



Evaporation and concentration gradients created by episodic river recharge in a semi-arid zone aquifer: Insights from Cl^- , $\delta^{18}\text{O}$, $\delta^2\text{H}$, and ^3H



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ARTICLE INFO

Article history:

Received 29 June 2015

Received in revised form 9 September 2015

Accepted 10 September 2015

Available online 21 September 2015

This manuscript was handled by Geoff

Syme, Editor-in-Chief

Keywords:

Darling River

Groundwater

Oxygen-18

Deuterium

Tritium

Recharge

SUMMARY

This study has significantly advanced our understanding of the origin of groundwater recharge in a semi-arid zone region of the Darling River catchment, Australia. The generally accepted hypothesis in arid zone environments in Australia that river water forms the primary groundwater recharge source has proven difficult to monitor. This is due to the time lags between large floods, the remoteness and expense of studying these hydrologically complex systems in detail. In addition, the highly episodic nature of dry-land rivers complicates the interpretation of the groundwater signal. A range of hydrochemical tracers (chloride, oxygen-18, deuterium and tritium) measured in rain, river water, soil water and groundwater were used in this multi-year study to trace the pathways of groundwater recharge under wet and dry climatic conditions. The evaporation and Cl concentrations observed in the unsaturated zone confirmed that small volumetric inputs from periodic rainfall were not the major recharge mechanism. Sampling which included an overbank flooding event in March 2012 provided firm evidence for groundwater originating from high flow episodic river recharge. The use of long-term environmental data to understand how economically important water resources respond to climate change with increasing temperatures is considered essential for future sustainability.

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1. Introduction

De-convoluting the river recharge component of groundwater contained in a semi-arid zone aquifer from other forms of recharge, such as rainfall, is not a trivial task. Groundwater recharge originating from rainfall in semi-arid to arid environments is usually very low i.e. $<10 \text{ mm yr}^{-1}$ and is difficult to measure (Allison and Hughes, 1983). The volume of this “direct” rainfall recharge will depend on the amount, intensity and distribution of rainfall together with the actual evaporation rate (Barnes and Allison, 1988) in the catchment.

However, rainfall is not the only source of groundwater recharge in most semi-arid zone aquifers (Harrington et al., 2002; Scanlon et al., 2006) and “indirect” recharge such as from rivers can provide a greater volume of water. River recharge originating from dryland rivers, such as the Darling River, is much more difficult to estimate because of the highly episodic nature of river flow (Bowling and Baker, 1996; Thoms and Sheldon, 2000; Thoms et al., 2005; Young et al., 2006) and longer term regional climatic controls on the catchment which need to be investigated.

Oxygen-18 and deuterium ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) data are routinely measured and reported for rainfall (Dansgaard, 1964; Hughes and Crawford, 2012; IAEA, 2002), surface water (Gibson et al., 2002, 2008; Kendall and Coplen, 2001) and groundwater (Fontes, 1980; Gat, 1971, 1981; Lloyd, 1981), but these data are not widely coupled and applied to the unsaturated zone for interpreting the resulting groundwater isotopic composition.

Zimmermann (1967) was the first to apply $\delta^{18}\text{O}$ and $\delta^2\text{H}$ to study the soil profile and following this work various laboratory, theoretical and field studies have been undertaken over the past +40 years in the soil zone (Allison, 1982; Allison and Barnes, 1985; Allison and Hughes, 1983; Barnes and Allison, 1983; Fontes et al., 1986). Following on from these seminal studies, we contribute to the science by directing considerable effort towards defining the river water (12 years of data) and rainfall (7 years of data) isotopic input values for the area, as well as observed soil and groundwater isotopic values. Long-term datasets are needed for understanding and tracing the bulk recharge signal that is transferred to groundwater over time and hence under varied climatic conditions. To the author's knowledge, this is one of the first studies in Australia to assess rain, river water, soil water and groundwater under variable dry and wet climatic conditions in a semi-arid zone catchment to understand groundwater recharge over time.

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It is widely acknowledged that sampling groundwater for environmental tracers such as chloride (Cl), $\delta^{18}\text{O}$, $\delta^2\text{H}$ and tritium (^3H) are essential for understanding groundwater recharge mechanisms in semi-arid to arid zone environments (Cook and Herczeg, 2000; Scanlon et al., 2002), but it is not common to see long-term, multi-year investigations, especially in semi-arid zone regions. In this study, we investigate a small 250 km² research site located adjacent to the Darling River with the aim of tracing the origin and magnitude of flood events needed to recharge a semi-arid zone aquifer. We measured the groundwater, rainwater, river water and soil water for a variety of environmental tracers along a transect that extended ~7 km from the river channel. The rationale was to capture the concentration and evaporation gradient at different depths and distances from the river. The $\delta^{18}\text{O}$, $\delta^2\text{H}$ and Cl profiles in the unsaturated zone were measured after a dry (June 2009) and wet period (June 2012) with the aim of calculating evaporation rates using the steady-state isotope model (Barnes and Allison, 1988) and provide estimates of Cl loads to groundwater.

The major hypothesis of this study was that most of the groundwater recharge occurred from overbank river recharge or bank storage release and not from direct rainfall. Tracing an overbank river flood event that occurred in March 2012 was expected provide evidence of groundwater recharge. It is anticipated that these findings will help improve our current knowledge of groundwater recharge processes within arid to semi-arid zone environments. This is important because groundwater is often the only available resource in these areas and understanding how economically important water resources respond to climate change with increasing temperatures is essential for future water sustainability.

2. Environmental setting

The Darling River is located in the northern section of the Murray Darling Basin (MDB). The study area, known as Glen Villa, is located approximately 30 km southwest of Bourke along the Darling River (New South Wales, Australia; Fig. 1) and has been described in Meredith et al. (2013). The area is arid to semi-arid climate with low rainfall (average 355 mm yr⁻¹ at Bourke Post Office and average 397 mm yr⁻¹ at Cobar MO (BOM, 2014)). The Glen Villa area contains a narrow riverine corridor with riparian vegetation such as River Red Gums (*Eucalyptus camaldulensis*) that run along the Darling River.

