vs. Cl shown in Fig. 8a are similar to those of Na/Cl vs. Cl, suggesting that weathering of muscovite and K-feldspar, both of which are present in the aquifer sediments (Table 4), contributes to the relatively high K concentrations in the lowest salinity groundwater. K/Cl ratios are lower than in rainfall, probably due to the formation of K-bearing clays such as illite.

Mg/Cl ratios increase with increasing salinity (Fig. 8c) probably due to ion-exchange between Mg and Na. The

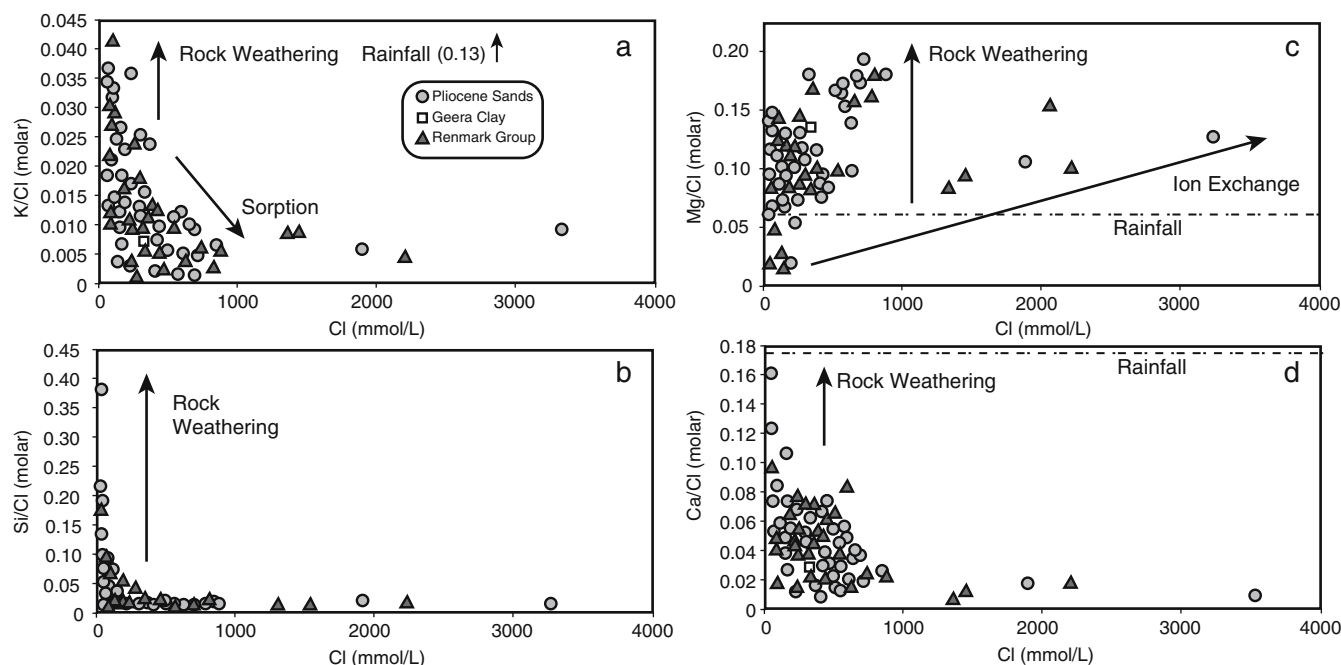


Fig. 8 Variations in **a** K/Cl vs. Cl, **b** Si/Cl vs. Cl, **c** Mg/Cl vs. Cl, **d** Ca/Cl vs. Cl. Arrows show trends expected for the rock weathering, ion exchange, and mineral precipitation and dissolution. Dashed lines show ratios in rainfall. Data from Table 2

