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# The hydrogeology and hydrogeochemistry of the Barwon Downs Graben aquifer, southwestern Victoria, Australia

B. Petrides · I. Cartwright

**Abstract** The Barwon Downs Graben lies on the northern flanks of the Otway Ranges and is situated approximately 70 km southwest of Geelong, Victoria, Australia. The major lower Tertiary Barwon Downs Graben aquifer comprises highly permeable sands and gravels interbedded with clays and silts of the hydraulically interconnected Pebble Point, Dilwyn and Mepunga Formations. Groundwater flows east into the Barwon Downs Graben from the Barongarook High, and yields  $^{14}\text{C}$  ages up to  $\sim 20$  ka implying that recharge rates are low and, consequently, that the resource could be impacted by overabstraction. The presence of three different lithological units has led to the development of localized flow systems that has resulted in a lack of regular spatial variations in groundwater chemistry. Stable isotopic data suggests that groundwater was recharged under similar climatic conditions as of today. The major ion chemistry of the freshest groundwater is dominated by Na and  $\text{HCO}_3$  while higher TDS groundwater, from the confining Narrawaturk Marl, is dominated by Na and Cl. Cl/Br ratios are close to rainfall suggesting that halite dissolution is not the principle source of salts. An excess of Na relative to Cl in fresher groundwater suggests that feldspar dissolution has occurred, however, water–rock interaction is limited. The concentrations of Ca, Mg, and  $\text{SO}_4$  are controlled by silicate dissolution and ion-exchange reactions with clays.

**Résumé** Le graben de Barwon Downs est situé sur le flanc nord de Otway Ranges, 70 km sud ouest de Geelong, Victoria, Australie. L'aquifère majeur inférieur d'âge tertiaire de Barwon Downs se compose de sables et de gravières, de grande perméabilité interconnectés avec des horizons d'argile et de limon qui sont en liaison hydraulique

avec les formations de Pebble Point, de Dilwyn et de Mepunga. La principale direction de l'écoulement des eaux souterraines est vers l'est tandis que le  $^{14}\text{C}$  indique un âge d'approximativement de 20 ka ce qui implique une faible recharge. En conséquence la ressource peut être affectée par une surexploitation. Les trois unités différenciées par la lithologie ont conduit aux systèmes d'écoulement locaux avec une variation importante de la composition chimique de l'eau. Les isotopes stables suggèrent que l'aquifère a été alimenté dans des conditions climatiques comparables avec les conditions actuelles. Les ions prédominants dans l'eau sont le Na et  $\text{HCO}_3$  tandis que l'eau avec des hautes valeurs en résidu sec provenant de marnes de Narrawaturk présente surtout des ions de Na et Cl. Le rapport Cl/Br dans les eaux souterraines et dans les précipitations présente des valeurs comparable en suggérant que la dissolution de l'halite n'est pas la principale source du sel. Un excès de Na par rapport au Cl suggère une dissolution des feldspaths mais que l'interaction avec la matrice rocheuse est assez limitée. Les concentrations en Ca, Mg et  $\text{SO}_4$  sont conditionnées par la dissolution des silicates ainsi que par les échanges ioniques avec les minéraux argileux.

**Resumen** El Graben de Barwon Downs yace en los flancos norte de las Montañas Otway y se sitúa aproximadamente 70 km suroeste de Geelong, Victoria, Australia. El mayor acuífero del Terciario Inferior, dentro del Graben Barwon Downs, comprende arenas y gravas muy permeables, interestratificadas con arcillas y limos que están interconectados hidráulicamente con las Formaciones Pebble Point, Dilwyn y Mepunga. El agua subterránea fluye hacia el este dentro del Graben Barwon Downs, proviene del Barongarook High y por  $^{14}\text{C}$  dió edades hasta de 20 mil años, que implican que las proporciones de la recarga son bajas y por consiguiente, que el recurso pudiera afectarse por sobre-explotación. La presencia de tres unidades litológicas diferentes ha llevado al desarrollo de sistemas de flujo locales, que han resultado en la carencia de las variaciones espaciales típicas en la química del agua subterránea. Los datos de isótopos estables hacen pensar en que el agua subterránea se recargó bajo condiciones climáticas similares a las de hoy. La química de los iones mayores del agua subterránea más dulce está dominada por el Na y  $\text{HCO}_3$ , mientras que el agua subterránea con los SDT más altos, de la Marga Narrawaturk de tipo confinado, está dom-

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inada por Na y Cl. La relación de Cl/Br está cerca de los valores para la lluvia, lo que hace pensar que la disolución de la halita no es la fuente principal de las sales. Un exceso de Na con relación al Cl, en las aguas subterráneas más dulces, sugiere que ha ocurrido la disolución del feldespato, sin embargo, la interacción entre agua-roca es limitada. Las concentraciones de Ca, Mg y  $\text{SO}_4$  son controladas por la disolución del silicato y por reacciones del intercambio iónico con las arcillas.

**Keywords** Hydrochemistry · Groundwater flow · Isotopes · Groundwater age · Barwon Downs Graben

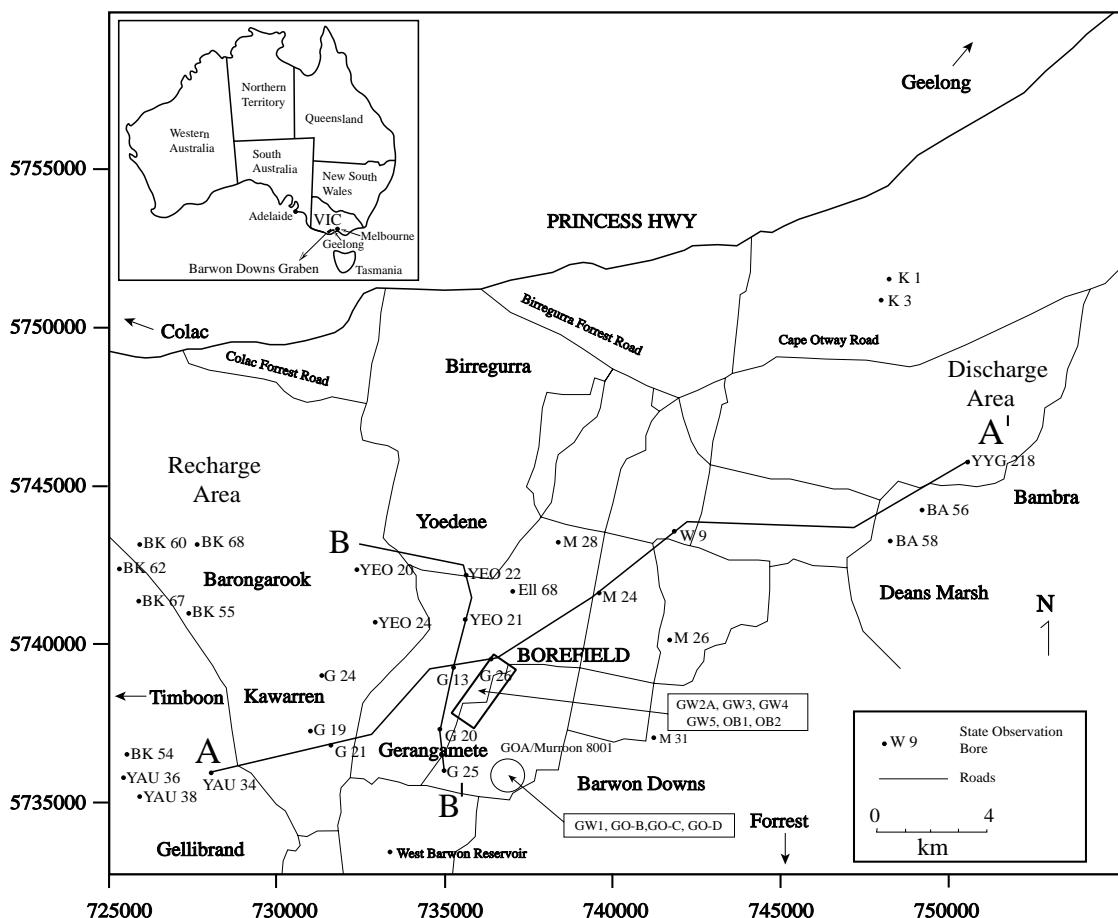
## Introduction

Australian rainfall is the most variable in the world (McMahon 1992) with years above annual rainfall punctuated by extended periods of drought such as in 2001–2003. Increased climatic uncertainty is the biggest threat to the municipal supply of potable drinking water. As surface water catchments become increasingly depleted due to increased water use (e.g., for irrigation or domestic supply) and the inevitability of drought, groundwater be-

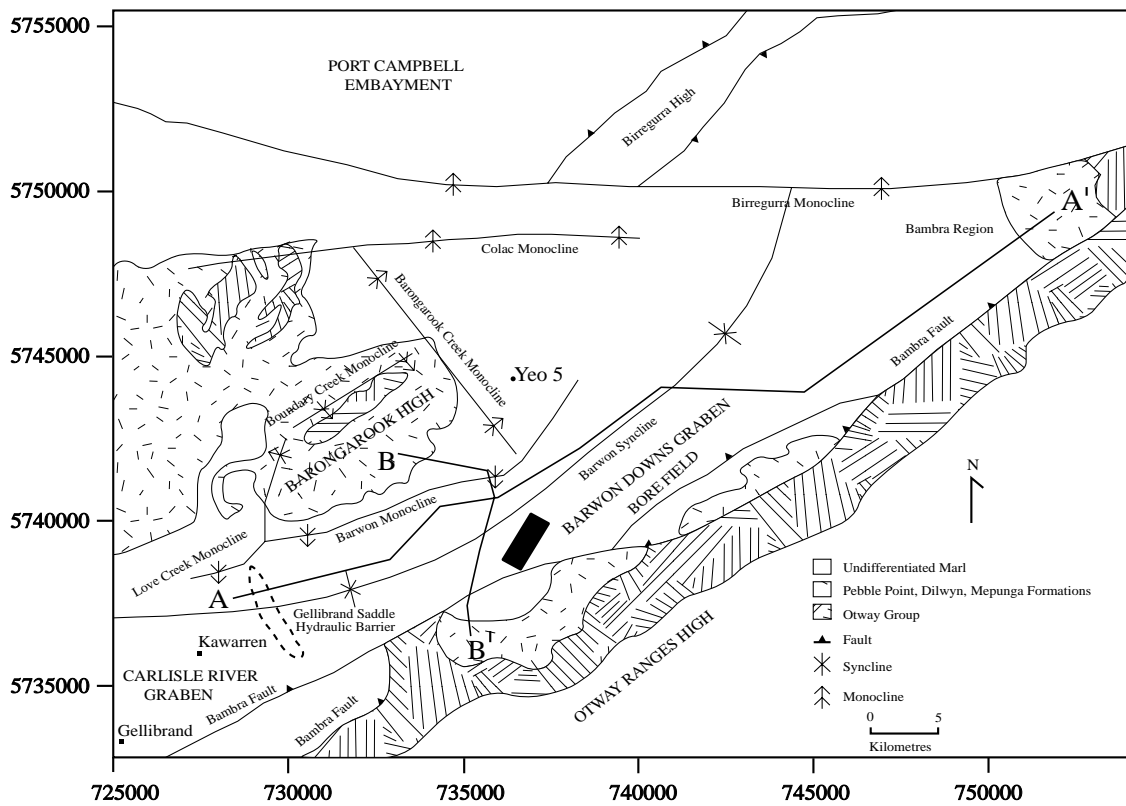
comes more important. As shown in Figs. 1 and 2, the Barwon Downs Graben is situated approximately 70 km southwest of Geelong on the northern flanks of the Otway Ranges. Groundwater investigations conducted in the Barwon Downs Graben since the early 1960s showed that it contained an extensive high-quality groundwater resource. This groundwater resource is an important source of water in Barwon Waters' drought management plan for Geelong. The Barwon Water bore field consists of four production bores with a combined capacity to extract up to 50 ML/day. This bore field provided a significant contribution to Geelong's water supply during the 1982/1983 drought.