The surficial geology of the study site comprises three unconsolidated alluvial aquifers; the shallow, intermediate and deep aquifers contained within the Narrabri (Quaternary), Gunnedah (Pliocene) and Cubbaroo (Miocene) Formations, respectively. These aquifers are part of an extensive, closed and internally draining groundwater basin. The deep aquifer is only found within a pre-Cenozoic palaeochannel that formed adjacent to the modern Darling River, within the underlying Great Artesian Basin (d'Hautefeuille and Williams, 2003) as seen in the cross section shown in Fig. 1. The other two aquifers are found extensively throughout the site and both have average thicknesses of 30 m (Fig. 1). The aquifer units at Glen Villa represent terrestrially sourced sediments that have originated from distal alluvial fan systems that were deposited in alternating wet/dry climates (Meredith et al., 2013).

3. Methodology

Groundwater, rainwater, river water, soil water and sediment samples were collected and measured for a number of different analytes from various locations throughout the study site. Most samples were collected along a transect that extended ~7 km from the river channel (cross section A–A'; Fig. 1).

3.1. Field techniques

River water was sampled from four locations (DR07, DR08, DR08a and DR08b) near the study site (Fig. 1). These were compared with a regional database of monthly surface water samples at three gauging stations near Bourke, Louth and Wilcannia collected from June 2002 to October 2005 (Meredith et al., 2009). Furthermore, 35 samples were analysed from the upstream (Bourke; ~40 km from Glen Villa) and downstream (Louth and Wilcannia; ~110 and 430 km respectively, from Glen Villa) gauging stations for 2011 and 2012.

Sediments were collected from boreholes drilled specifically to collect sediment samples in June 2009 during a dry period and again in June 2012 after a wet period. Sediment samples were collected off the auger for four boreholes drilled adjacent to existing groundwater monitoring wells using a motorised soil auger (Fig. 1). These boreholes were drilled in June 2009 until refusal (5, 4 and 5.5 metres below ground surface (m bgs)). In June 2012, new boreholes were drilled close to the original sites to 5 m bgs. Duplicate samples were collected from 0.5 m intervals for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis, volumetric moisture content and hydrochemical analysis. All soil samples were placed into sealed glass jars to prevent loss of soil water which could result in fractionation of this sample due to evaporation. The sample was then refrigerated until analysis.

Groundwater samples were collected from nested groundwater monitoring wells on August 2007, June 2009 and June 2012 (Fig. 1 see cross section A–A'). Sample depths varied between 12 and 126 m bgs and screen intervals ranged from 3 to 6 m long (Fig. 1). After standing water levels were measured, the wells were purged of three well-volumes and until stabilisation of field parameters (electrical conductivity, oxidation–reduction potential, dissolved oxygen, temperature and pH) prior to sampling. Groundwater samples were collected from an in-line 0.45 μm polyether-sulphone high capacity filter that was attached to the head of a submersible pump. For full details of the methodology for sample collection, the reader should refer to Meredith et al. (2012).

3.2. Analytical techniques

3.2.1. Sediments

One of the duplicate sediment samples was dried at 105 °C for 24 h to determine the gravimetric moisture content. Grain size was determined using a Malvern Mastersizer with a 300RF lens, 0.05–900 μm detection range and a beam length of 2.40 mm. The volumetric moisture content ($\text{m}^3 \text{m}^{-3}$) was calculated using a bulk density of 1.3 mg m^{-3} , multiplied by the gravimetric moisture content. Soil water extracts were performed at 1:5 dilutions on soil samples (Rayment and Higginson, 1992). Soil water samples were filtered through a 0.22 μm for major ion analysis using Ion Chromatography (IC) for anions and, after acidification, using Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES) for cations.

Soil water was extracted from the sediment by azeotropic distillation with kerosene, following the method outlined in (Revesz and Woods, 1990). After extraction, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were analysed by Isotope Ratio Mass Spectrometry (IRMS) according to methods outlined in Epstein and Mayeda (1953) and Dighton et al. (1997), respectively. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were reported as per mil (‰) deviations from the international standard V-SMOW (Vienna Standard Mean Ocean Water) and were reproducible to $\pm 0.1\text{‰}$ and $\pm 1.0\text{‰}$ respectively.

3.2.2. Water

The water samples were analysed by ICP–AES for cations and IC for anions. Cations and anions were assessed for accuracy by evaluating the charge balance error percentage and >85% of the

