The Department of
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Biodiversity
Conservation

Recharge mechanisms to Quaternary sand aquifers in the Willunga Basin, South Australia

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Cover Photograph

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Foreword

South Australia’s water resources are fundamental to the economic and social wellbeing of the State. Water resources are an integral part of our natural resources. In pristine or undeveloped situations, the condition of water resources reflects the equilibrium between rainfall, vegetation and other physical parameters. Development of surface and groundwater resources changes the natural balance and causes degradation. If degradation is small, and the resource retains its utility, the community may assess these changes as being acceptable. However, significant stress will impact on the ability of a resource to continue to meet the needs of users and the environment. Degradation may also be very gradual and take some years to become apparent, imparting a false sense of security.

Management of water resources requires a sound understanding of key factors such as physical extent (quantity), quality, availability, and constraints to development. The role of the Resource Assessment Division of the Department for Water Resources is to maintain an effective knowledge base on the State’s water resources, including environmental and other factors likely to influence sustainable use and development, and to provide timely and relevant management advice.

Bryan Harris
Director, Resource Assessment Division
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EXECUTIVE SUMMARY

There are growing concerns regarding the long-term sustainability of the groundwater resources in the Willunga Basin, and thus the horticultural developments that they support. With these concerns comes a requirement to determine more accurately the various components of the groundwater budget, in particular recharge rates.

Widespread (diffuse) groundwater recharge occurs in most parts of the basin, however the importance of direct recharge via stream-bed infiltration is yet to be determined. Primary Industries and Resources South Australia obtained funding from the Natural Heritage Trust in 2001 (Project no. 012181) to investigate stream–aquifer interactions at two field sites near McLaren Vale. Numerous wells were drilled at each site and completed as nests of multi-level piezometers equipped with water level logging devices.

This report presents the results of a detailed hydraulic and hydrochemical investigation at one site (Pedler Creek in D'Arenberg's vineyard) which involved a review of historical water level data and the sampling of all wells for major ion, stable water isotope, radiocarbon and chlorofluorocarbon analyses.

Groundwater level trends for the site show that aquifer heads have been below the base elevation of the creek on a few occasions since monitoring began in July 2000. This suggests that the potential for groundwater recharge by infiltration from the creek occurs rarely and for short periods of time.

Major ion compositions revealed a plume of relatively fresh groundwater originating near the creek and more saline groundwater deeper in the aquifer profile. The fresher samples, which were most likely recharged by infiltration of partially-evaporated creek water, have compositions that are dominated by Ca–Cl and reflect very little interaction with soil and/or aquifer minerals. Conversely, the more saline groundwater samples (electrical conductivity >~3000 μS/cm) are Na–Cl dominated and reflect evaporative concentration prior to recharge and interactions with predominantly carbonate minerals in the aquifer.

Groundwater ages determined using chlorofluorocarbon (CFC-12) data range from 21 to >36 years. It was not possible to obtain more accurate estimates of the groundwater ages for the oldest samples because they exceed the time scale over which chlorofluorocarbons can be used. Furthermore, groundwater radiocarbon concentrations have been severely affected by water–rock interactions in the aquifer, and therefore cannot be used to estimate groundwater ages. Nevertheless, the chlorofluorocarbon data revealed an interesting trend of groundwater ages becoming younger with increasing depth. When coupled with the hydraulic data, this reversed age gradient provides unequivocal evidence that this section of Pedler Creek is usually a groundwater discharge feature.

Groundwater recharge via stream-bed infiltration only occurs at this site after very large rainfall events in the winter months when the creek stage exceeds aquifer head elevations. Groundwater discharge to the creek may have an important impact on the shallow groundwater budget and therefore future groundwater allocations, particularly if other ephemeral creeks in the basin behave in a similar manner.

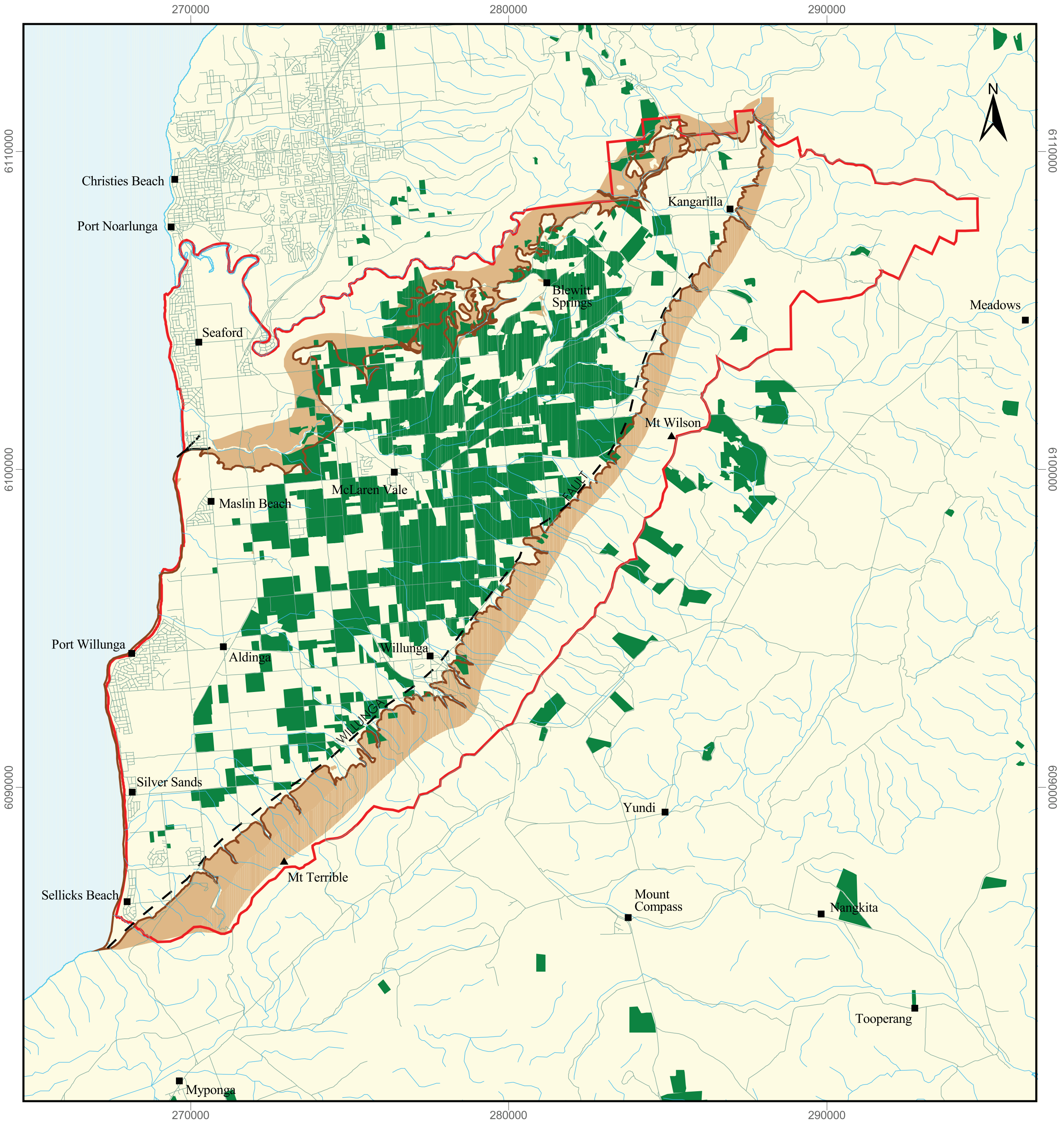
INTRODUCTION

The sedimentary aquifers that constitute the Willunga Basin to the south of Metropolitan Adelaide are a vital source of groundwater for the long-established horticulture and wine making industries in the region. Constant expansion of these activities combined with recent years of below average rainfall in the area has raised concern about the long-term sustainability of the groundwater resources. The Department for Water, Land and Biodiversity Conservation (DWLBC) is currently undertaking several groundwater investigations in the basin to determine aquifer recharge rates, groundwater salinity and age distributions. This information is vital for refining estimates of sustainable yield for the resource, and therefore should be considered in future management policies and procedures for the region.

Background and scope of study

Numerous streams drain the surface of the Willunga Basin (Fig. 1) and thereby provide a potential source of direct recharge to the underlying Quaternary sands and, in northeastern portions of the basin, Tertiary aquifer systems. Although many of these watercourses are ephemeral and only flow for three or four months each year, they may play an integral role in the recharge (or discharge) of the shallow aquifer systems. Therefore, with funding from the National Heritage Trust, a project was initiated in 1998 to investigate the importance of stream-bed infiltration as a groundwater recharge mechanism at two sites on Pedler Creek near McLaren Vale (Fig. 2). Several wells have been drilled at various distances from the creek bed at each of the two sites and are now completed as nests of multi-level piezometers (Martin and Sereda, 2002). Groundwater level monitoring in these piezometers is undertaken on a regular basis via either in situ data loggers or manual measurements.

The purpose of the current study is to sample groundwater from each of the piezometers for a suite of chemical and isotopic constituents to determine the spatial extent and, if possible, the rate of recharge from the stream into the aquifer. This report presents the hydraulic, chemical and isotopic results from investigations at Site 1 (Fig. 2) which is located in the D'Arenberg vineyard. The data is combined with historical rainfall, bore hydrographs and creek flow records to construct a conceptual model of the groundwater – stream water interactions occurring at the site.



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WILLUNGA BASIN
Locality plan

🟩 Irrigated areas

🟫 Neoproterzoic outcrop

□ McLaren Vale Prescribed Water Resource Area

0 5 10 Kilometres

Datum: GDA94
Projection: MGA Zone 54

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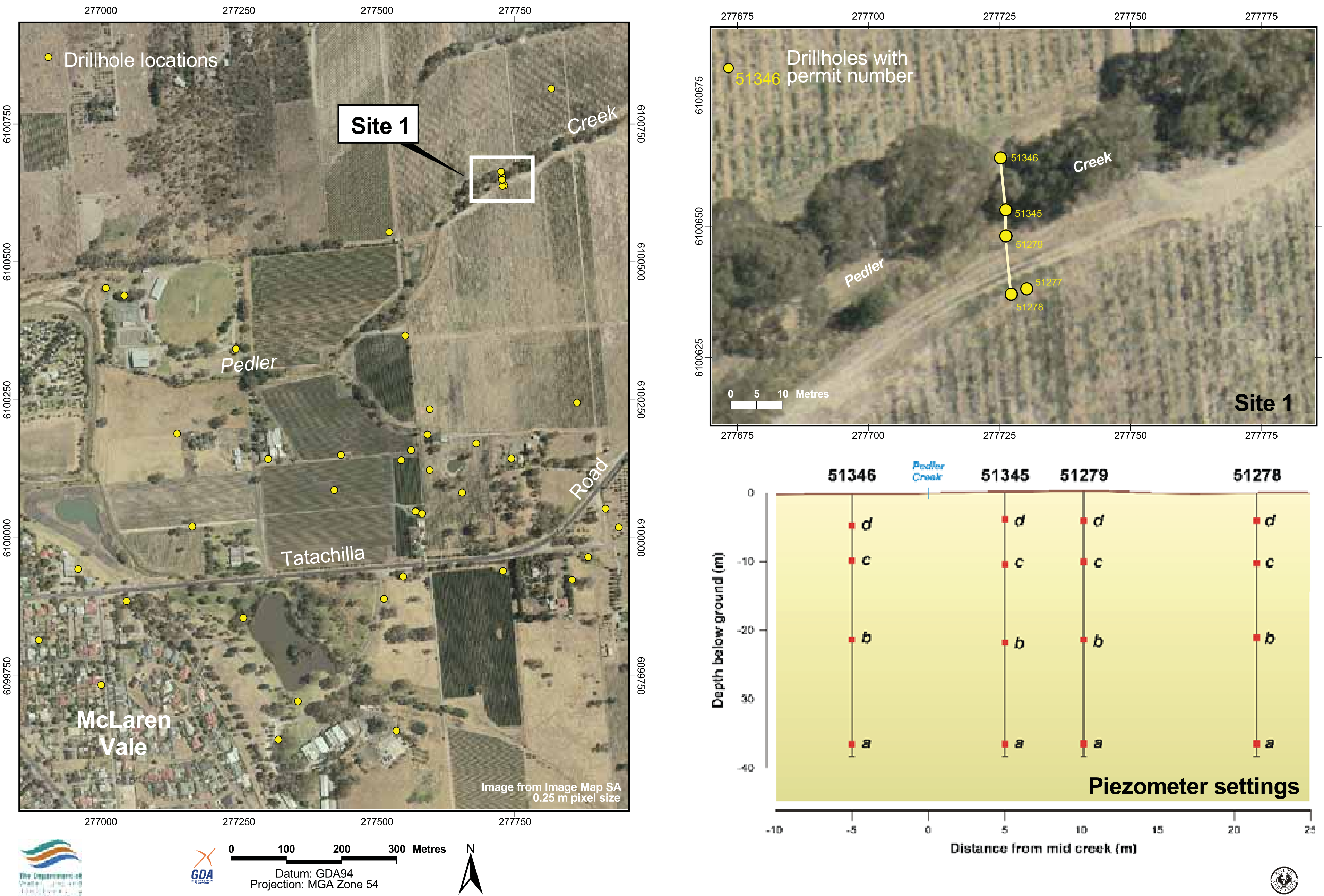
Figure 1



WILLUNGA BASIN

Location of Site 1 and individual boreholes

Figure 2

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METHODS

Groundwater samples were obtained from individual piezometers by pumping with a Grundfos MP1 submersible pump until at least three casing volumes of water had been purged. Large volumes of fine, grey sand and silt were recovered during the well purging process. This meant that either the piezometers had not been properly developed since the time of completion, or that the screen size was not properly matched to the aquifer material returned by drilling. Hence, individual piezometers could not be sampled until the desired pump out volume was achieved and the discharge water remained free of any solids. Electrical conductivity (EC) was also measured at the discharge pipe to ensure the salinity of the sample water remained constant, and thereby reflected aquifer water.