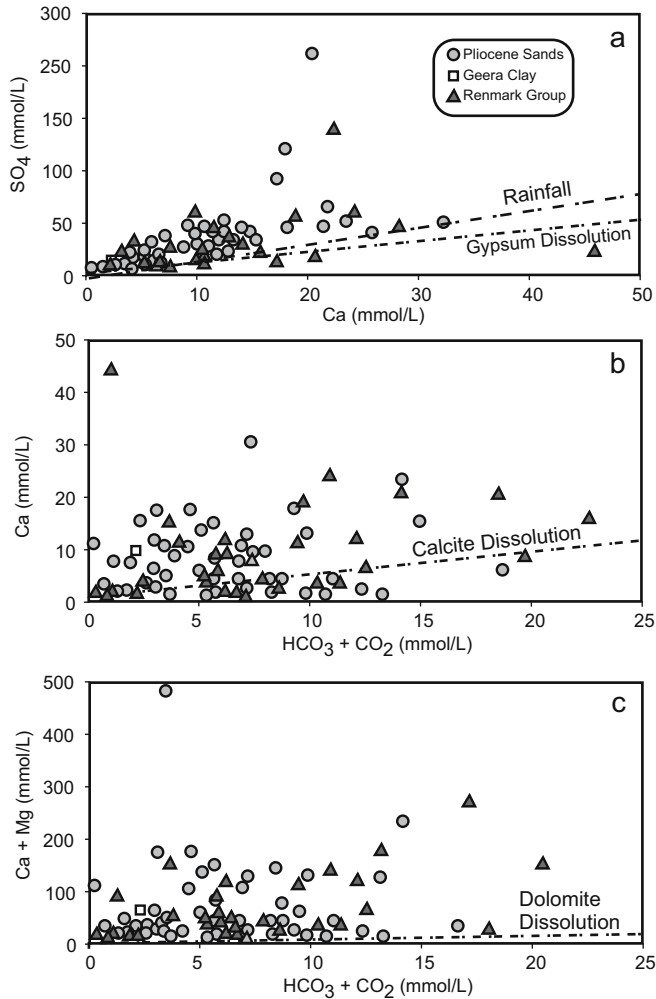


Fig. 9 a Variations in Ca vs. SO_4 , indicating that gypsum dissolution does not control the groundwater chemistry in the Tyrrell Catchment groundwater. b Total C vs. Ca and, c. Total C vs. Ca+Mg for Tyrrell groundwater. Data from Table 2

low salinity samples with high Mg/Cl ratios probably reflect the input of Mg from silicate weathering. High Ca/Cl ratios in the freshest groundwater (Fig. 8d) probably reflect weathering of Ca silicate minerals (e.g. plagioclase feldspar). Many of these samples are close to saturation with respect to calcite, dolomite, and gypsum (Table 2), suggesting that precipitation of these minerals may limit Ca and S concentrations in the groundwater. Gypsum dissolution is one possible source of S. However, as shown in Fig. 9a, Ca/S ratios are generally <1, especially in the Pliocene Sands groundwater. Alternatively, much of the S may be derived from evaporation of rainfall, which locally has a Ca/S ratio of 0.6–0.8 (Blackburn and McLeod 1983), similar to that of many of the groundwater samples. The low Ca/S ratios reflect Ca sorbing onto kaolinite at low salinities, and the formation of Ca-montmorillonite clays. On a $\log(a\text{Na}^+/a\text{H}^+)$ vs. $\log(a\text{SiO}_2)$ diagram (Fig. 10) the groundwater from the Tyrrell Catchment spans the stability fields of kaolinite and montmorillonite. It was shown by Tardy (1971) that