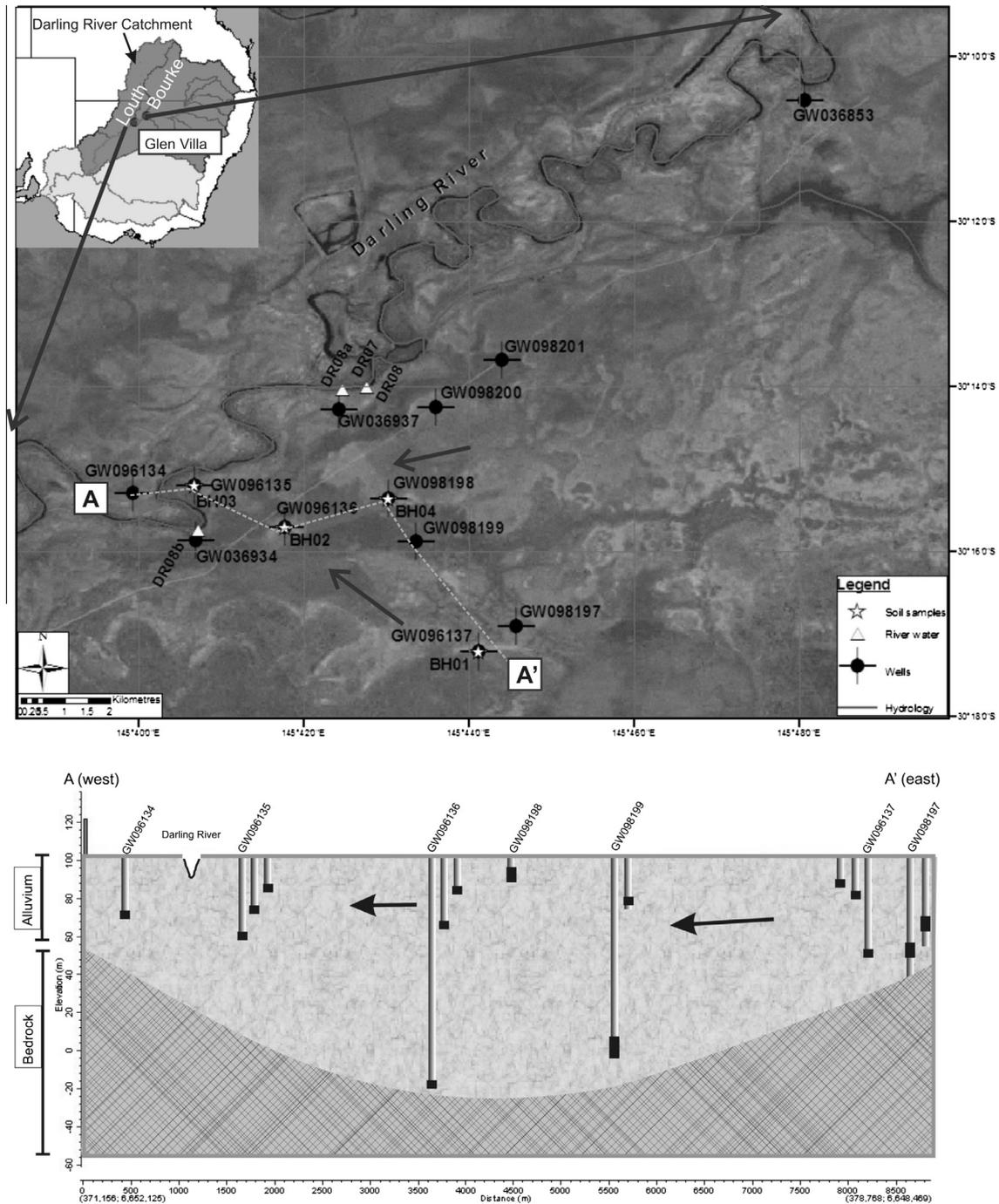


Fig. 1. Location of the Glen Villa study site (dashed lines show the location of cross section A–A’ with reference to the limits of the Murray–Darling Basin (left top corner insert: light grey + dark grey extent) and the Darling River catchment (left top corner insert: dark grey extent). Locations of groundwater wells, soil and river water sample sites are shown. Arrows show the generalised groundwater flow direction at the site during low flow conditions in the river. The geological cross section below the location map runs from A–A’. The locations of screens are depicted as black rectangles near the bottom of the wells. The contact and extent of the alluvium and bedrock are shown.

samples fell within $\pm 5\%$. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were analysed by IRMS for the groundwater samples and saline river samples, and a Picarro L2130-i Cavity Ring-Down Spectrometer was used to measure the fresh river water samples. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are reported as per mil (‰) deviations from the international standard V-SMOW and were reproducible to $\pm 0.1\text{‰}$ and $\pm 1.0\text{‰}$, respectively for the IRMS, and $\pm 0.2\text{‰}$ and $\pm 1.0\text{‰}$, respectively for the Picarro. The ^3H activities were expressed in tritium units (TU) with an uncertainty of $\pm \leq 0.1$ TU and quantification limit of ≤ 0.1 TU, and were analysed by liquid scintillation counting. Extended methods for ^3H activities can be found in Meredith et al. (2012).

3.3. Modelling

The $\delta^{18}\text{O}$ profiles in the unsaturated zone were modelled using the steady-state isotope model (Barnes and Allison, 1988) to determine the evaporation rate, E . Assuming that isotopes move only by diffusion in the liquid and vapour phases, the steady-state isotope profile below the evaporation front, δ , is given by (Barnes and Allison, 1988)

$$\delta - \delta_{ref} = (\delta_{ef} - \delta_{ref}) \exp \left[- \int_{z_{ef}}^z d\zeta / (z_l + z_v) \right] \quad (1)$$

where z is depth, δ_{ref} is a reference isotope concentration at depth, z_{ef} is a reference depth below the evaporation front but close to the surface, δ_{ef} is the isotopic concentration at z_{ef} , and z_l and z_v are the diffusion length scales for the liquid and vapour phase, respectively. In the liquid phase, the diffusion length scale

$$z_l = D^*/E \quad (2)$$

where D^* is the effective diffusivity of $H_2^{18}O$ in the liquid phase and E is the evaporation rate through the surface. In the vapour phase

$$z_v = (\alpha^* \sigma^v D_v^* N_{sat})/E\rho \quad (3)$$

where D_v^* is the effective diffusivity of $H_2^{18}O$ in the vapour phase, α^* is the equilibrium fractionation factor of $H_2^{18}O$, σ^v is the kinetic fractionation factor, N_{sat} is the saturated water vapour density, and ρ is the density of liquid water (Table 1).

The effective diffusivities take into account the effect of the porous medium in reducing the net diffusion rate. They were modelled as functions of the volumetric water content and soil properties so that

$$D^* = \theta\tau D \quad \text{and} \quad (4)$$

$$D_v^* = (\epsilon - \theta)\tau D_v \quad (5)$$

where θ is the volumetric water content, τ is the tortuosity of the soil matrix, ϵ is the dry soil porosity, D is the free water and D_v air diffusion coefficient.

The parameters in Eqs. (4) and (5) were taken from measurements or set to representative values (Table 1) leaving the evaporation rate as the only unknown. To evaluate the integral in Eq. (1), volumetric soil moisture was linearly interpolated between measurement points and then theoretical profiles were fitted to data using a nonlinear least-squares optimisation routine from SciPy (Jones et al., 2014). The samples collected from the unsaturated zone during the dry period (June 2009) are modelled in this study because of the extended period between rainfall events created ideal conditions to study evaporative effects on the development of isotope profiles (Barnes and Allison, 1983).