Groundwater levels were measured both before and during pumping to provide data suitable for hydraulic conductivity determination using standard pump-test analysis. However, large drawdowns were observed during pumping due to the low yield of most wells and, because pumping rate decreased with increasing drawdown, it was difficult to maintain a constant discharge rate at the surface. Although measured drawdowns can sometimes be corrected for changes in pumping rate, this approach can lead to large errors in the final estimate of aquifer transmissivity. Therefore, estimates of transmissivity from the pumping test cannot be presented.

Water samples were collected for major ion and stable hydrogen and oxygen isotope analysis in 1 L plastic bottles and 50 mL glass McCartney bottles, respectively. Measurement of carbonate alkalinity by titration with strong acid in the field enabled the volume of water required to supply 2 g of dissolved inorganic carbon for ^{14}C and $^{13}C/^{12}C$ analyses to be determined. This volume generally ranged from 30–60 L. Samples were then treated with saturated barium chloride solution, Magnafloc® and sodium hydroxide to form a white barium carbonate precipitate, which was later decanted into 5 L plastic bottles. Samples for chlorofluorocarbon (CFC) analysis were collected into 150 mL glass ampoules using a gas bailer and nitrogen evacuation system. Major ion analyses were performed by Australian Water Quality Centre at Bolivar, while all isotope and CFC measurements were undertaken by CSIRO Land and Water at Waite.

RESULTS

Aquifer hydraulics

Watertable elevations plotted relative to the ground surface and Pedler Creek profile are presented diagrammatically in Figure 3. Given that there was <0.1 m of water in the creek over the duration of the sampling program, this plot suggests that there is potential for groundwater discharge from the aquifer into the creek. Inspection of bore hydrographs from the site (Appendix) reveals only a few occasions when aquifer heads have been below 56 m AHD (the base elevation of the creek) since monitoring began at the site in July 2000. Therefore, based on the hydraulic data, groundwater recharge from the creek appears to be minimal.

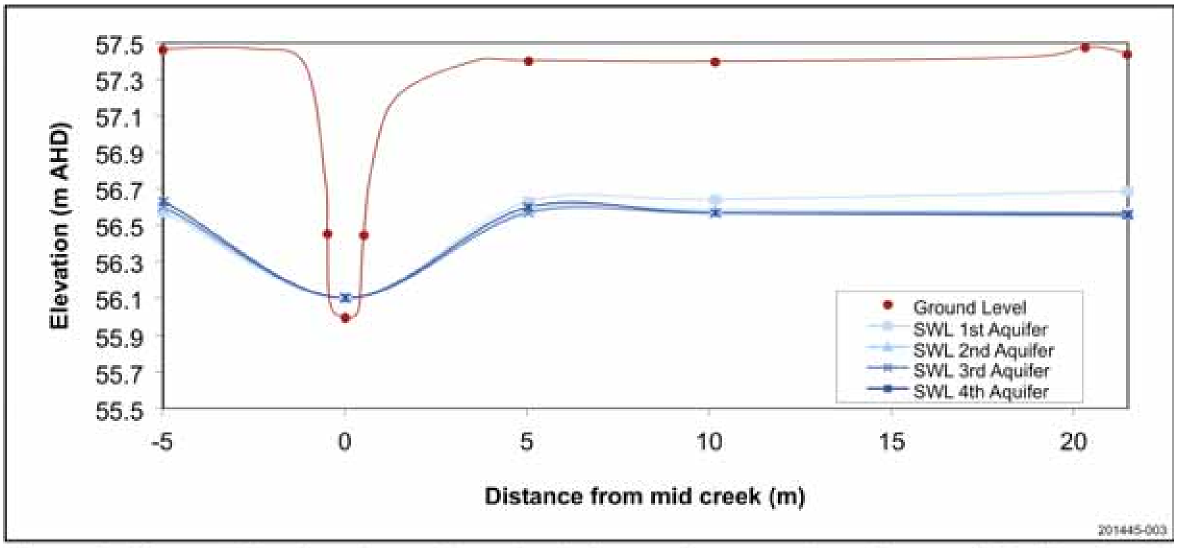


Figure 3 Watertable elevations plotted relative to the ground surface and Pedler Creek profile.

Groundwater chemistry

Field measurements of EC, pH and alkalinity as $CaCO_3$ in each piezometer are plotted spatially in Figures 4a–c respectively. Each of these profiles displays similar spatial trends: EC, pH and alkalinity are all generally lowest near the creek and in a gradually deepening arc away from the creek towards the south. This 'plume' of fresh water may reflect infiltration from the creek into the aquifer (discussed below).

Towards the bottom of the profile EC, pH and alkalinity reach the maximum observed values of 4650 µS/cm, 7.09 and 500 mg/L respectively.

Concentrations of major cations and anions, fluoride, bromide and total sulfur (as SO_4^{2-}) in groundwater samples collected from the piezometers are listed in Table 1. Fluoride, bromide, nitrate and nitrite concentrations are all below 1.0, 2.6, 3.3 (one sample returned 12.8 mg/L) and 0.2 mg/L respectively.

Whilst sulphate is usually the primary dissolved inorganic S species in groundwater, several observations suggest that other species (e.g. H_2S, HS^-) may be dominant at this site. Firstly, it was noticed while pumping many of the deeper piezometers that the groundwater was often black in colour and had a pungent H_2S smell. In addition, seven of

Table 1. Field measurements and major ion concentrations of groundwater samples and creek water from Site 1. Dissolved CO2 concentrations were determined using PHREEQC (Parkhurst, 1995).

Sample	**Well permit no.**	**Distance to mid creek** (m)	**SWL** (m AHD)	**Mean depth below ground** (m)	**EC** (µS/cm)	**pH**	**Alkalinity** (mg/L) (as $CaCO_3$)	**Ca** (mg/L)	**Mg** (mg/L)	**Na** (mg/L)	**K** (mg/L)	**CO_3** (mg/L)	**HCO_3** (mg/L)	**Cl** (mg/L)	**S** (mg/L)	**F** (mg/L)	**Br** (mg/L)	**NO_3.N** (mg/L)	**NO_2.N** (mg/L)	**CO_2** (M)
1	51278c	21.50	56.56	10.25	2440	6.49	260	228	33.9	206	7.3	11	252	465	102.7	0.29	1.5	0.741	0.008	0.0026
2	51278d	21.50	56.55	4	3150	6.85	380	182	70.9	329	12.3	15	330	711	63.7	0.41	2.28	2.89	0.049	0.0015
3	51279d	10.17	56.57	4.02	3640	6.68	380	215	85.4	384	9	0	446	848	78.7	0.34	2.57	0.492	0.014	0.0029
4	51279c	10.17	56.57	10.07	2230	6.59	260	144	42.2	218	8.4	12	265	468	48.0	0.31	1.5	0.251	0.005	0.0022
5	51345c	5.03	56.57	10.34	2560	6.7	320	210	39.7	240	8.3	0	261	473	96.3	0.39	1.52	0.182	0.005	0.0017
6	51345d	5.03	56.60	3.78	2900	6.61	320	165	61.3	304	8.6	6	290	652	57.7	0.31	2.03	0.424	0.006	0.0023
7	51345b	5.03	56.58	21.84	2800	7.01	400	162	42.5	348	13.3	5	307	534	110.0	0.55	1.78	0	0.005	0.0010
8	51345a	5.03	56.63	36.52	4650	6.96	460	559	110	401	17.3	0	402	517	566.7	0.75	1.77	0.003	0.006	0.0013
9	51279b	10.17	56.58	21.4	3980	6.99	500	401	84.1	364	14.4	0	472	555	353.3	0.96	1.85	0	0.005	0.0015
10	51279a	10.17	56.64	36.5	4490	7.09	–	544	98.7	398	17.5	0	430	545	510.0	0.9	1.81	0	0.005	0.0010
11	51278b	21.50	56.57	21.1	4080	6.95	380	410	88.9	373	14.5	0	472	595	360.0	0.84	1.98	0	0.005	0.0016
12	51278a	21.50	56.69	36.5	4340	6.92	380	528	77.8	372	16	0	403	593	446.7	0.62	1.98	0.003	0.021	0.0014
13	51346d	-5.00	56.63	4.75	2450	6.46	260	109	51.2	284	6.5	16	234	572	33.2	0.28	1.78	0.466	0.006	0.0027
14	51346c	-5.00	56.60	9.9	2310	6.86	380	153	41.2	234	8.8	0	256	456	44.3	0.47	1.47	0.127	0.005	0.0012
15	51346b	-5.00	56.59	21.35	3940	6.95	500	386	90.2	371	13.8	0	559	517	353.3	0.85	1.71	0.103	0.005	0.0019
16	51346a	-5.00	56.57	36.55	4510	7.02	400	497	119	416	16.8	0	516	515	520.0	0.8	1.63	0	0.005	0.0015
Creek	–	0	–	–	–	–	–	180	77.8	340	8.9	0	319	842	37.7	0.3	2.68	0	0.005	–

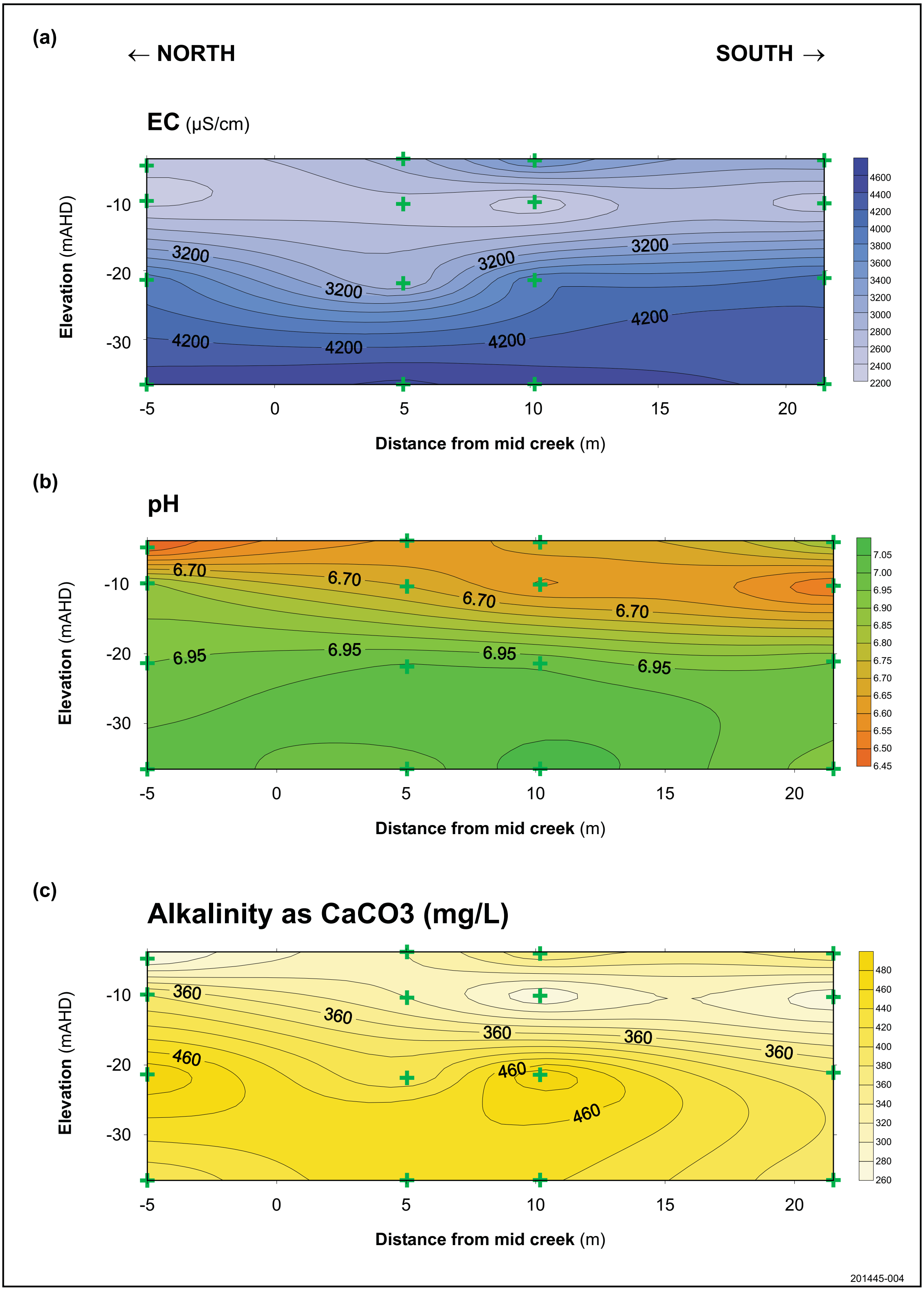


Figure 4a–c Profiles showing distribution of groundwater EC, pH and carbonate alkalinity at Site 1. X-axis is distance from mid creek (m) and y-axis is depth below ground level (m). Sampling points are denoted by green crosses, and orientation is shown at the top of the page.

