Lower Balonne Airborne Geophysical Project

GROUNDWATER AGES, SOURCES OF SALT AND RECHARGE MECHANISMS IN THE LOWER BALONNE AREA, SOUTHERN QUEENSLAND, AUSTRALIA: ISOTOPE AND GEOCHEMICAL DATA

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This report is one of six CRCLEME Open File Reports contributing to the Lower Balonne Airborne Geophysical Project funded by the National Action Plan for Salinity and Water Quality. The project is providing new knowledge and developing methodologies for improved natural resource management in the Murray Darling Basin area of southern Queensland. This integrated project has a multidisciplinary team with skills in regolith geology, geomorphology, bedrock geology, hydrogeology, geophysics and soil science, working to understand the processes and controls on salinnity in a variable regolith terrain.

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SUMMARY

Groundwaters of the Lower Balonne region of south-western Queensland are of marginal to brackish quality with a dominantly seawater-like composition. Twenty four groundwater samples from the two main Cainozoic alluvial aquifers, upper alluvial (UA) and lower alluvial (LA), the middle confining bed (MCB) and the Cretaceous Griman Creek meta-sedimentary formation (GCF) were collected in August-September 2003 and analysed for major and minor ion chemistry as well as a suite of environmental isotopes.

Sodium and chloride ions make up >85% of the salt load in the groundwaters with SO_4^{2-}, Ca^{2+} and Mg^{2+} making up most of the remaining. Cl^-/Br^- mass ratios of the groundwaters are the same as seawater (270-290) indicating a marine origin for dissolved salts. The ratios are much less than that which would be derived from dissolution of halite or rock-forming minerals, which have Cl^-/Br^- >5,000; therefore marine aerosols deposition via rainfall is the dominant source of salt in all the main aquifers. The linear relationship between the dominant ions Na^+ and Cl^-, with a slope of 0.56 identical to seawater, indicates evapo-transpiration is responsible for concentration of the ions prior to recharge. Isotope ratios of $^{34}S/^{32}S$ from dissolved sulphate are slightly less then seawater indicating marine sulphate and organic sulphur are the sources of dissolved sulphate in these groundwaters, rather than from dissolution of reduced sulphur minerals such as pyrite.

Recharge rates based on chloride mass balance calculations and median groundwater chloride concentrations indicate median recharge rates of 0.1 mm/yr for the Griman Creek formation, 0.25 mm/yr for the UA and about 0.5 mm/yr for the MCB and LA. However, individual recharge estimates range from 0.05 mm/yr for the highly saline UA and GCF waters to 5 mm/yr for the fresh groundwaters in the UA and MCB.

Stable isotope compositions of the groundwaters ($\delta^{18}O$ and δ^2H) indicate a meteoric composition and form a trend to the right of the global meteoric water line on a $\delta^{18}O$ versus δ^2H plot with a slope of 5.8. This suggests that recharge is dominated by rainfall and evaporation has altered the isotopic composition prior to recharge.

Radiocarbon ages for the lower alluvial aquifer tend to be much older (>5,000 - >25,000 years) than the upper alluvial aquifer (<2,500 year) suggesting that vertical leakage occurs at a very slow rate. There is no apparent trend in ages of the lower alluvial aquifer from the NE to SW part of the study area. Fresh, relatively young (<50 years) groundwater may be restricted to near the rivers suggesting flood recharge is limited in lateral extent via surface tributaries, but further work would be required to confirm this. There is evidence for vertical exchange of the groundwaters amongst the various aquifer systems (indicated by chemistry and stable isotope data) but this occurs on time scale of 10^3 to 10^4 years as indicated by 'old' ^{14}C groundwater ages at depths >20 m below the water table.

1.   INTRODUCTION

1.1   Scope

Increasing irrigation using surface water diversions and groundwater has raised some concerns for the possibility of land salinisation in the lower Balonne area near St. George-Dirranbandi, south western Qld. Although the water table is presently >20 m below the surface throughout most of the area, the low hydraulic gradient and variable hydraulic properties may limit to the rate of removal of the added water and salt outside the study area.

Predicting response times and extent of salinisation as a result of increasing irrigation, and potential for displacement of saline groundwater requires a robust groundwater conceptual model. This report presents geochemical and isotopic information in an attempt to evaluate a conceptual hydrogeological model developed by Pearce et al. (2004) and complements the data from pore fluids (Coram, 2004) and ^{36}Cl data (Cresswell, 2004). This report also presents ^{14}C data to determine groundwater ages and residence times of the various groundwater aquifer systems in this region. The groundwater conceptual model presented by Pearce et al. (2004) suggests that groundwater flows in general from a NE to SW direction and that the series of aquifers Upper Alluvial (UA), Middle Confining Bed (MCB), and Lower Alluvial (LA) behave as a single inter-connected aquifer. The model is based primarily on hydraulic head data, major element chemistry collected from the observation bore network, and lateral interpolation of bore logs. Because hydraulic gradients are very low, there will be some uncertainty on inferred flow systems and flow rates, further investigation using environmental tracers was conducted to evaluate and validate the model. Long-term recharge rates and integration of flow dynamics that can be inferred from groundwater chemistry and isotopes can add substantially to the robustness of a conceptual model built from basic hydrogeological principles.

The objectives of this study are to address the following questions:

1. What is the extent of horizontal and vertical migration of saline groundwater to the less saline aquifers?

2. What are the lateral flow rates, and potential for lateral migration of highly saline groundwater?

3. What are the main sources of salt to the groundwater?

4. What is the relative importance of proposed recharge mechanisms to the groundwaters?

The study area is described in detail in Pearce et al. (2004), but in summary is has very low topography and a semi-arid climate with occasional flooding. Rainfall at St. George is 520 mm year, with 63% falling in the summer months (October – March). There is minor flooding of the Balonne River every 3-4 years, and major widespread flooding about every 10-12 years.

The region is underlain by a series of Cainozoic aquifers and aquitards which have been described in detail elsewhere (McAlister, 2001; Pearce et al. 2004) and which are mostly of marginal quality and not suitable for irrigation. The weathered equivalent of the Cretaceous meta-sedimentary Griman Creek formation outcrops in the western part of the study area. The weathered zone is of variable thickness but has very low yield and generally high salinity (Pearce et al. 2004).

1.2   Methodology

The approach taken here is complementary to both the conventional groundwater conceptual model, and the subsequent simple numerical model. Groundwater chemistry data (both salinity and chemical composition of the water) can provide qualitative and quantitative information on recharge rates. For example, rapid recharge (shorter contact time with soil and aquifer minerals) would be characterised by lower major ion concentrations. Long-term recharge rates (using chloride mass balance) can be used where surface runoff is low, provided that the input Cl^- concentration in rainfall can be estimated. The chemistry of groundwater end-members will be used to establish the extent of mixing, both laterally and vertically.

Stable isotopes of water are used to characterize groundwater end-members to estimate mixing between aquifers as well as evaluate recharge mechanisms (flood recharge vs. diffuse recharge). It is expected that waters that have infiltrated directly from the flood waters will be distinctly different in their $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios than that which infiltrates through the soil zone.

Groundwater dating is best done in this system using ^{14}C to estimate groundwater residence time and pre-clearing flow velocities (provided that suitable boreholes can be found along flow paths). We assume that the very low hydraulic gradients and consequent low horizontal groundwater flow velocities are commensurate with the ^{14}C time scale between 500-20,000 years.

Other environmental tracers (e.g., $\delta^{34}S$, $^{87}Sr/^{86}Sr$) may also be used to provide additional evidence for the extent of connectivity amongst the various aquifers if the major ions and stable isotopes of water are ambiguous. The latter in particular is distinctive of aquifers from different lithological units and behaves conservatively during the mixing process. Sources of salt may be traced using Br^-/Cl^- ratios as well as major ion compositions and possible $\delta^{34}S$ data. These can identify the extent of contribution from marine sources atmospheric aerosols, evaporite deposits or mineral weathering.

2.   SAMPLING AND ANALYTICAL METHODS

Twenty four groundwater samples were collected in August – September 2003 from 14 sites installed with up to 3 piezometers screened at various depths (Fig. 1 and 2). At least two standing volumes of water in the boreholes were pumped using a Grundfos MP1 pump. When the pH, temperature and EC were constant, water samples were collected in separate containers for the following chemical and isotopic parameters: major and minor ion chemistry (including Br^- and SiO_2), stable isotopes of water (δ^2H and $\delta^{18}O$), stable sulphur isotopes of dissolved sulphate ($\delta^{34}S_{SO4}$), stable carbon isotopes dissolved inorganic carbon ($\delta^{13}C_{DIC}$), strontium isotopes of dissolved Sr^{2+} ($^{87}Sr/^{86}Sr$), and the radioisotopes carbon-14 on dissolved inorganic carbon ($^{14}C_{DIC}$) and radon-222 (^{222}Rn).