## Geological setting and hydrostratigraphy

The Barwon Downs Graben extends from the Gellibrand Saddle in the southwest to the Birregurra Monocline in the east covering an area of approximately 500 km<sup>2</sup> (Fig. 2). The region is dominated by a series of NE/SW-trending folds and faults shown in Fig. 2, that make up the major structural elements of the graben (Witebsky et al. 1995). The Barwon Downs Graben is a small synclinal structure bounded by the Otway Ranges to the south and the Barongarook High to the west. Cross-sections A-A' and B-B',



**Fig. 1** Location map of the Barwon Downs Graben showing bore locations, roads, and settlements. The circled area shows where the first production bore was situated. The rectangular box displays where the bore field now lies. Eastings and Northings refer to the Australian map grid



**Fig. 2** Structural elements within and surrounding the Barwon Downs Graben. The Barwon Downs Graben extends from the Gellibrand Saddle to the Bambrab Region in the northeast (Adapted from Witebsky et al. 1995)

shown in Figs. 3a and b, demonstrate the structural relationship of the Tertiary sediments to the uplifted Otway Group rocks. The isolated nature of the graben suggests that the availability of groundwater for sustainable water supply is limited.

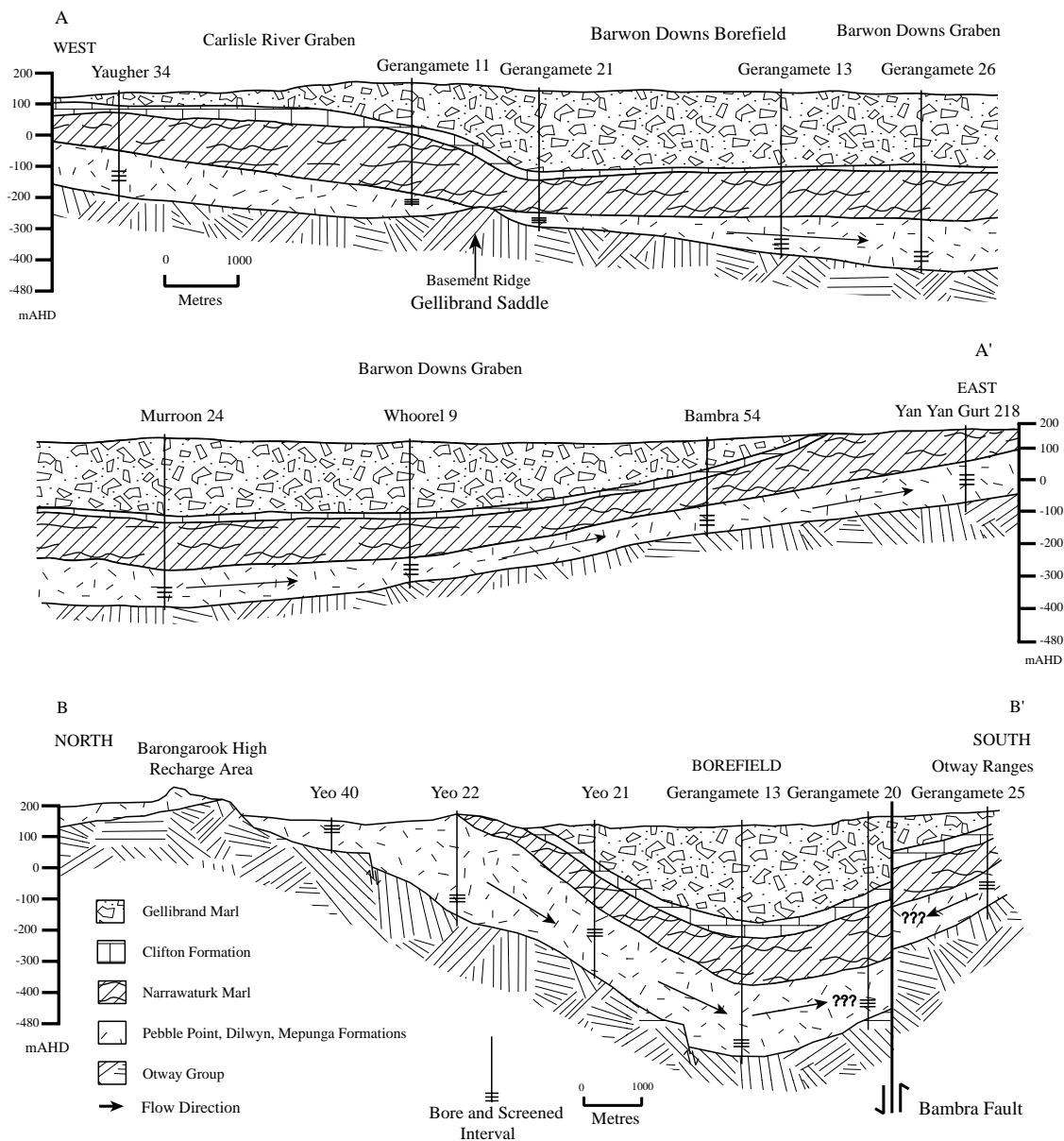
As shown in Table 1, the Barwon Downs Graben contains a complex suite of Mesozoic and Cainozoic sediments reflecting several depositional and tectonic events. The lower Cretaceous Otway Group (Eumeralla Formation), the basement aquifer, is thickly bedded, light grey volcanogenic sandstone dominated by lithic clasts and feldspar with little quartz that is interbedded with mudstone, shale, quartz pebble conglomerate, and thin bituminous coal beds (Witebsky et al. 1995). Uplifted Otway Group rocks crop out on the Barongarook High. These rocks constitute poor aquifers and have low primary porosity and hydraulic conductivity. Bore yields are low ranging from 0.1 to 1.26 L/s and Total Dissolved Solids (TDS) range from 1,000 to 3,000 mg/L (Lakey and Leonard 1982).

The basal Tertiary Pebble Point Formation unconformably overlies the Otway Group. This marine unit consists predominantly of quartzose sand with small quantities of grey lithic pebbles, sandstone, chert, and hornfels. The overlying Dilwyn Formation was deposited in a fluvial channel and coastal plain environment consisting of clean quartz sands, interspersed with thinner beds of yellow to light brown clayey sand (Blake 1980). A regional unconformity separates the Mepunga Formation from the Dilwyn Formation. The Mepunga Formation was deposited

in a beach and near shore environment and consists of very well-sorted reddish brown limonitic quartz sand, calcareous limonitic-sand, and limonitic sandy-limestone. The Pebble Point, Dilwyn, and Mepunga Formations are in direct hydraulic continuity and together form the lower Tertiary aquifer system that, in the Barwon Downs Graben, locally attains a thickness in excess of 250 m (e.g., in Yeo 5, Fig. 2). The thickness of the lower Tertiary aquifer is considerably reduced on the Barongarook High due to post-depositional erosion and subsequent uplift (Witebsky et al. 1995).

A minor marine transgression during the Late Eocene to Late Oligocene deposited the Narrawaturk Marl, which is thickest in the central portion of the graben. The Narrawaturk Marl is a low hydraulic conductivity unit that locally confines the lower Tertiary aquifer. The Late Oligocene Clifton Formation was deposited in a shallow marine high-energy environment (Table 1). It consists of limonitic quartz to limonitic sandy limestone (Lakey and Leonard 1982), and disconformably overlies the Narrawaturk Marl. The overlying Upper Oligocene Gellibrand Marl consists predominantly of greyish marl, varying to calcareous clay and silt and clayey-limestone. It is exposed throughout the graben and attains a maximum thickness of 250–300 m.

Previous work on augmenting recharge to the Barwon Downs Graben aquifer (Johnston 1990, 1992) also showed that variability exists in terms of the stratigraphy and layering present in the unsaturated zone. At the ground surface the sands contained varying amounts of roots and



**Fig. 3** **a** Cross-section A-A'. The Gellibrand Saddle separates the Carlisle River Graben from the Barwon Downs Graben. **b** Cross-section B-B'. Also shown are the locations of the boreholes used in this study. The Bamba Fault has resulted in the juxtaposition of low permeability basement rock on the south side against the aquifer on the north

other organic matter up to a depth of 0.1 m. At greater depths (up to 1 m) coarse white and orange sands are evident. Below 1 m the soils tend to be of a heterogeneous nature with the presence of mottling, silty clay material, variable grain size ( $<2\ \mu\text{m}$ –1 mm), and very hard cemented layers. The variability of soils in the unsaturated zone leads to inconsistent recharge rates and flow paths.

The lower Tertiary aquifer system occupies approximately  $2.3 \times 10^{10}\ \text{m}^3$  of the graben (Witebsky et al. 1995). Assuming an average porosity of 0.15, it would contain approximately 3,500,000 ML of water of which approximately 30,000 ML is held in elastic storage (Witebsky et al.

1995). Barwon Water is licensed to extract 80,000 ML over a 10-year period with a maximum of 12,500 ML in any year. While this represents only 0.125% of total volume in storage, understanding recharge rates is essential for sustainable use of this resource. This paper integrates hydraulic, chemical, and isotopic data to constrain the groundwater flow paths, the groundwater solutes, and the age of the groundwater.

### Climate

The region has a temperate climate with warm dry summers and cool wet winters. Data from the Bureau of Meteorology



**Table 1** Stratigraphic column (adapted from Witebsky et al. 1995)

Period	Group	Formation/Member
PLIOCENE		Newer Volcanics Moorabool Viaduct
MIOCENE	Heytesbury	Gellibrand Marl
OLIGOCENE		Clifton Formation
EOCENE	Nirranda	Older Volcanics Narrawaturk Marl Yaughar Volcanics Mepunga Formation
PALEOCENE	Wangerrip	Dilwyn Formation Pebble Point Formation
UPPER CRETACEOUS	Sherbrooke	Timboon Sand
LOWER CRETACEOUS	Otway	Pretty Hill Sandstone Eumeralla Formation

show that average daily maximum temperature between 1990 and 2000 in summer was 21.5 and 11.3 °C in winter. The mean annual rainfall for the region, between 1990 and 2000, was approximately 1,200 mm, with distinct spatial variations: 1,041 mm in Colac; 1,937 mm along the Gellibrand River in Forrest; 1,067 mm in Timboon; and 1,025 mm in Forrest (Fig. 1). The average monthly rainfall from June to September (winter) was approximately 110 mm, but less than 50 mm between the months of January and March (summer). Potential evaporation exceeds rainfall from December to March, implying that most recharge occurs from May to September.