the eight deepest piezometers yielded the highest total S concentrations which, when expressed as SO_4^{2-}, are unusual for fresh groundwaters in this type of environment. When plotted on a graph of total dissolved solids concentration (TDS, assuming all S is SO_4^{2-}) versus EC, these seven most saline samples plot on a distinctly different linear trend compared to the fresher samples (Fig. 5). Therefore these samples must have a proportion of their S present as either H_2S, HS^- in addition to SO_4^{2-}, and thus the real TDS will be lower than that calculated assuming all S is SO_4^{2-}.

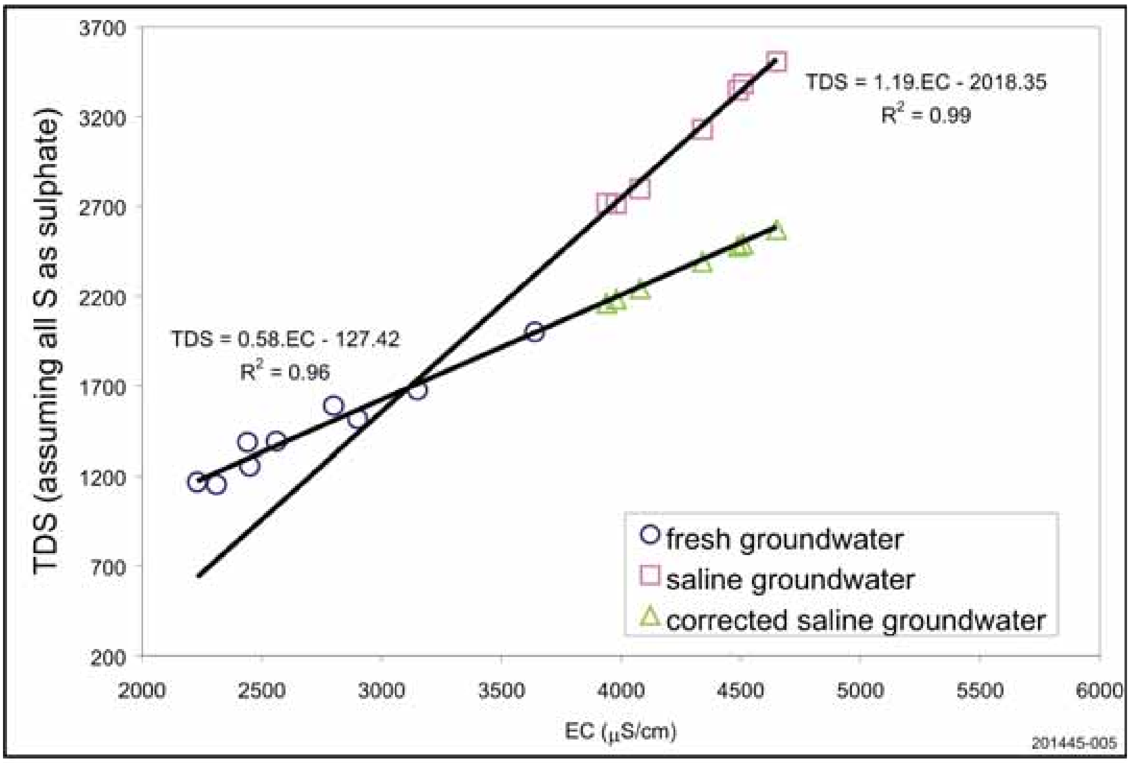


Figure 5 TDS (assuming all S is SO_4^{2-}) versus EC showing the seven most saline samples plot on a distinctly different linear trend compared to the fresher samples.

Analysis of groundwater samples for individual S species was not undertaken at the site nor in the laboratory. One method for estimating the speciation of S is via the use of computer-aided geochemical modelling software such as PHREEQC (Parkhurst, 1995). However, in the absence of reliable redox potential (Eh) data, this type of analysis can yield highly ambiguous results. Thus, a novel approach has been developed to estimate the proportions of SO_4^{2-} and 'other' dissolved inorganic S species in these groundwater samples. Firstly, it is assumed that all of the total inorganic S concentration occurs as either SO_4^{2-} or H_2S (any HS^- or S^{2-} is considered as H_2S due to their very similar molecular masses). Accordingly:

$$[S]=\frac{32}{96}\left[SO_4^{2-}\right]+\frac{32}{34}\left[H_2S\right] \tag{1}$$

Where: 32 = atomic weight of S
34 = molecular weight of H_2S
96 = molecular weight of SO_4^{2-}.

Rearranging (1) gives:

$$[H_2S] = \frac{34}{32}[S] - \frac{34}{96}[SO_4^{2-}] \tag{2}$$

Field EC values of the most saline samples are then used to estimate the TDS concentration for those samples using the linear regression equation calculated from the fresher samples (i.e. TDS = 0.58.EC – 127; Fig. 5). For TDS defined as:

$$TDS = \sum[cations] + \sum[anions] - \frac{1}{2}[HCO_3^-] + [H_2S] \tag{3}$$

Where $[H_2S]$ again includes $[HS^-]$ and $[S^{2-}]$, we obtain an expression for $[SO_4^{2-}]$:

$$[SO_4^{2-}] = TDS - \sum[cations] - \sum[anions\ other\ than\ SO_4^{2-}] + \frac{1}{2}[HCO_3^-] - [H_2S] \tag{4}$$

It should be noted that if TDS is defined as the sum of anions and cations (i.e. without removing half of the $[HCO_3^-]$ to enable comparison with TDS determined by drying) then the ½$[HCO_3^-]$ term in (3) and (4) should be omitted. Substituting the above expression for $[SO_4^{2-}]$ into equation (2) yields:

$$[H_2S] = \frac{102}{62}[S] - \frac{34}{62}\left(TDS - \sum[cations] - \sum[anions\ other\ than\ SO_4^{2-}] + \frac{1}{2}[HCO_3^-]\right) \tag{5}$$

Therefore, using TDS concentrations estimated from field EC values, and measured cation, anion and total S concentrations, the $[H_2S]$ of a particular groundwater sample can be estimated with equation (4). Once obtained, this value can then be substituted into equation (1) to provide $[SO_4^{2-}]$.

Estimates of TDS, H_2S and SO_4^{2-} concentrations for groundwater samples obtained from the current study are presented in Table 2. Due to the inherent design of the above approach for estimating concentrations of various S species, groundwater samples which plot along the more 'normal' TDS versus EC trend (i.e. the relatively fresh samples, Fig. 5) will have no H_2S, and this is reflected in Table 2.

The range of major ion compositions measured in the groundwater samples, incorporating 'corrected' sulphate concentrations, is best illustrated in a Piper diagram (Fig. 6). Clearly there is a continuum of compositions from Ca–Cl dominated at the fresh (low TDS) end towards Na–Cl dominated in the most saline samples. Whether this trend is reflecting chemical evolution of groundwater by water–rock interaction or mixing between the two 'end-members' is unknown and will be investigated further below.

Stable hydrogen and oxygen isotopes in groundwater

Stable hydrogen and oxygen isotope compositions of water samples are generally expressed in delta (δ) notation relative to the standard V-SMOW (Vienna Standard Mean Ocean Water):

$$\delta(‰, VSMOW) = \frac{R_{SAMPLE} - R_{VSMOW}}{R_{VSMOW}} \times 1000 \tag{6}$$

Where: R_{SAMPLE} is the isotopic ratio ($^2H/^1H$ or $^{18}O/^{16}O$) of the sample R_{VSMOW} is the isotopic ratio of the standard.

Table 2. TDS concentration corrected using field EC values, and estimated H2S and SO4 concentrations (mg/L).

Sample	Corrected TDS	H_2S	SO_4
1	1385	0	308
2	1676	0	191
3	2000	0	236
4	1169	0	144
5	1391	0	289
6	1515	0	173
7	1588	0	330
8	2570	513	252
9	2181	292	235
10	2477	478	181
11	2239	306	216
12	2390	405	197
13	1255	0	100
14	1154	0	133
15	2158	307	194
16	2489	490	177

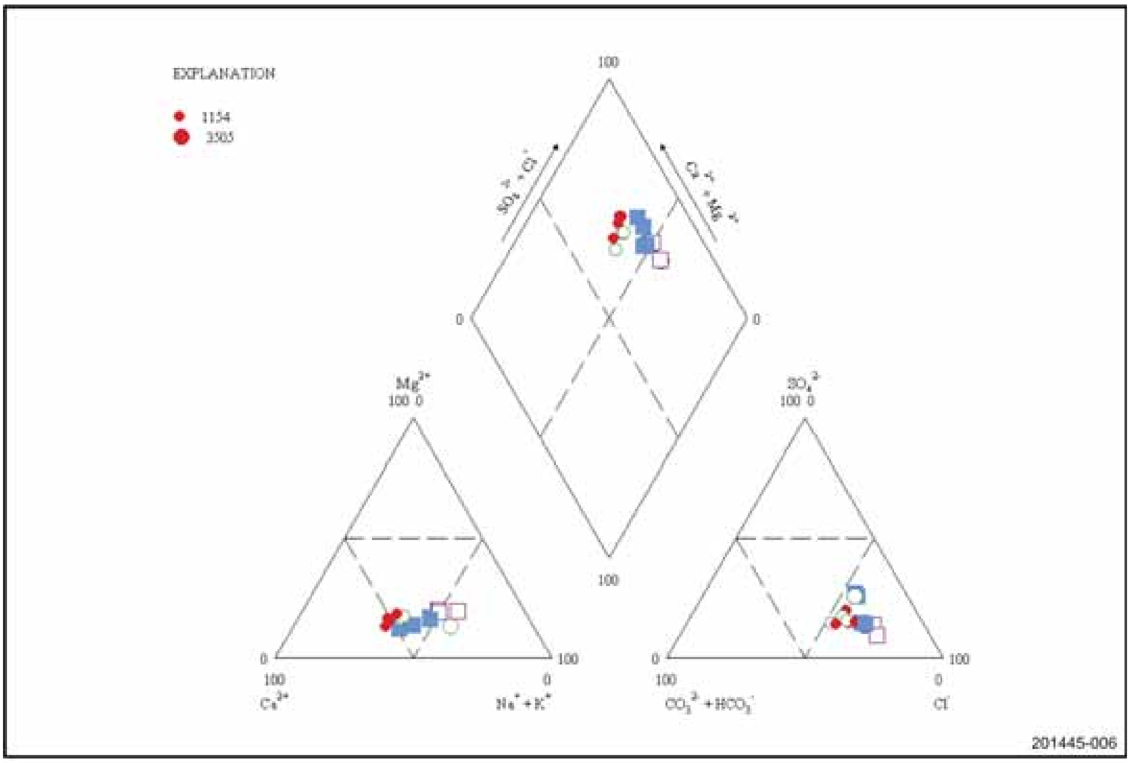


Figure 6 Piper diagram illustrating evolutionary trend of Site 1 groundwater compositions from Ca–Cl dominated to Na–Cl dominated as salinity (TDS concentration) increases. Different symbols correspond to individual aquifers and symbol size is proportional to TDS concentration.

Compositions of groundwater samples from the piezometers at Site 1 range between –29.9 and –25.2 ‰ for δ^2H and between –5.86 and –4.29 ‰ for δ^{18}O (Table 3).

