



## Groundwater dependent pools in seasonal and permanent streams in the Clare Valley of South Australia



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### ABSTRACT

#### 1. Study region

The Clare Valley region of South Australia.

#### 2. Study focus

Continuing extraction of groundwater threatens pools in seasonal and permanent streams. In order to determine this groundwater dependence, the pools and groundwater from corresponding fractured rock aquifers were investigated using environmental tracers ( $\delta D$ ,  $\delta^{18}O$ ,  $^{87}Sr/^{86}Sr$ , and major and minor elements). For the 11 paired pool-groundwater sites in the four different catchments, groundwater dependence was evaluated over a four season sampling period.

#### 3. New hydrological insights

In this Mediterranean climate with cool wet winters and dry hot summers strong salinity changes (up to 2.5 times) due to seasonal cycles of wetting and drying were observed in surface water. Oxygen and hydrogen isotope values from pool sites showed strong evaporative enrichment during the dry season with up to 50% net evaporation calculated. Water isotopes from groundwater, however, cluster at the depleted end of the local meteoric water line and most do not show change despite significant seasonal salinity changes. Strontium isotope values and concentrations from the pools over the one year period do *not* define a mixing relationship. Instead, most pool sites have unchanging strontium isotope values despite the large seasonal change in salinity indicating strong evaporation of groundwater fed pools during this drought year.

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## 1. Introduction

The last two decades have seen a substantial increase in understanding of the interactions between surface water and groundwater (SW-GW), especially in semi-arid and arid environments that are common to the Australian setting (Jolly et al., 2008). Historically, studies of groundwater and surface water have been quite distinct and separate (Sophocleous, 2002). An

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example of the interconnectedness of surface water and groundwater systems is the recognition that aquatic biota have the ability to move between surface water and groundwater with the hyporheic zone linking these two domains (Ward, 1998).

Most surface water studies have focused on flowing systems (Murray et al., 2003). This is understandable given the methods used to assess SW–GW exchange are often reliant on the presence of flowing water. For example, the use of radon as a tracer of groundwater inputs into streams is a popular method that is reliant on the short residence time of radon gas in surface water (e.g. Cook et al., 1999, 2003; Gilfedder et al., 2015). However, within semi-arid seasonal and ephemeral systems permanent water is most often found as pools with significant sediment–water interactions making the interpretation of radon measurements much more difficult (Cook et al., 2008). In ephemeral or intermittent surface water systems with important springs or pools, groundwater–surface water interactions and the source of surface water has been assessed using strontium isotope environmental tracers (Rango et al., 2010; Paces and Wurster, 2014).

Wetland ecosystems in seasonal or ephemeral systems commonly have a level of groundwater dependency, and the degree and timing of the dependency are fundamental issues for managing such river systems (Murray et al., 2003; McMahon and Finlayson, 2003). Where dependency occurs, surface water and groundwater exchange varies with seasonal changes of flow conditions (Brunke and Gonser, 1997; Sophocleous, 2002). Most previous research has focused on pool systems entirely dependent on groundwater; however Hatton and Evans (1998) suggest that systems with variable dependency on groundwater are of greater importance since variable dependency may be more common and as such play a large role in maintaining surface water refuges during drought and low-flow conditions.

Investigations of groundwater discharge into pools in seasonal and ephemeral systems are few (Sophocleous, 2002). It is often presumed that the presence of water in pools is direct evidence of groundwater inputs, particularly during drought conditions. This presumption is problematic since many dryland rivers retain standing pools without having an obvious direct connection with the underlying groundwater. Such pools can be maintained by residual surface flows, irregular flow pulses and perched stream bed or hyporheic water due to what Sophocleous (2002) terms a clogged stream bed. For example, within the Lake Eyre Basin, Hamilton et al. (2005) found that surface water was essentially isolated from underlying groundwater and that water levels within waterholes of semi-permanent channel segments were controlled by evaporation.

Surface water–groundwater interactions become important to land management when they attempt to account for the sustainable level of water use and water quality in seasonal and ephemeral systems. For example, within the Border Rivers catchment (Murray–Darling Basin, Australia) SW–GW interactions were examined to determine the potential for saline groundwater discharge into surface water sources (Baskaran et al., 2009). Many groundwater dependent ecosystems in Australia are under threat due to both groundwater extraction and recent land–scape changes (Hatton and Evans, 1998). South Australia, New South Wales, and Victoria use more than 60% of extracted groundwater for irrigation, and between 1985 and 1997 groundwater extraction nearly doubled (Plazinska, 2007). The expansion of irrigated vineyards in the Clare Valley area has relied on both efficient capture of surface water and on groundwater pumping both of which have been shown to lower the groundwater level beneath rivers and streams and thereby lengthening the time a stream has no or very low flow (Dahm et al., 2003; Evans, 2007). Since institutional arrangements in Australia have divided the management of surface water and groundwater (Fullagar et al., 2006), understanding the degree of groundwater dependence of surface water pools is essential for appropriate water resource planning and management.

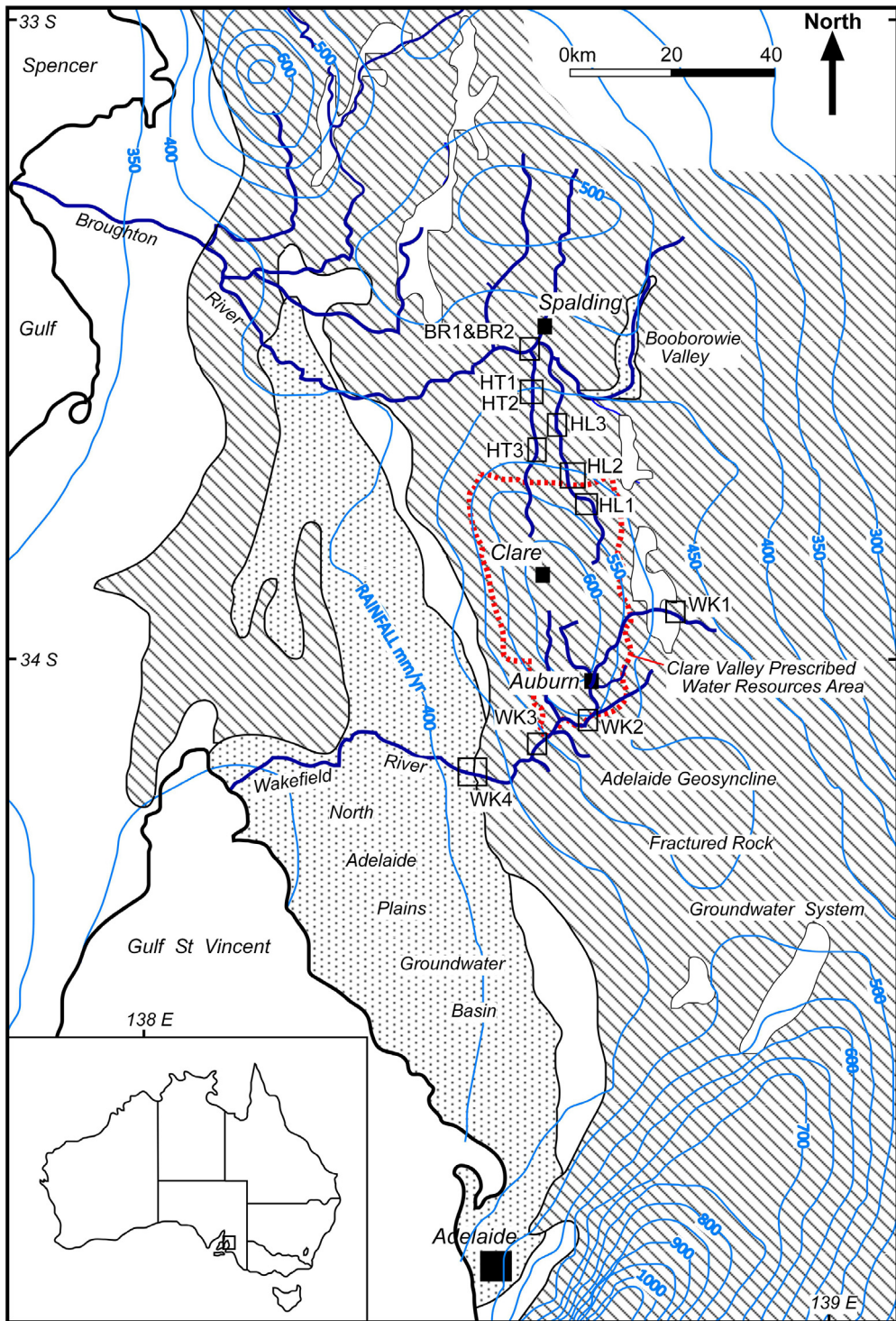
Determining the degree of groundwater dependence of surface water pools can be achieved by sampling paired groundwater–permanent pool sites and analysing for environmental tracers (Walker and Krabbenhoft, 1998). A multi-isotope approach takes advantage of the fact that unreactive tracers (water isotopes) and reactive tracers (strontium isotopes) provide different information on how a catchment functions (Bullen and Kendall, 1998). Water isotopes are useful for determining water sources and evaporation whereas tracers such as strontium isotopes and major ions are useful for understanding water–rock and water–soil interactions along flow–paths (Shanley et al., 1998; McNutt, 2000). The strontium isotope ratio of  $^{87}\text{Sr}/^{86}\text{Sr}$  has been commonly used to trace the source and mixing of waters. Because  $^{87}\text{Sr}$  is the only strontium isotope to vary over geologic time, variations in the strontium isotope ratio reflect strontium from different sources as water passes through strontium containing materials (McNutt 2000). Strontium isotope ratios can be used to discern subtle differences in the interaction of water with different mineral types or the contact time with minerals (Bullen et al., 1996; Walker and Krabbenhoft, 1998).