### Sampling and analytical techniques

A total of 34 observation bores screened in the Mepunga, Dilwyn, Pebble Point, Narrawaturk Marl, or Clifton Formations were sampled between May 2001 and February 2002 using a bailer, foot-valve, or low-flow bladder pump. Three production bores were also sampled at the outflow. Depth to water, pH, EC, alkalinity, dissolved CO<sub>2</sub>, dissolved O<sub>2</sub>, and temperature were measured in the field. An Orion 290 m with an Orion Ross electrode was used to measure pH and was calibrated against pH buffers at each location. EC and temperature were measured using an Orion 240 conductivity meter and probe. Alkalinity, dissolved CO<sub>2</sub>, and dissolved O<sub>2</sub> were determined using Hach digital or drop titrators 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 Thermo Jarrel Ash ICP-AES at ALS Environmental (Melbourne) on samples that had been filtered through 0.45 µm cellulose nitrate filters and acidified to pH 2 using 16N ultrapure HNO<sub>3</sub> immediately after collection. Lithium and silica was analysed by ALS Sydney on an ICP-MS. Anions were analysed in unacidified samples using a Metrohm ion chromatograph at Monash University. Charge balances determined using PHREEQC (Parkhurst and Appelo 2003) were mainly within ±10%, which is acceptable for waters

of moderate TDS (Eaton et al. 1995). All samples outside these limits have high HCO<sub>3</sub> concentrations suggesting errors in field titration. Chemical analysis and field parameters are presented in Table 2. Stable isotope ratios presented in Table 3 were measured at Monash University using a Finnigan MAT 252 mass spectrometer. δ<sup>18</sup>O values were measured via equilibration with CO<sub>2</sub> at 25 °C for 24–48 h. δ<sup>2</sup>H values were measured via reaction with Cr at 850 °C using an automated Finnigan MAT H/Device. δ<sup>18</sup>O and δ<sup>2</sup>H values were measured relative to internal standards that were calibrated using IAEA SMOW, GISP, and SLAP standards. Data were normalized following Coplen (1988) and are expressed relative to V-SMOW where δ<sup>18</sup>O and δ<sup>2</sup>H values of SLAP are –55.5‰ and –428‰, respectively. CO<sub>2</sub> from dissolved inorganic carbon (DIC) was liberated by acidification under vacuum in sealed sidearm vessels. δ<sup>13</sup>C values are expressed relative to PDB. Many samples were analysed at least twice and the precision (1σ) is: δ<sup>18</sup>O=±0.1‰ ; δ<sup>2</sup>H=±1‰ ; δ<sup>13</sup>C=±0.2‰ . <sup>14</sup>C contents were determined by AMD on the 14UD tandem electrostatic accelerator at the Australian National University. Ages are expressed in years before present, and the results are presented in Table 4.

### Groundwater flow regime

#### Recharge/regional and localised flow

Recharge to the lower Tertiary aquifer system is achieved via direct infiltration into the Pebble Point, Dilwyn, and Mepunga Formations where they crop out on the Barongarook High. Blake (1980) computed the recharge for the Graben as 5,340 ML/year by using an overall effective recharge rate of 5% of the annual rainfall of 890 mm and a potential aquifer outcrop of 120 km<sup>2</sup>. Prior to bore field pumping, both regional and local groundwater systems could be distinguished. The regional groundwater system flows through the Barwon Downs Graben. Recharge calculations based on flow net and base flow techniques (Lakey and Leonard 1984) indicate recharge from the Barongarook High into the lower Tertiary aquifer system may be up to 14% of precipitation, equivalent to 4,800 ML/year. On the Barongarook High, Boundary Creek flows eastwards and was considered by Witebsky et al. (1995) to receive base flow. Witebsky et al. (1995) calculated from vertical hydraulic gradients that about 1,000 ML/year discharges from the groundwater system to parts of Boundary Creek (Fig. 4). Pumping from the bore field has lowered the water table on the Barongarook High and reduced base flow to these streams. If enough stress is placed on the system, the water table will fall below the elevation of the creek and the entire area of outcropping aquifer will provide recharge to the Barwon Downs Graben aquifer.

Water table and potentiometric surface contours (Figs. 4 and 5) show that groundwater mainly flows radially from the Barongarook High eastward into the Barwon Downs Graben and south into the Carlisle River Graben. Horizontal hydraulic gradients are 0.0021. A second flow system is to the southwest under the surface catchment divide of the

**Table 2** Hydrochemistry of Barwon Downs Graben groundwater samples

Bore ID	EC $\mu\text{S}/\text{cm}$	TDS	pH	Eh (mV)	DO (mg/L)	HCO <sub>3</sub> (mg/L)	CO <sub>2</sub> (mg/L)	Cl (mg/L)	Br (mg/L)	F (mg/L)	NO <sub>3</sub> (mg/L)	SO <sub>4</sub> (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Fe (mg/L)	Mn (mg/L)	Si (mg/L)	Ba (mg/L)	Li (mg/L)	SlCc	SlG	SlQ
Barongarook 54	404	229	6.8	247	7	122	35	73	0.23	<0.03	0.02	0.30	48	14	5	3	2.00	0.24	3.10	0.02	0.009	-1.48	-4.65	-0.2
Yeo 21	812	449	8.6	543	2	93	<1	216	0.61	0.05	0.00	0.08	94	26	13	6	0.11	0.03	0.02	4.69	0.047	0.4	-4.97	-2.41
Barongarook 55	684	315	5.5	551	5	<1	144	202	0.74	0.10	0.71	1.84	93	3	12	2	0.06	0.02	4.91	0.09	0.005	-6.05	-4.58	0
Barongarook 60	916	428	4.8	401	5	<1	140	257	0.88	0.03	0.62	12.25	143	2	12	<1	<0.01	0.02	4.77	0.02	0.002	-6.38	-3.96	-0.01
Yeo 20	235	124	6	562	4	5	46	52	0.17	0.02	8.40	3.14	36	3	3	1	0.13	0.02	3.47	0.06	0.004	-4.27	-4.23	-0.15
Yeo 24	398	219	6.0	123	<1	98	60	64	0.20	<0.03	0.02	1.72	45	<1	2	<1	35.90	0.39	2.31	0.04	0.003	-3.48	-5.07	-0.33
Barongarook 62	1460	668	6.8	479	1	6	6	445	1.55	bd	0.03	0.68	184	6	11	9	81.20	5.09	<0.01	0.08	0.008	-3.04	-5.16	bd
Barongarook 67	1016	459	6.4	262	<1	<1	6	301	0.97	0.05	bd	0.18	135	9	9	4	23.80	3.35	<0.01	0.06	0.006	-5.22	-5.13	bd
Barongarook 68	484	328	4.3	441	5	<1	90	131	0.46	<0.03	0.03	10.68	72	1	7	<1	0.38	0.03	3.76	0.08	0.005	-6.66	-4.27	-0.11
Elliminyt 68	578	319	6.6	166	7	61	35	139	0.45	0.08	0.02	0.41	78	5	9	<1	12.60	0.56	1.17	0.03	0.022	-2.45	-4.98	-0.61
Yeo 22	236	142	5.7	238	7	49	30	42	0.14	<0.03	0.02	7.52	23	2	2	<1	14.60	0.23	3.70	0.02	0.003	-3.74	-4.04	-0.12
Murroon 28	590	350	6.9	71	<1	161	78	104	0.35	0.07	0.05	0.09	66	5	7	6	24.60	0.57	3.27	0.07	0.046	-1.73	-5.62	-0.18
Whoorel 9	424	157	10.9	339	1	46	<1	82	0.28	0.13	0.00	0.60	59	2	<1	10	0.01	0.00	0.01	0.01	0.023	-0.11	-5.18	bd
Murroon 26	881	403	11.4	554	<1	43	<1	210	0.93	0.24	0.01	0.60	109	29	<1	10	<0.01	<0.001	<0.01	0.26	0.024	0.48	-4.13	bd
Murroon 31	6220	4032	7.2	71	<1	476	120	1957	3.92	0.69	2.45	13.50	1000	33	126	8	23.80	0.48	4.22	0.64	0.058	-0.48	-1.77	-0.06
Yan Yan Gurt 218	1406	676	8.8	255	1	5	<1	415	1.00	0.10	0.03	0.13	200	22	16	17	<0.01	0.07	<0.01	0.08	0.148	-0.82	-5.1	bd
Murroon 24	551	306	7.3	540	2	83	20	121	0.42	0.05	0.05	2.65	82	3	6	8	1.51	0.53	0.79	0.03	0.064	-1.82	-4.38	-0.8
Yaughter 36	402	242	7.9	548	1	99	2	64	0.24	0.06	0.02	0.09	63	6	3	7	<0.01	0.02	0.23	<0.01	0.009	-0.64	-5.48	-1.33
Yaughter 36	319	156	7.2	560	2	22	2	74	0.26	0.04	0.02	bd	48	5	3	4	0.08	0.01	<0.01	<0.01	0.016	-2.23	-6.52	bd
Yaughter 34	393	185	9.1	283	2	39	<1	70	0.25	0.02	0.05	4.09	64	4	<1	4	0.04	0.01	1.10	<0.01	0.02	-0.31	-4.02	-0.71
Kamgun 3	7910	4353	8.9	548	2	57	<1	2415	6.94	bd	1.60	0.40	1420	5	110	28	<0.01	0.05	0.54	0.01	0.183	-0.57	-2.67	-1
Kamgun 1	2370	1566	9.2	317	<1	506	<1	491	1.59	0.48	0.10	0.10	521	<1	<1	13	0.54	0.01	0.34	<0.01	0.052	0.33	-3.84	-1.24
Bambra 54	1290	657	9.3	506	3	15	<1	384	1.00	0.14	0.10	0.35	205	17	9	13	0.08	0.03	<0.01	0.06	0.043	-0.03	-4.58	bd
Bambra 56	847	402	9.1	303	2	<1	<1	242	0.68	bd	0.15	0.20	134	10	5	10	0.03	0.01	<0.01	0.02	0.019	-1.99	-5.03	bd
Gerangamete 19	798	452	6.9	223	9	98	15	194	0.65	0.13	0.03	0.05	78	30	18	8	0.20	0.19	0.61	0.01	0.005	-2.12	-6.17	-0.91
Gerangamete 26	824	592	8.2	512	2	327	32	91	0.32	0.18	0.13	0.17	141	6	14	12	0.31	0.04	0.75	<0.01	0.022	-0.09	-5.31	-0.82
Gerangamete 20	840	478	7.2	247	7	73	50	200	0.69	0.13	0.04	0.75	82	38	15	10	0.09	0.22	0.58	0.01	0.021	-0.91	-3.94	-0.93
Gerangamete 25	173	80	6.6	234	<1	18	2	44	0.14	0.09	0.01	0.10	23	4	<1	<1	0.07	0.01	0.06	0.00	0.002	-3.02	-5.56	-1.91
Gerangamete 24	743	439	8.3	274	9	104	20	174	0.57	0.09	0.03	0.87	98	14	13	5	<0.01	0.02	0.32	0.01	0.028	-0.09	-4.27	-1.2
Gerangamete 13	439	218	5.3	521	2	20	2	122	0.39	<0.03	0.02	2.88	70	2	3	5	0.02	0.15	<0.01	0.02	0.03	-4.56	-4.47	bd
Gerangamete 21	383	158	10.0	563	2	32	<1	85	0.26	<0.03	0.02	0.10	59	2	<1	7	<0.01	0.04	<0.01	0.00	0.024	-0.06	-6.66	bd
GW2A	373	167	6.2	121	4	73	0	74	0.26	0.07	0.05	0.25	43	1	4	5	21.90	0.75	1.51	0.04	0.027	-3.39	-5.83	-0.51
GW4	454	233	6.4	192	6	82	20	84	0.29	0.01	0.08	6.03	50	3	5	5	30.10	0.32	4.80	0.11	0.034	-0.59	-4	-0.01
GW5	601	535	5.7	116	0	56	32	353	0.46	0.04	0.00	5.15	66	4	5	5	38.80	0.51	4.75	0.09	0.032	-3.52	-4.06	-0.01
Barwon River	158	106	6.2	587	9	20	10	27	0.10	0.03	0.53	4.63	16	4	3	<1	0.06	0.22	4.23	0.02	0.001	bd	bd	bd

bd = below detection

Log Saturation Indices (SI) of calcite (Cc), gypsum (G), quartz (Q)