Although no rainfall samples have been collected from the site for stable isotope analysis, an historical record of monthly rainfall compositions is available for Adelaide between 1962 and 1986, when the International Atomic Energy Agency had a global network of isotopes in precipitation (GNIP) recording station located in the city (IAEA/WMO, 2001). This rainfall data is plotted, together with the groundwater data from Site 1, on a conventional δ^2H-δ^{18}O plot (Fig. 7) and defines a local meteoric water line (LMWL):

$$LMWL : \delta^2 H = 7.25 \times \delta^{18} O + 7.89 \tag{7}$$

Figure 7 also shows the amount-weighted, annual mean composition of Adelaide rainfall (–24.13 and –4.47 ‰ for δ^2H and δ^{18}O respectively), which is slightly more enriched in the heavier isotopes than all of the groundwater samples.

Chlorofluorocarbons

Chlorofluorocarbon (CFC-11 and CFC-12) concentrations and implied recharge dates of groundwater samples are presented in Table 3. Most of the samples yielded recharge dates of between 1967 and 1980, however five of the samples returned dates <1965, which implies they could be any age in excess of 36 years. Whether their ages are still of the order 10 years or greater (i.e. 10^2–10^4 years) cannot be determined from the CFC concentrations, however radiocarbon data may be able to provide some insight to this.

Table 3. Stable isotope, CFC and radiocarbon compositions of groundwater samples

Sample	Well permit no.	δ^{18}O (‰, VSMOW)	δ^2H (‰, VSMOW)	CFC-11 (pg/kg)	CFC-12 (pg/kg)	CFC-12 date (y)	δ^{13}C (‰, PDB)	^{14}C (pmC)
1	51278c	-5.27	-25.9	<25	39	1966	-13.6	63.7
2	51278d	-4.55	-25.8	148	130	1977	-12.7	92.8
3	51279d	-4.69	-26.3	–	–	–	-14.6	92.5
4	51279c	-5.24	-27.8	<25	<25	<1965	-12.7	47.1
5	51345c	-4.88	-28.1	<25	66	1970	-12.6	45.4
6	51345d	-4.29	-25.2	<25	74	1972	-14.5	83.4
7	51345b	-4.92	-29.1	<30	94	1974	-12.3	5.2
8	51345a	-5.06	-28.5	<25	28	<1965	-13.9	12.8
9	51279b	-5.11	-28.3	<25	84	1973	-12.6	9.1
10	51279a	-5.1	-28.8	<25	45	1967	-15.4	12.6
11	51278b	-5.06	-28.7	<25	45	1967	-13.5	8.2
12	51278a	-5.51	-26.8	<25	<30	<1965	-14.9	13.9
13	51346d	-5.03	-27.6	<25	<25	<1965	-16	77
14	51346c	-5.86	-29.9	<25	<20	<1965	-11.6	>30
15	51346b	-5.29	-29.4	<25	147	1980	-14.7	9.8
16	51346a	-4.93	-27.3	181	154	1980	-16.1	17.9

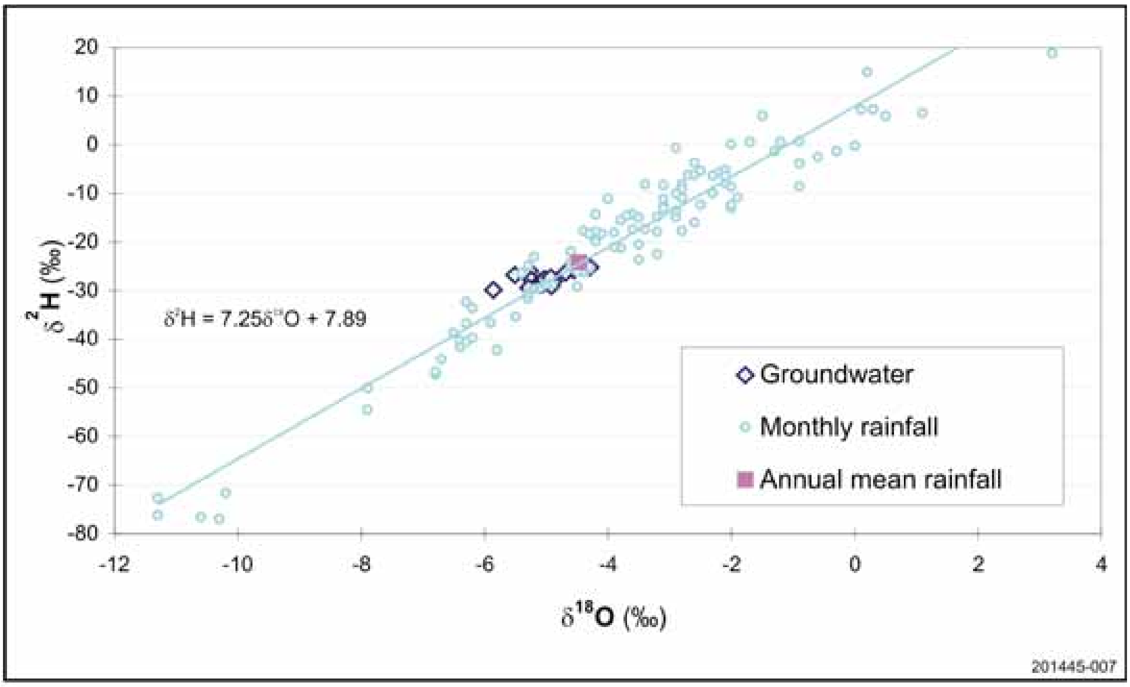


Figure 7 Stable isotope compositions of Adelaide monthly rainfall (IAEA/WMO, 2001) and groundwater from Site 1. The rainfall data produce a LMWL with slope 7.25 and deuterium excess 7.89.

Carbon isotopes

Stable carbon isotope compositions of the dissolved inorganic carbon (DIC) in groundwater samples is presented in δ-notation equation (6) in Table 3. Results range from –16 to –11.6 ‰ relative to the standard PDB (Pee Dee Belemnite Formation of South Carolina) and display a slight positive correlation with the reciprocal of DIC concentration (Fig. 8). This suggests that progressive addition of DIC to the groundwater may result in more depleted (i.e. more negative) δ^{13}C compositions.

Radiocarbon (^{14}C) concentrations of DIC in groundwater samples range between 5.2 and 92.8 pmC (Table 3), which equate to 'uncorrected' groundwater ages of between 0 and 24 000 years. However, the calcareous nature of the Quaternary aquifers at the site (Martin and Sereda, 2002) coupled with variations in major ion compositions (Fig. 6), DIC concentrations and stable carbon isotope data (Fig. 8) suggest that radiocarbon concentrations in these groundwaters have most likely been diluted by the addition of 'dead' carbon through water–rock interactions. Thus, the true ages of the groundwater may be much younger than the raw radiocarbon data suggests. Numerous models are available in the literature for correcting observed radiocarbon concentrations for water–rock interactions and these will be explored later.

Figure 9 shows the relationship between radiocarbon concentration and sampling depth below SWL. The ^{14}C concentrations decrease in an approximately exponential fashion with depth, indicating that groundwater becomes older with increasing depth.

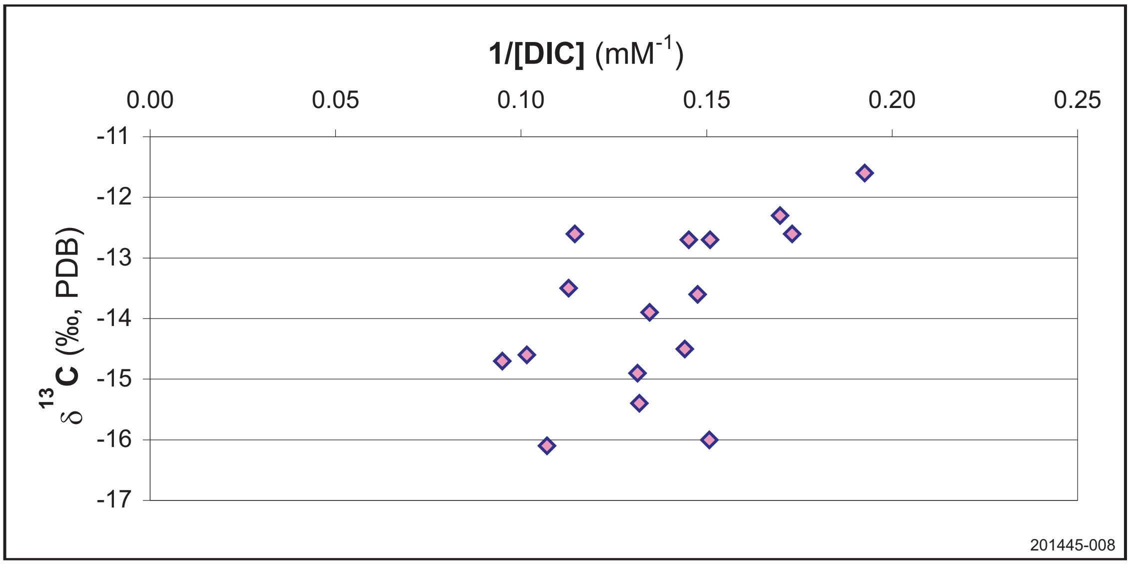


Figure 8 Relationship between the reciprocal of DIC concentration and stable carbon isotope composition of groundwater samples from Site 1. A slight positive trend in the data suggests that addition of DIC to the groundwater may result in more depleted δ^{13}C values.

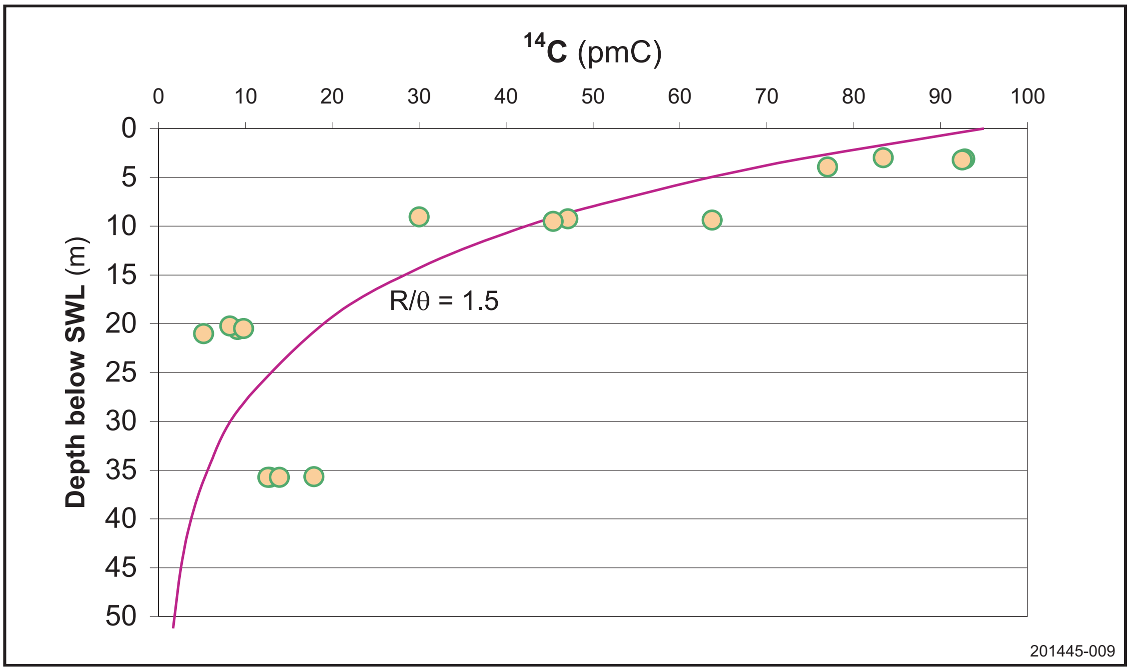


Figure 9 Radiocarbon (^{14}C) concentration versus sampling depth below SWL. The curved line was calculated assuming only vertical flow and uncorrected ^{14}C ages (i.e. $z = (R/\theta).(1/\lambda).\ln(^{14}C_0/^{14}C)$; where $^{14}C_0$ = 95 pmC).

DISCUSSION

Relationship between rainfall, creek flow and aquifer head

Borehole hydrographs constructed using water level logger data from selected piezometers at the site show rapid rises in groundwater level following high daily rainfall amounts (Fig. 10a). The hydrographs also mirror stream flow records from Pedler Creek for the same period; steep rises in groundwater level are virtually concurrent with high flow rates in the creek (Fig. 10b). These trends clearly demonstrate that active groundwater recharge occurs at the site following the intense rainfall – run-off events. However it is not possible to determine from this data whether the recharge occurs via widespread (diffuse) infiltration of rainwater or leakage from Pedler Creek.

Given that aquifer heads have rarely been lower than the base elevation of Pedler Creek over the last two years (Appendix), groundwater recharge via stream-bed infiltration cannot be considered as an annual event.