The chemical analyses were done at the CSIRO Analytical Laboratories at CSIRO Land and Water, Urrbrae using standard Inductively Coupled Plasma-Optical Emission Spectroscopy and Ion Chromatography techniques for all species, except alkalinity which was analysed by potentiometric titration. All isotopic analyses, except $^{87}Sr/^{86}Sr$, were carried out at the CSIRO Land and Water Laboratories, Urrbrae. Stable isotopes of water (δ^2H and $\delta^{18}O$) were analysed using a water equilibration system (WES) coupled to a PDZ Europa Geo 20-20 mass spectrometer and are reported relative to the international standard Vienna-Standard Mean Ocean Water (V-SMOW). Sulphur isotopes on dissolved sulphate ($\delta^{34}S_{SO4}$) are analysed by precipitation of $BaSO_4$ and analysis by continuous flow mass spectrometry and results reported relative to the international Vienna-Canon Diablo Troilite (VCDT) standard. ^{222}Rn

was determined by liquid scintillation counting of 14 ml of water by alpha/beta separation on an LKB Quantulus low level liquid scintillation counter.

Eighteen of the ^{14}C samples were precipitated as $BaCO_3$ in the field and the precipitated $BaCO_3$ subsequently converted to CO_2 and determined for ^{14}C activity by liquid scintillation counting using the direct absorption method (Leaney et al., 1994). δ^{13}C composition was measured on an aliquot of CO_2 produced from the ^{14}C $BaCO_3$ sample using a PDZ Europa Geo 20-20 mass spectrometer. Six of the radiocarbon samples were sent to the Rafter Radiocarbon Laboratories, GNS, Lower Hutt, New Zealand, for analysis by accelerator mass spectrometry (AMS) due to insufficient DIC for analysis by the direct absorption method. ^{87}Sr/^{86}Sr on dissolved strontium were analysed at CSIRO Petroleum Resources, North Ryde using Thermal Ionisation Mass Spectrometry.

3. RESULTS AND DISCUSSION

Twenty four groundwater samples from a range of nested sites were sampled for a suite of environmental isotopes as well as full chemistry. The chemistry data here supplements the 78 chemistry samples that are reported by Pearce et al. (2004). The samples were collected on a NE-SW trending axis roughly parallel to the Lower Balonne river (Figs. 1 and 2) and are in or surrounding the area flown for airborne geophysics as part of the Lower Balonne NAPSWQ salinity investigation.

Figure 1. Location map of study area boreholes sampled for geochemistry and environmental isotopes shown with respect to NAPSWQ airborne geophysics area.

3.1 Groundwater chemistry

The data collected here are given in Tables A1-A3 at the back of this report, and some of the following interpretation also includes data from Pearce et al. (2004). Salinity of the groundwaters range from very fresh to seawater salinity (EC values range from 580 to 57 000 μS/cm). The freshest groundwaters (<1,000 μS/cm) tend to be located in the upper alluvial aquifer and are near to the Lower Balonne river, or adjacent to an irrigation area. The more saline waters tend to be from the upper aquifer, with waters collected from >50 m below ground typically <12,000 mg/L. The groundwaters from the Griman Creek Formation are relatively saline, typically 20 000 to 35 000 μS/cm.

The relationship between major ions versus chloride given by Pearce et al. (2004 – Fig. 63 in that report) shows linear correlations between most major ions and chloride (with the exception of HCO_3^-). Data from this study show similar relationships (see example using Na^+ and Cl^- in Fig. 3) and plot on a line similar that of seawater dilution except for slight chloride enrichment for the most saline waters. The linear relationship across all aquifers and formations indicate that similar processes in the entire aquifer system are responsible for the salinity distributions amongst them. Evapo-transpiration of a single source (namely marine aerosols) is the primary source of dissolved salts in the Lower Balonne groundwaters, including the GCF.
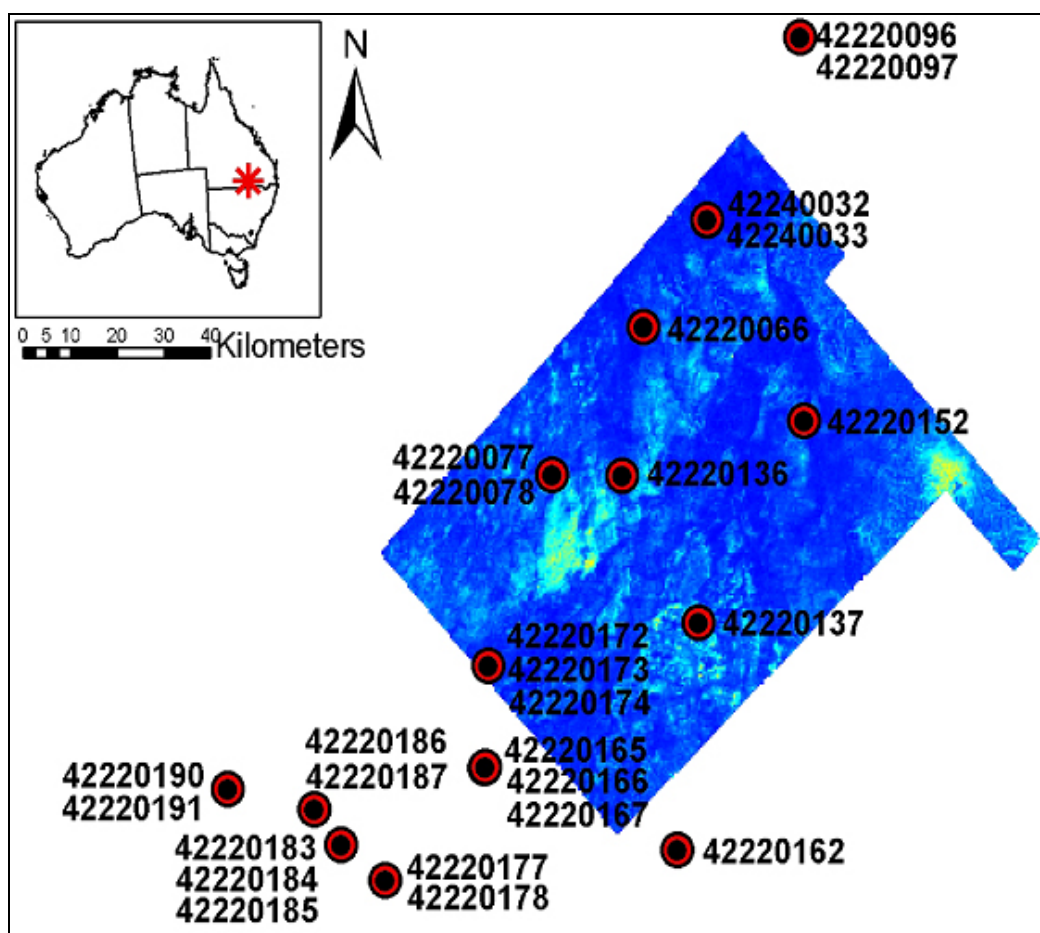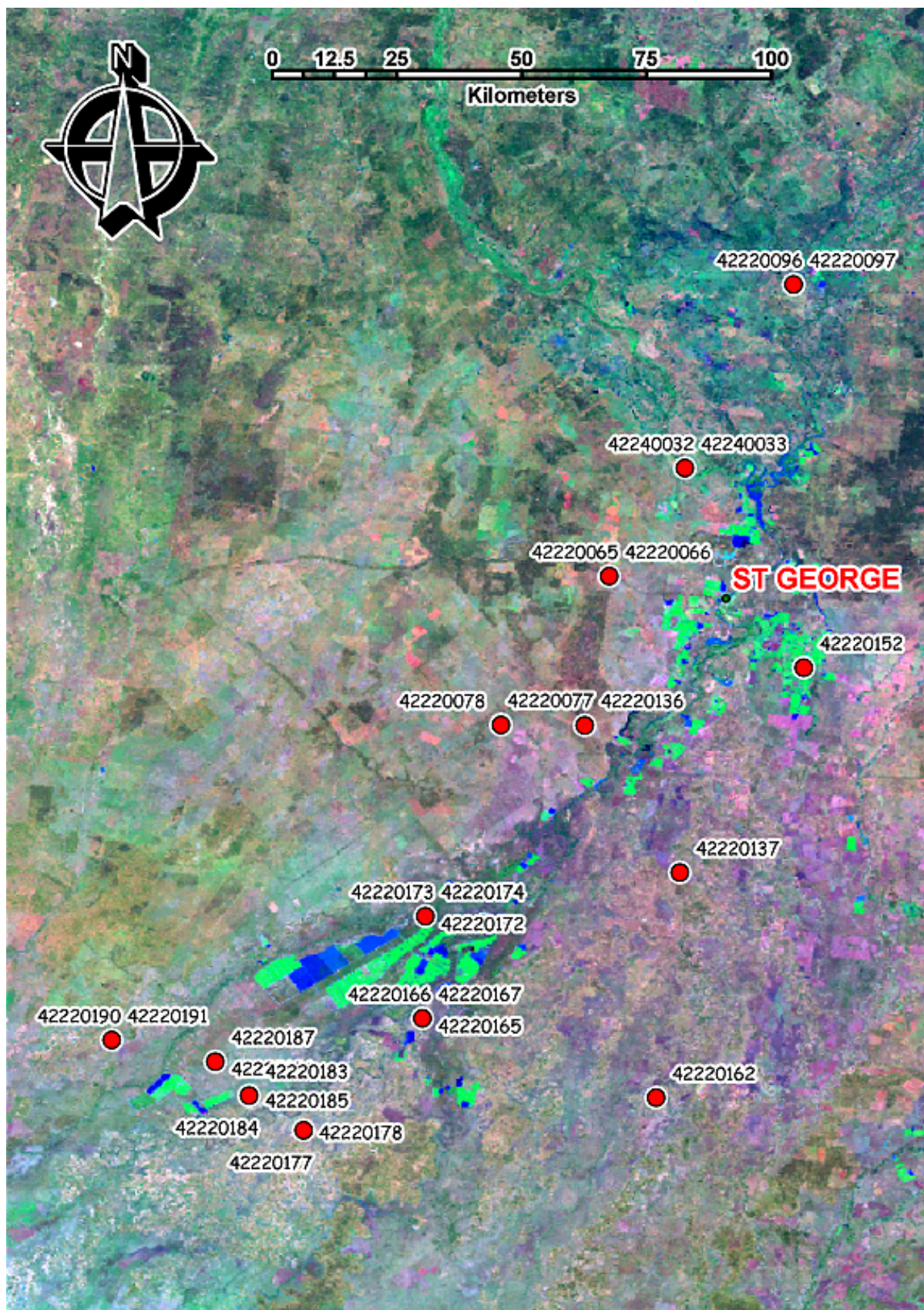
Figure 2. Location map of study area boreholes sampled for geochemistry and environmental isotopes with respect to Lower Balonne River and the irrigation areas.