Soil moisture flux to the unsaturated zone was calculated by dividing solute flux by the soil water concentration (Scanlon, 2000; Sharma and Hughes, 1985). The solute flux for the study site was estimated by multiplying the mean precipitation (397 mm yr⁻¹) by the weighted average Cl concentration in rainfall for the Cobar region May 2007 to June 2010 (1.2 mg L⁻¹; Crosbie et al., 2012) giving a value of 0.5 g m⁻² yr⁻¹, which is similar to that observed in South Australia (0.1 g m⁻² yr⁻¹) (Allison et al., 1985).

We also use the Craig and Gordon model (Craig and Gordon, 1965) outlined in (Gonfiantini, 1986) to determine the fraction of soil water remaining, where heavy-isotope enrichment is a function of relative humidity, temperature and isotopic composition of water vapour (δ_A). We assume a relative humidity of 45%, a temperature of 20 °C and δ_A from -13.6‰ for $\delta^{18}O$ (Gibson et al., 2008)

and -108.4‰ (multiplying $\delta^{18}O$ by 8) for δ^2H . The initial water composition was chosen as -4.70‰ and -27.6‰ for $\delta^{18}O$ and δ^2H , respectively (Meredith et al., 2009), representing the weighted-mean isotopic composition of input waters to the catchment.

4. Results

4.1. Rainfall

Monthly rainfall data (1963–2012) are examined using a cumulative residual curve (CRC), which shows periods where the rainfall has been higher or lower than average for Cobar, 130 km south of the study site. Fig. 2a shows sections of the curve that are declining represent “drier” periods such as from the start of 2004 to mid-2007 i.e. when the August 2007 water samples were collected. Samples collected in June 2009 were collected during a declining rainfall period also but those collected in June 2012 were collected after a rising curve reflecting a “wetter” than average period for rainfall.

Monthly composite rainfall samples for Cobar, have been collected as part of a larger Australia-wide programme since 2007 run by ANSTO (Fig. 2b). Samples were analysed for $\delta^{18}O$ and δ^2H and a Local Meteoric Water Line (LMWL) of $\delta^2H = 6.97\delta^{18}O + 8.3$ was constructed based on monthly averages from 2007 to 2013 (using ordinary least squares regression). The amount weighted mean $\delta^{18}O$ and δ^2H values were -4.63‰ and -22.8‰, respectively, and monthly winter values were more depleted than in summer.

4.2. River water

River water samples were collected from within the study area (Fig. 1). They were collected from upstream (Bourke) and downstream (Louth and Wilcannia) of the study area for two periods; (1) June 2002 to October 2005 (Meredith et al., 2009) and (2) 2011 to 2012. The rainfall data suggests that the river level is governed by trends in long-term rainfall conditions rather than localised events (Fig. 2a and b). The wetter than average rainfall (increasing CRC) from 2010 to 2012 did coincide with periods of elevated river levels. The Darling River is a regulated system with weirs and structures controlling existing flow (Bowling and Baker, 1996). But the amount of flow is governed by the variable climatic conditions within the catchment (Thoms and Sheldon, 2000). Therefore, “wetter” than average climatic trends result in greater river flows. The river discharge event in March 2012 recorded the highest river level during the sampling period resulting in the river bank level of 10.6 m being exceeded (Fig. 2b).

River water was generally fresher than groundwater but varied significantly in Cl concentrations ranging from fresh (1 mmol L⁻¹) to saline (>550 mmol L⁻¹). The most saline samples were collected when the river was not flowing and the water contained in the river channel was dominated by saline groundwater input (Meredith et al., 2009). The $\delta^{18}O$ and δ^2H values (average: +0.35‰ for $\delta^{18}O$ and -4.7‰ for δ^2H ; $n = 151$) for river water were enriched relative to groundwater samples. Since the lighter isotope is preferentially lost during evaporation, enriched river samples highlight the significance of evaporation on surface water. As seen in Meredith et al. (2009), river water chemistry, including $\delta^{18}O$ and δ^2H was found to vary significantly over time due to variable flow conditions, evaporation and groundwater influx. The $\delta^{18}O$ values during low flows are greater than 0‰ but after large flow events such as the April 2010 flood, depleted values of ~ -8.0 ‰ were observed (Fig. 2b).

Table 1
Evaporation model parameters.

Symbol	Value	Definition
T	25 °C	Temperature
α^*	0.990740	Equilibrium fractionation factor
τ	0.66, 0.2	Tortuosity for sand, clay
ϵ	0.3	Porosity
D	$2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	Diffusivity of water in liquid phase (Mills, 1973)
D_v	$2.5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$	Diffusivity of water vapour in air (Braud et al., 2005)
ρ	1000 kg m ⁻³	Density of liquid water
σ^v	1	Kinetic fractionation factor
z_{ef}	0.5 m	Reference depth of below evaporating front