Groundwater recharge from Pedler Creek

The spatial distribution of groundwater salinity (as EC, Fig. 4a) suggests that a plume of relatively fresh groundwater is entering the watertable beneath or slightly to the north of Pedler Creek. Groundwater sampled from the shallow aquifer to the south of the creek and the deeper aquifers is more saline and may reflect a higher degree of evaporative concentration prior to recharge and/or a greater influence of water–rock interactions.

The groundwater chloride mass balance (CMB) method for estimating recharge rates was originally proposed by Eriksson and Khunakasem (1969), and has since been adopted in hundreds of studies around the world in a range of different environments. Essentially the method assumes that the only source of chloride in groundwater is via deposition in rainfall. Providing the rate of chloride accession to the landscape is constant, and that there are no sources nor sinks of chloride in the subsurface, the following steady-state mass balance equation can be used to estimate recharge:

$$P.C_P = R.C_R \tag{8}$$

Where: P = precipitation rate [$L \cdot T^{-1}$]
C_P = chloride concentration in precipitation [$M \cdot L^{-3}$]
R = recharge rate [$L \cdot T^{-1}$]
C_R = chloride concentration in recharge water [$M \cdot L^{-3}$].

Use of the CMB method to estimate recharge at the current study site is valid because there are no documented occurrences of any Cl-bearing minerals in the area. Recharge rates obtained using equation (8) range between 4.7 and 8.8 mm y^{-1} (P = 572 mm y^{-1}, C_P = 7 mg L^{-1} and C_R as groundwater Cl concentrations; Table 1). Highest rates are observed in samples collected from the second shallowest set of piezometers (i.e. at about 10 m below ground level), and the lowest rates are generally associated with the more saline groundwater to the south of Pedler Creek and in the deeper aquifers (Fig. 11).

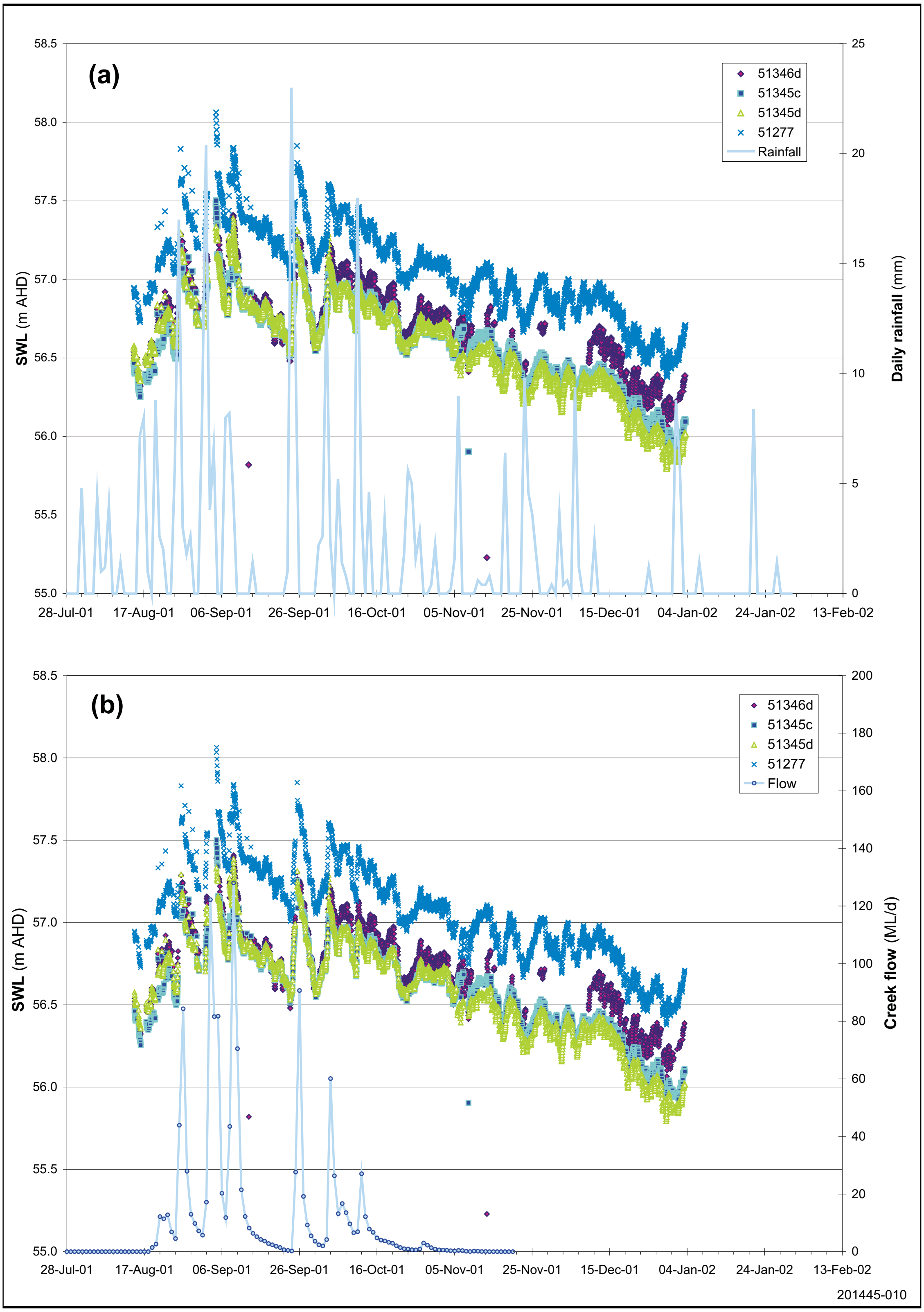


Figure 10 Response of groundwater levels to (a) rainfall events and (b) flow rate in Pedler Creek.

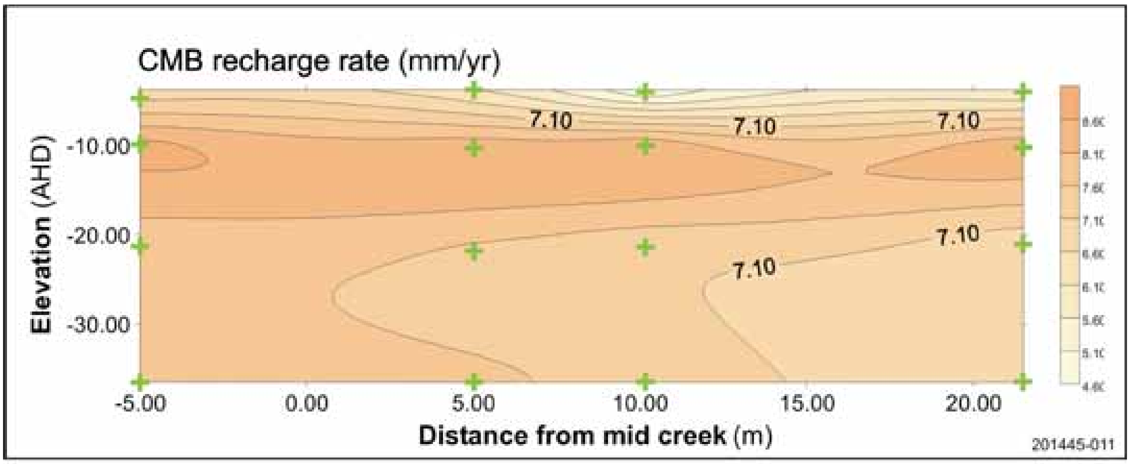


Figure 11 Distribution of recharge rates determined for individual groundwater samples using the steady-state, CMB approach.

The highest CMB recharge rates estimated for the site occur on the northern (left hand) side of the profile (Fig. 11), particularly in the second aquifer, which suggests that groundwater recharge from another source to the north may be as important as recharge from Pedler Creek.

Groundwater δ^2H and δ^{18}O compositions plot on or very close to the local meteoric water line for Adelaide, and are slightly depleted relative to the mean annual composition of rainfall (Fig. 7). This may reflect either recharge from only the large rainfall events (an ‘amount effect’) or recharge by predominantly winter rainfall. Support for the latter hypothesis can be observed in Figure 12 where the majority of groundwater δ^2H compositions correspond to weighted mean monthly rainfall compositions between April and July.

Deuterium excess (D-excess) provides a measure of the degree of isotopic enrichment that a water sample has undergone due to evaporation prior to recharge; and is defined by the following relationship:

$$D\text{-}excess = \delta^2 H - 8 \times \delta^{18} O \tag{9}$$

Where 8 represents the slope of the global meteoric water line (GMWL, Craig, 1961). The slope of the LMWL should be used instead of that of the GMWL, but due to their similarity for this site (i.e. 7.25 cf. 8) the latter has been used. The range of D-excess values determined for the current study range from 9.1 to 17.3 ‰ and, whilst difficult to interpret, exhibit distinct spatial variations in the profile (Fig. 13).

It should be stressed that all of the contour maps presented in this report could be different if an algorithm other than ‘kriging’ was used to produce the contours. Assuming the contour positions in Figure 13 are correct, then the lowest D-excess values (least evaporated groundwater) beneath the creek and down through the centre of the profile may be reflecting direct recharge from Pedler Creek.

The distribution of groundwater recharge dates, calculated using CFC-12 concentrations (Table 3), is plotted in Figure 14. Piezometers which returned recharge dates of <1965 were plotted in Figure 14 as 1965 to facilitate contouring, however these points may be much older. The most recent groundwater recharge is evident in the shallow aquifer to the south of the creek, and in the northern piezometers in the two deepest aquifers. Therefore, the most important recharge mechanism for the groundwater system, at least

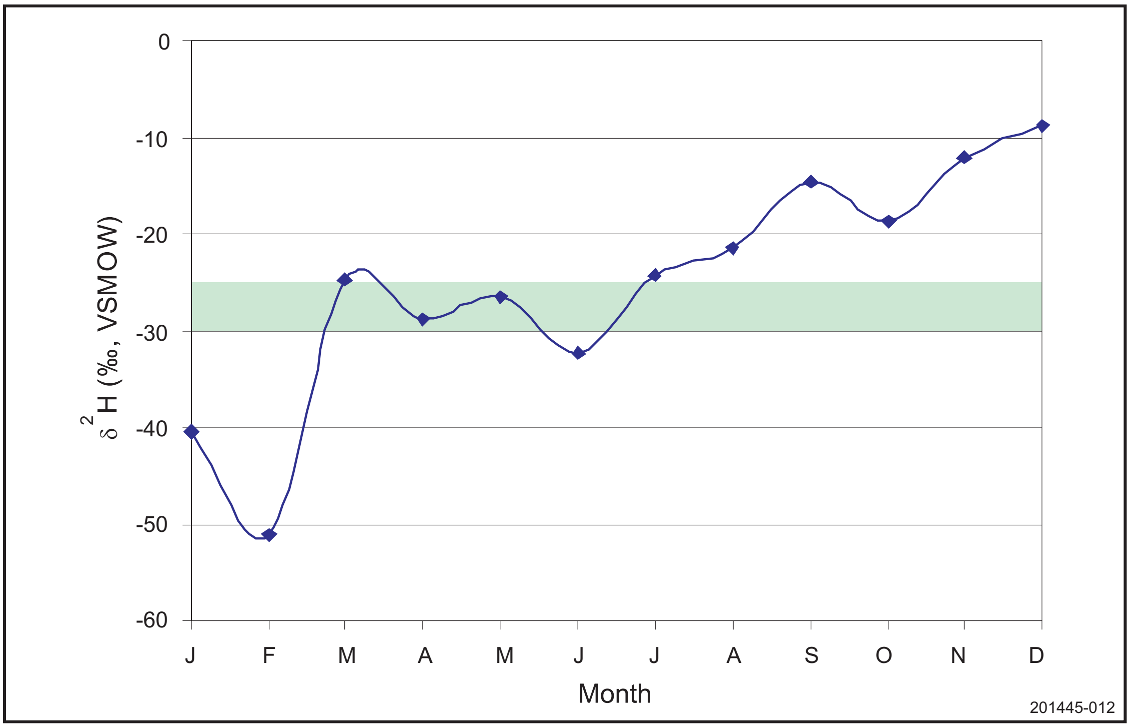


Figure 12 Mean δ^2H compositions of Adelaide monthly rainfall (series) and range of observed δ^2H compositions in groundwater at Site 1 (shaded band).