The close correlation between Na^+ and Cl^- and maintenance of seawater ratio over the entire concentration range indicates that weathering of aquifer minerals is not a significant source of salt to the groundwaters. Because aquifer minerals contain significant amounts of sodium but negligible chloride, weathering would result in substantial Na^+ enrichments over the seawater ratio. Note also that the Na^+/Cl^- ratio of the mineral halite is 0.65 whereas these data plot close to the seawater value of 0.56 indicating that halite dissolution does not contribute significant dissolved salt to the groundwaters.

Figure 3. Na^+ versus Cl^- for lower Balonne groundwaters. The data points represent the Upper Alluvial Aquifer (UA), Middle Confining bed (MCB), Lower alluvial Aquifer (LA) and Griman Creek Formation (GCF). Also shown is the seawater dilution line (slope = 0.56) and halite dissolution line (slope = 0.65).

Bromide and chloride are also well correlated and follow a seawater dilution trend, except for two outliers in the shallow groundwaters at the fresh and very saline end of the spectrum (Fig. 4). Because Br^- is not incorporated during formation of halite, the dissolution of halite would result in very high Cl^- enrichment as indicated by a line with very low slope in Figure 4. The conclusion from this plot is that salinity distributions in all but one groundwater sample are controlled by evaporation of a single seawater-like source. This source is most likely marine aerosols that are deposited with rainfall. Although it is likely that addition of other ions such as Ca^{2+}, Mg^{2+} and SO_4^{2-} may be partly contributed by mineral dissolution, these constitute <15% of total salt load and therefore mineral weathering (including halite dissolution) is not a significant mechanisms for delivering salt to these groundwaters.

Figure 4. Br⁻ versus Cl⁻ for lower Balonne groundwaters. The data points represent the Upper Alluvial Aquifer (UA), Middle Confining bed (MCB), Lower alluvial Aquifer (LA) and Griman Creek Formation (GCF). Also shown is the seawater dilution line (slope = 0.00347) and the approximate halite dissolution trend.

3.2   Chloride mass balance

Recharge rates can be estimated using the simple form of the chloride mass balance if we assume that vertical recharge >> lateral input. The recharge rate can be estimated by rearranging the chloride steady-state expression where:

$$R = (P.C_P)/C_R \qquad (1)$$

Where   R = recharge rate (L T^{-1})
        P = mean annual rainfall (L T^{-1})
        C_P = concentration of chloride in rainfall (M L^{-3})
        C_R = concentration of chloride in groundwater (M L^{-3})

If we assume a mean annual rainfall for the region of 500 mm yr^{-1}, and an maximum estimate of chloride in rainfall based on data from Inverell and Charleville as reported by Blackburn and McLeod (1983) of 2 mg L^{-1}, then recharge rates can be estimated for the minimum, maximum and median chloride values for the suite of groundwaters reported here and data compiled by Pearce et al (2004) (Tables 1 & 2).

Table 1. Compilation of minimum, maximum and median chloride values for Lower Balonne groundwaters (this study and Pearce et al. 2004)

	Min. Cl (mg/L)	Max. Cl (mg/L)	Median Cl (mg/L)
UA	210	21 600	4,000
MCB	250	6400	2100
LA	1150	5,150	2,180
GCF	700	19 500	11 400

Table 2. Compilation of minimum, maximum and recharge rates for Lower Balonne groundwaters (based on chloride values in Table 1 and using Eq. 1).

	Min. R (mm yr^{-1})	Max. R (mm yr^{-1})	Median R (mm yr^{-1})
UA	0.05	4.5	0.25
MCB	0.16	4	0.5
LA	0.2	1.1	0.45
GCF	0.05	1.5	0.1

Recharge rates based on chloride mass balance and median groundwater chloride concentrations suggest recharge rates ranging from 0.1 mm/yr for the Griman Creek formation, to 0.25 mm/yr for the UA and about 0.5 mm/yr for the MCB and LA. However, individual recharge estimates range from 0.05 mm/yr for the highly saline UA and GCF waters to 4-5 mm/yr for the fresh groundwaters in the UA and MCB. The recharge rates quoted above would be lower if the actual concentration of Cl$^-$ in rainfall in the past was lower than 2 mg/L.

These recharge rates are similar to those given by Kellett (2004) and Cresswell (2004). They are typical for a semi-arid region with two main recharge mechanisms: indirect diffuse recharge and direct river/flood recharge. The latter would tend to provide higher recharge rates, but over a relatively restricted part of the entire landscape. A large range of recharge estimates is to be expected for such a large range of chloride values. It may be possible to estimate a spatially distributed recharge rate using individual groundwater chloride data. For the time being, using a median value of 0.25 mm yr^{-1} for the UA and 0.5 mm yr^{-1} for the MCB and LA will provide adequate input to any water balance model.

3.3   Sulphur and strontium isotopes

Additional constraints on sources of solutes can be obtained from sulphur and strontium isotopes of dissolved sulphur and strontium respectively. The sulphur isotopic values are all depleted in ^{34}S relative to seawater sulphate (Tables A1-A3 and Fig. 5) and all have varying amounts of 'excess' sulphate relative to seawater. In other words, the SO$_4$/Cl ratios are all 20-40% higher than the seawater value of 0.14 and δ^{34}S values are less than the value of seawater (<20‰, CDT). This is commonly observed in groundwaters that have a predominantly marine origin of dissolved sulphate, with some additional sulphate from ^{34}S depleted organic sulphur, either from atmospheric dimethyl sulphide sources, or soil organic matter. There is no evidence of significant contributions from oxidation of mineral sulphides because they typically have δ^{34}S values <-40 ‰, CDT, and the observed values are much more enriched in