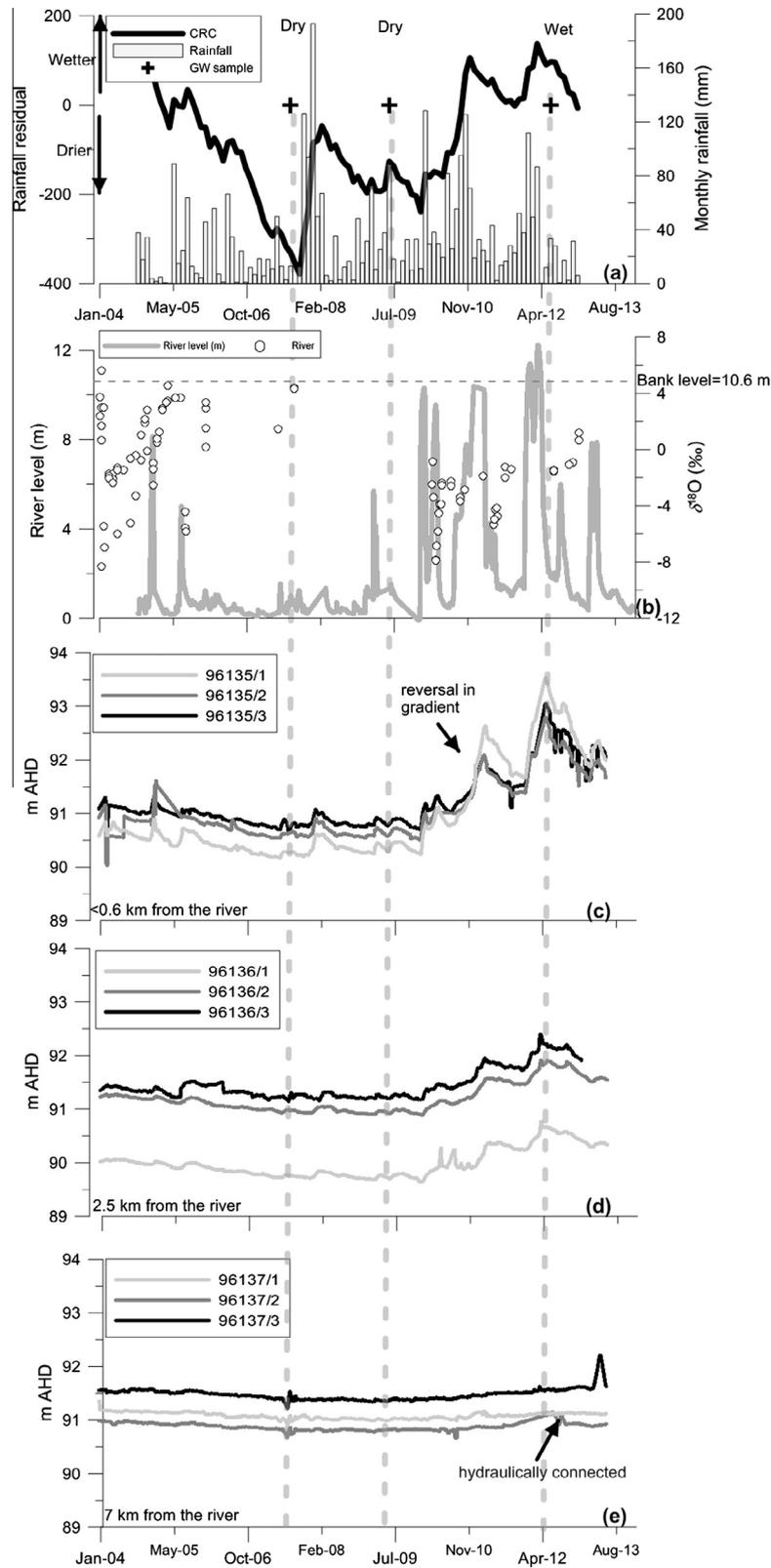


Fig. 2. Time series splice 2004–2013 of (a) long term rainfall cumulative residual curve (CRC) for Cobar from 1963 to 2012 with monthly rainfall data from October 2004 to December 2012 for Cobar and groundwater sampling events for the dry periods in August 2007, June 2009 and the wet period in June 2012 (b) River level height at Glen Villa weir (DR07; Fig. 1) with bank level of 10.6 m and surface water $\delta^{18}O$ values from upstream of the site (Bourke) and downstream (Louth and Wilcannia) (c) water level measurements close to the river (<0.6 km) for shallow (96135/1: well screen midpoint at 16 m bgs), intermediate (96135/2: 28 m bgs) and deep (96135/3: 42 m bgs) (d) water level measurements at 2.5 km from the river for shallow (96136/1: 17 m bgs), intermediate (96136/2: 37 m bgs) and deep (96136/3: 119 m bgs) (e) water level measurements at 7 km from the river for shallow (96137/1: 15 m bgs), intermediate (96137/2: 22 m bgs) and deep (96137/3: 52 m bgs). Please note water levels have been adjusted to AHD (Australian Height Datum) and daily measurements have been filtered using a 5 day median calculation to remove instrumental noise produced by removing the logger for sampling.

4.3. Groundwater

4.3.1. Water levels

Water level loggers were emplaced in shallow (15–17 m bgs), intermediate (22–37 m bgs) and deep wells (42–119 m bgs) located <0.6 km (GW096135), 2.5 km (GW096136) and 7 km (GW096137) from the channel. Hydrographs were constructed from the 2004–2013 dataset with data filtered using the 5 day median to remove instrumental noise and highlight the general trends in water levels over time. The main source of instrumental noise was when water loggers were removed from the wells for sampling at various times throughout the study period. For example on 19 January 2005, wells GW096135/1 and GW096137/3 experienced a 0.4–0.5 m water level decrease, respectively.

Water levels generally showed an upward hydraulic gradient in the deeper sections of the aquifer (i.e. from wells located between 42 and 119 m bgs). Water levels within the shallow aquifer close to the river responded to long-term rainfall trends that were driving high flow conditions in the river (Fig. 2c). From June 2009 to March 2012, water levels in the shallow aquifer increased by 3 m near the river suggesting hydraulic connection to the river. The reversal in hydraulic gradient between the shallow and deeper sections of the aquifer observed after the December 2011 flood was indicated by vertical flow from the shallow aquifer downwards. The subsequent flow events in 2012 and 2013 have been sufficient to sustain vertical flow between the aquifers. The largest recorded flood event during this study was in March 2012 which was the only one to exceed the river bank level of 10.6 m (Fig. 2b). Because the other events did not exceed the river bank it shows that the aquifer was in hydraulic connection with the river receiving groundwater recharge via bank storage exchange or hyporheic exchange processes.