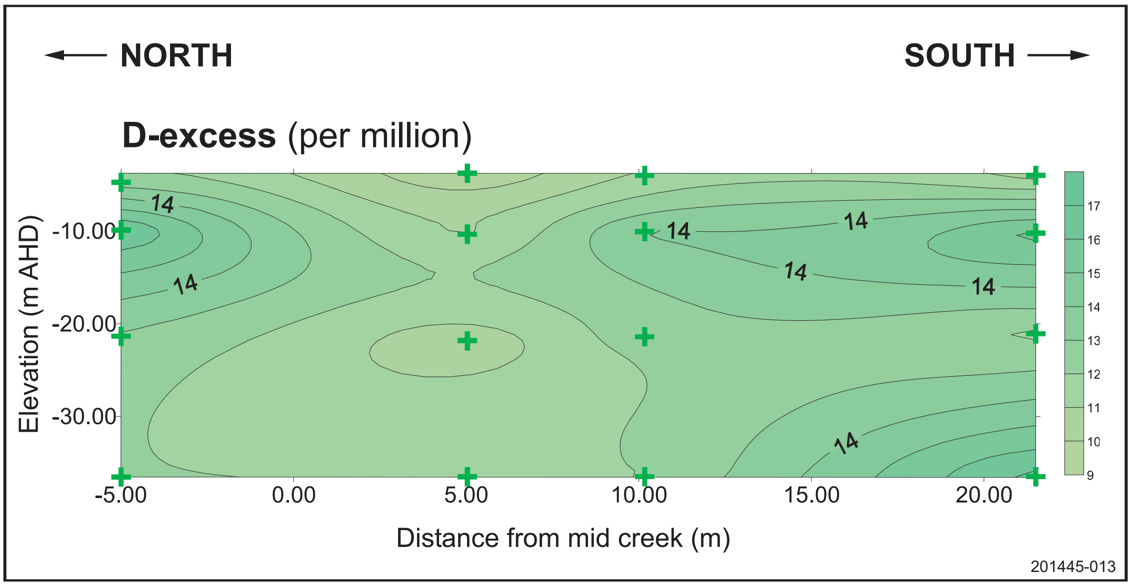


Figure 13 Profile of D- excess distribution at Site 1.

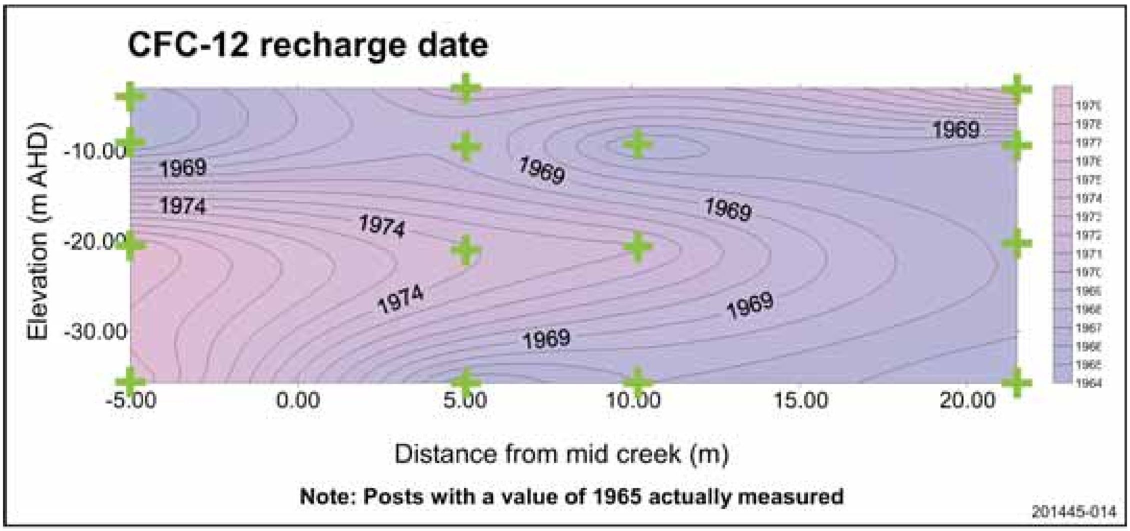


Figure 14 Groundwater recharge dates obtained from CFC-12 concentrations. Groundwater is youngest in the shallow aquifer to the south of the creek and in the deeper aquifers on the northern side of the profile.

over the time scale encapsulated within the groundwater ages, is likely to be a diffuse source to the north and south of the creek; albeit the distribution of EC, pH and D-excess indicates that some direct recharge occurs from Pedler Creek.

The apparent reversed age gradient (i.e. groundwater becoming younger with increasing depth) observed beneath the creek in Figure 14 is characteristic of a groundwater discharge zone. This finding supports the hydrograph data (Appendix) where aquifer heads are usually above the base elevation of the creek, thereby creating potential for discharge of groundwater. Therefore Pedler Creek is (for most of the time) a groundwater discharge feature which only serves to recharge the shallow aquifers when hydraulic heads permit after intense winter rain–runoff events.

Groundwater ages estimated from the raw (uncorrected) radiocarbon data (Table 4) are generally much older than the CFC-12 data suggests. Only those five samples which yielded recharge dates <1965 could possibly be in agreement with the ^{14}C ages. However, given that two-thirds of the groundwater samples from the site had CFC-12 ages <36 years, and the error associated with CFC-12 ages is much smaller than for ^{14}C ages, it is unlikely that any significantly older (i.e. >1000 years) groundwater exists at the site.

Therefore, the groundwater radiocarbon concentrations must have been diluted by addition of dead carbon through water–rock interactions. Fortunately there are many existing models in the literature for correcting groundwater ^{14}C data, and the most common of these are the chemical (Tamers, 1967) and isotope (Ingerson and Pearson, 1964) mass balance methods, and chemical mass balance with isotope exchange (Fontes and Garnier, 1979). When applied to the current study with appropriate chemical and stable carbon isotope data, these models provide varying degrees of correction to the groundwater ages (Table 4). While each of the models does bring the ^{14}C age of some groundwater samples back to 0 years (with an uncertainly of ± 100 to 200 years), there are still several samples (e.g. 7, 9, 11, 15) where ^{14}C ages are >10 000 years and CFC-12 ages are <36 years. Thus, it appears that none of these models can adequately account for the water–rock interactions that have led to diluted radiocarbon concentrations in this groundwater system.

Table 4. Radiocarbon ages (y) of groundwater samples. Obtained using uncorrected data (initial ^{14}C = 95 pmC), CMB (Tamers, 1967), isotope mass balance (Ingerson and Pearson, 1964) and CMB with isotope exchange (Fontes and Garnier, 1979) models.

Sample	Uncorrected age	Tamers age	Ingerson and Pearson age	Fontes and Garnier age
1	2857	0	0	0
2	0	0	0	0
3	0	0	0	0
4	5353	2089	92	0
5	5657	2034	330	0
6	630	0	0	0
7	23570	19111	18044	17723
8	16124	11723	11609	11577
9	18944	14493	13617	13357
10	16254	11576	12586	12845
11	19805	15444	15049	14935
12	15442	11146	11501	11597
13	1290	0	0	0
14	9082	5011	3072	2442
15	18331	13973	14279	14362
16	13351	8818	10051	10362

Chemical evolution of groundwater

Groundwater compositions at the site tend to evolve from Ca–Cl type to Na–Cl type as salinity (TDS concentration) increases (Fig. 6). Figure 4a revealed that the freshest (lowest EC) groundwater exists immediately beneath the creek and in a downward arc away from the creek towards the south. The more saline groundwater was observed in shallow aquifers away from the creek and with increasing depth below ~10 m. Similar trends are observed between chloride (Cl^-) concentration and depth (Fig. 15a); lowest Cl concentration occurs at ~10 m corresponding to the freshwater plume, with relatively higher concentrations above and below that depth.

Major ion (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}) and bromide (Br^-) concentrations all increase with respect to Cl concentration as sampling depth increases (Fig. 15b–g). The chemical composition of Pedler Creek also forms an end-member to these trends, which is not surprising given that the groundwater was discharging into the creek at the time of sampling (Fig. 3). Plotting ion concentrations as molar ratios with respect to Cl enables the variable influence of evapotranspiration on each sample to be removed (providing Cl is conservative, which is a reasonable assumption in this environment). Thus, the observed increases in ionic ratios with depth must be reflecting addition of solutes by water–rock interactions. Interactions which may be important controls on the major ion composition of groundwater at the site include carbonate dissolution or precipitation,

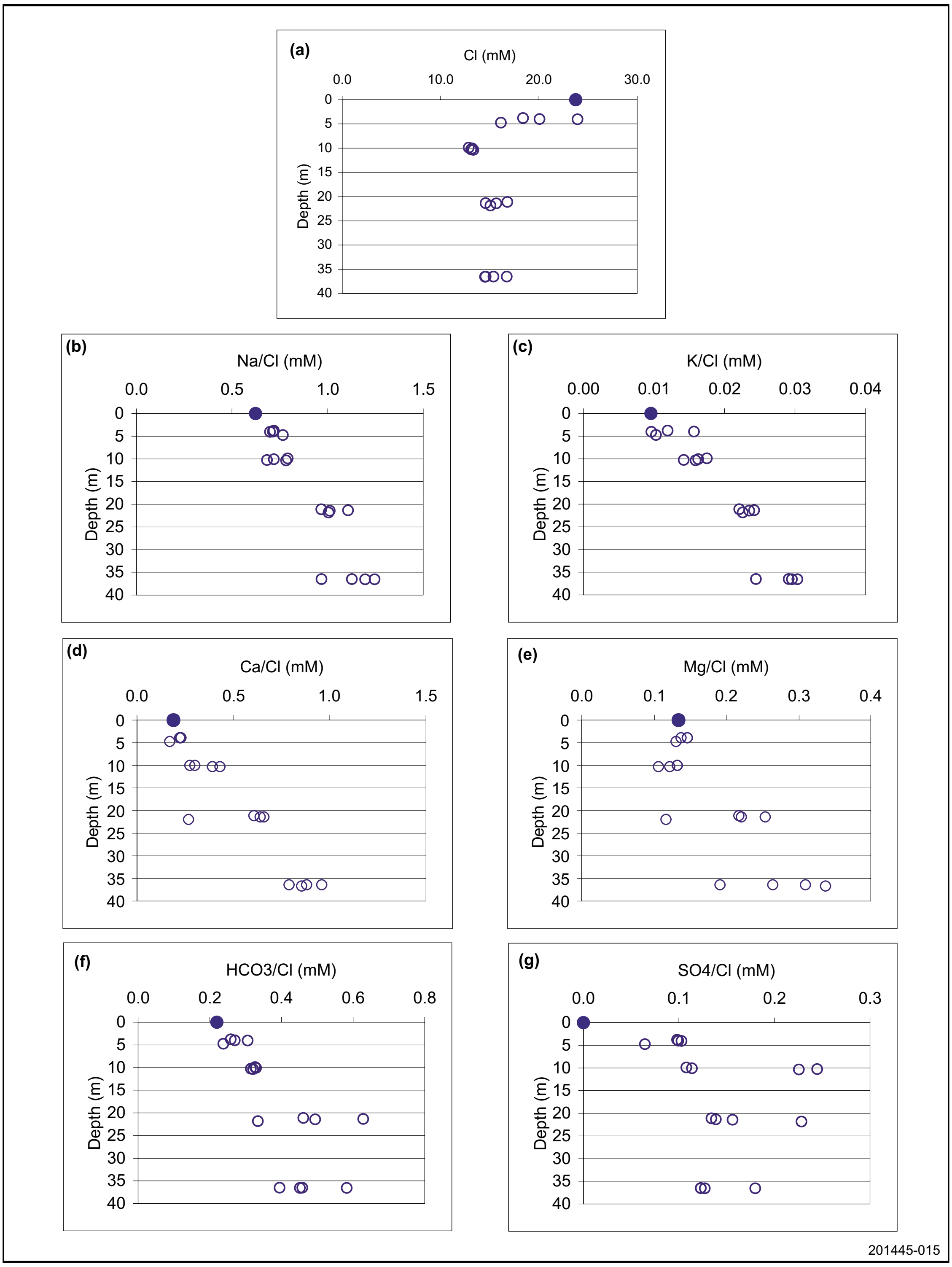


Figure 15a–g Chloride concentration and major ion/Cl mole ratios versus sampling depth. Blue dots represent creek water compositions.

cation exchange on clay minerals and silicate hydrolysis; with the first two being most likely given the aquifer mineralogy and groundwater residence times.

Ion/Cl ratios for Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} are all significantly higher than those observed in sea water and therefore rainfall of marine origin (Fig. 16a–f). The source of Ca^{2+}, Mg^{2+} and HCO_3^- ions is most likely dissolution of Mg-calcite minerals, because calcareous horizons have previously been identified in the soil zone and most parts of the aquifer (Martin and Sereda, 2002). Profiles of the saturation index (SI) of each groundwater sample with respect to calcite (Fig. 17b) and dolomite (Fig. 17c) support this hypothesis. The relatively fresh groundwater plume originating near the base of the creek is highly under-saturated with respect to both minerals. As groundwater–aquifer contact time increases, either as a result of increasing flow path length (deeper parts of the aquifer) or lower recharge rates (shallow aquifer to the south of the creek; Fig. 11), the SI increases to positive values indicating saturation with respect to both calcite and dolomite.