[34]S than that. The contribution of gypsum dissolution is also not significant because the waters are all under-saturated with respect to gypsum, and the saline waters have Ca:SO_4^{2-} molar ratios much greater than 1.
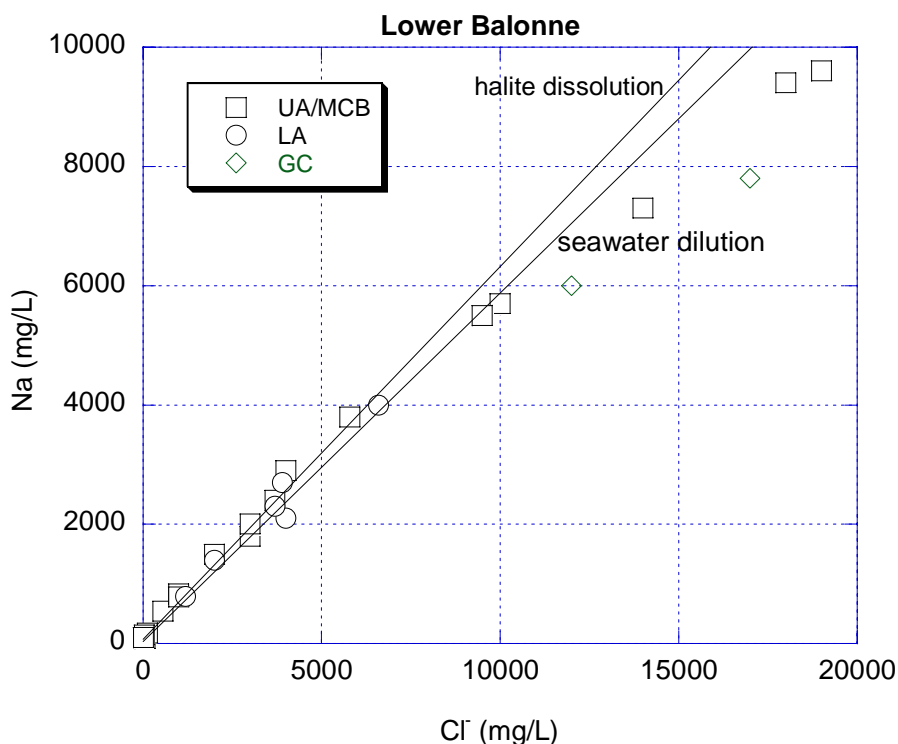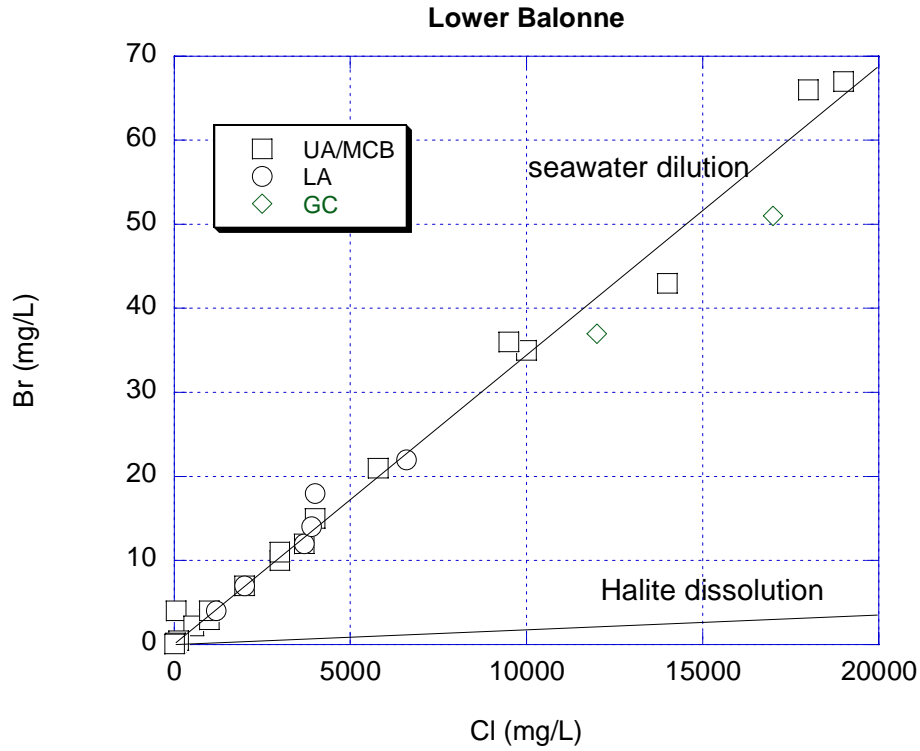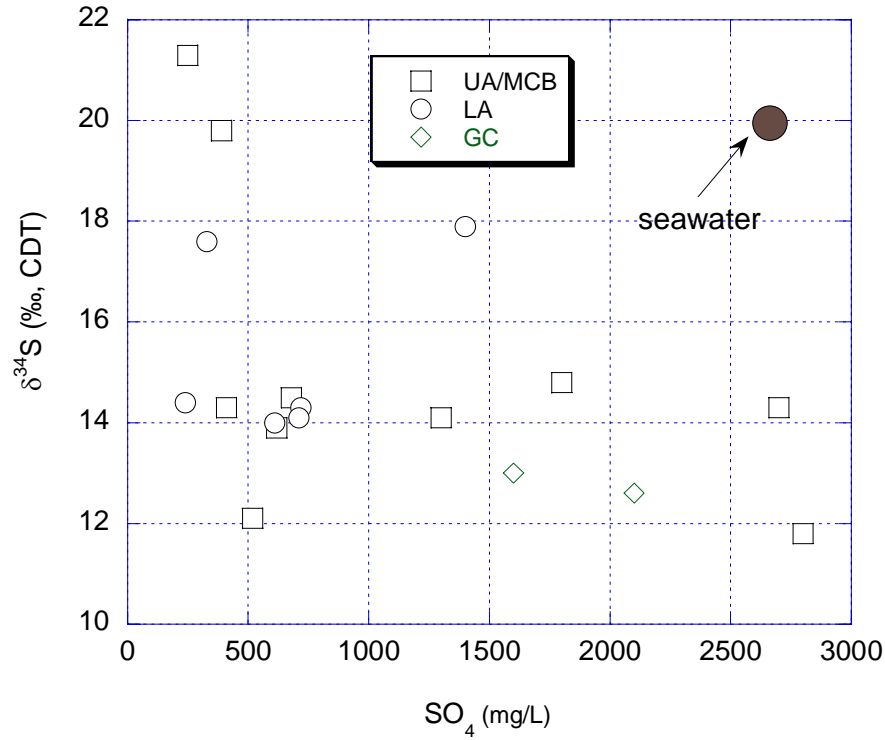

Figure 5. $\delta^{34}S$ versus sulphate concentration for Lower Balonne groundwaters. The data points represent the Upper Alluvial Aquifer (UA), Middle Confining bed (MCB), Lower alluvial Aquifer (LA) and Griman Creek Formation (GCF).

Strontium isotope data are limited to 12 samples collected from the UA and LA aquifer and all show a spread of values from 0.712 to 0.7172 and 0.714 – 0.7165 respectively (Fig. 6). These values are much higher than the marine limestone (0.7082 – 0.7092) of the Tertiary and Cretaceous, and higher than modern marine derived rainfall (0.7079). These values are typically of strontium derived from silicate weathering rather than carbonate dissolution, indicating that the bulk of the Sr^{2+}, and by implication dissolved carbonate, is derived to a large extent from non-marine carbonate sources. The two main alluvial aquifers also display similar range in $^{87}Sr/^{86}Sr$ values indicating connectivity between the two systems, or that they have similar mineralogy that contribute Sr^{2+} to the waters.
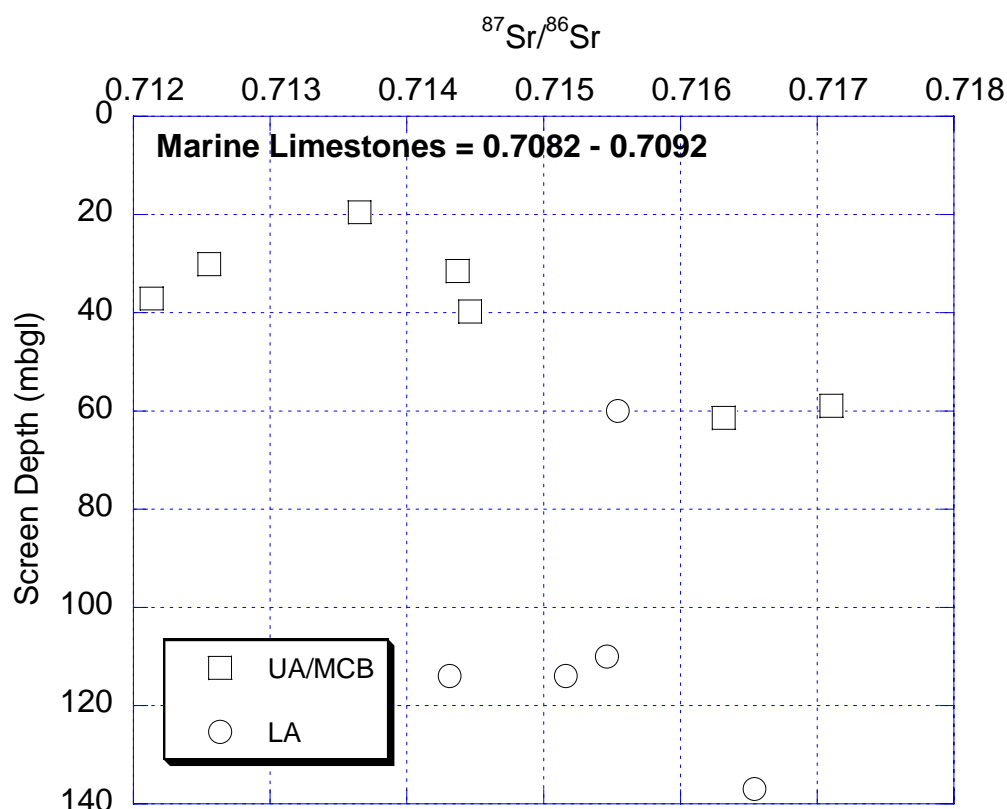
Figure 6. $^{87}Sr/^{86}Sr$ as a function of screen depth for the lower Balonne alluvial aquifers. The data points represent the Upper Alluvial Aquifer (UA), Middle Confining bed (MCB) and Lower alluvial Aquifer (LA). Note the estimated marine carbonate value lies well off the left hand scale on this plot.