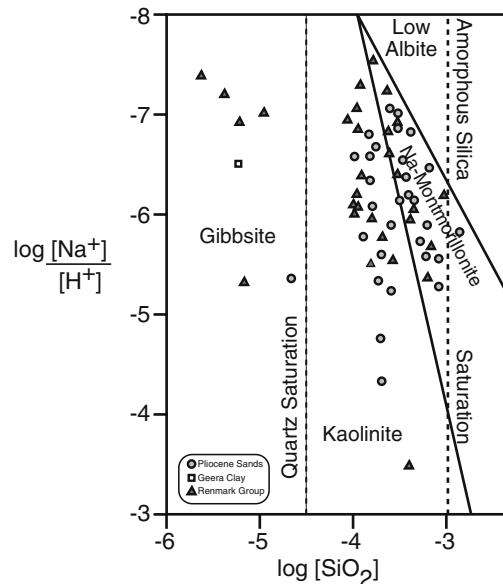


Fig. 10 Stability field diagram for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system at 25°C. Groundwater falls in the kaolinite and Na-montmorillonite fields (after Wallick 1981)

waters from arid regions or areas with basic rocks tend to plot in the montmorillonite field, while those from cooler regions or granitic areas plotted in the kaolinite field.

Calcite or dolomite dissolution is unlikely to be a significant source of solutes as there is no significant calcite or dolomite present in any of the lithologies, and there is no correlation between Ca, Mg and HCO_3 (Fig. 9b,c). This implies that the increase in Mg concentration is most likely attributed to Mg-silicate dissolution and ion-exchange. However, $\delta^{13}\text{C}$ values of groundwater from both aquifer systems range from -21.3 to 0.7‰ (Table 4). The lower values are close to those expected from carbon derived primarily from the soil zone or from fossil organic material that in the Renmark Group has $\delta^{13}\text{C}$ values of $-26 \pm 0.5\text{‰}$ within the typical range for coals: -28 to -25‰ (Hoefs 1980). The higher values

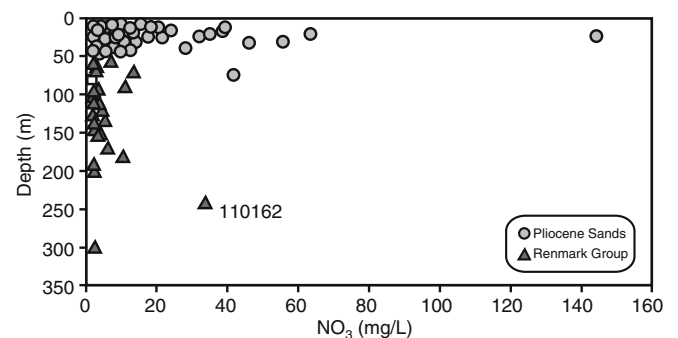


Fig. 11 Variations in NO_3 concentrations with depth in Tyrrell groundwater. Data from Table 2. Bore 110162 is screened in the deeper part of the Renmark Group (247.5 m) and also contains high nitrate concentrations (32 mg/L), suggesting some leakage of recent water from the surface

reflect calcite dissolution; however, dissolution of calcite with a typical limestone $\delta^{13}\text{C}$ value of 0‰ in a system open to CO_2 , produces maximum $\delta^{13}\text{C}$ values of DIC in groundwater of -5 to -6 ‰. Methanogenesis may increase $\delta^{13}\text{C}$ values, but this is unlikely in the oxygen-bearing groundwater of the southern Murray Basin. Rather, the data imply that incongruent carbonate dissolution occurred in a system closed to CO_2 , where $\delta^{13}\text{C}$ values approach those of the matrix carbonates (Clarke and Fritz, 1997). This implies carbonate dissolution occurs within the saturated zone. There is no correlation of $\delta^{13}\text{C}$ values with position in the flow system, suggesting that any carbonate is heterogeneously distributed.