This paper aims to determine the level of groundwater dependence of 11 surface water pools in seasonal and ephemeral streams over one water year in the Clare Valley area north of Adelaide, South Australia (Figs. 1 and 2; Table 1). The level of groundwater dependence and the degree of surface water evaporation are determined using strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ), stable water isotopes ( $^{18}\text{O}/^{16}\text{O}$ ; D/H), and major ion analysis.

### 1.1. Clare Valley region

The Clare Valley region is located approximately 100 km north of Adelaide within the Northern Mount Lofty Ranges of South Australia with elevations ranging from about 400 to 650 m (Fig. 1). The Broughton and Wakefield river systems are the main surface water catchments within the Clare Valley region. These two river systems are separated by an east–west topographic high which causes the Broughton River system to flow northward to the Spencer Gulf, while the Wakefield system flows south–west to the Gulf St Vincent.

The climate of the Clare Valley area is generally semi-arid to sub-humid with hot, dry summers and cool moist winters. Despite higher elevation areas exhibiting higher rainfall (mean annual rainfall at the highest elevation in the area is 653 mm)



**Fig. 1.** Location map showing the Clare Valley Prescribed Water Resources Area, stream catchments, samples sites along the Hutt (HT), Hill (HL), Broughton (BR) and Wakefield (WK), and overall location in Australia. Groundwater basins and rainfall isohyets from Alcoe and Berens, 2011.

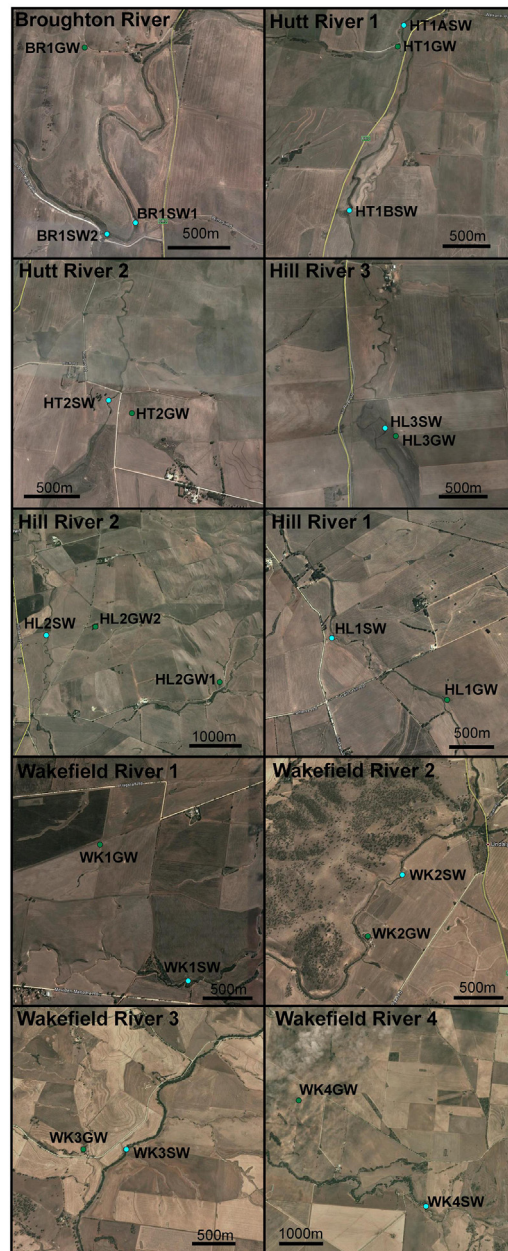


Fig. 2. Aerial images of the paired surface water-groundwater sites.

the variation in rainfall across the region maintains its semi-arid climatic classification. As a result of the strong precipitation and temperature variation in this climate, rivers are seasonal with very low flows or no flows during summer and autumn and moderate to low flows during winter (Fig. 3).

The soils of this region are dominated by Red Brown Earth or duplex soils (Stace et al., 1968; Oades et al., 1981) that are approximately 0.5–1.0 m thick. These soils, where not extensively modified, have a sandy or coarse silty A horizon which is 10–30 cm thick and commonly abruptly overlays a clayey red-brown B horizon. In much of the region, soil carbonate occurs between 0.5 and 1.0 m depth in the lower B and/or upper C horizon. Below the B horizon is weathered bedrock or saprolite which has variable thickness (Fig. 4).

The Clare Valley region is part of the Mt Lofty and Flinders Ranges geologic province. Rock types include metamorphosed shale, quartzite, and limestone (marble) including dolomite and dolomitic shale. Geologic formations in the region have been folded into broad folds that trend north-south and plunge to the south. This bedrock comprises the host rock for the fractured rock aquifer which dominates the groundwater system in the region. The fractured rock aquifer has an upper, moderately permeable zone at depths of 20–40 m that has relatively low salinities (Love et al., 2002) and a deeper, low