3.4   Stable isotopes of water and mechanisms of recharge

The stable isotopes of water all plot to the right of the global meteoric water line with a slope of about 5.6 (Fig. 7). None show any evidence of any residual seawater which by definition has a composition of 0 for both δ^2H and $\delta^{18}O$. The trend in these data is similar to that observed for many groundwater systems throughout the Murray-Darling basin. They show a predominantly meteoric signature and some evidence of evaporation in the upper part of the unsaturated zone. Extrapolating these data back to the Global Meteoric Water line (GMWL) gives an intercept at about $\delta^2H=-46‰$ and $\delta^{18}O=-7.4‰$ which is approximately the mean annual rainfall for the region (as indicated by interpolation between Brisbane and Alice Springs rainfall data). Because transpiration by plants does not affect the isotopic composition of residual waters, the concentration by that mechanism will increase salinity but not isotope composition of the water molecules. There is a general trend of waters that have Cl concentrations <5,000 mg/L to be the most depleted in ^2H and ^{18}O (plotting to the lower left) and may be indicative of flood recharge rather than diffuse recharge
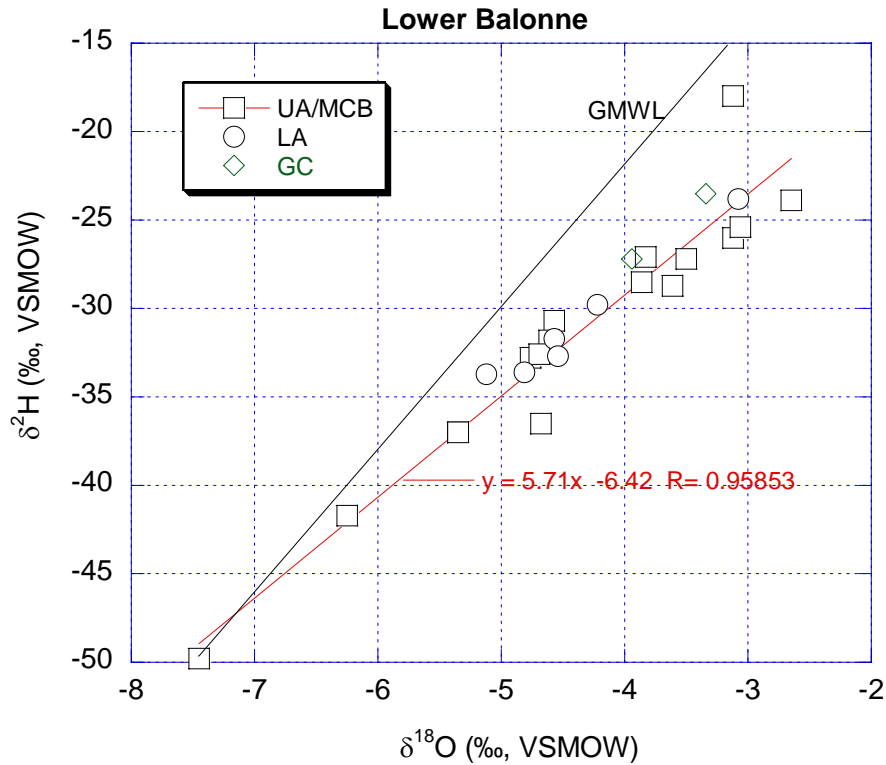
Figure 7. δ^2H versus $\delta^{18}O$ for Lower Balonne groundwaters. The data points represent the Upper Alluvial Aquifer (UA), Middle Confining bed (MCB), Lower alluvial Aquifer (LA) and Griman Creek Formation (GCF). The line of best fit shows an evaporation line with a slope of 5.71.

3.5   Groundwater dating

The ^{14}C concentration of the Lower Balonne groundwaters ranges over the full spectrum of possible values (i.e., from <3 % modern carbon (%mc) to 100 %mc – Tables A1b – A3b and Fig. 8). The UA samples cover spectrum from <0.5% mc to 98.7 %mc, while the data from the LA tend to plot in a clump at about 5 – 10%mc, although one sample has a value of 41 %mc. The two GCF samples have ^{14}C concentrations between 22 – 26 %mc. Note that the three samples that are below our detection limit of 0.5 %mc are plotted arbitrarily at 0 %mc. Most of the groundwater samples that were taken where screens are <10 m below the water table have ^{14}C concentrations >50 %mc, with the exception of two samples from the UA and one from the Griman Creek Fm. The remaining samples, where screened intervals are >10 m below the water table have ^{14}C concentrations <30 %mc with the exception of one sample from the LA at about 41 %mc. None of the samples from >40m below the water table have ^{14}C concentrations >10 %mc.
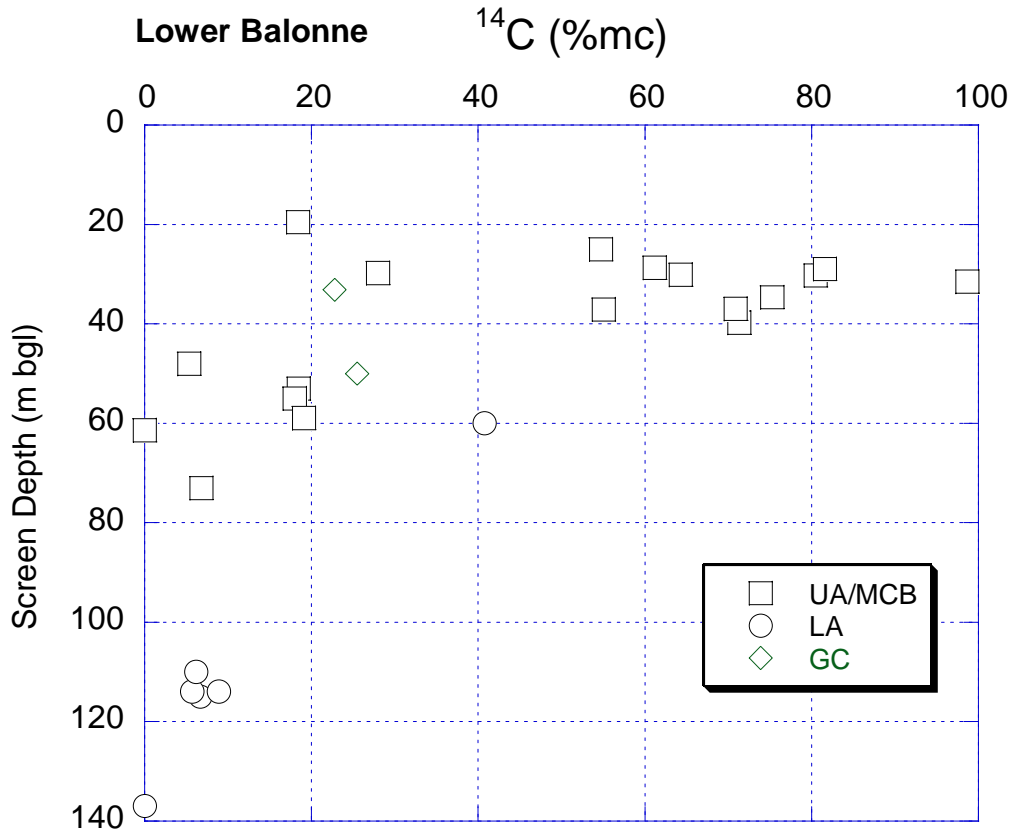
Figure 8. [14]C concentrations for Lower Balonne groundwaters expressed as percent modern carbon (%mc). The data points represent the Upper Alluvial Aquifer (UA), Middle Confining bed (MCB), Lower alluvial Aquifer (LA) and Griman Creek Formation (GCF). The lower limit of detection is about 0.5 %mc. The water table is between 20 – 25m below ground level (bgl) at the time of sampling.

The results of groundwater ages using four different methods of calculations are given in Table 3. Estimates of groundwater [14]C "age" can be made from measured ^{14}C data according to the rearrangement of the basic decay equation according to the following expression:

$$t = -\ln 8033(A/A_0) \tag{2}$$

where

t = time or age in years
A = measured ^{14}C activity of total dissolved inorganic carbon (TDIC)
A_0 = estimated initial radiocarbon content of TDIC at the time of recharge

The age estimated from Eq. 2 is what is often referred to as the uncorrected age because there is no consideration for chemical processes within the soil or groundwater affecting ^{14}C concentrations. This age is usually, but not always, an underestimate of the true ^{14}C age. Estimates of ^{14}C groundwater "model" age are usually made by using geochemical and other isotopic data to reconstruct the initial ^{14}C concentrations (A_0) using chemical and isotopic data and applying several of the most common correction schemes. A short summary of four common correction methods known as Tamers correction (chemical approach), Pearson correction (isotopic approach), the Fontes-Garnier correction (a combined chemical/isotope approach) and the Fontes-Garnier equilibrium correction (an extended combined chemical/isotope approach with equilibrium between soil bicarbonate and soil gas CO_2) is given in Appendix 2.

The concentrations and mole fraction of the dissolved CO_2 and of the HCO_3^- in the bore water samples are required as input data for corrected ages using the Tamers and Fontes-Garnier models, whereas the Pearson scheme requires only $\delta^{13}C$ data. Estimates of these were calculated using field measurements of pH and temperature and laboratory analyses of major anions and cations of water sampled from the bores and running the analyses through a hydrochemical model (PHREEQC – see Parkhurst and Appelo, 1999).