Nitrate concentrations are up to 150 mg/L, however, they generally are <30 mg/L. As shown in Fig. 11, nitrate concentrations tend to be higher in the shallower Pliocene Sands groundwater and in the younger Renmark Group groundwater, which probably reflect contamination from modern agricultural practices. However, despite the evidence for vertical flow in the Tyrrell Catchment, there appears to be much less evidence for modern surface water infiltrating to depth than in the Goulburn Valley (Cartwright and Weaver 2005). This may reflect the

differences in sediments in the two areas. The deep lead systems tend to be dominated by a high proportion of gravels and sand that allow locally rapid vertical infiltration, while the Tyrrell Catchment is dominated by finer grained sands and clays.

Oxygen and hydrogen isotopes

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of groundwater from the Renmark Group and Pliocene Sands aquifers in the Tyrrell Catchment range from -42 to -12 ‰ and -5.8 to -3.8 ‰, respectively. Most of the groundwater falls to the right of the global and local meteoric water lines (Fig. 12a). The groundwater defines a single trend with a slope of 4.9 that is consistent with evaporation in a semi-arid climate (Clarke and Fritz 1997).

The stable isotopic data provide compelling evidence that all groundwater is derived from rainfall, and that all of the original seawater has been flushed out of the aquifers. Although groundwater in the Murray Basin is known to vary in age from modern to $>20,000$ years, there is no suggestion of different groups of water in the Tyrrell Catchment. While climate has changed within this time