**Table 3** Stable isotope data for Barwon Downs Graben groundwater

Bore ID	Aquifer	$\delta^{18}\text{O}$ (‰ SMOW)	$\delta^2\text{H}$ (‰ SMOW)	$\delta^{13}\text{C}$ (‰ PDB)
Barongarook 54	Mepunga Fm	-5.0	-29	-8.2
Yeo 21	Mepunga Fm	-5.4	-31	-7.3
Barongarook 55	Dilwyn Fm	-5.9	-31	-20.8
Barongarook 60	Dilwyn Fm	-4.7	-30	-19.6
Yeo 20	Dilwyn Fm	-5.5	-32	-10.1
Yeo 24	Dilwyn Fm	-5.3	-36	-13.2
Barongarook 62	Pebble Point Fm	-5.2	-29	IC
Barongarook 67	Pebble Point Fm	-4.8	-33	-21.2
Barongarook 68	Pebble Point Fm	-5.4	-35	-19.9
Elliminyt 68	Pebble Point Fm	-5.5	-36	4.5
Yeo 22	Pebble Point Fm	-5.8	-34	-20.2
Murroon 28	Mepunga Fm	-4.9	-34	-11.2
Whoorel 9	Mepunga Fm	-5.0	-35	-2.8
Murroon 26	Dilwyn Fm	-5.2	-33	-2.8
Murroon 31	Dilwyn Fm	-5.0	-29	-10.9
Yan Yan Gurt 218	Dilwyn Fm	-5.6	-33	-8.5
Murroon 24	Pebble Point Fm	-5.1	-32	-3.4
Yaugher 38	Mepunga Fm	-5.4	-32	-14.1
Yaugher 36	Mepunga Fm	-5.2	-31	-14.8
Yaugher 34	Dilwyn Fm	-4.6	-32	0.2
Karngun 3	Gellibrand Marl	-4.9	-30	-14.2
Karngun 1	Dilwyn Fm	-4.8	-31	4.3
Bambra 54	Mepunga Fm	-5.4	-29	-5.3
Bambra 56	Dilwyn Fm	-5.4	-33	-3.7
Gerangamete 19	Clifton Fm	-5.2	-34	-9.6
Gerangamete 26	Narrawaturk Marl	-5.5	-34	-15.7
Gerangamete 20	Mepunga Fm	-5.5	-29	-11.7
Gerangamete 25	Mepunga Fm	-5.4	-33	-6.5
Gerangamete 24	Dilwyn Fm	-5.1	-30	-1.4
Gerangamete 13	Pebble Point Fm	-5.5	-34	-7.9
Gerangamete 21	Pebble Point Fm	-5.3	-35	-10.6
GW2A	Dilwyn Fm	-5.4	-31	-7.14
GW4	Dilwyn Fm	-5.4	-30	-11.1
GW5	Dilwyn Fm	-5.3	-30	-11.5
Barwon River		-4.2	-25	-9.9

IC=insufficient carbon

Barwon River into the Gellibrand River catchment. Flow in this latter direction is restricted by a topographical barrier, the Gellibrand Saddle (Fig. 2).

The Dilwyn and Mepunga aquifers are composed of discontinuous beds of sand, gravel, clay, and silt deposited in different continental settings. The variation in lithology affects the hydrogeological characteristics of the aquifers, for example, river channel sands have high horizontal hydraulic conductivity, whereas the more clayey flood-plain deposits have low hydraulic conductivity. The responses of adjacent bores to bore field pumping illustrate the heterogeneous nature of the lower Tertiary aquifer. As shown in Fig. 6, Gerangamete 13 and Murroon 24 show similar response during pumping and Whoorel 9 which is further from the bore field also shows significant drawdown.

Vertical head gradients between the Mepunga Formation and the underlying Dilwyn Formation were estimated from localities with nested or adjacent bores and are shown in Table 5. A few localities, dominantly the central portion of the graben and discharge areas show upward head gradients between the Dilwyn and Mepunga Formations. For example, Murroon 24 and 25 are 65 m apart and are screened in the lower Dilwyn and Mepunga Formations, respectively and have an upward vertical hydraulic gradient of 0.025. Similarly Gerangamete 17 and 24, which are 10 m apart are screened in the Mepunga and Dilwyn Formations, respectively, have an upward vertical hydraulic gradient of 0.0076. By contrast, in the recharge area, head gradients are typically downwards. The hydrographs of adjacent bores allows assessment of whether the groundwater system is hydraulically connected. Karngun 3 lies in the Gellibrand

**Table 4** Radiocarbon data for Barwon Downs Graben groundwater

Bore ID	Formation	Depth (m)	Region	Corrected pmc <sup>a</sup>	Age (raw) <sup>b</sup>	Age (qstat) <sup>c</sup>	Age ( $\delta^{13}\text{C}$ ) <sup>d</sup>	Age (alk) <sup>e</sup>
GW5	Dilwyn Fm	550	Borefield	24.4±1.1	11218±361	9818	5939	8692
Karngun 1	Dilwyn Fm	494	Discharge Area North	35.3±0.8	8360±191	6763	modern	2797
Gerangamete 24	Dilwyn Fm	232	Extraction Area	52.3±2.0	5272±306	3577	modern	1236
Gerangamete 20	Mepunga Fm	359	Extraction Area	7.4±0.3	20964±275	19679	18502	18497
Whoorel 9	Mepunga Fm	421	Flow Path North	36.8±0.9	8032±186	6419	modern	2462
Murroon 24	Dilwyn Fm	585	Flow Path North	33.1±0.8	8892±193	7295	modern	5170
Yeo 21	Mepunga Fm	56	Recharge Area	13.9±1.0	15867±576	14468	10283	10283
Yeo 24	Dilwyn Fm	46	Recharge Area	62.9±1.4	3718±175	1988	modern	1196

<sup>a</sup>percent modern carbon<sup>b</sup>age calculated assuming no dilution by matrix carbon<sup>c</sup>corrected using qSTAT (c.f. Vogel 1970)<sup>d</sup>corrected using  $\delta^{13}\text{C}$  values (see text)<sup>e</sup>corrected using alkalinity (c.f. Clarke and Fritz 1997)

Marl and shows no response to pumping, whereas Gerangamete 26 lies in the Narrawaturk Marl and responds to pumping. This implies that the Narrawaturk Marl may act as a leaky aquitard.

### Discharge

The discharge area in the Barwon Downs Graben is not well known, but the potentiometric contours indicate that vertical flow may occur either through the thick late Tertiary marine marls or along faults in the northeast towards Bambra. The second option is unlikely as most of the faults die out within the late Cretaceous and early Tertiary, with very few penetrating through to the surface (Blake 1980). Even those that do penetrate through the late Tertiary are unlikely to be significant pathways of groundwater flow as the clays and marls are highly plastic and unconsolidated and would tend to seal any fault surfaces developed (Blake 1980).

### Structures affecting groundwater movement

The Bambra Fault forms the southern boundary of the graben and acts as a groundwater barrier for most of its length. Hydrograph analyses of bores on either side of the fault clearly indicate that the fault acts as a barrier to groundwater flow and that the lower Tertiary aquifer units on either side are not connected. Gerangamete 25 is screened in the Mepunga Formation and lies on the southern side of the Bambra Fault. Water levels in this bore show very little response to the 3 years of production from the Barwon Downs bore field. Gerangamete 21 is situated on the northern side of the fault and only 200 m away from Gerangamete 25 and water levels show a response to pumping. The fault has resulted in the juxtaposition of low permeability basement rock on the south side against the aquifer on the north (Fig. 3b).

While the Bambra Fault acts as a groundwater barrier to the south, the existence of a groundwater barrier southwest

of the bore field was postulated after preliminary modeling of the Barwon Downs aquifer system by Blake (1980). Witebsky et al. (1995) suggested that the thinning of the aquifer over a basement ridge creates a barrier in the southwest (Fig. 3a). The barrier separates the Barwon Downs groundwater system from the Kwarren/Gellibrand system to the southwest. Its location has been inferred from observation bore response to production from the Barwon Downs bore field. Aquifer thickness is reduced from over 150 m in the Barwon Downs borefield area to 20 m in Gerangamete 21 (Witebsky et al. 1995). On the western side of the ridge the lower Tertiary unit then thickens to 100 m in Gerangamete 11 (Fig. 3a). This barrier is termed the Gellibrand Saddle.