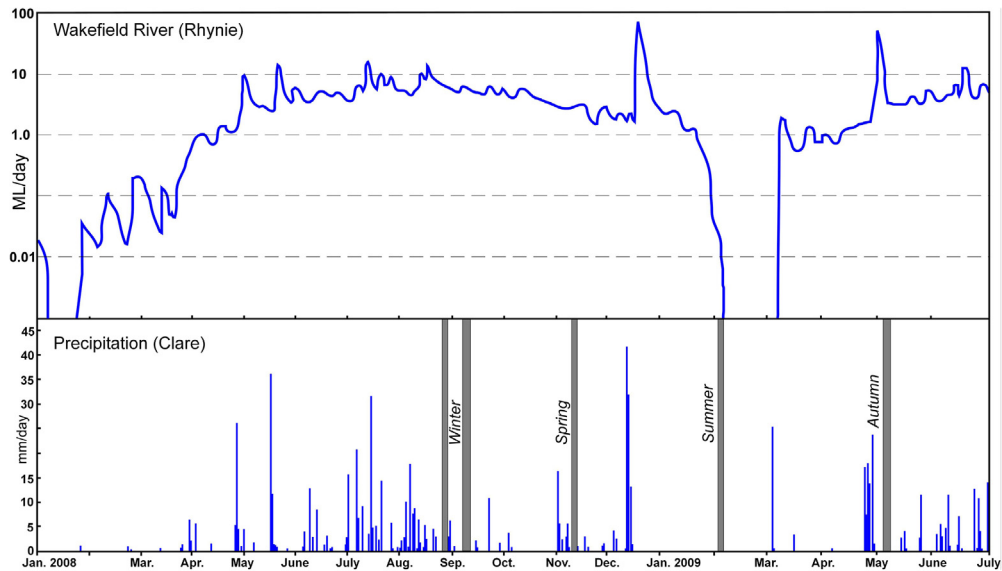
**Table 1**  
Location and elevation details of paired groundwater-surface water sites.

Groundwater bores	Catchment	Latitude	Longitude	Elevation mAHD	Approx. depth m	Distance from pool m	Unit Number Water Connect	Comments
BR1GW	Broughton	33°30'43.87"S	138°35'37.84"E	297	20–40 m	1620 1670	n/a	Stock production bore with holding tank
HL1GW	Hill	33°45'11.90"S	138°41'05.27"E	379	20–40 m	1080	6630–1659	Stock production bore
HL2GW1	Hill	33°43'07.93"S	138°41'38.92"E	423	20–40 m	4030	n/a	Stock production bore with holding tank
HL2GW2	Hill	33°42'25.35"S	138°39'52.23"E	377	20–40 m	1130	n/a	Stock production bore with holding tanks
HL3GW	Hill	33°37'57.06"S	138°38'08.73"E	329	20–40 m	110	n/a	Stock production bore
HT1GW	Hutt	33°34'24.01"S	138°35'53.18"E	291	33 m	280 2200	6630–3314	Stock production bore with tank
HT2GW	Hutt	33°40'13.52"S	138°36'31.84"E	320	24 m	290	6630–2136	Stock production bore
WK1GW	Wakefield	33°54'23.23"S	138°48'21.29"E	440	38 m	1790	6630–526	Stock production bore
WK2GW	Wakefield	34°05'06.59"S	138°40'46.15"E	265	20–45 m	760	6629–1749	Domestic production bore
WK3GW	Wakefield	34°07'11.05"S	138°36'02.76"E	192	35 m	590	6629–1178	Stock production bore with holding tanks
WK4GW	Wakefield	34°08'45.15"S	138°31'11.67"E	94	32 m	3790	6529–311	Stock production bore
Surface water								
BR1SW1	Broughton	33°31'32.07"S	138°36'01.87"E	260	–	–		Upstream pool of three closely spaced pools
BR1SW2	Broughton	33°31'35.80"S	138°35'54.01"E	259	–	–		Downstream pool of three closely spaced pools
HL1SW	Hill	33°44'58.15"S	138°40'26.13"E	369	–	–		Small pool in bend of channel
HL2SW	Hill	33°42'32.93"S	138°39'08.91"E	353	–	–		Many pools
HL3SW	Hill	33°37'55.49"S	138°38'04.40"E	328	–	–		Many pools
HT1ASW	Hutt	33°34'14.71"S	138°35'54.19"E	287	–	–		Pool under bridge
HT1BSW	Hutt	33°35'34.46"S	138°35'46.94"E	298	–	–		Many pools
HT2SW	Hutt	33°40'09.54"S	138°36'20.55"E	318	–	–		A few pools
WK1SW	Wakefield	33°55'12.06"S	138°48'59.78"E	426	–	–		A few pools
WK2SW	Wakefield	34°04'43.93"S	138°40'58.09"E	264	–	–		One pool
WK3SW	Wakefield	34°07'12.99"S	138°36'25.79"E	180	–	–		One pool
WK4SW	Wakefield	34°10'05.49"S	138°31'11.67"E	103	–	–		One pool

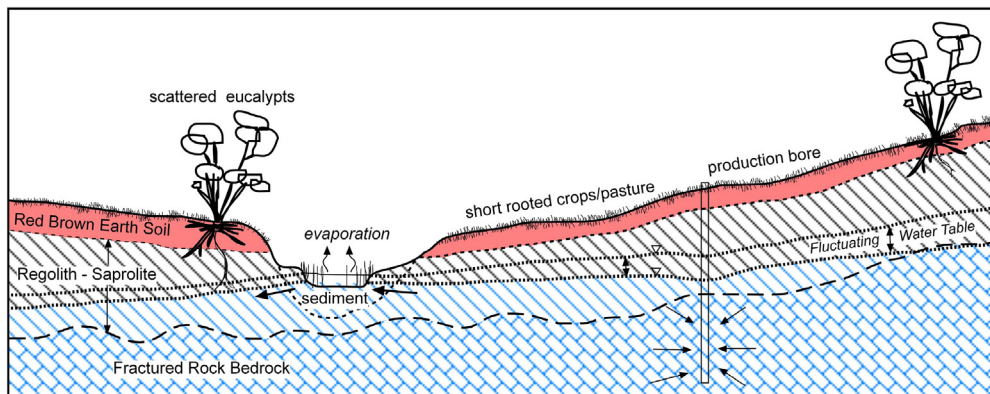
permeability zone with generally higher salinity and low fracture spacing (Love et al., 2002). The fractured rock aquifer standing water level has pronounced seasonal fluctuations as well as fluctuations from drought and wet year cycles due to variation in rainfall and the low storage capacity of the aquifer (Love et al., 2002; Stewart, 2005). Seasonal water table rise and fall can range up to 10–20 m within a year (Love et al., 2002; Stewart, 2005). There are salinity variations recorded in some bores situated in the upper part of the aquifer such that as the water table rises, salinity falls and as water table falls, salinity rises. These standing water level changes can double groundwater salinity values (Stewart, 2005) and demonstrates the occurrence of a saline cap.

As a highly developed agricultural and viticultural region, the Clare Valley experiences increasing and on-going demands for water resources. Currently, 30% of the Wakefield River system (Cresswell, 1999) and 12% of the Broughton River System (Cresswell, 2000) are designated as the Clare Valley Prescribed Water Resources Area which is bound by regulations outlining the sustainable use of both surface and groundwaters to maintain the long-term integrity of the water resources. Water resources outside of the prescribed area have limited protection from continued water resource development and extraction. Despite the protection of some portion of each of these river catchments, continued water use development combined with drought conditions has resulted in an 80% loss of permanent pools within the Clare Valley region between 1998 and 2008 (George et al., 2008, 2009). This loss of permanent pools initiated the work reported here in which the sources of water for permanent pools were examined.

The abundance of farm dams in this area is a major cause of reduced surface flows within the Clare Valley. Cresswell (1999) estimated that over a 25 year period farm dams reduced the median flow in the Hutt river by 24% and in the Hill river



**Fig. 3.** Hydrographs of Wakefield River stream flow and rainfall at Clare during and before the sampling period. Four season sampling is indicated by grey bars on rainfall hydrograph.



**Fig. 4.** Conceptual model of the study area for most ephemeral stream pools in relation to soil, regolith (saprolite), fractured rock bedrock and major land use-vegetation type.

by 21%. [Deane and Graves \(2008\)](#) supported this by highlighting that farm dams are primarily located in the higher rainfall areas which supply flow to the river catchments of the region and were capturing an average of 47% of the median annual runoff.