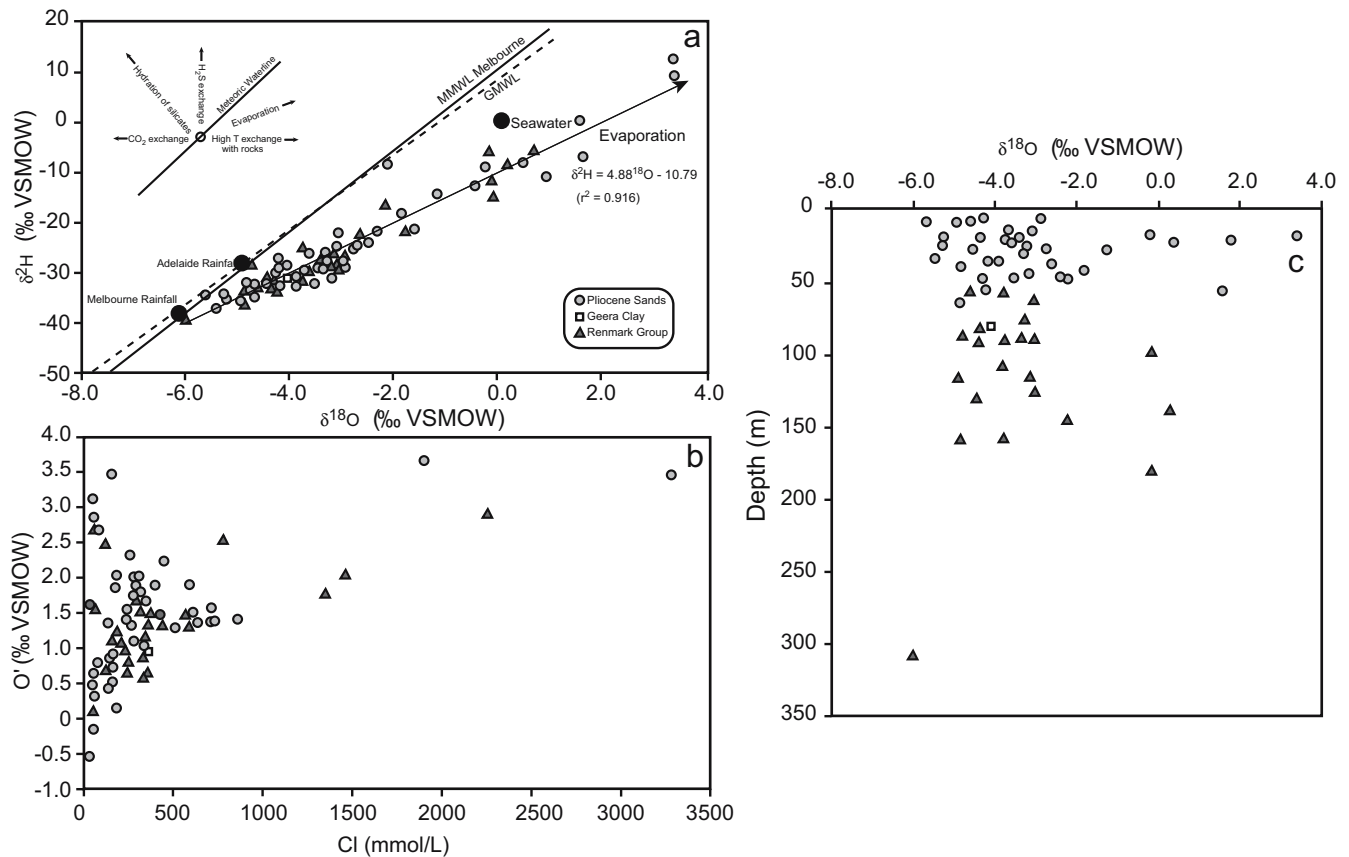


Fig. 12 a $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ values for Tyrrell groundwater. *MMWL* is the local meteoric water line for Melbourne, *GMWL* is the global meteoric water line and the *shaded circles* are the mean isotopic composition of Melbourne and Adelaide rainfall (Cartwright, personal observations, Monash University December 2005).

b Deviation of $\delta^{18}\text{O}$ from the MMWL (O') vs. Cl concentrations. Data show a scattered array of points suggesting that evaporation and evapotranspiration are important. **c** $\delta^{18}\text{O}$ vs. depth for Tyrrell groundwater. Shallower groundwater shows greater impact of evaporation. Data from Table 4

period, the groundwater does not reflect such changes. This may be a function of slow infiltration rates and vertical flow that has caused mixing and homogenization of groundwater in the Tyrrell region.

The intercept of a line through the data points extrapolated to the global meteoric water line (GMWL) should indicate the isotopic composition of infiltrating rainwater. The isotopic composition of this point ($\delta^2\text{H} \sim -40\text{‰}$, $\delta^{18}\text{O} \sim -6\text{‰}$; Fig. 12a) is somewhat lower than the weighted mean of present day precipitation ($\delta^2\text{H} \sim -35\text{‰}$, $\delta^{18}\text{O} \sim -5.8\text{‰}$) in Melbourne and ($\delta^2\text{H} \sim -27\text{‰}$, $\delta^{18}\text{O} \sim -4.6\text{‰}$) in Adelaide, which are the best estimates of the isotopic composition of rain for the recharge areas of the Murray Basin. This indicates that winter precipitation, which tends to be lighter than the mean annual isotopic composition because of the colder temperatures, contributes the dominant portion of recharge water. Allison et al. (1984) also noted this trend in soil water in the Mallee Province of South Australia.

The samples that lie at the high $\delta^{18}\text{O}$ and $\delta^2\text{H}$ extremity of the evaporation trend belong to the group of samples with high salinities but near oceanic Cl/Br ratios that, as discussed above, experienced evaporation. An estimate of water lost by evaporation can be calculated from the enrichment of ^2H . Using a value of $0.8 \pm 0.2\text{‰}$ in $\delta^2\text{H}$ per 1% of water volume lost by evaporation (Herczeg et al. 1993), implies up to 40% water loss by evaporation in the Tyrrell Catchment. The high salinity of the groundwater requires a higher degree of concentration than this, suggesting that transpiration is the more important process in controlling groundwater chemistry. Additionally, the plot of O' (deviation of $\delta^{18}\text{O}$ from the MMWL) against Cl (Fig. 12b) shows a scattered distribution. If evaporation was the only process influencing the solute load of groundwater, O' values would increase with increasing Cl concentration. Groundwater with high Cl concentrations and low O' values indicate that transpiration is important. $\delta^{18}\text{O}$ variations with depth (Fig. 12c) and distance along the Tyrrell Catchment are similar to the pattern of Cl/Br ratios. The shallower groundwater samples have a wide range of $\delta^{18}\text{O}$ values, which suggests that these waters have not mixed sufficiently to homogenize variations in the isotopic composition of recharge waters. While at depth, there is a general homogenization of $\delta^{18}\text{O}$ values.