Progressive addition of Ca^{2+}, Mg^{2+} and HCO_3^- ions to groundwater through dissolution of marine-derived carbonate minerals should result in $\delta^{13}C$ compositions of DIC in groundwater tending towards the $\delta^{13}C$ of the carbonates (i.e. 0 ± 2 ‰; Salomons and Mook, 1980). However, the groundwater data plotted in Figure 8 exhibits a slight positive trend, which indicates that addition of DIC to the groundwater is actually decreasing the $\delta^{13}C$ value. This may reflect other chemical processes which have not been defined but can exert an important control on carbon geochemistry, isotope compositions and radiocarbon concentrations.

Elevated SO_4^{2-} concentrations are often attributed to dissolution of gypsum or anhydrite, however this mineral is rarely present in temperate environments such as the Willunga Basin. A more likely source is oxidation of reduced sulfur compounds, albeit such minerals were not identified during drilling. An alternative source (which the author is unaware if it has ever been explored) is inputs of sulfur beneath vineyards. Sulfur is commonly used to control fungal disease in grapevines, and therefore could be leached to the watertable following rainfall and/or irrigation. Groundwater entering the profile from the north between 15 and 35 m depth has a relatively high EC (Fig. 17a) and high SO_4^{2-}/Cl^- ratio (Fig. 15d). Application of sulfur to the vineyard located immediately north of the creek at this site, and subsequent leaching of oxidised sulfur compounds to the watertable following irrigation (with groundwater that already has a relatively high EC), could explain this part of the profile. Whilst all sulphate concentrations estimated for this study (Table 2) pose no threat to agricultural nor horticultural production, the complex sulfur speciation and geochemistry at the site warrants further investigation.

Na^+/Cl^- and K^+/Cl^- mole ratios of groundwater samples are all slightly above or below sea water ratios and therefore the ratios expected in rainfall of marine aerosol origin. These deviations are most likely the result of cation exchange of Na^+ and/or K^+ for Ca^{2+} and/or Mg^{2+} (or vice versa) on clay minerals.

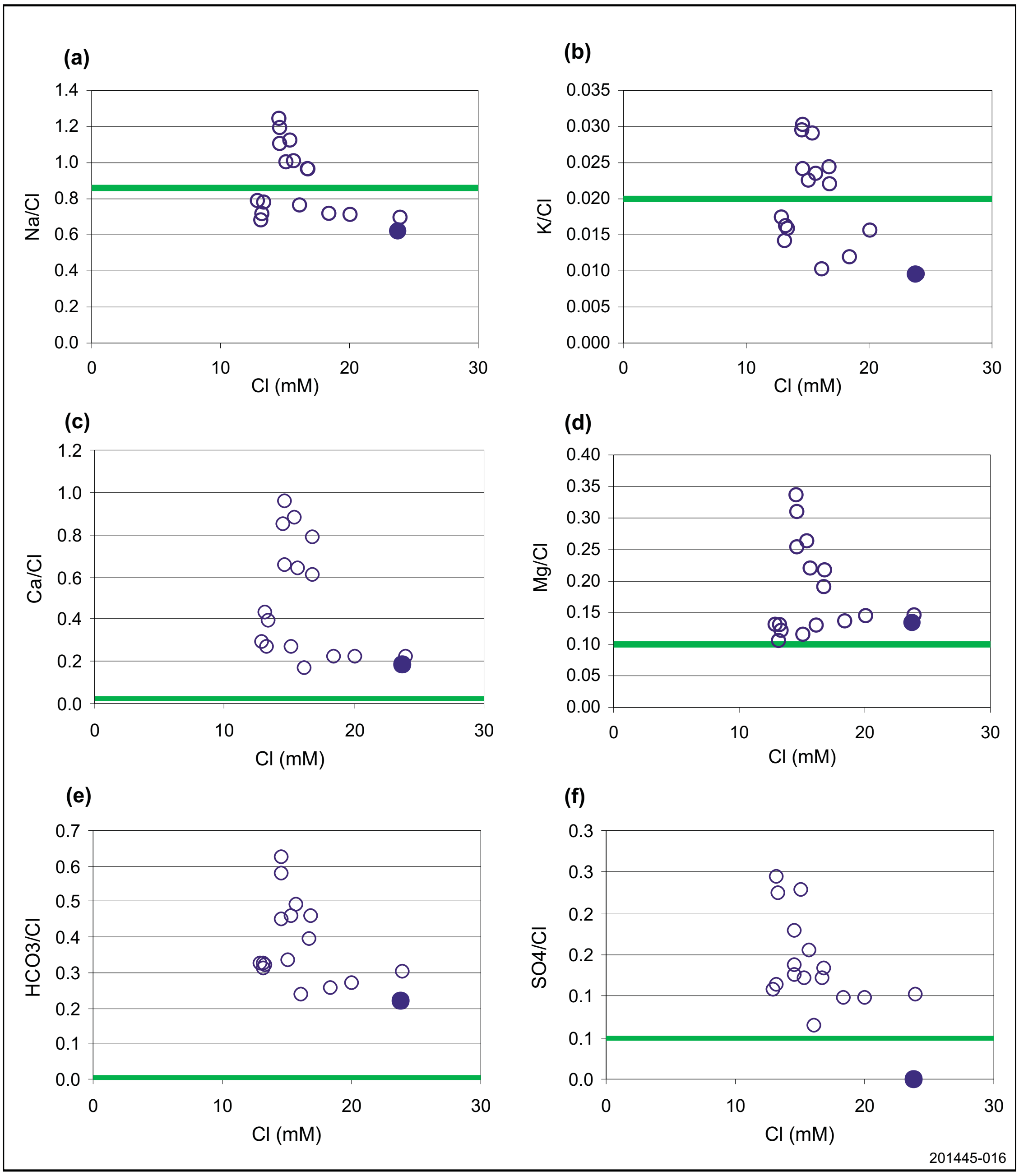


Figure 16a–f Groundwater major ion/Cl mole ratios versus chloride concentration. The green lines represent ion/Cl ratios of sea water and thus rainfall of marine origin. Calcium, magnesium, bicarbonate and sulfate concentrations are all significantly higher than would be expected from evaporated rainfall. Blue dots represent creek water compositions.

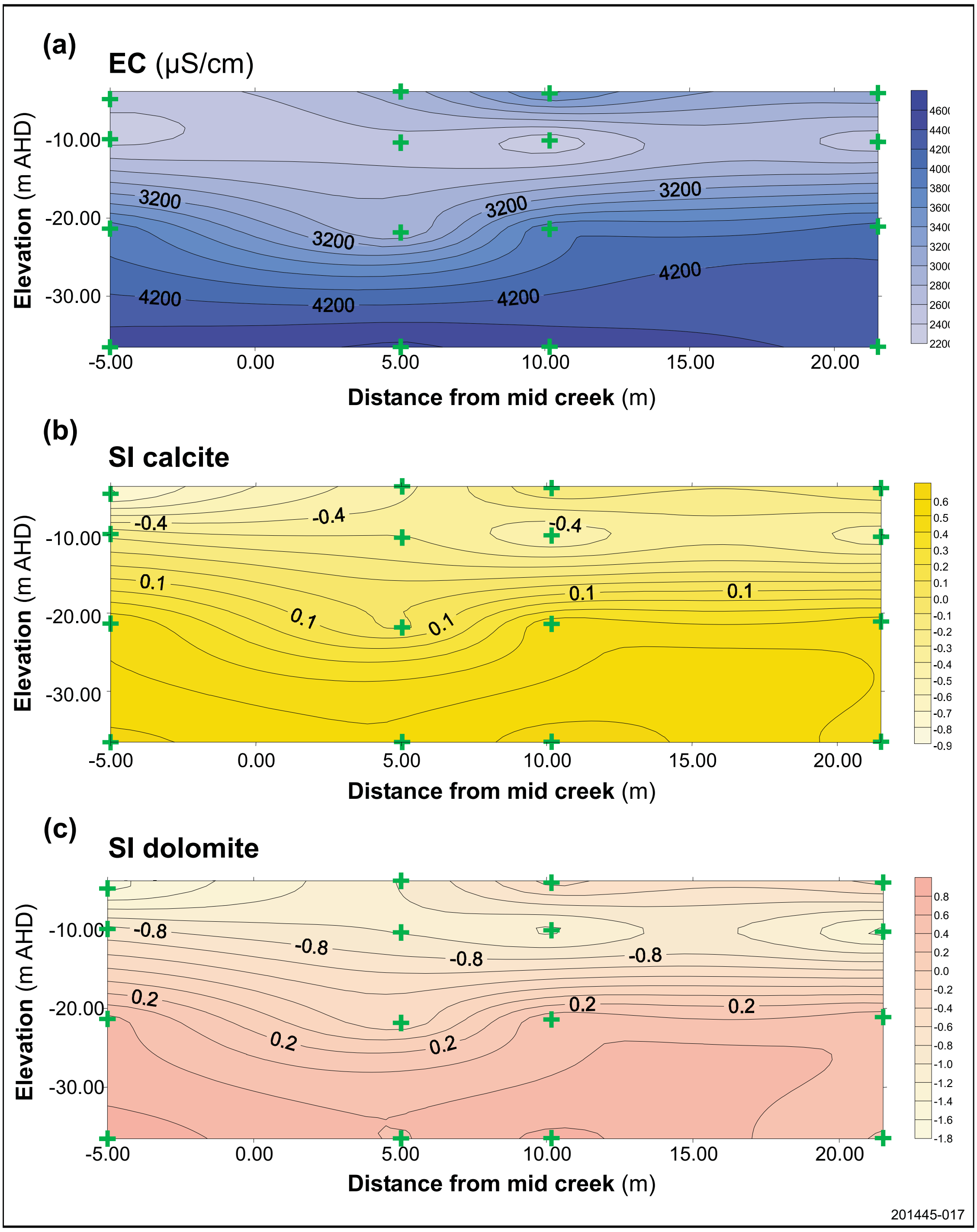


Figure 17 Groundwater EC distribution (as Fig. 4a) compared with saturation indices with respect to (b) calcite and (c) dolomite. Relatively fresh groundwater near the watertable is under-saturated with respect to both minerals, but the more saline groundwater at depth is over-saturated with respect to both.

SUMMARY OF STREAM–AQUIFER INTERACTIONS

The reach of Pedler Creek investigated in this study has a complex relationship with the underlying groundwater system. Hydraulic head records and groundwater age distributions indicate that the creek is most often a groundwater discharge feature, rather than a source of recharge. However, after large rainfall events in the winter months, the stage of the creek can exceed aquifer head elevations and thereby create potential for groundwater recharge via stream-bed infiltration. The occurrence of these events is supported by the existence of a plume of relatively fresh, lower pH groundwater originating near the creek and moving in a southerly direction. This fresh groundwater is Ca–Cl dominated and highly under-saturated with respect to both calcite and dolomite. With increasing residence time, groundwater that has been recharged either via stream-bed infiltration or a diffuse source to the north of the site begins to mix with the ambient groundwater and interact with the aquifer mineralogy. Primary water–rock reactions in the sub-surface include dissolution of carbonate minerals (Mg-calcite) and cation exchange.

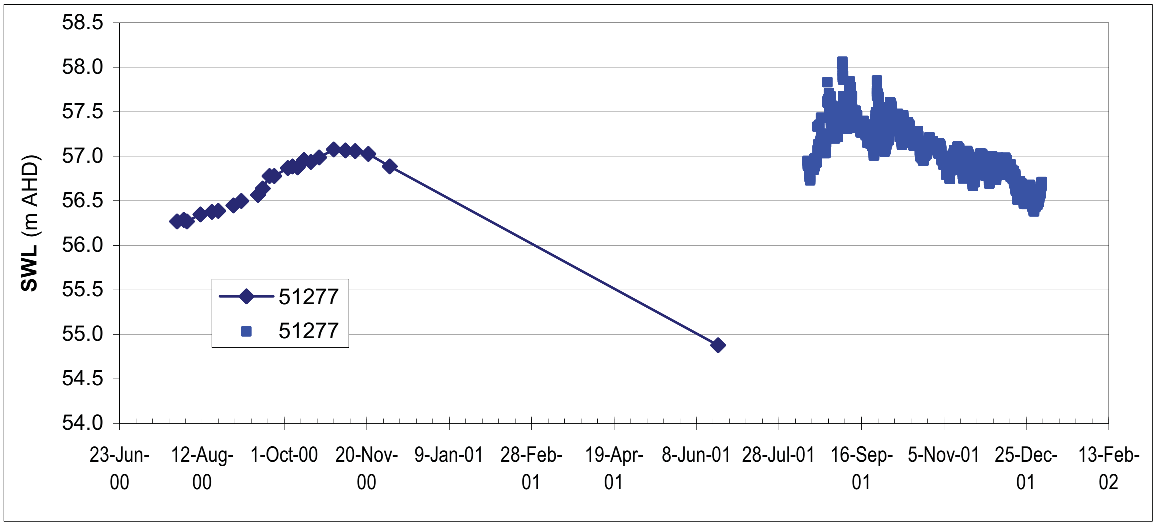
CONCLUDING REMARKS AND RECOMMENDATIONS

The principal aim of this project was to investigate the importance of stream-bed infiltration from Pedler Creek as a groundwater recharge mechanism. Whilst the results from Site 1 clearly indicate that the creek is more often a discharge feature than a source of recharge, the investigation has provided valuable insight to the complexity of stream–aquifer interactions (both physical and chemical) in this groundwater system.