Groundwater levels at 2.5 km (GW096136) from the river experienced a similar rise in head to those located close to the river (GW096135) but with a reduced response (1.5 m) over the same period (Fig. 2d) and no reversal in hydraulic gradient. This suggests recharge is not reaching the deeper section of the aquifer and less connection to the river. Water levels located the furthest from the river (7 km) showed little response to rainfall or river flow conditions over the past 10 years (Fig. 2e). However after the March 2012 flood, the shallow and intermediate aquifer became hydraulically connected suggesting downward flow but limited to the shallow aquifers (Fig. 2e).

4.3.2. Hydrochemistry

Similar salinity range was observed in groundwater as in the river water, where Cl values ranged from fresh (2.5 mmol L⁻¹) to saline (586 mmol L⁻¹) but 85% of the 42 samples were greater than 285 mmol L⁻¹ and commonly Na–Cl-rich. The presence of shallow groundwater with low Cl concentrations (dilute) located close to the river (<0.6 km), implies fresh water interaction (Fig. 3a).

Groundwaters were depleted relative to V-SMOW with average values of $\delta^{18}\text{O}$ of -3.70‰ and $\delta^2\text{H}$ of -29.3‰ ($n = 42$) and plotted on a regression line of $\delta^2\text{H} = 4.4\delta^{18}\text{O} - 12.8$. The shallow fresh or “dilute” waters close to the river had the most variation in the $\delta^{18}\text{O}$ values (from -4.64‰ to -3.52‰ ; $n = 5$). Other than for dilute samples, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values did not vary greatly in the groundwater even with depth and distance from the river (Fig. 3b).

Groundwaters generally contained low measurable ^3H with an average 0.3 TU ($n = 42$) (Fig. 3c). The highest ^3H activity was found close to the river (<0.6 km). Recent groundwater recharge close to the river is supported by ^3H and Cl concentrations in groundwater. When groundwater was sampled from various depths (16, 28 and 42 m bgs) close to the river (GW096135) during the dry period (August 2007), groundwater was low in ^3H (0.3 TU) and high in Cl (469, 485 and 491 mmol L⁻¹, respectively). But the same wells

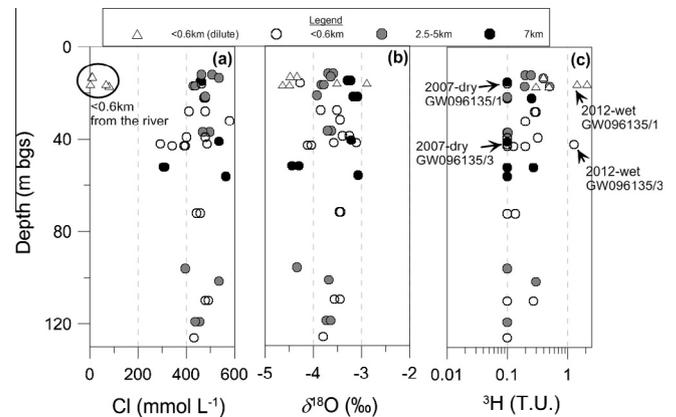


Fig. 3. Depth distribution plots of groundwater along the transect (a) Cl⁻ concentration (b) $\delta^{18}\text{O}$ and (c) ^3H presented in log scale for the x-axis with GW096135/1 and GW096135/3 depicted for the dry and wet sample event. The ^3H activities were expressed in tritium units (TU) with an uncertainty of $\pm \leq 0.1$ TU and quantification limit of ≤ 0.1 TU.

were sampled after the wet period (June 12) and had ^3H activities of 1.4, 0.3 and 1.3 TU, with increasing depth (Fig. 3c). These ^3H values were well above the quantification limit of 0.05 TU. Similarly lower Cl concentrations (67, 417 and 297 mmol L⁻¹, respectively) after the wet period (2012) provide compelling evidence of recent groundwater recharge even at depths of up to 42 m bgs near the river.

4.4. Unsaturated zone sediments

Volumetric moisture contents, Cl and major ion concentrations in the 1:5 soil water extracts generally increased with depth and distance from the river and were not found to be influenced by lithology (Fig. 4a–c). Variations in Cl concentrations in the soil water between the dry and wet periods also provided information on water infiltration in the unsaturated zone. After the wet period, the Cl concentration at 7 km from the river decreased by 800 g m⁻³ at 5 m bgs (Fig. 4c) suggesting Cl was diluted or is being transported down the profile. The concentration of Ca also decreased after the wet period below 2 m bgs (Fig. 4e) suggesting the presence of mobile mineral phases such as evaporite minerals. It is likely that evaporite minerals are precipitating after long periods of evaporation and partially dissolved after recharge events (Drever, 1997) hence the decrease in concentration after the wet period.

4.4.1. $\delta^{18}\text{O}$ profiles in the unsaturated zone

Irrespective of distance from the river, isotope profiles formed a classic shape with intermediate values at the surface, a maximum at ~ 0.5 m bgs and then a monotonic decrease towards a constant relatively depleted value at depth (Fig. 4d), regardless of the lithology (Fig. 4a). These isotope profiles are characteristic of water loss by evaporation through an unsaturated soil (Barnes and Allison, 1983). Below the evaporation front, the net diffusive water flux was constant and equal to the surface evaporation rate. But the heavy isotopes also diffused down the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ concentration gradient away from the evaporation front, eventually forming a profile where the net flux balanced the isotope flux (Barnes and Allison, 1982, 1983; Zimmermann, 1967).