Table 3. [14]C groundwater 'age' estimates as uncorrected and two calculated model ages (based on [1]mean of Pearson and Fontes & Garnier closed system correction schemes; [2] extended F&G system with partial CO_2 re-equilibration) for the St. George-Dirranbandi area. Both uncorrected and model ages assume a soil gas ^{14}C of 95 %mc.

sample ID	[14]C (pmC)	$\delta^{13}C$	Uncorrected Age (yrs)	Model Age[1] (yrs)	Model age[2] (yrs)
U Alluvial-MCB					
4224-0033	80.5	-14.8	1370	1900	70
4222-0078	71.3	-12.3	2370	Modern	Modern
4222-0097	98.7	-12.6	Modern	Modern	Modern
4222-0136	70.9	-12.2	2420	Modern	Modern
4222-0156	75.3	-16.6	1920	340	1420
4222-0162	54.7	-16.8	4560	3120	3750
4222-0065	6.8	-13.6	21 800	18 600	20 000
4222-0167	81.6	-13.9	1260	Modern	Modern
4222-0173	64.3	-15.0	3230	800	2210
4222-0177	61.2	-9.0	3640	Modern	Modern
4222-0190	28.0	-10.5	10 100	4870	9550
4222-0191	18.4	-10.2	13 570	8110	2250
4222-0201	55.1	-12.6	4500	680	2250
4222-0066	18.5	-13.9	13 530	10 500	11 840
4222-0165	18.0	-13.8	13 750	10 680	11 970
4222-0184	5.4	-11.3	23 700	19 020	20 670
4222-0186	<0.5	-12.7	>25 000	>25 000	<25 000
4222-0203	19.1	-11.2	13 260	8500	10 240
Lwr Alluvial					
4224-0032	6.7	-13.9	21 920	18 910	20 170
4222-0077	5.7	-13.8	23 260	20 190	21 470
4222-0096	40.8	-18.6	6990	6330	7170
4222-0172	8.9	-12.6	19 580	15 770	17 240
4222-0183	<0.5	-13.5	>25 000	>25 000	>25 000
4222-0200	6.2	-12.0	22 560	18 360	19 900
Griman Ck Fm					
4222-0163	25.5	-14.2	10 870	8070	8930
4222-0137	22.8	-13.4	11 800	8560	9220

The results in Table 3 show that the ^{14}C ages cover the full spectrum from modern to >25 000 years for the St. George – Dirranbandi area. The samples that are assigned as modern ages

mean that they are <50 years old. In other words, the groundwater contains some fraction of ^{14}C-labelled carbon derived from atmospheric nuclear weapons tests in the 1950's and 60's. In general, the uncorrected ages give the oldest ages, and the model ages from the P and F&G model give the youngest ages. This is because the model ages are determined from a 'corrected' initial ^{14}C value which is lower than that assigned as the soil gas concentration of 95 %mc. Therefore, six samples when corrected for 'dead' carbon, yield modern ages. The differences between the various estimates increases with increasing $\delta^{13}C$ values and are related to different estimates of initial [14]C (A_0).

Many of the groundwaters which have screens open in the Upper Alluvial aquifer have relatively high ^{14}C concentrations which translate to modern ages (negative values in Tables A1b, A2b and A3b). All of the model ages estimates give negative values which correspond to 'modern' ages. This means that recharge is potentially very rapid and some fraction of the groundwater was recharged since 1950. Uncorrected groundwater ages for other UA samples are grouped as follows: 9 from 1,000 – 5,000 yrs; 5 between 10 000 and 15 000 yrs, and three >20 000 years.

[14]C data plotted in terms 'uncorrected' groundwater ages are between modern and >25 000 years (Fig. 9). These results are shown for comparison only, and corrected ages shown in the next section are thought to be more reliable. In general, the LA is restricted to the ^{14}C concentration range between 0 and 40 %mc which translates to uncorrected ages of between 6,000 to >20 000 years, with most groundwaters at least 10 000 years old. Those samples where the screen mid-point is >70 m have ages >25 000 years. Three of the UA samples taken from areas that are not close to any known flooding recharge or irrigation area have ages of the order of 10 000 years. All the other UA samples have ^{14}C activities between 55%mc and 100%mc which indicate apparent ages of between modern and 5,000 years, or they may be equally well interpreted as mixing between 'old' groundwater and younger recharge water. The two apparently very old samples from the UA and LA aquifer should be read as > 25 000 years because the ^{14}C dating techniques cannot resolve ages greater than that due to assumptions and estimates of the initial ^{14}C at the time of recharge.

The three correction schemes give slightly different results, but give consistent differences in estimated ages amongst the various groundwaters sampled. The most appropriate groundwater ages from sampled in the St. George-Dirranbandi area are those estimated from the model ages determined from the partial soil gas CO_2 re-equilibration scenario (last RH column in Table 3) and are shown in Fig. 10 as a function of depth. This does not necessarily assume that there is limited interaction between the solution and the carbonate minerals, but only that there has been re-equilibration between the soil CO_2 and the dissolved bicarbonate, which essentially resets the A_0 value to 90-100 %mc prior to recharge. In general, the data also make sense from the point of view that those where the slots are deepest below the water table are the oldest, and those in the unconfined aquifer furthest from the rivers also have the lowest ^{14}C and are older.

$\delta^{13}C$ values of the Lower Balonne groundwaters cover a relatively small range, with 70% of samples ranging from -11 to -15 ‰, V-PDB. The $\delta^{13}C$ value is controlled by a combination of two processes: 1) isotopic exchange between DIC and carbonate minerals via carbonate dissolution re-precipitation processes, and 2) mixing between an old ^{13}C-enriched and 'young' ^{13}C-depleted end members. In this case, the ages represent a mean carbon age, but converting that to a mean water age is subject to large uncertainties given the unknown dilution with old carbon especially when $\delta^{13}C$ values are greater than about -12 ‰, (Pearson, 1992).
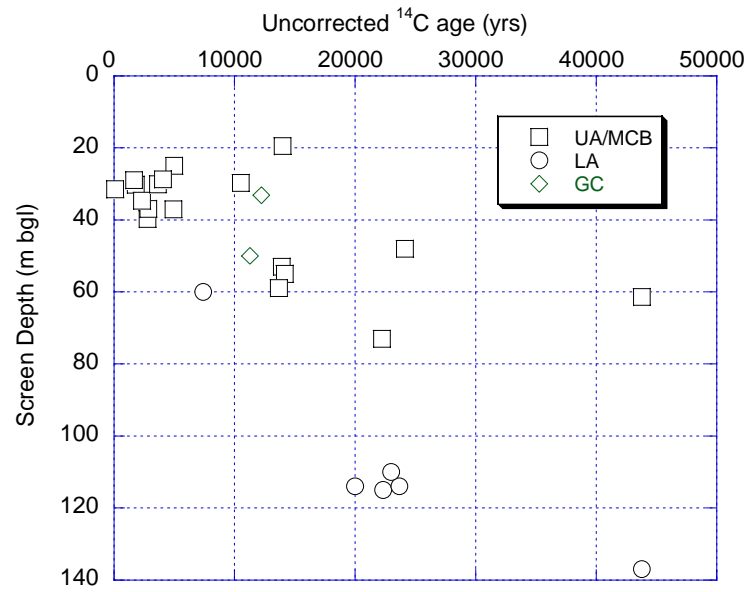
Figure 9. Uncorrected groundwater ages for Lower Balonne. The data points represent the Upper Alluvial Aquifer (UA), Middle Confining bed (MCB), Lower alluvial Aquifer (LA) and Griman Creek Formation (GCF).

Figure 10. Corrected groundwater ages for Lower Balonne groundwaters using the Fontes&Garnier method with partial CO_2 re-equilibration. The data points represent the Upper Alluvial Aquifer (UA), Middle Confining Bed (MCB), Lower Alluvial Aquifer (LA) and Griman Creek Formation (GCF).
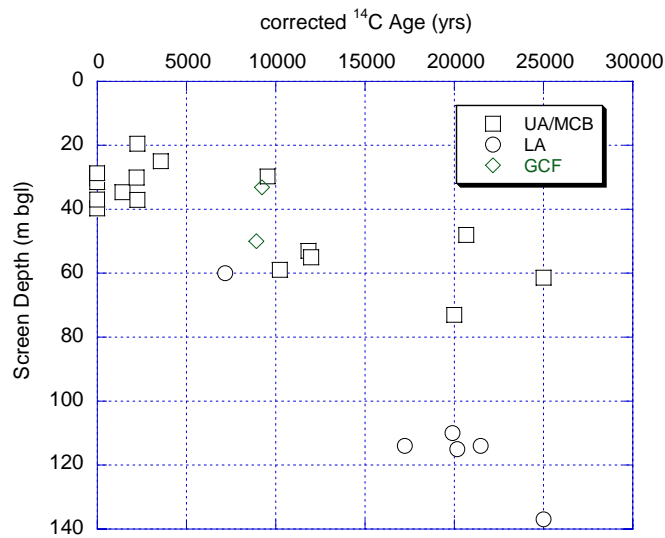
The relatively 'old' ages, or long residence times for most of the groundwater samples retrieved from >20 m below the water table indicate that rates of vertical groundwater flow, or

cross formational exchange, is of the order of thousands to tens of thousands of years. The similarity in the chemical composition and stable isotopic composition of the waters is consistent with the conceptual model of Pearce et al (2004) that the aquifers behave as a single inter-connected system, albeit vertical exchange occurs at a rate much less than any alterations in the hydrological balance due to land use change. This means that any increased recharge flux will have an effect on pressure but the movement of salt from the shallow systems to the deep systems will not occur on any management time frame. The relatively old ages recorded for most groundwaters sampled within the area does not support any preferential or highly transmissive flow systems in the LA or much of the UA or GCF in any part of the system that is not close to the river beds.