## 2. Methods

### 2.1. Sampling and field measurements

A total of 23 sites (12 groundwater, 11 surface water) were sampled along the Hutt, Hill, Wakefield, and lower Broughton Rivers ([Fig. 2](#), [Table 1](#)). Paired groundwater and surface water sites consisted of the selected permanent surface water pool and the closest groundwater well. The groundwater well water was assumed to be representative of the groundwater in the vicinity of the pools. Four season sampling of the wells was conducted to test this assumption. Ten clear pairs of surface and groundwater locations resulted from the site selection ([Fig. 2](#)). The remaining three sites represented one surface water site on the Broughton that was only present during winter and was dry for all other seasons of the sampling period, one surface water site on the Hutt for which no nearby groundwater well could be located, and one additional groundwater site on the Hill sampled only during summer.

Each site was visited during each of the four seasons between August 2008 and May 2009 ([Fig. 3](#)). The sampling seasons include winter wet (Aug–Sept 2008), spring drying (Nov. 2008), dry summer (Feb. 2009), and wetting autumn (May 2009). Within each season, water samples were collected during a two-day period. Surface water samples were collected directly

from pools by manually filling the sampling containers from the middle depth of the pool in order to gain a representative water sample. The pools are relatively shallow (mostly less than 2 m in depth). Electrical conductivity depth profiles of the pools did not show any significant salinity stratification. At each pool, a standard range of physicochemical parameters (pH, electrical conductivity (EC), total dissolved solids (TDS), and temperature) were measured from the middle depth of the pool using a YSI® multi-parameter meter (Table 2; Supplementary file).

Groundwater samples were obtained from privately owned and fully equipped bores. Four of the 11 wells are not incorporated in the State's drill hole data base (WaterConnect: [www.waterconnect.sa.gov.au](http://www.waterconnect.sa.gov.au)) so detailed information about these wells was unavailable, except for ad-hoc information given by the land-owners; this information about the depth of the bore and the depth to water table was not deemed to be of sufficient quality to report here. Department for Water groundwater monitoring bores were located outside of the acceptable distance for this study (Stewart, 2005). Based on groundwater levels measured in bores with similar physiographic and geologic settings (Dept. for Water, 2010) to the paired sites in this study, depth to water table at the bores was estimated to be 20–40 m. All but two of the groundwater wells used for this study were closed and topped with windmills. Water from the windmill sites was collected after purging from each bore assuming 10 m of casing depth and purging three casing volumes and noting that the physicochemical parameters had stabilised. The two open wells were located on the Hill and Wakefield rivers. The well on the Hill River was a new bore and was capped and closed by the final sampling season; the well on the Wakefield was an old bore no longer used as a water resource. Depth to water at this bore averaged 1.2 m. At these two sites, water was directly pumped from the bore purging three casing volumes and noting that the physicochemical parameters had stabilised. As with the surface water samples, the standard range of physicochemical parameters (pH, electrical conductivity (EC), total dissolved solids (TDS), and temperature) were measured using a YSI® multi-parameter meter in the field. The YSI was calibrated before each field trip with standardized solutions that covered the range of pH and EC encountered. Both surface and groundwater samples were collected in 5L HDPE jerry cans. Samples were kept cool and transferred to the lab where they were refrigerated until processed for analysis of major ions, stable isotopes of water and strontium isotope ratios.

Rainfall was limited during the sampling period and was only able to be collected once during the sampling year. This measured rainfall value was augmented with monthly bulked rainfall values obtained from a similar area in the Mt Lofty Ranges near Adelaide (Table 2; Supplementary file). The rainwater sample was collected using a 200-mm-wide funnel inserted into a 1.25 L bottle held 1 m above ground in 100 mm PVC stormwater pipe. Approximately 10 mm of paraffin oil was added to each new collection bottle prior to deployment to prevent isotopic fractionation from evaporation of the rainfall sample.

## 2.2. Laboratory analyses

All samples were processed in the laboratory within 48 h of collection using coarse filtration (1 µm) followed by fine filtration (0.45 µm). Filtered samples were divided into subsamples and, for major, trace and strontium isotopes, acidified with nitric acid to bring the sample to a pH of ~2. Major elements were analysed by ACME Analytical Laboratories Ltd. in Canada; precision of ICP-MS was based on replicate analyses of internal standards of wastewater within runs as well as replicate analyses of unknown samples with analyses within 5% or better of the standard.

The UC Davis Stable Isotope Facility analysed oxygen isotopes ( $^{18}\text{O}/^{16}\text{O}$ ) and hydrogen isotopes (D/H) using a Laser Water Isotope Analyser V2 (Los Gatos Research, Inc., Mountain View, CA, USA). Sample ratios are standardized using a range of working standards calibrated against IAEA standard reference materials with precision of  $\leq 0.3\%$  for  $\delta^{18}\text{O}$  and  $\leq 2.0\%$  for  $\delta^2\text{H}$ . Water isotope results are reported relative to Vienna Standard Mean Ocean Water (vs. VSMOW) in per mil (‰) difference using the delta ( $\delta$ ) notation. The local meteoric water line (LMWL) with values for Australia of  $\delta^2\text{H} = 7.10 \times \delta^{18}\text{O} + 8.21$  (Liu et al., 2010) were used following Hughes and Crawford (2012).

Strontium isotope ratios were analysed at the University of Adelaide using a Finnigan MAT262 thermal ionization mass spectrometer (TIMS), in static measurement mode. Strontium analyses were compared to a standard strontium reference material with an average  $^{87}\text{Sr}/^{86}\text{Sr}$  value of 0.710229. Strontium ratios are reported with 2 SE measurement precision after a two sigma rejection test (Table 2; Supplementary file).

## 2.3. Water isotope data analysis

The isotopic compositions of the groundwater and surface water samples were compared with modelled values for water undergoing evaporation at a defined relative humidity in order to refine the magnitude of potential evaporation from the surface water pools or groundwater reservoir. A similar approach to Tweed et al. (2011) was followed and is outlined in Cartwright et al. (2009) and Confiantini (1986). Stable isotope values of the residual groundwater or surface water undergoing evaporation were given by:

$$\delta^{18}\text{O}_{\text{gw}} = (\delta^{18}\text{O}_i - A/B)f^B + A/B \quad (1)$$

where  $\delta^{18}\text{O}_i$  is the initial isotopic composition of the recharging rainfall, in this setting is  $\sim -5.5\%$ , obtained from linear interpolation to the LMWL (described above),  $f$  is the fraction of groundwater evaporating and  $A$  and  $B$  are constants defined by:

$$A = \left( \frac{h}{a\text{H}_2\text{O}_{\text{gw}}} \delta^{18}\text{O}_v + \Delta\varepsilon + \frac{\varepsilon}{a} \right) / \left( 1 - \frac{h}{a\text{H}_2\text{O}_{\text{gw}}} + \frac{\Delta\varepsilon}{1000} \right) \quad (2)$$

and

$$B = \left( \frac{h}{a\text{H}_2\text{O}_{\text{gw}}} - \frac{\Delta\varepsilon}{1000} - \frac{\Delta\varepsilon}{1000a} \right) / \left( 1 - \frac{h}{a\text{H}_2\text{O}_{\text{gw}}} + \frac{\Delta\varepsilon}{1000} \right) \quad (3)$$