Steady-state evaporation was assumed and the profiles were modelled using the method presented in Barnes and Allison (1988) to determine the evaporation rate, E (see methods). Curves matched observations for sites located near the river (GW096135) and 7 km from the river (GW096137) yielding steady-state

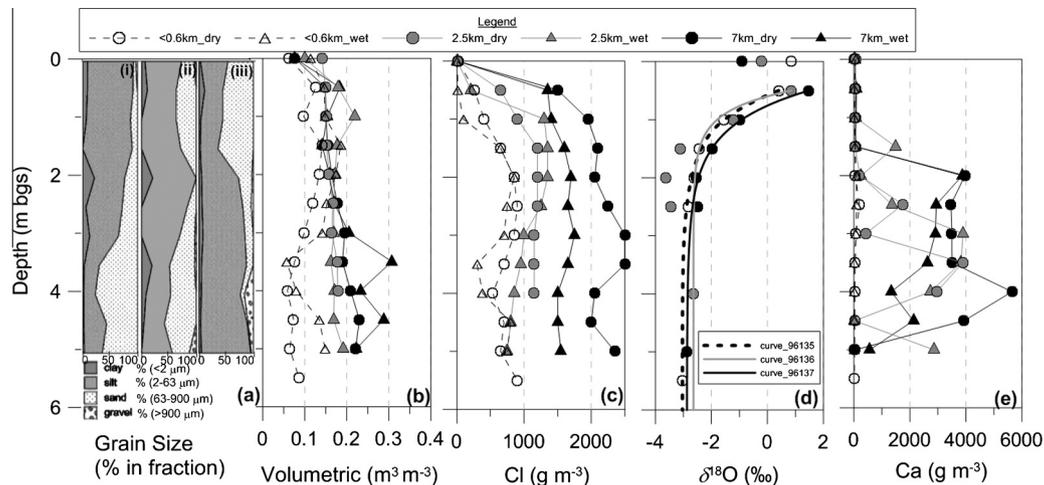


Fig. 4. Depth distribution plots through the top 6 m of the unsaturated zone along the transect (<0.6 km = BH03, 2.5 km = BH02, 7 km = BH01) according to different sampling periods (dry = June 09 and wet = June 12) (a) grain size distribution % of clay (<2 μm), silt (2–63 μm), sand (63–900 μm) and gravel (>900 μm) for (i) BH03, (ii) BH02 and (iii) BH01; (b) volumetric soil moisture content; (c) 1:5 soil water Cl concentration; (d) 1:5 soil water $\delta^{18}\text{O}$ and steady-state isotope model curves; (e) 1:5 soil water Ca concentration.

evaporation rates of 11 and 15 mm yr^{-1} , respectively. The evaporation rate at the site located 2.5 km from the river was estimated to be 26 mm yr^{-1} but with a weaker fit to the model, so the value was considered a slight over estimation of the evaporation rate. Using the Craig and Gordon model (see methods) it was calculated that a maximum of 25% of the initial soil water could be evaporated at the evaporation front based on the input values of 4.70‰ and -27.6‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively (Meredith et al., 2009).

5. Discussion

5.1. Groundwater origin

This study is a classic example of why we need to capture as many components of the hydrological cycle over extended time periods to understand the origin of groundwater. Initially we compared our groundwater $\delta^{18}\text{O}$ and $\delta^2\text{H}$ results in the traditional way against the GMWL (Global Meteoric Water Line) (Rozanski et al., 1993), LMWL and LEL (Local Evaporation Line) (Meredith et al., 2009) but we found that groundwater $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were offset from rainfall when compared to the LMWL and weighted means for annual and seasonal rainfall. They were also found not to have originated from the evaporated river water for the region because they plotted to the right of the LEL (Fig. 5). Therefore we tested whether the groundwater could contain various contributions of rainfall and evaporated soil waters from the unsaturated zone. To do this we then included the soil water line from regressed $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, and found a much closer fit, however, groundwater samples still plotted slightly left of this line implying a less evaporated origin (Fig. 5).

The soil waters have been estimated to contain only 75% of the original water source when experiencing evaporation rates of 11–15 mm yr^{-1} in the unsaturated zone at this site. Therefore we would expect the regression line of these soil waters to have a slope of between 4 and 6 in the $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ space (Allison, 1982; Barnes and Allison, 1983), where the slope is governed by the temperature and relative humidity at which the evaporation occurred (Gonfiantini, 1986). The soil waters from below the evaporation front (i.e. <1 m depth) resulted in a slope of 3.9 (Fig. 5). This provides evidence that the soil water signal is not composed of intermittent rainfall events because we would expect to have isotopic values below the evaporation front that produce a similar

slope to the LMWL (i.e. 6.97) (Allison et al., 1985; Fontes et al., 1986). The increasing Cl concentrations that have resulted in the unsaturated zone with distance from the river also disproves the constant Cl flux from rainfall model, because we would see similar soil Cl concentrations along the transect if similar moisture fluxes occurred (Scanlon, 1991).

Therefore we can discount rainfall and soil water as the main source of groundwater recharge, the source that remains unexplained in this system is river flood waters. We added a further 35 river water samples from upstream (Bourke) and downstream (Louth and Wilcannia) from a wetter than average period for the region from 2011 to 2012, and we found that groundwaters plot almost directly on this river water regression line ($\delta^2\text{H} = 6.78\delta^{18}\text{O} - 4.0$) (Fig. 5). Suggesting groundwaters originate from high flow river waters that were recharged quickly and not subjected to excessive open-water evaporation. Increasing Cl concentration in the unsaturated zone with distance from the river also confirms that the aquifer is recharged from varied moisture fluxes. Episodic river flooding events that vary in magnitude and spatial extent across the transect would explain this trend. Therefore, the site located the greatest distance from the river (i.e. 7 km), would receive significantly less water, and hence less transport of ions away from the area of recharge, resulting in a higher Cl accumulation, as observed in the data. These various lines of evidence have not only clearly highlighted the river water origin of groundwater, but also that higher flow events (with more depleted values) dominated the signal. Without this long-term river water and rainfall data, the true origin of groundwater i.e. river water vs. rainfall and high flow vs. low flow contributions would have only been inferred.