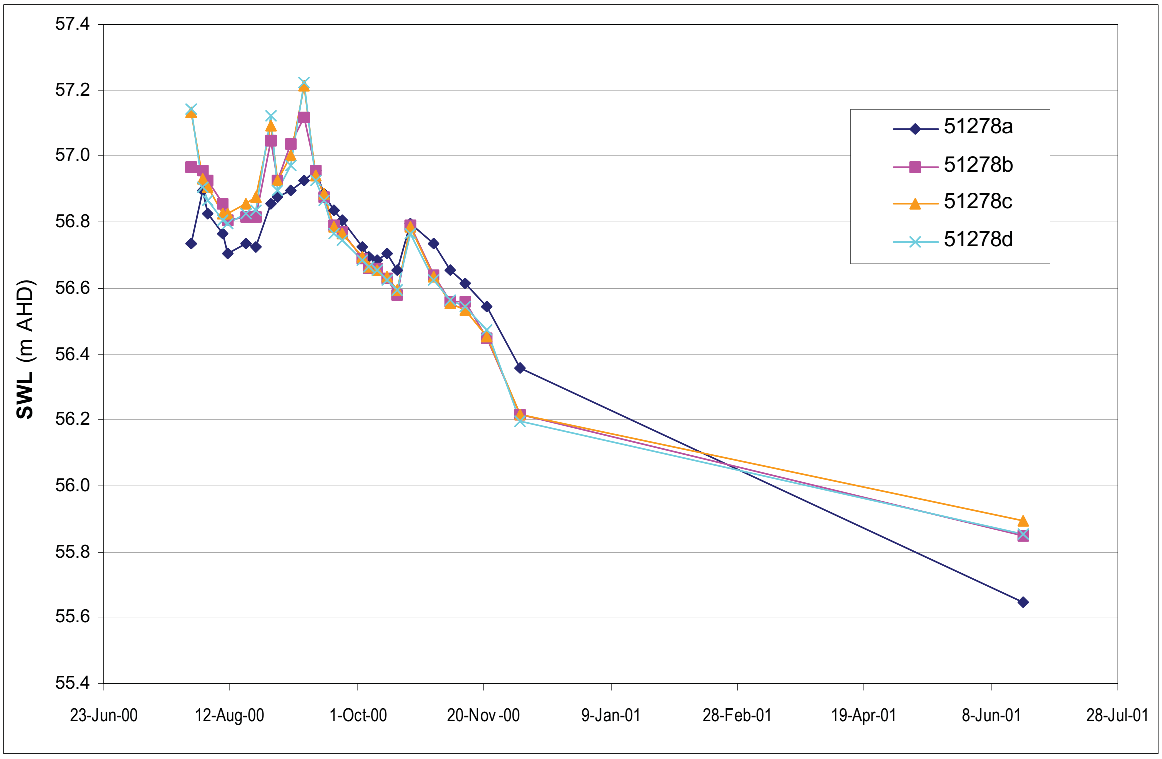
Site 2 has a different physiographic (and possibly hydrologic) setting and may therefore behave differently to Site 1. Therefore, it is proposed that selected chemical and isotopic samples be collected from Site 2 in the near future to investigate the stream–aquifer processes occurring at that site. Due to the range of groundwater ages identified at Site 1, it would not be necessary to sample groundwater for radiocarbon analysis at Site 2, thereby reducing analytical costs by almost 50%.

APPENDIX

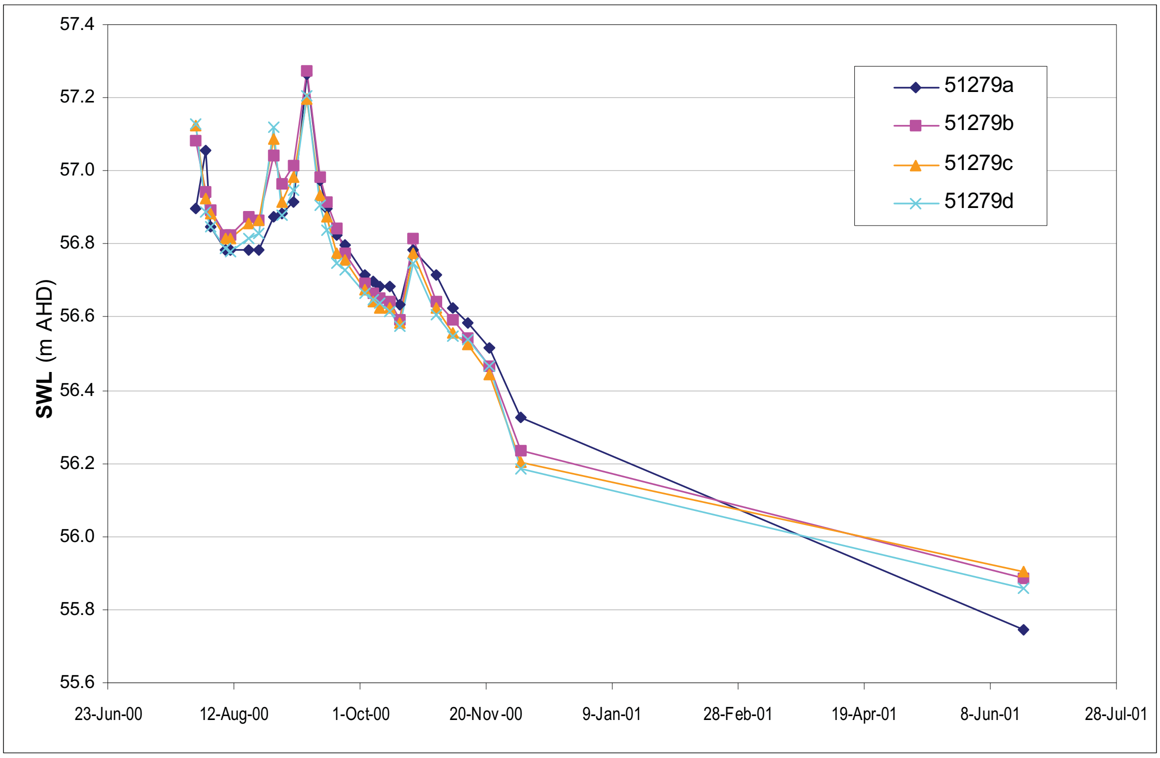
Hydrographs — well permit numbers 51277–51279, 51345 and 51346



Well hydrograph 51277

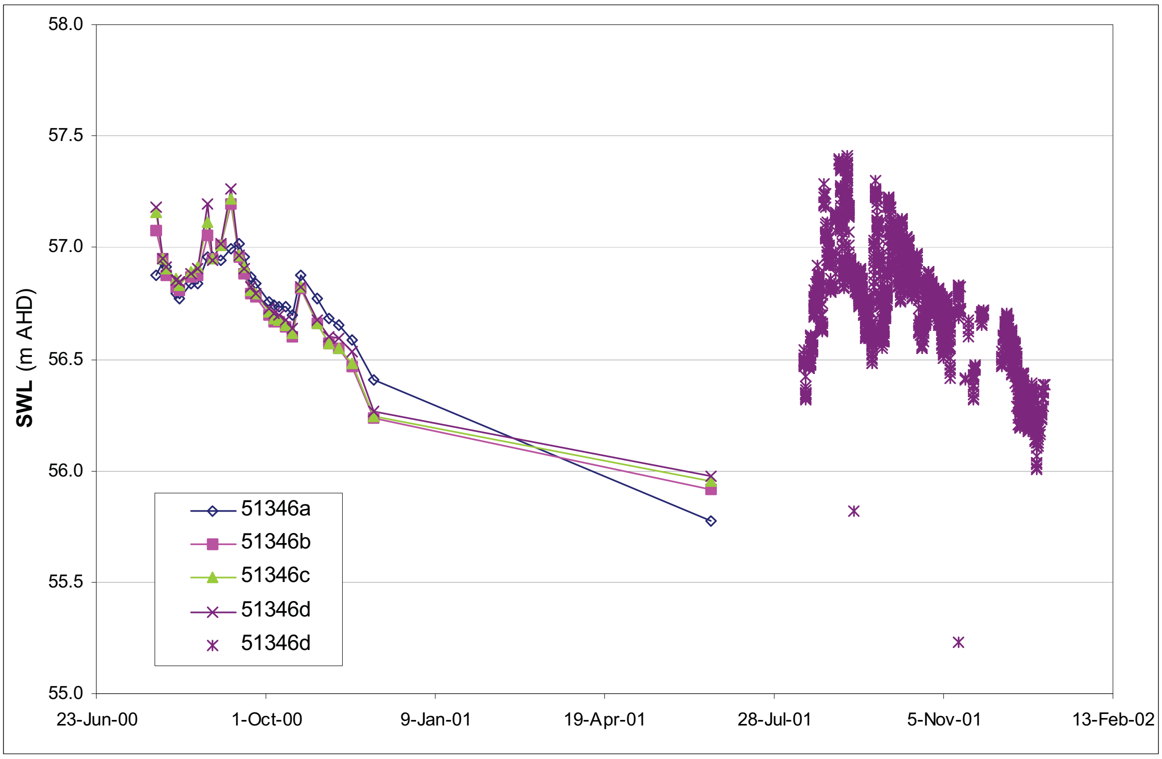


Well hydrograph 51278



Well hydrograph 51279

Well hydrograph 51345



Well hydrograph 51346

SHORTENED FORMS

Measurement

Most units of measurement used in this volume are those of the International System of Units (SI).

Name	Symbol	Expressed in terms of other SI units	Quantity
Centimetre	cm	10^{-2} m	Length
Day	d	86.4×10^{3} s	Time interval
Gram	g	10^{-3} kg	Mass
Kilogram	kg	Base unit	Mass
Litre	L	10^{-3} m^{3}	Volume
Megalitres	ML	10^{6} L	Volume
Metre	m	Base unit	Length
Microsiemens	µS	10^{-6}S	Electric conductance
Microsiemens per centimetre	µS/cm	—	—
Milligram	mg	10^{-6} kg	Mass
Milligrams per litre	mg/L	—	—
Millilitre	mL	10^{-6} m^{3}	Volume
Millimetre	mm	10^{-3} m	Length
Millimolar	mM	10^{-3} M	Concentration (amount of substance)
Molar	M	Mole per litre	Concentration (amount of substance)
Picogram	pg	10^{-12} g	Mass
Second	s	Base unit	Time interval
Seimens	S	Ampere per volt	Electric conductance

Species

Symbol	Name
Br	Bromine
C	Carbon
^{14}C	Carbon 14
Ca	Calcium
CO_2	Carbon dioxide
CO_3	Carbonate
Cl	Chloride
F	Fluoride
H	Hydrogen
HCO_3	Bicarbonate
H_2S	Hydrogen sulphide
K	Potassium
Mg	Magnesium

Na	Sodium
NO_3–N	Nitrate as N
O	Oxygen
S	Sulphur
SO_4	Sulphate

General

Shortened form	Description
λ	Radioactive decay constant
δ	Delta notation relative to a standard
θ	Porosity
‰	Parts per thousand
AHD	Australian height datum
CFC	Chloroflurocarbons
CMB	Chloride mass balance
C_0	Initial carbon-14 concentration
C_P	Chloride concentration in precipitation
C_R	Chloride concentration in recharge water
D-excess	Deuterium excess
DIC	Dissolved inorganic carbon
EC	Electrical conductivity
Eh	Redox potential
GMWL	Global meteoric water line
GNIP	Global network of isotopes in precipitation
IAEA	International Atomic Energy Agency
LMWL	Local meteoric water line
P	Precipitation rate
pH	Measure of acidity
PDB	Pee Dee Belemnite Formation of South Carolina
PHREEQC	A computer program for speciation, reaction-path, advective transport, and inverse geochemical calculations
pmC	Percent modern carbon
R	Recharge rate
SI	Saturation index
SWL	Standing water level
TDS	Total dissolved solids
V-SMOW	Vienna standard mean ocean water
WMO	World Meteorological Organisation
y	Year
z	Depth

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