where  $h$  is humidity,  $a\text{H}_2\text{O}_{\text{gw}}$  is the activity of groundwater (isotopic ratio),  $\delta^{18}\text{O}_v$  is the isotopic composition of the water vapour,  $\alpha$  is the equilibrium isotopic fractionation,  $\varepsilon$  is the isotopic enrichment and  $\Delta\varepsilon$  is the kinetic enrichment. Relative humidity values of 0.3 and 0.5 were used as these are representative of the mean 3pm relative humidity of the summer months in the Clare region (Average 35%; Bureau of Meteorology 2015; [www.bom.gov.au/climate/data](http://www.bom.gov.au/climate/data)). Values of  $\Delta\varepsilon$  for oxygen and hydrogen were obtained by the relationships of  $14.5(1-h/a\text{H}_2\text{O}_{\text{gw}})$  and  $12.5(1-h/a\text{H}_2\text{O}_{\text{gw}})$  from Gonfiantini (1986), reported in Cartwright et al. (2009). The activity of groundwater was calculated using chloride concentrations following the relationship outlined in Cartwright et al. (2009):

$$a\text{H}_2\text{O}_{\text{gw}} = 1 - 6 \times 10^{-9}[\text{Cl}]^2 - 2 \times 10^{-5}[\text{Cl}] \quad (4)$$

with chloride concentration in mmol/kg. The isotopic composition of vapour was calculated using the procedure outlined in Jacob and Sonntag (1991), using  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of precipitation:

$$\delta^2\text{H}_v = 0.84\delta^2\text{H}_{\text{precip}} - 91 \quad (5)$$

$$\delta^{18}\text{O}_v = 0.84\delta^{18}\text{O}_{\text{precip}} - 12.2 \quad (6)$$

Relevant  $\delta^2\text{H}$  values were then substituted into the same series of equations to calculate the  $\delta^2\text{H}$  value of evaporated groundwater.

### 3. Results and discussion

At all of the surface water sites the closest available groundwater was compared hydro chemically with surface water samples (Table 1; Tables 2 and 3; Supplementary file; Fig. 5). Sample sites have been arranged in a run-of-river order with samples grouped by river catchment. For example, each site numbered 1 is the upstream site for each catchment. The numbers indicate the direction of river flow from sites 1 (upstream) to 4 (downstream). The absence of values for summer at two sites along the Wakefield indicates that no water was present at the site.

#### 3.1. Chloride and major element concentrations and molar ratios

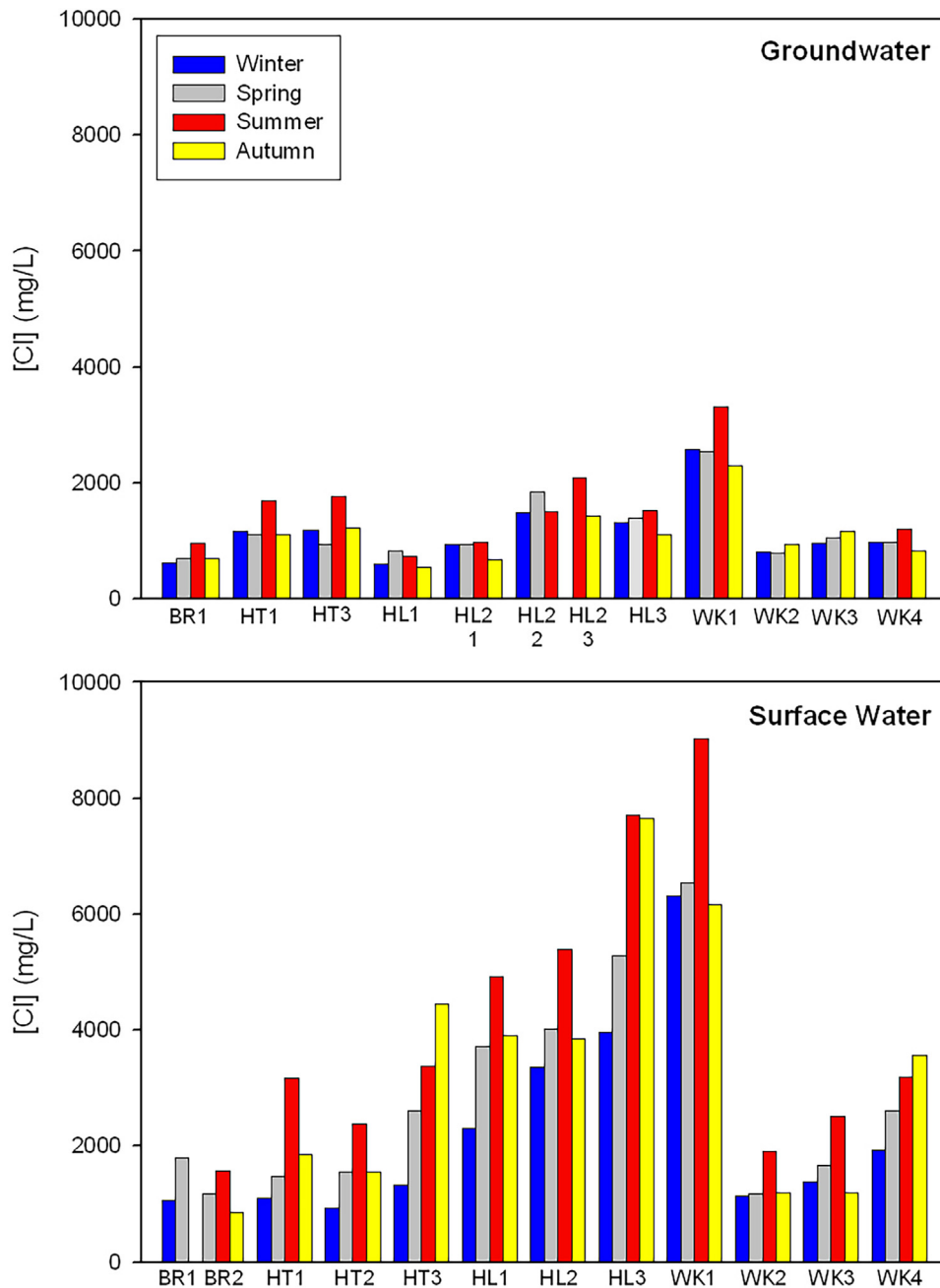
In order to assess hydrogeochemical processes such as ion exchange, weathering reactions, evaporation, and bioaccumulation, chloride concentrations were compared with elemental concentrations and molar ratios to illustrate possible relationships between groundwater and surface water. Rainwater ratios were included in order to represent initial elemental composition.

Groundwater samples generally had lower, and in most cases much lower, levels of chloride concentration compared to their paired surface water pools (Fig. 5). Chloride concentrations in the groundwater ranged between 550 and 3318 mg/L whereas surface water concentrations were nearly three times as high as groundwater with values of 864–9036 mg/L. This difference between ground and surface water was evaluated using permutation multivariate analysis of variance (PERMANOVA) in Primer v6. The test indicated a statistically significant difference between chloride concentration of groundwater and surface water samples (Pseudo  $F=6.48$ ,  $p(\text{perm})=0.001$ ). Further evaluation of the data to determine if this difference was less significant during seasons was also assessed using PERMANOVA. While there were single significant differences within surface water and groundwater samples (summer vs autumn for groundwater, and summer vs winter for surface water), overall the statistically significant difference between surface and groundwater samples remained throughout the year.

Hydrochemical relationships between groundwater and surface water were evaluated with scatterplots of chloride concentrations vs. Na, Ca, Si, K and Cl/Br (Fig. 6). These plots evaluate the behaviour of major elements compared to chloride as surface water and groundwater undergo water-rock-soil reactions and evapo-concentration. Hydrochemical relationships were analysed using scatterplots of chloride molar concentrations vs. Na/Cl, Si/Cl, K/Cl and Ca/Cl (Fig. 7). Only data from the Wakefield catchment are shown since this catchment represented the general data spread for all catchments.