### Aquifer parameters

Nine pumping tests were performed on the lower Tertiary aquifers in the Barwon Downs Graben and adjoining Kwarren/Gellibrand area. Aquifer parameters estimated from these tests are summarized in Table 6. The average value for the hydraulic conductivity and storage coefficient over the intervals tested were 6 m/day and  $2.4 \times 10^{-4}$ , respectively (Witebsky et al. 1995). In confined aquifer tests the storage coefficient is typically around  $4 \times 10^{-4}$  (Witebsky et al. 1995). The specific yield of the aquifer, a clean moderately sorted fine to medium sand, could reasonably be expected to fall in the range of 0.1–0.2 (Lakey and Leonard 1982). Slug tests (Lakey and Leonard 1982) conducted on 33 bores in the aquifer material in the Gellibrand area, indicate that the hydraulic conductivity of aquifer material ranges from 0.2 to 40 m/day with a medium value of about 12 m/day. However, the values of hydraulic conductivity obtained from these tests are not representative of the overall aquifer. Observation bores are usually screened in coarser grained intervals which are more permeable and pumping test results tend to be weighted towards these coarser units. Lakey and Leonard



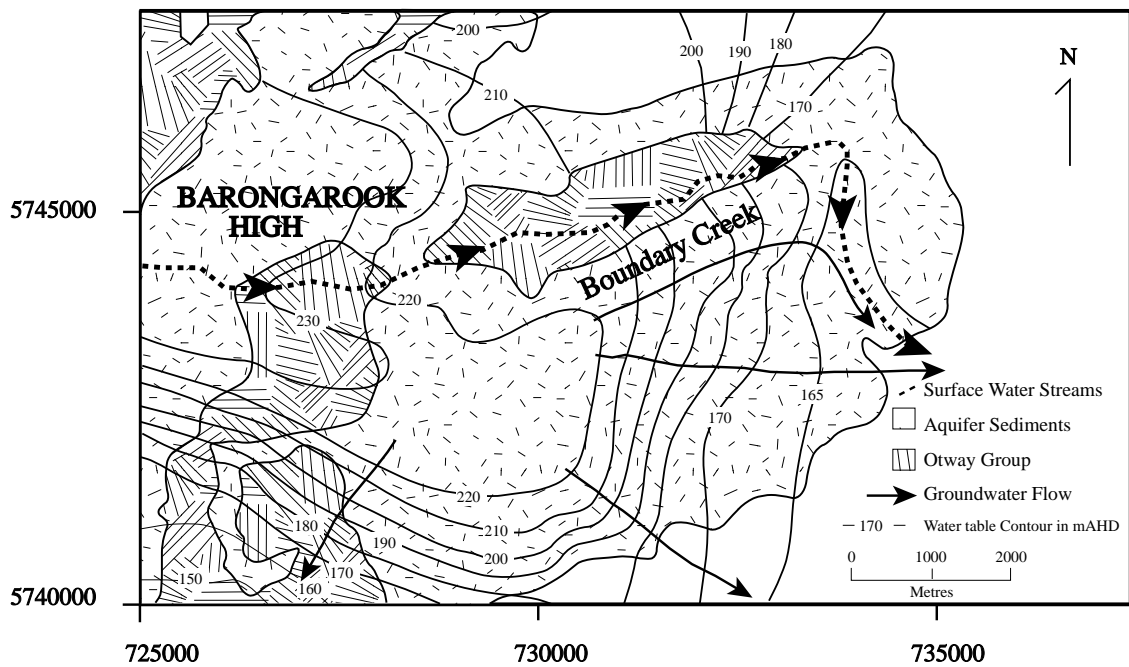


Fig. 4 Water table contour map of the Barongarook High. Groundwater flows radially from the Barongarook High into the graben

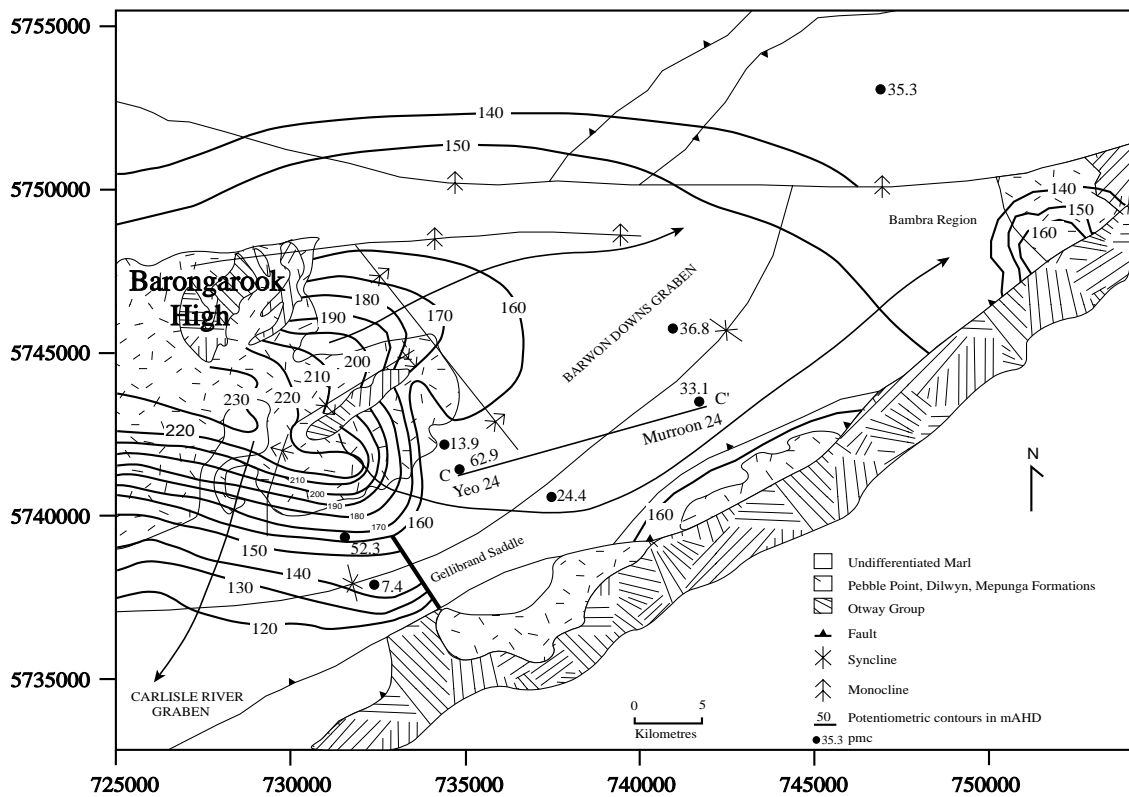


Fig. 5 Potentiometric surface. Groundwater elevations, head gradients, and flow directions in the Barwon Downs Graben aquifer. Line transect C-C' used for calculating groundwater velocities from Darcy's Law. Distribution of pmc values in the lower Tertiary Barwon Downs Graben aquifer are also shown

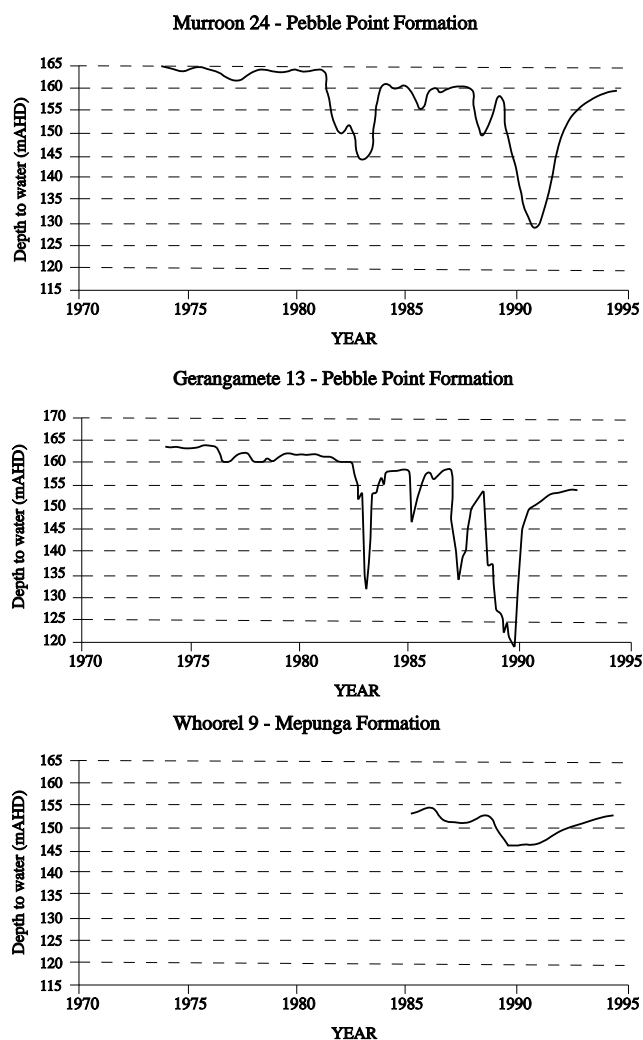


Fig. 6 Hydrographs of Murroon 24, Gerangamete 13, and Whoorel 9. A low transmissivity exists between these nested bores

(1984) considered an effective hydraulic conductivity value of 4 m/day to be more representative of the full aquifer sequence.

## Groundwater residence times

Sustainable use of groundwater resources requires that groundwater ages are known. Two common approaches to estimate groundwater ages are based on groundwater velocities calculated from Darcy's Law, and radiometric dating such as  $^{14}\text{C}$  ages.

### Darcy's Law

Using Darcy's Law, the estimated groundwater velocity between Yeo 24 (Recharge Area) and Murroon 24 (Middle of Flow Path) (Fig. 5, Line Transect C-C'), assuming a porosity of 0.15, hydraulic conductivity between 1 and 10 m/day, and a hydraulic gradient of  $1.5 \times 10^{-3}$ , is 0.01–0.1 m/day

or 3.74–37.38 m/year. Therefore it would take 241–2,406 years for water to travel from Yeo 24 to Murroon 24.

### $^{14}\text{C}$ dating

As shown on Fig. 5, Percent Modern Carbon (pmc) values range from 13.9 to 62.9 in the Mepunga and Dilwyn Formation groundwater. As discussed below, in common with many parameters, there is no regular increase of pmc values with distance along the flow path or with depth. The Clifton Limestone Formation is the only major carbonate unit in this region. As the lower Tertiary aquifer is confined by the Narrawaturk Marl interaction of groundwater in this aquifer with the Clifton Limestone Formation is unlikely. However, carbonate cements may be present in the aquifer matrix making some dilution of old non-radioactive carbon likely. Three methods were applied to calculate the volume of carbon derived from the aquifer matrix and to calculate the groundwater residence times from the  $^{14}\text{C}$  data (Table 4).

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, which results in ages from 3.7 to 20.9 ka. This is a simple correction that makes no attempt to correct the age of individual samples that may have experienced different water–rock interaction histories. A second model uses the measured  $\delta^{13}\text{C}$  and pH values (Tables 2 and 3) to calculate the percentage of calcite dissolution assuming soil  $\text{CO}_2$  has a  $\delta^{13}\text{C}$  of  $-23\text{‰}$  and calcite to have a  $\delta^{13}\text{C}$  of  $0\text{‰}$  (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; the  $\delta^{13}\text{C}$  of the soil is dependant on the mix of C3 and C4 plants; and there are no measured  $^{13}\text{C}$  values of any carbonate cements in either the aquifers or the recharge area. This model results in ages ranging from Modern to 13.6 ka. A modern age suggests recharge post 1960s. It is unlikely that modern groundwater exists in the Barwon Downs Graben aquifer as it is confined by a thick low hydraulic conductivity aquitard. The third model applied is an alkalinity correction (Clarke and Fritz 1997) that predicts 26–50% dilution by carbon from the aquifer matrix, yielding ages from 1.1 ka to 18.5 ka.