Discussion and conclusions

Regional groundwater in the Tyrrell Catchment flows northward from recharge areas in the southern highlands towards regional discharge salt lakes in the north. There is a moderately low lateral hydraulic gradient within the Tertiary aquifers, suggesting relatively long groundwater residence times. This interpretation is confirmed by the ^{14}C ages. The distribution of groundwater ages, the observation that long-term hydrograph records of nested bores are in phase and the chemistry of the groundwater is similar suggests that these two aquifers are inter-

connected and there is a considerable component of vertical flow across the catchment.

The solutes in the groundwater in the Tyrrell Catchment are predominantly the result of evapotranspiration with minor halite dissolution and silicate weathering. Similar conclusions have been made for processes elsewhere in the southern Murray Basin (Arad and Evans 1987; Allison et al. 1990; Macumber 1991; Love et al. 1993; Herczeg et al. 2001; Cartwright et al. 2004; Cartwright and Weaver 2005). Sorption and ion-exchange reactions involving clays are also important in modifying groundwater chemistry. The similarity of the chemistry of the groundwater in the Renmark Group and Pliocene Sands aquifers together with the lack of systematic chemical trends along flow paths again suggests that vertical flow is also important.

The groundwater in the Tyrrell Catchment is generally more saline than that in the adjacent Goulburn or Campaspe deep leads; however, the processes that control groundwater chemistry are similar (Arad and Evans 1987; Cartwright and Weaver 2005). Given that there is no climatic difference between these regions, this most likely results from the presence of finer grained sediments in the Tyrrell Catchment that permit greater degrees of evapotranspiration than in the deep leads where vertical infiltration is more rapid. Both deeper and shallower groundwater have locally high salinities and there is no correlation between TDS contents and age, suggesting that evapotranspiration rates have been high in this catchment over at least the last several thousand years.

The major ion chemistry implies that Cl concentrations are largely controlled by evapotranspiration. Under such circumstances, if runoff is negligible, as is generally the case in semi-arid, low relief areas, chloride mass balance may be used to determine recharge rates (R) via

$$R = \frac{P\text{Cl}_p}{\text{Cl}_g}$$

(e.g. Allison et al. 1990), where P is annual precipitation and Cl_p and Cl_g are the chloride concentrations in precipitation and groundwater, respectively. Average annual rainfall for the Tyrrell region is ~ 450 mm (Bureau of Meteorology 2005) and Cl concentrations in precipitation are 2.9 mg/L (Blackburn and McLeod 1983). Typical Cl concentrations in the groundwater of 10,000–15,000 mg/L imply recharge rates of ~ 0.1 mm/year ($\sim 0.02\%$ of modern rainfall). These recharge rates are approximately an order of magnitude lower than those calculated using radiocarbon data.

The change in climate of the Australian continent and other parts of the Southern Hemisphere over the past 200,000 years is well documented (Bowler and Wasson 1984; Bowler 1990; Wasson and Donnelly 1991; Stute and Talma 1998) and shows alternating humid and dry periods. Therefore, variations in groundwater chemistry or stable isotopic ratios in the confined aquifer could represent a proxy record of these climate changes (Herczeg et al. 2001). However, the stable isotope and

major ion chemistry of all groundwater is similar, implying that climate change of this period is not recorded in the groundwater. This may indicate a high degree of mixing that has minimized any chemical fluctuations over time. Alternatively rainfall patterns and temperatures in this area may not have varied as much as in temperate coastal zones.

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