Relatively high ^{14}C concentrations were observed in several shallow UA groundwaters near the vicinity of surface tributaries (Bore #'s 4224-0033, 4222-0097; 4222-0167; and to a lesser extent 4222-0078, 4222-0136 and 4222-0156). Based on this data, there is evidence of rapid recharge to the shallow UA near the river beds, and adjacent to irrigation areas on a time scale of <50 years, but this may be limited in lateral extent. Those samples from the UA that were not near any obvious surface flooding or irrigation area had lower ^{14}C concentrations indicating natural rainfall recharge rates are much lower than that for irrigation and flood-out. However, this is limited in extent and probably contributes a much smaller fraction of recharge to the entire area than diffuse rainfall recharge.

4.   CONCLUSIONS

Sodium and chloride ions make up >85% of the salt load in the groundwaters with SO_4^{2-}, Ca^{2+} and Mg^{2+} making up most of the remaining. Cl^-/Br^- ratios of the groundwaters are the same as seawater (270-290) indicating a marine origin for dissolved salts. The dissolved salts are derived almost entirely from concentration of atmospheric marine derived aerosols deposited via rainfall.

Recharge rates based on chloride mass balance calculations and median groundwater chloride concentrations indicate median recharge rates of 0.1 mm/yr for the Griman Creek formation, 0.25 mm/yr for the UA and about 0.5 mm/yr for the MCB and LA. However, individual recharge estimates range from 0.05 mm/yr for the highly saline UA and GCF waters to 5 mm/yr for the fresh groundwaters in the UA and MCB.

Stable isotope compositions of the groundwaters (δ^{18}O and δ^2H) are of meteoric composition and lie to the right of the global meteoric water line on a δ^{18}O versus δ^2H plot with a slope of 5.8. Recharge is dominated by rainfall across the entire area and evaporation has altered the isotopic composition prior to recharge.

Radiocarbon ages for the lower alluvial aquifer tend to be much older (>5,000 - >25,000 years) than the upper alluvial aquifer (<2,500 year) suggesting that vertical leakage occurs at a very slow rate. There is no apparent trend in ages of the lower alluvial aquifer from the NE to SW part of the study area. Fresh, relatively young (<50 years) groundwater may be restricted to near the rivers suggesting flood recharge is limited in lateral extent via surface tributaries, but further work would be required to confirm this. There is evidence for vertical exchange of the groundwaters amongst the various aquifer systems (indicated by chemistry and stable isotope data) but this occurs on time scale of 10^3 to 10^4 years as indicated by 'old' ^{14}C groundwater ages at depths >20 m below the water table.

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APPENDIX 1: Groundwater Chemistry and Environmental Isotope data

Table A1a. Upper Alluvial aquifer – Chemistry data

Bore #	pH	Temp C	EC μS/cm	WT mbgl	Date	Cl mg/L	SO4 mg/L	Alk meq/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	Si mg/L	Br mg/L
4224-0033	6.64	25.0	0.7	23.59	1-9-2003	63	16	3.80	19	18	87	18	0.1	40	4.0
4222-0078				37.20	4-9-2003	2000	410	8.10	120	88	1500	32	2.3	25	7.0
4222-0097	6.70	25.4	2.6	16.86	1-9-2003	560	22	8.10	27	16	540	15	0.6	35	2.2
4222-0136				30.10	31-8-2003	4000	390	11.4	130	110	2900	31	3.1	13	15.0
4222-0156				23.08	3-9-2003	130	15	3.50	3	3	180	5	0.1	30	0.5
4222-0162	5.88	25.2	31.1	20.24	5-9-2003	10000	1500	3.20	1000	600	5700	112	20.0	32	35.0
4222-0065	6.69	25.2	4.1	32.93	4-9-2003	1000	250	3.80	40	26	830	11	0.9	25	3.0
4222-0167	6.85	24.1	0.7	24.60	30-8-2003	43	12	4.60	9	5	140	6.0	0.2	27	0.2
4222-0173	7.08	22.8	0.7	20.99	29-8-2003	23	5	5.90	35	14	100	4.0	0.4	21	0.1
4222-0177	6.35	24.8	39.0	21.44	30-8-2003	14000	2800	3.30	1500	770	7300	35	23	25	43.0
4222-0190	6.04	25.8	50.8	13.95	29-8-2003	19000	2700	2.20	1900	1200	9600	159	40	29	67.0
4222-0191	6.02	25.2	49.8	13.77	29-8-2003	18000	2700	2.10	1900	1100	9400	132	41	26	66.0
4222-0201	6.66	23.2	19.9	26.21	4-9-2003	5800	1300	11.7	310	340	3800	83	8.6	19	21.0
4222-0066	6.63	25.3	4.1	32.62	4-9-2003	1000	190	3.80	47	36	780	15	1.1	19	4.0
4222-0165	6.52	24.2	10.6	24.77	30-8-2003	3000	520	4.00	260	170	1800	23	4.6	34	10.0
4222-0184				21.24	30-8-2003	3000	620	5.10	240	150	2000	28	4.0	27	11.0
4222-0186	6.33	23.8	12.2	14.54	30-8-2003	3700	680	4.40	200	140	2400	23	4.0	25	12.0
4222-0203	6.57	24.5	29.7	35.37	5-9-2003	9500	1800	3.80	1100	490	5500	101	19.0	31	36.0

Table A1b. Upper Alluvial aquifer – Isotope data

Bore #	WT	depth	slots	Date	^{222}Rn	err	δ^2H	$\delta^{18}O$	^{14}C	$\delta^{13}C$	$\delta^{34}S$	$^{87}Sr/^{86}Sr$	Uncorr[1]	Corr[2]	Corr[3]
	mbgl	mbgl	mbgl		mBq/L		‰, V-SMOW		%mc	‰,PDB	‰,CDT				
4224-0033	23.59	30.29	27	1-9-2003		7.3	0.4	-41.7	-6.25	80.5	-14.8		1370	1900	70
4222-0078	37.20	39.75	36	4-9-2003			-30.7	-4.57	71.3	-12.3	14.3	0.71446	2370	M	M
4222-0097	16.86	31.53	29	1-9-2003	12.2		0.4	-23.9	-2.65	98.7	-12.6	0.71437	M	M	M
4222-0136	30.10	37.00	28	31-8-2003			-18.0	-3.12	70.9	-12.2	19.8		2420	M	M
4222-0156	23.08	34.67	33	3-9-2003		1.5	0.2	-49.8	-7.45	75.3	-16.6		1920	340	1420
4222-0162	20.24	25.00	24	5-9-2003		21.1	0.5	-28.5	-3.86	54.7	-16.8		4560	3120	3750
4222-0065	32.93	73.00	71	4-9-2003		14.9	0.4	-37.0	-5.35	6.8	-13.6	21.3	21800	18600	20000
4222-0167	24.60	28.95	27	30-8-2003			-36.5	-4.68	81.6	-13.9			1260	M	M
4222-0173	20.99	30.10	28	29-8-2003	5.5	0.4	-32.0	-4.59	64.3	-15.0		0.71256	3230	800	2210
4222-0177	21.44	28.67	28	30-8-2003	5.8	0.3	-27.2	-3.50	61.2	-9.0	11.8		3640	M	M
4222-0190	13.95	29.83	33	29-8-2003	4.8	0.3	-26.0	-3.12	28.0	-10.5	14.3		10100	4870	6290
4222-0191	13.77	19.53	17	29-8-2003	8.2	0.4	-25.4	-3.06	18.4	-10.2		0.71366	13570	8110	9550
4222-0201	26.21	37.15	35	4-9-2003	9.7	0.3	-27.1	-3.83	55.1	-12.6	14.1	0.71213	4500	680	2250
4222-0066	32.62	53.00	54	4-9-2003	26.4	0.6	-32.8	-4.76	18.5	-13.9			13530	10500	11840
4222-0165	24.77	54.99	54	30-8-2003	2.9	0.3	-37.0	-5.35	18.0	-13.8	12.1		13750	10680	11970
4222-0184	21.24	48.00	51	30-8-2003			-31.8	-4.61	5.4	-11.3	13.9		23700	19020	20670
4222-0186	14.54	61.40	61	30-8-2003			-32.6	-4.69	0.0	-12.7	14.5	0.71632	>25000	>25000	>25000
4222-0203	35.37	59.00	51	5-9-2003			-28.7	-3.61	19.1	-11.2	14.8	0.71711	13260	8500	10240

[1] Uncorrected ^{14}C ages determined from initial ^{14}C of 95 %mc; [2] Corrected ^{14}C ages determined from mean of closed-system correction assuming dilution with ^{14}C-free carbonate prior to recharge using the closed-system 'isotope dilution' method of Ingerson and Pearson (1964) and 'chemical and isotope dilution method' of Fontes and Garnier (1979) (see Appendix 2); [3] Corrected ^{14}C ages determined from modified Fontes and Garnier model incorporating partial exchange with soil gas CO_2 with ^{14}C content of 95 %mc prior to recharge (open-system isotope dilution).