5.2. Tracing Cl input from a flood event

We have identified that river flooding events are the primary source of groundwater recharge, so now we use one of these events to identify how this influences Cl concentrations in groundwater. The largest flood event recorded during this study in March 2012 exceeded the river bank level of 10.6 m, peaking at 12.2 m on 8 March 2012. Evidence of inundation up to 15 km away from the river channel was captured by the TerraMODIS satellite over the Darling River on 7th March 2012. Hydraulic modelling of the area completed for the 1974, 1976 and 1998 floods which were of

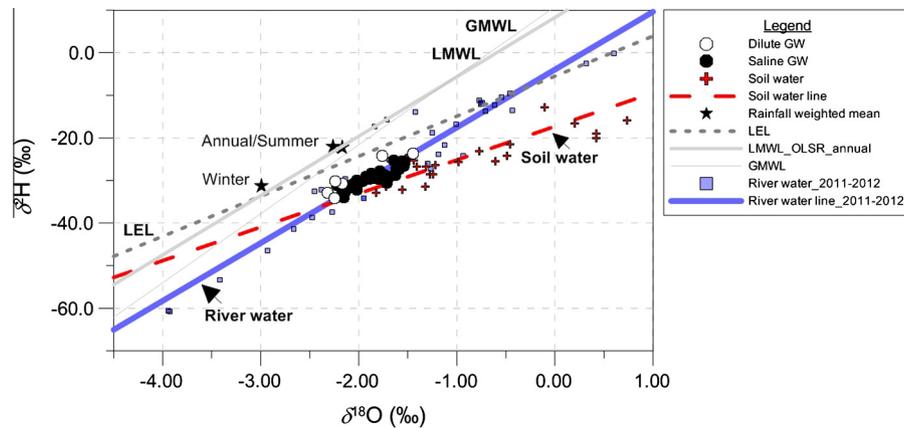


Fig. 5. Bivariate plot of $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ for river water, soil water and groundwater with respect to the GMWL ($\delta^2\text{H} = 8.1\delta^{18}\text{O} + 10.8$), LMWL_OLSR ($\delta^2\text{H} = 6.97\delta^{18}\text{O} + 8.28$) and LEL ($\delta^2\text{H} = 4.7\delta^{18}\text{O} - 5.5$) for the region. The soil water regression line (excluding the top 1 m evaporated samples) ($\delta^2\text{H} = 3.9\delta^{18}\text{O} - 17.3$) and river water line for 2011–2012 ($\delta^2\text{H} = 6.78\delta^{18}\text{O} - 4.0$) are included for comparison. The amount weighted mean summer, winter and annual rainfall for value are also included.

similar magnitude also suggested that 1.0–2.0 m of floodwater could result over the study area (Benning and Dalglish, 2009).

Here we use the wells located 2.5 and 7 km from the river because we know they are only influenced by overbank recharge. We observe an increase in Cl concentration in the shallow groundwater of between 200 and 300 mg L^{-1} in June 2012 after the flood event. Considering this concentration increase, the average flood water concentration (12 mg L^{-1} ; Meredith et al., 2009) and a 1 m average inundation depth from this event, the mass balance suggested 40–60 mm of infiltration water was needed to produce the observed Cl concentration increase in the groundwater. When we considered that these large flood events typically happen approximately every 26 years (based on the average time between the previous major floods for the region in 1864, 1890, 1950, 1974, 1976, 1998 and 2012), we calculated it would take 1.3–2.1 ka to create the observed Cl concentration in the shallow groundwater (15–17 m bgs) from riverine input.

It is also important to note that the large episodic recharge pulse observed in March 2012 had enough hydraulic head to push the Cl that was accumulating in the soil profile downwards and the recharge was fast enough to not be influenced by evaporation. Clearly these are initial estimates and provide a guide to Cl accumulation and the time taken for the observed groundwater Cl concentration to form. Being able to trace the Cl concentration increase in the groundwater was especially useful in this semi-arid zone environment because the presence of evaporite minerals such as NaCl in the soil profile away from the river (>2.5 km) will affect calculations involving (1) Cl mass balance (Wood, 1999) or (2) residence time of the Cl in the unsaturated zone (Scanlon, 1991). The next step with this work is to refine these estimates by modelling groundwater dynamics with a coupled flow and chemical transport model.

6. Conclusion

This study has significantly advanced our understanding of how groundwater is being recharged in the dryland region of the Darling River catchment. Groundwater recharge originating from rainfall in most semi-arid to arid environments is usually very low. It is generally hypothesised that river recharge is the dominant groundwater recharge source, but providing evidence for such can be difficult, especially when evaporative concentration obscures standard geochemical processes and long time periods (decades) exist between river flooding events. The highly episodic

flow of the Darling River adds another layer of complexity to the interpretation of the hydrology and makes it particularly difficult to interpret the groundwater chemical and isotopic signals. Long-term studies such as ours, which use a range of hydrochemical tracers measured in rain, river water, soil water and groundwater, are important in furthering our understanding of groundwater recharge processes. This study is unique to the Australian setting because we provided 12 years of river water and 7 years of rainfall data, as well as measurements from the unsaturated zone and groundwater over time, all used to understand groundwater recharge after a large river flood event.

The major hypothesis of this study was that groundwater recharge occurred mostly from overbank river recharge during flooding, and not from direct rainfall. The isotopic and Cl concentrations observed in the unsaturated zone confirmed this. In addition, we traced a large river recharge pulse from an overbank flooding event in March 2012, which provided convincing evidence of groundwater recharge. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ profiles were modelled to determine the evaporation rate, and also provide evidence that small volumetric inputs from rain on a yearly basis were not the major recharge mechanism. Soil water chemistry also proved to be useful for characterising the groundwater where Cl concentrations suggest a history of moisture flux variations created from high flow episodic river recharge. In addition, the solute load increase in the groundwater after a large flood event suggests a period of 1.3–2.1 ka to attain the observed salinity level.

Globally, further research in arid to semi-arid zone groundwater is essential as groundwater resource models are often designed using limited, short-term monitoring data. Understanding how economically important water resources respond to climate change with increasing temperatures will be essential for future sustainability.

Acknowledgements

The authors would like to thank various Australian Nuclear Science and Technology Organisation personnel such as Barbora Gallagher, Scott Allchin and Kellie-Ann Farrawell for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and ^3H analysis. Thank you to Stuart Hankin and Chris Dimovski for their help in the field. We would also like to thank the New South Wales Government, Department of Primary Industries, Office of Water, Australia for providing assistance with accessing the site and providing the water level data with special mention to Hari Haridharan.

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