Ages from these models should be treated with caution. The alkalinity correction does not take into account Ca produced or lost by ion-exchange or derived from silicate weathering. The  $\delta^{13}\text{C}$  correction requires assumptions to be made about the  $\delta^{13}\text{C}$  values of the soil  $\text{CO}_2$  and the carbonate in the aquifer matrix (both of which are unconstrained in this study). The  $\delta^{13}\text{C}$  correction also suggests that in some cases all carbon is derived from calcite dissolution, which is unlikely. Additionally, neither model takes into account changes in major ion chemistry or  $\delta^{13}\text{C}$  values resulting from carbonate precipitation. As a result of the uncertainty in the alkalinity and  $\delta^{13}\text{C}$  models, and the conditions and

**Table 5** Vertical hydraulic gradients of nested bores in the Barwon Downs Graben

Bore ID	Depth (m)	Formation	Region	Easting	Northing	RLNS (mAHD)	Head (m)	Grad h (m/m)
Yeo 21	54	Mepunga Fm	Recharge Area	736500	5743950	137.3	157.15	
Yeo 24	46	Dilwyn Fm	Recharge Area	734400	5743820	161.79	160.33	−0.3975 <sup>DM</sup>
Murroon 24	576.7	Dilwyn Fm	Flow Path North	742052	5743756	155.97	165.24	
Murroon 25	460.2	Mepunga Fm	Flow Path North	742052	5742463	158.35	162.33	0.0254 <sup>DM</sup>
Yaugher 38	139.59	Mepunga Fm	Flow Path South of Barongarook High	725950	5736300	123.97	112.94	
Yaugher 34	196.87	Dilwyn Fm	Flow Path South of Barongarook High	725950	5736305	123.88	113.49	0.0096 <sup>DM</sup>
Gerangamete 17	148.9	Mepunga Fm	Extraction Area South	734200	5739752	171.45	158.57	
Gerangamete 24	229.2	Dilwyn Fm	Extraction Area South	734200	5741500	171.52	159.18	0.0076 <sup>DM</sup>

RLNS: Depth to groundwater in metres relative to Australian Height Datum (mAHD)

Vertical Head Gradient (Grad h) in m/m (XXX<sup>DM</sup>=between Dilwyn and Mepunga Formations)

Negative values indicate downward gradient, positive values indicate upward gradient

constraints of the groundwater system, the qSTAT model will be used to correct for <sup>14</sup>C ages.

The <sup>14</sup>C groundwater ages are approximately 5,000–8,000 years older than the groundwater ages determined using Darcy's Law. The oldest groundwater is from the extraction area, and is ~20 ka. Paradoxically, relatively old groundwater of ~10 ka is present in the Mepunga Formation in the recharge area. This is probably due to the high clay contents in the Mepunga Formation that result in locally low hydraulic conductivities. Extraction bores are usually screened in coarser grained intervals, which are more permeable, thus flow is more rapid to these bores. The heterogeneity of the aquifer system which leads to variable groundwater velocities can explain the variation in distributions of groundwater ages.

## Groundwater chemistry

### Stable isotopes

$\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of 34 groundwater samples are shown in Fig. 7 and Table 3. The groundwater in the graben has  $\delta^{18}\text{O}$  values ranging from −4.6 to −5.9‰ and  $\delta^2\text{H}$  values from −29 to −36‰ and plot in a close group around the local meteoric water line (LMWL) for Melbourne indicating that it has undergone minor isotopic fractionation due to evaporation, water–rock interaction, or gas exchange. Barwon Downs lies between Melbourne and Adelaide, and groundwater plots between the average isotopic composition of meteoric water for Melbourne and Adelaide. The small variations in isotopic values suggest that the Barwon Downs Graben aquifer is a well-mixed groundwater system.

$\delta^{13}\text{C}$  values of dissolved inorganic carbon (DIC) range from 4.5 to −21.2‰ (Table 3). While this range is broad,

most values are consistent with the carbon in the groundwater being derived from organic matter in the soil zone (Clarke and Fritz 1997). This agrees with the geochemistry data (Fig. 8) that indicate that carbonate dissolution played an insignificant role in determining the geochemistry of these waters. The higher  $\delta^{13}\text{C}$  values, however, suggest some calcite dissolution, possibly calcite cements. Calcite dissolution can explain the high pH values of some of the groundwater, which is also implied by a broad correlation of pH and  $\delta^{13}\text{C}$  values (Tables 2 and 3).

### 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; Herczeg et al. 1991, 1993; Macumber 1991, 1992; Weaver and Bahr 1991; Acworth and Jankowski 1993; Kimblin 1995; Weaver et al. 1995; Elliot et al. 1999; Edmunds and Smedley 2000; Herczeg and Edmunds 2000;).

The major ion chemistry of groundwater from a variety of hydrological settings (recharge area, flow paths, discharge areas) is shown in Table 2. pH values vary between 4.32 and 11.35. The majority of groundwater in the Barwon Downs Graben is oxidized, with dissolved oxygen (DO) ranging up to 9 mg/L. The bores situated on the Barongarook High recharge area tend to have higher DO concentrations. However, most groundwater, even at depth in the Mepunga and Dilwyn Formations, contain measurable dissolved oxygen, suggesting that reactions with the aquifer matrix have not been sufficient to consume all available oxygen. A series of bores located in the extraction area and bore field have low DO values, and are also acidic, pH<5. These more acidic waters also tend to have high Fe concentrations. The iron content of some groundwater is above the WHO limit of 1 mg/L for potable drinking

**Table 6** Summary of aquifer parameters determined from pumping tests (Adapted from Witebsky et al. 1995)

Test Site	Pumping bore	Aquifer tested	Total length of screened interval (m)	Pumping rate (m/day)	Test duration (days)	Drawdown in production bore (m)	Transmissivity (m <sup>2</sup> /day)	Hydraulic conductivity (m/day)	Storage coefficient	Reference
Barwon Downs	GW1	Mepunga Fm	40	7197	1.6	50.60	366	9.2	$3 \times 10^{-4}$	Blake 1978
Gerangamete	GW2	Dilwyn Fm	75	5564	5	25.75	512	6.8	$3.2 \times 10^{-4}$	Blake 1978
Borefield	GW2A	Mepunga Dilwyn Fms	78	7732	0.08	21.45	650	8.3	$2.8 \times 10^{-4}$	Layton Groundwater Consultants 1982
Borefield	GW5	Mepunga Dilwyn Fms	79	7776	0.02	37.25	—	—	—	Layton Groundwater Consultants 1982
Wire Lane Kawarren	Murroon 23 Yaughar 37	Dilwyn Fm Mepunga Dilwyn Fms	13 72	985 5413	0.83 6.5	9.50 —	64 970	4.9 13.5	$1.8 \times 10^{-5}$ $3 \times 10^{-4}$	Blake 1978 Lakey and Leonard 1982

waters but it is site specific reflecting the variability in chemical composition of the sediments in the aquifer. The iron is probably derived from oxidation of pyrite, which also lowers the pH of groundwater, and is relatively abundant in the upper Dilwyn, and lower Mepunga Formations, (Tickell et al. 1991).

TDS contents of the groundwater range from 80 to 4,353 mg/L. Murroon 31 nested in the Dilwyn Formation in the recharge area contained groundwater with a TDS of 4,032 mg/L. Bore logs indicate that this bore is screened in a clay lens that may contain saline water. Groundwater in the Gellibrand Marl has the highest TDS contents (4,353 mg/L). Groundwater in the Narawaturk Marl had TDS values of 1,102 mg/L; however, there is only one bore sampling this marl so it may not be representative of the overall groundwater chemistry. Low TDS groundwater in the Narawaturk Marl may be the result of upward vertical gradients leading to fresher groundwater infiltrating from the lower Tertiary aquifer.

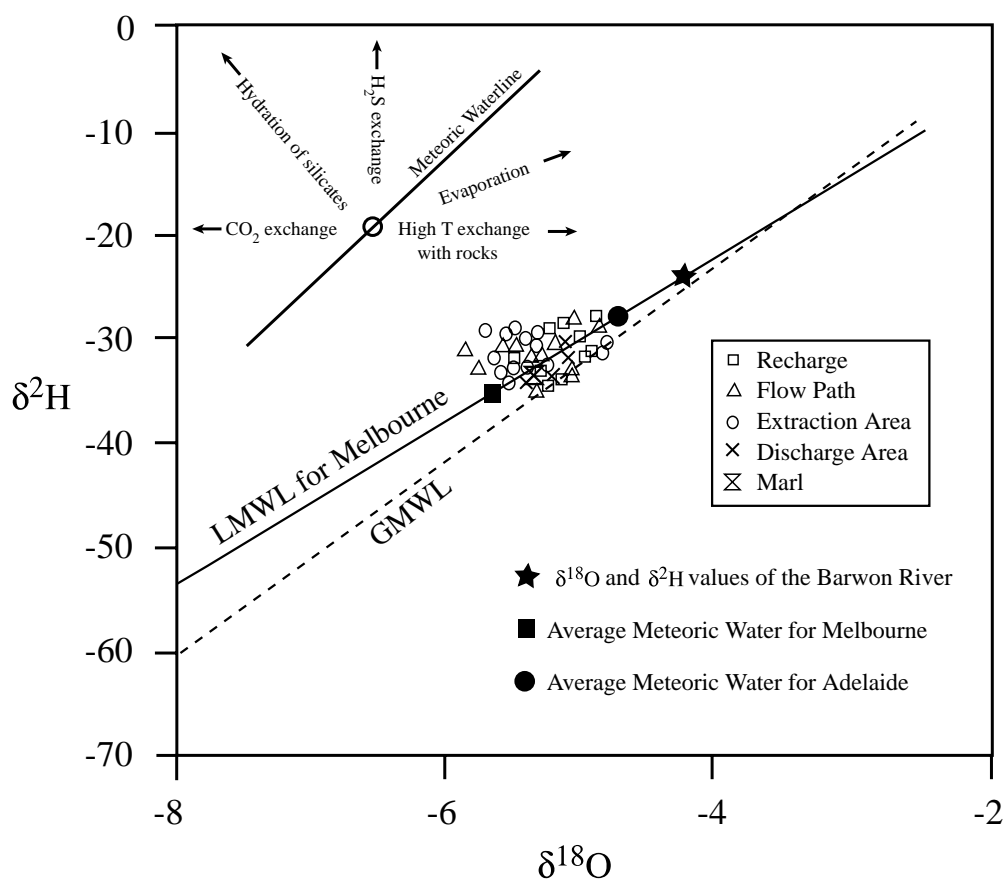
There is no regular spatial or depth variation in TDS, pH, or DO implying that the aquifer matrix is heterogeneous and that water-rock interaction is spatially variable. This is in agreement with the distribution of the <sup>14</sup>C ages. Given this, groundwater chemistry will be discussed with respect to salinity variations. The freshest waters, which occur in the recharge area on the Barongarook High, are dominated by Na (up to 80% total cations), Cl (>50% total anions), and HCO<sub>3</sub>. These waters contain limited amounts of Ca, Mg, and K. With increasing TDS, Cl becomes the dominant anion (up to 90% of total anions) while Na remains the dominant cation (up to 90% of total cations).

The chemistry of surface waters (i.e., Boundary Creek and the Barwon River, Table 2) within the Barwon Downs Graben show a similar composition to the groundwater system. The TDS within surface waters is lower than in groundwater (TDS ~106 mg/L) and also has a high oxidizing potential. Elemental ratios and isotopic compositions (i.e., anions, cations, stable isotopes) are similar to that of groundwater.

### Correlation coefficients

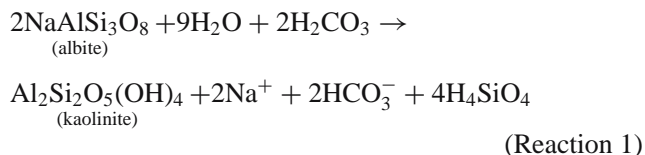
A cluster analysis (e.g., Davis 1973) performed on groundwater chemistry from the lower Tertiary aquifer shows four main clusters (Fig. 9): 1) Na, Cl, and Br concentrations have strong mutual correlations (>0.96) and Mg is correlated with this group (0.89); 2) Ca, K, and Li concentrations are strongly mutually correlated (>0.74), Fe, Mn, and Ba are also strongly mutually correlated (>0.78) and correlated to Ca, K, and Li (0.68); and 3) C, F, and N concentrations also show strong mutual correlation (0.81) and weak correlation to the other groups of ions; and 4) Si and S that have a mutual correlation of (0.68) but are not correlated with the other groups of ions. These clusters form the basis for discussing the sources of the solutes.