Rainwater ratios are displayed as dashed lines in Figs. 6 and 7 so that comparisons with this assumed starting composition can be made. One rainwater sample was collected during the course of this investigation. Another five rainfall samples





**Fig. 5.** Chloride concentration in groundwater and surface water sites over the four seasons for the Clare Valley catchments. BR-Broughton, HT-Hutt, HL-Hill, WK-Wakefield.

collected in 2007 by Flinders University staff and students in the Scott Creek area of the Mt Lofty Ranges are reported in Table 2 (Supplementary file). These values were averaged together to produce an average rainwater chemistry.

The significantly higher chloride concentrations in the surface water sites than the paired groundwater sites as well as gains and losses of elements compared to closed system evaporated rainfall composition are illustrated in Figs. 6 and 7. Closed system evaporation of rainfall refers to evaporation with no gains or losses such as addition of a different water source or precipitation and removal of a mineral. Sodium has overall gains in both surface and groundwater samples compared to the evaporated rainfall composition. Silicon shows both gains and losses; most groundwater samples have gained silicon and most surface water samples have lost silicon compared to rainwater. Surface water sites show very significant loss of silicon. Calcium has both gained and lost minor amounts compared to evaporation of rainwater. Both groundwater and surface

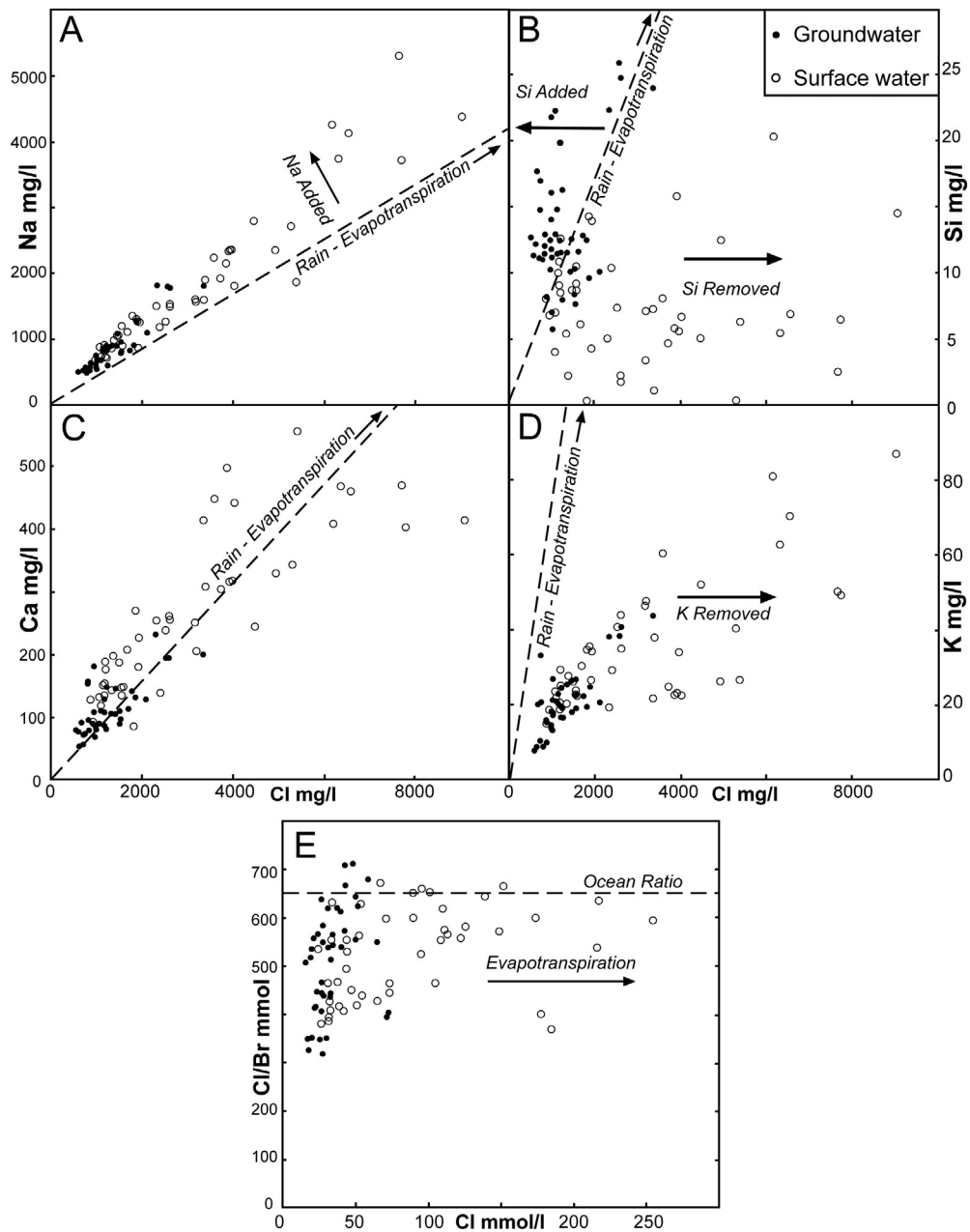


Fig. 6. Scatter plots of concentrations of Na, Si, Ca, and K vs. Cl. Molar ratio of Cl/Br vs. Cl mmol is also plotted.

water have lost potassium compared to evaporated rainwater; surface water samples have greater losses with increasing chloride concentration.

Almost all of the groundwater and surface water sites have Cl/Br ratios lower than the marine ratio (Fig. 6E). There is however slightly lower Cl/Br ratio of groundwater sites ( $486 \pm 135$ ) compared to surface water sites ( $526 \pm 94$ ). Molar Cl/Br of groundwater and surface water are poorly correlated (GW:  $r^2 = 0.15$ ; SW:  $r^2 = 0.13$ ); thus despite Fig. 6E appearing to have a relationship between chloride concentration and Cl/Br ratio, there is no significant relationship.

In most paired surface water-groundwater sites the Na/Cl ratio decreases significantly with increased chloride concentration indicating a decrease in sodium relative to chloride in surface water compared to groundwater (Figs. 6 and 7). A few sites are exceptions such as Wakefield site WK4 and Hutt sites HT2 and HT1A (not shown in Fig. 7) which have no trends. Ratios of Na/Cl are almost exclusively higher than rainfall. Calcium/chloride ratios vs. chloride are variable in the paired surface water-groundwater sites and plot both higher and lower than rainfall ratio. All four catchments have both