Table A2a. Lower Alluvial Aquifer – Chemistry data

Bore #	pH	Temp Deg C	EC µS/cm	WL mbgl	Date	Cl mg/L	SO$_4$ mg/L	Alk meq/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	Si mg/L	Br mg/L
4224-0032	6.52	25.3	4.70	33.84	1-9-2003	1200	240.0	2.9	94.0	68.0	790.0	15	2.3	22	4.00
4222-0077	6.52	25.6	7.39	36.50	4-9-2003	2000	330.0	5.8	140	69.0	1400	22	2.4	18	7.00
4222-0096	6.42	25.2	21.7	19.89	1-9-2003	6600	1400	3.4	560	310	4000	33	10	15	22.0
4222-0172	6.56	23.1	11.9	24.32	29-8-2003	4000	610.0	2.6	300	180	2100	42	5.2	27	18.0
4222-0183	6.33	25.6	12.9	19.08	30-8-2003	3700	720.0	4.5	290	180	2300	22	5.0	24	12.0
4222-0200	6.53	23.8	13.9	26.21	4-9-2003	3900	710.0	8.6	210	190	2700	48	5.2	32	14.0

Table A2b. Lower Alluvial Aquifer – Isotope data

Bore #	WL mbgl	depth m	slots mbgl	date	radon mBq/L	err	δ^2H ‰, V-SMOW	δ^{18}O	^{14}C %mc	δ^{13}C ‰,PDB	δ^{34}S ‰,CDT	^{87}Sr/^{86}Sr	^{14}C Age (years) uncorr[1]	Corr[2]	Corr[3]
4224-0032	33.84	115	113	1-9-2003	4.2	0.30	-33.7	-5.12	6.70	-13.9	14.4		21920	18910	20170
4222-0077	36.50	114	111	4-9-2003	4.5	0.20	-33.6	-4.81	5.70	-13.8	17.6	0.71516	23260	20190	21470
4222-0096	19.89	60.0	59	1-9-2003	5.5	0.30	-23.8	-3.08	40.8	-18.6	17.9	0.71554	6990	6330	7170
4222-0172	24.32	114	110	29-8-2003	5.5	0.40	-31.7	-4.57	8.90	-12.6	14.0	0.71431	19580	15770	17240
4222-0183	19.08	137	131	30-8-2003	3.0	0.30	-32.7	-4.54	0.00	-13.5	14.3	0.71654	>25000	>25000	>25000
4222-0200	26.21	110	99	4-9-2003	6.0	0.30	-29.8	-4.22	6.20	-12.0	14.1	0.71547	22560	18360	19900

[1-3] See explanation on Table A1b

Table A3a. Griman Creek Formation – Chemistry data

Bore #	pH	Temp Deg C	EC µS/cm	WL mbgl	Date	Cl mg/L	SO4 mg/L	Alk meq/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	Si mg/L	Br mg/L
4222-0163	5.95	24.7	34.0	19.98	5-9-2003	12000	1600	1.9	1100	680	6000	116	24	32	37
4222-0137	6.56	20.8	39.6	18.05	5-9-2003	17000	2100	1.8	2200	1300	7800	73	34	23	51

Table A3b. Griman Creek Formation – Isotope data

Bore #	WL mbgl	depth m	slots mbgl	Date	^{222}Rn mBq/L	err	δ^2H ‰, V-SMOW	δ^{18}O	^{14}C %mc	δ^{13}C ‰,PDB	δ^{34}S ‰,CDT	^{14}C Age (yrs) uncorr[1]	Corr[2]	Corr[3]
4222-0163	19.98	50.0	48	5-9-2003	15.5	0.4	-27.2	-3.9	25.5	-14.2	13.0	10870	8070	8930
4222-0137	18.05	33.2	27	5-9-2003	22.5	0.5	-23.5	-3.3	22.8	-13.4	12.6	11800	8560	9220

[1-3] See explanation on Table A1b

APPENDIX 2: Hydrochemical/Isotopic Models for Correction of ^{14}C in Groundwater

Radiocarbon laboratories routinely report results of ^{14}C analyses as years before present (yr BP), percent modern carbon (pmC or %mc) or Delta (Δ^{14}C). The convention most often used for reporting ^{14}C activity in groundwater is as %mC, with 100 %mc equivalent to the ^{14}C concentration of the atmosphere. For groundwater samples, the results refer to the age or activity of the dissolved inorganic carbon (DIC) in the groundwater and rarely to the age or activity of the groundwater itself. The principle behind ^{14}C dating of groundwater is that carbon dioxide containing a known amount of ^{14}C decays at a well known rate (half life of 5730 years) and the age calculated using equation 1:

$$t = -\ln 8033 A/A_o \qquad\qquad (1)$$

where

t = time in years
A = measured activity of total dissolved inorganic carbon (TDIC)
A_o = Initial radiocarbon content of TDIC at the time of recharge

High concentrations of CO_2 build up in the unsaturated zone due to root respiration and microbial oxidation of organic matter. This CO_2 is considered to be modern (100 %mC) or near modern (if there is oxidation of old carbon within the unsaturated zone).

In areas where there are appreciable amounts of carbonate minerals in the soil zone, dissolution of carbonate ($CaCO_3$) takes place according to reaction 2:

$$CO_{2(aq)} + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^- \qquad\qquad (2)$$

Two sources of TDIC are involved during the recharge process, namely the ^{14}C active component from the soil and the ^{14}C-free carbonate. If reaction 2 proceeds to completion, about half the resultant HCO_3^- will be derived from soil CO_2, and half from the $CaCO_3$ that is free of ^{14}C. This occurs in what is generally known as dissolution under closed conditions and the initial ^{14}C composition of the water (A_0) is considered to be ~50%.

At the other extreme is dissolution under open conditions where the TDIC of soil water is continually exchanging with a very large reservoir of ^{14}C active soil CO_2. In this case, the initial ^{14}C activity of the TDIC, A_0 remains unchanged at or near 100 %mC modern. In practice, what happens is somewhere in between the two extreme conditions and most groundwaters reach calcite saturation somewhere during transition from open to closed conditions.

There have been numerous 'correction schemes' developed over the past 40 years to estimate A_0. One of the simplest methods, presented by Tamers (1975), is known as the "chemical" correction approach. It is based on the initial and final DIC concentrations and nearly always results in an A_0 value of ~50 %mC because it assumes fully closed conditions.

It is possible to use the δ^{13}C composition of the DIC in groundwater to indicate the fraction of open and closed dissolution during the evolution of groundwater. The δ^{13}C mixing model, as suggested by Ingerson and Pearson (1964), used the δ^{13}C composition of the groundwater relative to the soil CO_2 and the $CaCO_3$ to determine the extent of dissolution. Hence, if the δ^{13}C composition of the groundwater is half way between that of the soil CO_2 and the $CaCO_3$, A_0 is estimated to be ~50 %mC.

The decision on which method to use for any particular situation is based on some knowledge of the climatic regime and soil type. Each of the methods summarised, along with others not discussed here, have strengths and weaknesses. Clark and Fritz (1997) suggest that "the best approach is to collect as much field data as possible, including samples from the recharge area, and compare results with various models". A summary of the relative merits of the different models is given in various reviews, the most recent of which is by Kalin (1999). Many of these models are incorporated in the USGS

Computer code NETPATH (Plummer et al., 1994) which can be down-loaded from the WEB at http://water.usgs.gov/software/geochemical.html.

When determining corrected ages using the Pearson and Fontes-Garnier models, it is necessary to estimate the $\delta^{13}C$ composition of carbonate material in the aquifer, and of the soil gas in the unsaturated zone. The $\delta^{13}C$ composition of carbonate material in the aquifer is primarily determined by the origin of carbonate material in the aquifer and the unsaturated zone. Marine carbonates usually have $\delta^{13}C$ compositions ~ 0 ‰, PDB while non-marine carbonate material may be as negative (depleted) as –8 ‰, PDB. For this study, a value of 0 ‰, PDB was used.

CO_2 gas in the unsaturated zone is generated primarily by root respiration. Hence, the $\delta^{13}C$ composition of the soil CO_2 gas will be dependent on the $\delta^{13}C$ composition of the vegetation in the area. $\delta^{13}C$ composition of vegetation ranges from approximately –10 ‰ PDB for plants that have a C4 metabolism to approximately –30 ‰ PDB for peat and humus derived from plants that have a C3 metabolism. In tropical parts of Australia, the values lie somewhere between the two because of a mixture of plants with C3 and C4 type metabolism. A $\delta^{13}C_{sw}$ value of   –20 ‰, PDB was assumed given the absence of measured soil gas data for the study area.

The measured $\delta^{13}C$ composition of the DIC for the groundwaters in this study range from –18.7 ‰ to –6.9 ‰, PDB (with an average composition of approximately –11.8‰, PDB). It is probable that the $\delta^{13}C$ composition of the soil gas would be at more negative than these values. When using the Pearson and Fontes-Garnier models, we have used –20 ‰, PDB for the $\delta^{13}C$ composition of the soil gas for all groundwater samples. This value is consistent with plants having a predominantly C3 metabolism, at least at the time when recharge took place.