**Fig. 7** Stable isotopic ratios for Barwon Downs Graben groundwater. Inset shows the predicted isotopic shifts resulting from a wide range of processes. Average precipitation for Melbourne and the Melbourne Meteoric Water Line (MMWL) are from the IAEA GNIP database and I. Cartwright, Monash University (unpublished data), 2003. Global Meteoric Water Line (GMWL) from Clarke and Fritz (1997)



### Na, Cl, and Br

Despite the strong correlation between the concentrations of these ions there is some variation in their ratios, as shown in Fig. 8. Molar Na/Cl ratios ranged from as high as 2.41 to 0.67, with many between 0.8 and 1.0 (Fig. 8a). The high Na/Cl ratios of the freshest groundwater are probably controlled by water–rock interaction, for example, albite weathering by



Reaction 1 also produces kaolinite, which is common in the weathered rocks in the region. Samples with Na/Cl ratios of 0.8–0.9 are probably due to evaporation of rainfall which in this region has a Na/Cl ratio of 0.86 (Arad and Evans 1987). Samples with low Na/Cl ratios are probably the result of Na loss or exchange onto soils and clays. As discussed below, the Ca and Mg data support this idea.

Oceans have molar Cl/Br ratios of 550–700 (Davis et al. 1998, 2001). Coastal precipitation has similar Cl/Br ratios, however, inland precipitation, especially in arid or semiarid climates, may have lower Cl/Br ratios due to the tendency for Cl to be removed in early rainfall near coastal areas (Herczeg et al. 1991; Davis et al. 1998, 2001). Cl/Br ratios

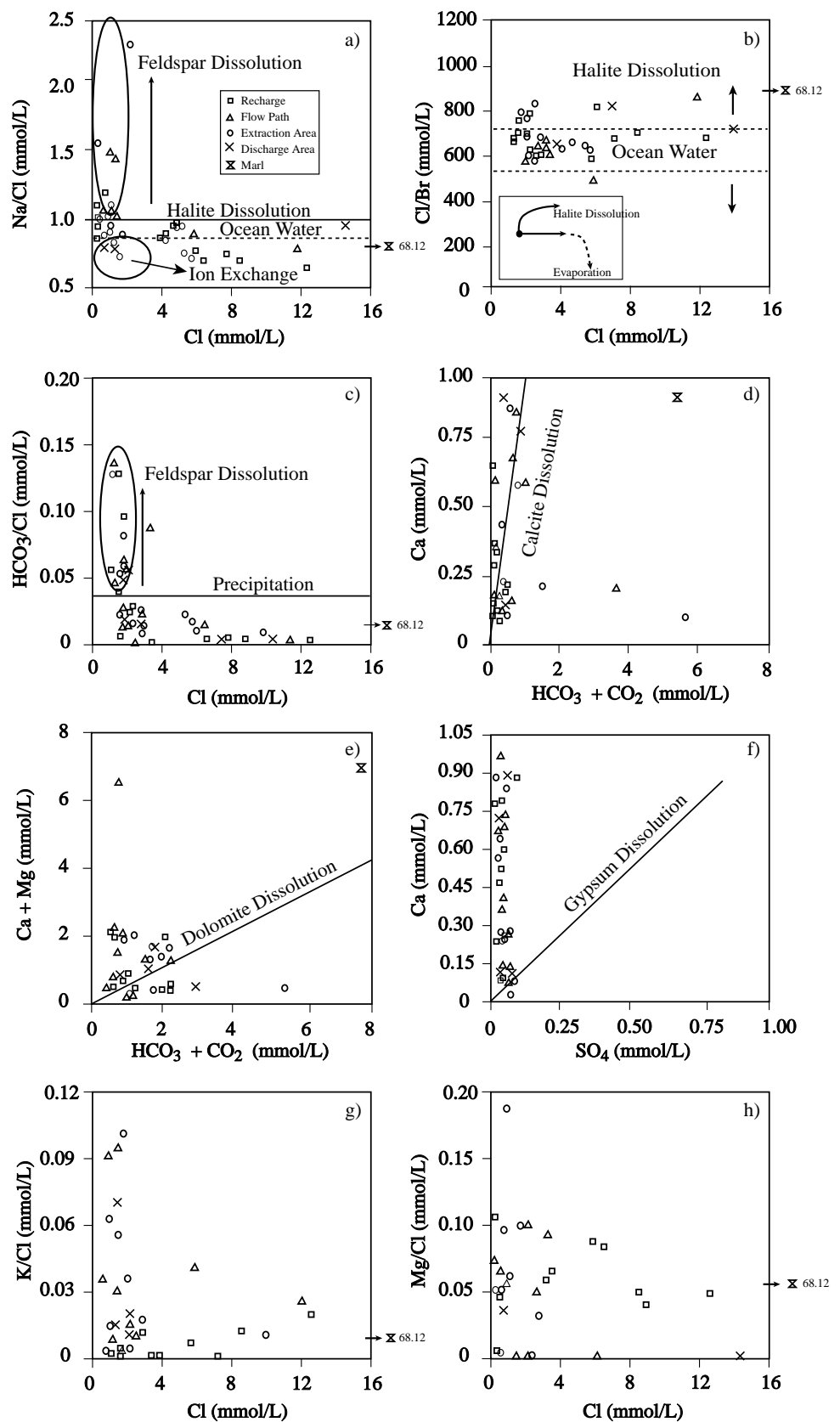
in the Barwon Downs Graben range from 512 to 1124 (Fig. 8b) and most of the groundwater plots within the Cl/Br range for ocean water (550–700). Cl/Br ratios show some evidence of ongoing halite dissolution as a cause of increasing salinity, however, even this must be relatively minor since halite has Cl/Br ratios of  $10^4$ – $10^5$  (e.g., Cartwright et al. 2003). The groundwater from the Gellibrand Marl has a Cl/Br molar ratio of 812 and this reflects minor halite dissolution.

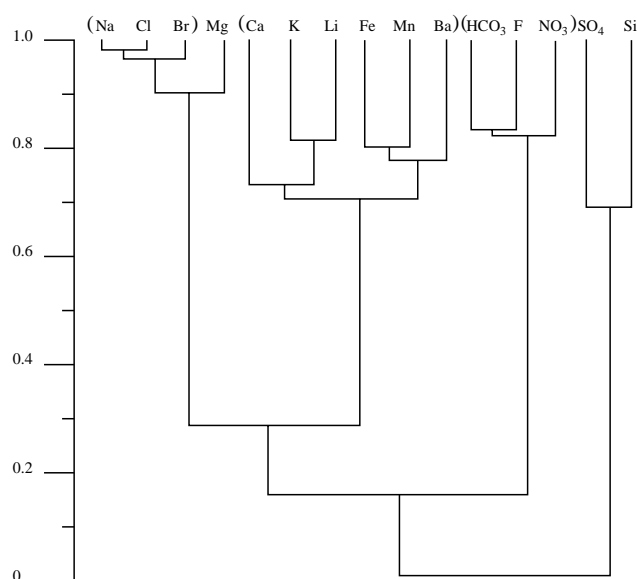
### Other cations

These remaining cations may be derived by dissolution of silicate minerals (e.g., plagioclase feldspar, chlorite, or biotite), carbonates (dolomite or calcite), gypsum, and/or cation exchange of Na for Ca and Mg on clay minerals. Thick carbonate deposits are absent in the Barwon Downs Graben, but as discussed above carbonate cements may be present. As shown in Figs. 8c–e, a lack of correlation between Ca and Mg and total dissolved inorganic carbon, DIC, indicates that carbonate dissolution (calcite and dolomite) is not the major process controlling the Ca and Mg contents of the Barwon Downs Graben groundwater. The saturation indices with respect to calcite ( $\log \text{SI} = 0.05$  to  $-11.54$ ) and dolomite ( $\log \text{SI} = -1.45$  to  $-15.67$ ) also showed that the groundwater is undersaturated with respect to these minerals (Table 2). However, as pH increases, groundwater approaches saturation with respect



**Fig. 8** Molar ratios for Barwon Downs Graben groundwaters. The data imply that calcite, dolomite, and gypsum dissolution does not control Ca or Mg abundances, while dissolution of K-feldspar may be the major source of K





**Fig. 9** Diagram showing correlation coefficients between the major and selected minor ions in Barwon Downs Graben groundwater constructed using methods outlined in Davis (1973). Brackets show groupings of ions discussed in the text

to calcite and the  $\delta^{13}\text{C}$  of groundwater approaches values that are close to marine carbonates. Also the high pH waters, (Whoorel 9, Murroon 26, and Gerangamete 21) also contain relatively high carbon concentrations. Total carbon measurements ranged from  $<1$  to 506 mg/L. The pH of most natural waters is controlled by reactions involving the carbonate system. The saturation indices with respect to calcite and the  $\delta^{13}\text{C}$  data suggest that these high pH groundwaters are the result of calcite dissolution or precipitation. Dissolution of a small amount of calcite from minor cements will overcome the buffering capacity of fresh groundwater allowing its pH to rise. There is no sequential correlation of  $\delta^{13}\text{C}$  values with position in the flow system, suggesting that the carbon source is heterogeneous. Given the above discussion, most of this carbon will initially be derived from the soil zone, and changes in alkalinity will reflect the degree of weathering and the heterogeneity of the sediments.

The low sulphate contents ( $<1$  mmol/L), low S/Ca ratios of the groundwater (Fig. 8f), and low saturation indices with respect to gypsum (Table 2) likewise imply that gypsum dissolution does not control Ca concentrations although gypsum dissolution is one potential source of sulfate. Alternatively, much of the S may be derived from evaporation of rainfall.

Overall, Ca and Mg are most likely to be derived mainly from the weathering of silicates. As discussed above, exchange of Ca and Mg for Na may occur but is unlikely to be a dominant process at the low salinities (TDS  $<800$  mg/L) in the Barwon Downs groundwater (c.f., Stumm and Morgan 1981). The high  $\text{HCO}_3/\text{Cl}$  ratios (up to 1.07, Fig. 8c) in the fresher groundwater are due to the weathering of feldspars (e.g., Reaction 1), which occurs during the initial stages of water–rock interaction.

Concentrations of K are weakly correlated with Na (Fig. 9), yet K/Cl vs. Cl trends (Fig. 8g) are similar to those of Na/Cl vs. Cl (Fig. 8a). An analogous reaction to Reaction (1) may be written for K-feldspar that would explain the relatively high K/Cl ratios of the freshest waters. K concentrations may also be governed by reactions between the clay minerals as K is preferentially sorbed onto clays relative to Na due to its smaller ionic radius. If this were the case, it would result in decoupling of K and Na concentrations.