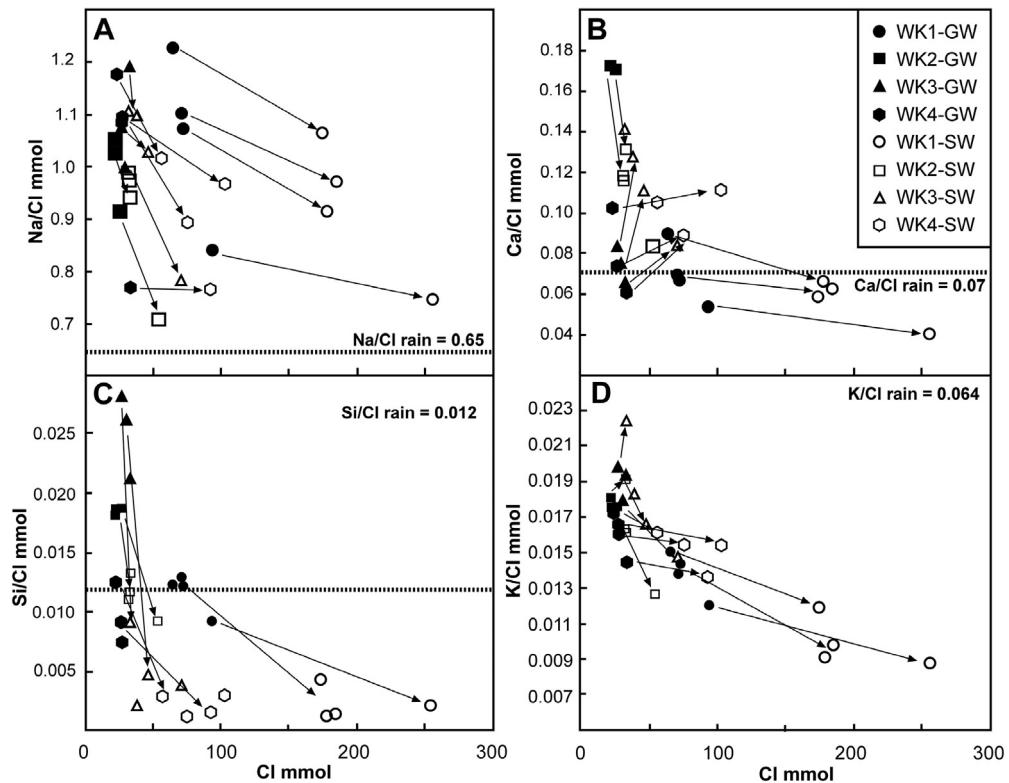


Fig. 7. Molar ratios vs. chloride molar concentration for the Wakefield River. Arrows indicate paired groundwater-surface water sites.

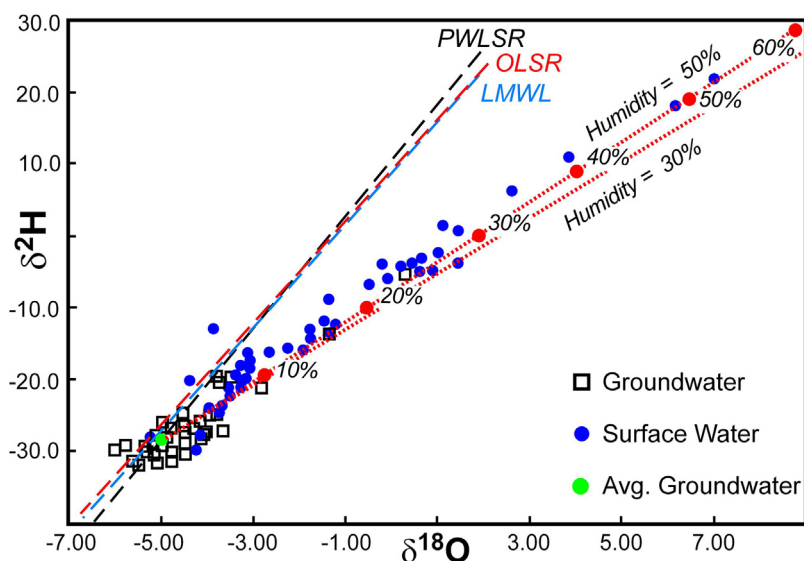
decreasing and increasing trends of Ca/Cl with increasing chloride concentration. Similar to Na/Cl, Si/Cl ratios vs. chloride for all paired sites show a strong decrease of the ratio with increase in chloride.

Potassium/chloride vs. chloride for most sites display strong decrease of the ratio with increase in chloride. A few sites have exceptions with increases in the ratio with increase in chloride. All sites have K/Cl ratios much lower than the rainfall ratio.

### 3.2. Discussion of major and minor elements

The Cl/Br ratios of groundwater and surface water are almost all significantly lower than the ocean ratio. This relationship is most likely due to raintout of chloride relative to bromide (Davis et al., 1998). Other factors to consider are organic activity at the sea surface and organic activity from the terrestrial environment which has been shown to lower the Cl/Br ratios (Risacher et al., 2006; Butler et al., 2007; Alcalá and Custodio, 2008). In areas with sources of gypsum (with some halite) and/or halite, Cl/Br ratios would be elevated from the marine ratio. Along windy arid coasts the ratio would be expected to go up due to crystallisation of halite from sea spray. Because the ratio is lower than marine, the presence of gypsum and/or halite in the rocks and dust can be ruled out.

A few basic interpretations can be made from the molar ratio plots. Evaporation of surface water pools during summer and autumn to produce higher salinity is a dominant process. Overall, with increasing salinity, molar ratios decline for most elements (Fig. 7A–D). Sodium/chloride ratios above the rainfall ratio most likely indicate sodium input into the groundwater system from weathering reactions of sodium bearing minerals such as feldspar following basic water chemistry arguments of Garrels and Mackenzie (1967). The decrease in the Na/Cl ratio observed in almost all of the paired sites is probably due to ion exchange (sorption) of sodium with other cations on clay mineral surfaces (Hem, 1985). Calcium/chloride ratios also show decreasing trends with increasing chloride concentration and indicate either exchange (sorption) of calcium on clay minerals and/or precipitation of soil/vadose zone calcium carbonate. Calcium carbonate mineral precipitation is a common process in semi-arid river systems (Meybeck, 2004). Conversely, increasing Ca/Cl ratio trends with increasing chloride at sites HL2, WK3, HT1A, and BR1 could indicate weathering of soil/vadose zone calcium carbonate and/or exchange of calcium for other cations on clay minerals. Calcium/chloride ratios lower than the rainfall ratio support mineral precipitation of soil/regolith calcium carbonate and ratios trending higher support weathering. High Ca/Cl ratios of two Wakefield catchment groundwater samples probably indicate input from dissolution of carbonate bedrock units. The strong decrease of the Si/Cl ratios with increasing chloride concentration from groundwater to surface water indicates silica is being removed from the surface water system. Silicon values and Si/Cl higher than rainfall for many of the groundwater sites indicates significant input of



**Fig. 8.** Stable isotopes of water showing groundwater and surface water values, PWLSR refers to precipitation weighted least squares regression, OLSR refers to ordinary least squares regression (Hughes and Crawford, 2012). LMWL (local meteoric water line) is from Liu et al., 2010). Evaporation line calculations are explained in the methods section. Percentage points along the calculated evaporation line represent percentage water evaporated. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

silica into the groundwater system presumably from silicate mineral weathering. In the surface water, silica is probably taken up by aquatic organisms. Diatoms actively use silica particularly during evaporation phases of surface waters since increased nutrient loads provide suitable conditions for enhanced bioproductivity (Wolyn and Stone, 1999). The presence of clay minerals in the surface waters may also incorporate silica (Siever and Woodford, 1973). The strong decrease in K/Cl ratios with increasing chloride concentration and the much lower ratios in all sites compared to rainwater ratio document the removal of potassium during evaporation of surface water. Waters that have interacted with decomposing organic matter through processes such as overland flow and soil through-flow normally have high levels of potassium compared to their overall salinity (Chaudhuri et al., 2007). In the Mt Lofty Ranges near Adelaide, Bestland et al. (2009) records potassium concentrations from soil water from Red Brown Earth soils ranging from 4 to 9 mg/L with K/Cl ratios (molar) of 0.08–0.2. Corresponding stream water has lower potassium concentrations (2–3 mg/L) and lower K/Cl ratios (0.025–0.04 molar). Clare Valley pools have much higher salinities and higher potassium concentrations than soil and stream water reported in Bestland et al. (2009), however, the K/Cl ratios (molar) of 0.009–0.023 of Clare Valley pools are much lower than soil water reported by Bestland et al. (2009). The low K/Cl ratios and decreasing trends with increase in chloride suggest low amounts of soil water input to the surface water pools. Alternatively, K sorption onto clay minerals during evaporative concentration in the pools is a viable interpretation.