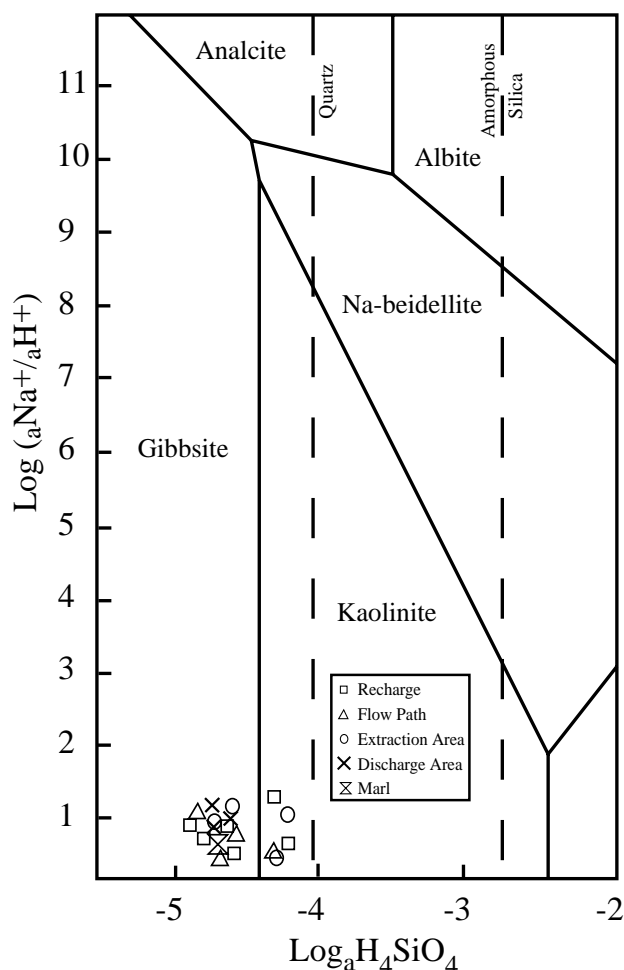
Mn, Li, and Ba elements are present in negligible quantities in rainfall but are common minor components in many rock-forming minerals, where they substitute for Fe and Mg, Si, Li, or K. The presence of these ions is interpreted to indicate water–rock interaction within the flow system. Their correlation with K and Ca concentrations is consistent with all these cations being predominantly derived from the weathering of silicates.

### Silica

Silica in groundwater originates from two sources; the dissolution of quartz and from the dissolution of other silicates in particular aluminosilicates. Figure 10 shows the stability of various minerals in the system  $\text{Na}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}-\text{SiO}_2$  in the Barwon Downs Graben groundwater plot close to the boundary between the gibbsite and kaolinite fields. This suggests that the reaction between gibbsite and kaolinite may buffer silica concentrations causing their decoupling from the concentration of elements such as Na, Mg, and Ca. Natural gibbsite and kaolinite will also contain Na and Ca as well as K; however, the relative amount of K contained within the clay minerals with respect to the concentrations in groundwater is probably much larger than Ca or Na. Hence, the reactions amongst the clay minerals are likely to cause larger relative changes in K than in Ca or Na. This may explain the poorer correlation of K with many other cations (Fig. 9). The degree of weathering or water–rock interaction is low as saturation with respect to amorphous silica has yet to be reached. The groundwater with the highest silica concentration is mainly situated along flow paths and discharge areas. However, there is groundwater along flow paths that have low silica concentrations indicating that water–rock interaction is spatially variable probably due to the heterogeneous nature of the sediments.

### F and N

The concentrations of these two ions are not strongly mutually correlated, nor are they correlated with other ions. Fluoride and nitrate concentrations are low ( $<0.69$  and  $<8.40$  mg/L, respectively, Table 2), and given the lack of nitrate and fluoride sources in the aquifer, it appears that all of these ions are predominantly derived from the atmosphere, surface, or unsaturated zone.



**Fig. 10** Log ( $a\text{Na}^+/a\text{H}^+$ ) vs. log  $a\text{H}_4\text{SiO}_4$  diagram at 25°C showing mineral stability fields calculated using the Geochemists Workbench (Bethke 1998) and the composition of Barwon Downs Graben groundwater

## Conclusions

The use of chemical and isotopic data in combination with hydraulic heads has improved the understanding of groundwater movement in the Barwon Downs Graben. Two different scales of groundwater flow are recognized. Local flow systems in the lower Tertiary sequence on the Barongarook High provide base flow to Boundary Creek and other surface water bodies. The regional flow system also recharges on the Barongarook High, and groundwater flows both southwest into the Carlisle River Graben and east into the Barwon Downs Graben. Groundwater discharge is probably into surface water streams and springs in the Bamba region. The Bamba Fault forms the southern boundary of the Barwon Downs Graben. Hydrographs show that the lower Tertiary sediments south of this fault are not hydraulically connected with the lower Tertiary aquifer in the Barwon Downs Graben to the north. Hydrographs also show that the Clifton Formation and the Gellibrand Marl are not hydraulically connected to the lower Tertiary aquifer. However, the Narrawaturk Marl, which acts as a confining layer to the lower Tertiary aquifer, does show a minor response to

bore field pumping, implying that it acts as a leaky aquitard. This may pose a threat to groundwater quality in the lower Tertiary aquifer if diffusion of this nonpotable groundwater was induced by groundwater extraction.

To determine whether groundwater use in this area is sustainable an understanding of the total flow system and not just the area surrounding the bore field is necessary.  $^{14}\text{C}$  ages in the recharge avenue are  $\sim 3$  ka while  $^{14}\text{C}$  ages in the extraction area are in the vicinity of  $\sim 20$  ka. The combination of old groundwater, slow residence times, and a limited supply of recharge (4,800 ML/year) suggests that this resource is not finite and sustainable yields need to be quantitatively modeled.

Potentiometric surface contours indicate a relative low lateral hydraulic gradient within the lower Tertiary aquifer, suggesting relatively long groundwater residence times, which is confirmed by the  $^{14}\text{C}$  ages. The Dilwyn, Mepunga, and Pebble Point Formations contain discontinuous beds of sand, gravel, silt, and clay and consequently have heterogeneous hydraulic conductivities. Considerable disparities in potentiometric head drawdowns as a response to pumping between adjacent bores is also probably due to heterogeneities in the aquifer. This also poses a threat to groundwater quality as groundwater in the clay lenses is highly saline and pumping may induce flow from these layers.

Approximate hydraulic parameters may be derived from the  $^{14}\text{C}$  and head data. For the Mepunga Formation the head gradient between Yeo 21 in the recharge avenue and Gerangamete 20 in the extraction area is  $3 \times 10^{-3}$ . The relative difference in groundwater residence times between these two localities is 5–8 ka (depending on the age correction model used), suggesting an average linear velocity of 0.62 to 1 m/year. For an effective porosity of 0.15, the average hydraulic conductivity estimated from Darcy's Law is 31–50 m/year. The relatively low hydraulic conductivities in the Mepunga Formation result from the high clay content. For the Dilwyn Formation the head gradient between Karngun 1 in the discharge area and Gerangamete 24 in the extraction area is  $2.5 \times 10^{-3}$ . The relative difference in groundwater residence times between these two localities is 3–4 ka, suggesting an average linear velocity of 6–8 m/year and a hydraulic conductivity of 360–480 m/year for a porosity of 0.15. The high hydraulic conductivities of the Dilwyn Formation are due to the presence of coarse sands and gravels. However, locally the Dilwyn Formation still contains relatively old (up to 10 ka) groundwater. This reflects the heterogeneous hydraulic continuity in the Mepunga, Dilwyn, and Pebble Point Formations that form the Barwon Downs Graben aquifer due to the local presence of clay layers. Hydraulic conductivity values in the Mepunga Formation determined from slug tests (e.g., Darcy's Law) are  $\sim 4$  m/day. Groundwater pumping tests usually overestimate the hydraulic conductivity of a system because groundwater is preferentially pulled from the higher permeability lenses and sediments, thus resulting in higher yields. Paradoxically, the hydraulic conductivity values determined from radiocarbon data are an order of magnitude higher than those determined from hydraulic values. Groundwater pumping by Barwon Water will have

changed the flow system and hydraulic properties of the aquifer over time. This has led to inconsistent estimates of hydraulic conductivity values using both hydraulic and radiocarbon techniques.

Oxygen and hydrogen isotopes of groundwater in the lower Tertiary aquifer indicates that it was recharged under climatic conditions similar to those of today and has subsequently undergone little fractionation due to water–rock interaction, evaporation, or gas–water exchange. Unlike in some other large aquifer systems, such as the Quaternary alluvium aquifer of the Comarca Lagunera, in Northern Mexico (Brouste et al. 1997), and the Late Paleozoic – Early Mesozoic sedimentary cover in central Europe (Barth 2000), no variation in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values with age or position along the flow path is observed. However,  $^{14}\text{C}$  ages suggest that groundwater residence times are up to  $\sim 20$  ka. Based on palynology, fossil remains, and reconstructed water levels in local lakes, the Late Pleistocene (16,000–10,000 years BP) in Victoria was arid with increasing temperatures and decreasing precipitation (D'Costa 1989; Kershaw 1998). That this climatic variation is not seen in the groundwater stable isotopes may be due to the area's proximity to the coast and consequent lower variability of local climate over the last 20,000 years than in some inland areas.

Groundwater in the graben is fresh ( $<300$ – $700$  mg/L TDS), however groundwater in the Narrawaturk Marl and clay lenses in the aquifer sediments are more saline (TDS  $>1,000$  mg/L). Groundwater is mainly oxidizing and has a circum neutral pH. Reducing groundwater is found in the bore field extraction area where pyrite is present in the Dilwyn Formation. No spatial trend in groundwater chemistry exists; however, groundwater chemistry changes with increasing TDS from being dominated by bicarbonate and sodium to chloride and sodium becoming the dominant ions. Cl/Br ratios are close to oceanic values, indicating that the principle source of solutes is evapotranspiration with only very minor halite dissolution. The high salinity groundwater in the marls may have also undergone minor halite dissolution. High Na/Cl ratios and bicarbonate concentrations in the fresher waters indicate weathering of feldspar contributes to the solute load. Gypsum and carbonate dissolution are minor with most Ca, Mg, and K derived from silicate weathering. Reactions between gibbsite and kaolinite may buffer silica concentrations. Overall, water–rock interaction is limited and heterogeneous within the aquifer reflecting the variability of the aquifer lithologies.

A major concern for groundwater use in this region was whether bore field pumping would induce groundwater flow from the Narrawaturk Marl into the lower Tertiary aquifer and compromise the quality of this potable groundwater resource. Groundwater chemistry has not appreciably changed prepumping and postpumping; however, continued monitoring is required to assess the long-term sustainability of the system. In particular, extended extraction may result in the input of saline water from the over and underlying aquitards or clay lenses in the aquifer. Another concern was whether groundwater abstraction would decrease baseflow to overlying streams and wetlands. Anecdotal evidence shows that such streams do dry up during periods

of pumping from the borefield. However, the hydrographs demonstrate little hydraulic interconnectivity between the lower Tertiary aquifer and the formations above the Gellibrand Marl. As groundwater is mainly abstracted during periods of low rainfall, it is most likely that changes to surface water bodies reflect the lack of recent rains that lower water tables in the near surface systems.

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