### 3.3. Water isotopes

Comparison of the stable water isotopic values of surface water pools and groundwater illustrates their relationship to meteoric water lines and the degree of evaporation (Figs. 8 and 9). Three different meteoric water lines are presented. The Local Meteoric Water Line (LMWL) is based on Global Network of Isotopes in Precipitation (GNIP) from 7 Australian stations for the period 1962–2002 (Liu et al., 2010). The ordinary least squares regression (OLSR) and precipitation weighted least square regression (PWLSR) are for Adelaide GNIP site (Hughes and Crawford, 2012).

Groundwater samples collected throughout the sample period and from all catchments cluster at the negative (or depleted) portion of the LMWL (Figs. 8 and 9). Some groundwater samples, such as in the Wakefield Catchment, plot to the right of the LMWL. The groundwater samples have a weakly defined evaporative enrichment trend compared to the much stronger evaporation trend of surface water samples ( $R^2 = 0.72$ ), with the exception of one site from the Wakefield Catchment (Wakefield 3). While some groundwater samples deviate from the main groundwater cluster, these points represent only one particular site rather than a trend at the catchment scale. By comparison, the stable water isotopes for the surface water samples show a large degree of evaporative enrichment along a Local Evaporation Line equation ( $y = 4.14x - 6.26$ ;  $R^2$  of 0.96). Two surface water sites, one in the Hill Catchment (Hill 3) and one in the Hutt Catchment (Hutt 3) exhibit the greatest degree of evaporative enrichment. Both sites show highest evaporation in autumn and lowest values in winter. Isotopic enrichment range between winter and autumn for site Hill 3 is 10.5‰  $\delta^{18}\text{O}$  and 41.6‰  $\delta^2\text{H}$  and for Hutt 3 9.5‰  $\delta^{18}\text{O}$  and 37.9‰  $\delta^2\text{H}$ .

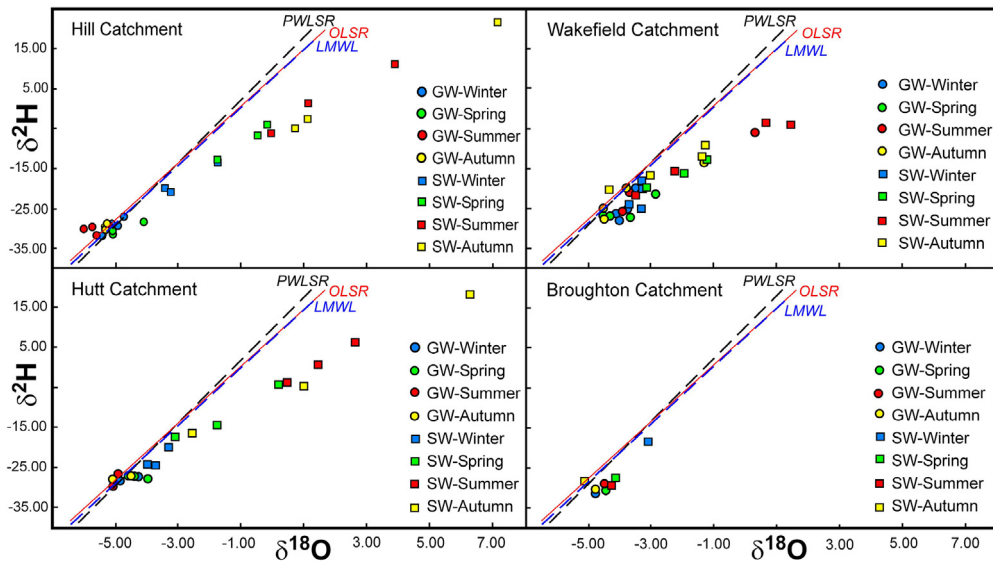


Fig. 9. Stable water isotopes separated for the four catchments and for season: A) Hill, B) Wakefield, C) Hutt, and D) Broughton.

### 3.4. Discussion of water isotope data

Comparison of the net evaporative enrichment of the Clare Valley pools to other groundwater-surface water systems is done in order to evaluate their degree of enrichment. The Clare Valley pools compare, and are in the same range of evaporative enrichment, as saline lakes reported by Cartwright et al. (2009) in nearby western Victoria, although maximum isotopic enrichment for the Victorian lakes was greater. Evaporative enrichment of the Clare Valley pools is much less than the evaporative range of the Darling River reported by Meredith et al. (2009) of 17.7‰  $\delta^{18}\text{O}$  and 123‰  $\delta^2\text{D}$ .

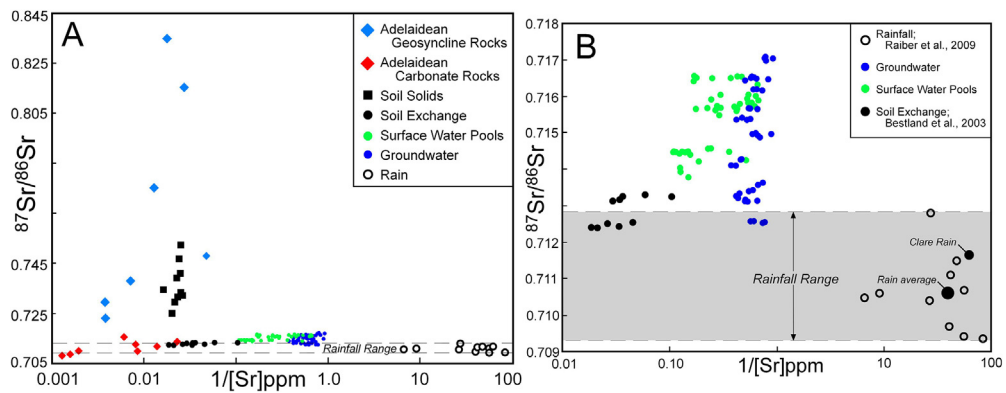
Evaporation from stream pools was compared to calculated net evaporation using an average stable water isotope value of groundwater (shown in Fig. 8), relative humidity of between 30 and 50%, based on the 3pm relative humidity of the Clare weather station during January through April, and as described in Section 2.3 of the methods section. Summer and Autumn months were used to estimate relative humidity because most evaporation occurs during these months. The evaporation lines (in dashed red) in Fig. 8 are the calculated net evaporation trend based on the above data and assumptions and shows points along the 50% relative humidity line for evaporation of 10% to 60%. Thus, maximum evaporation from stream pools of up to 50% during summer and autumn is indicated from these calculations and assumptions. Results showed that the component of water evaporating between winter and summer/autumn from the most enriched pools, Hill 3 and Hutt 3, was found to be 47% and 43% respectively. Most other pools showed less than 20% evaporation had occurred over the same time period. Most samples from other seasons have evaporation of 10% to 30% from the LMWL, and winter samples are less than 10%.

Most of the groundwater samples cluster close to the LMWL at the depleted end of the plot, indicating that groundwater in this region results from winter recharge events since winter rainfall is generally known to be more negative (depleted) than summer rainfall (Kayaalp, 2001; Guan et al., 2013). Recharge derived from summer rainfall would be dominated by heavier isotopes and would tend to be more positive (enriched), except when large monsoonal systems have crossed the Australian continent in which case such rains can be more depleted (Bestland et al., 2009; Guan et al., 2013). Some groundwater samples, such as in the Wakefield, plot to the right of the LMWL suggesting that in this catchment shallow groundwater sources may undergo evaporation prior to recharge. Calculations outlined in Section 2.3 indicate that approximately 20% of one of the groundwater samples from the Wakefield catchment (WK3) has been evaporated between winter and summer.

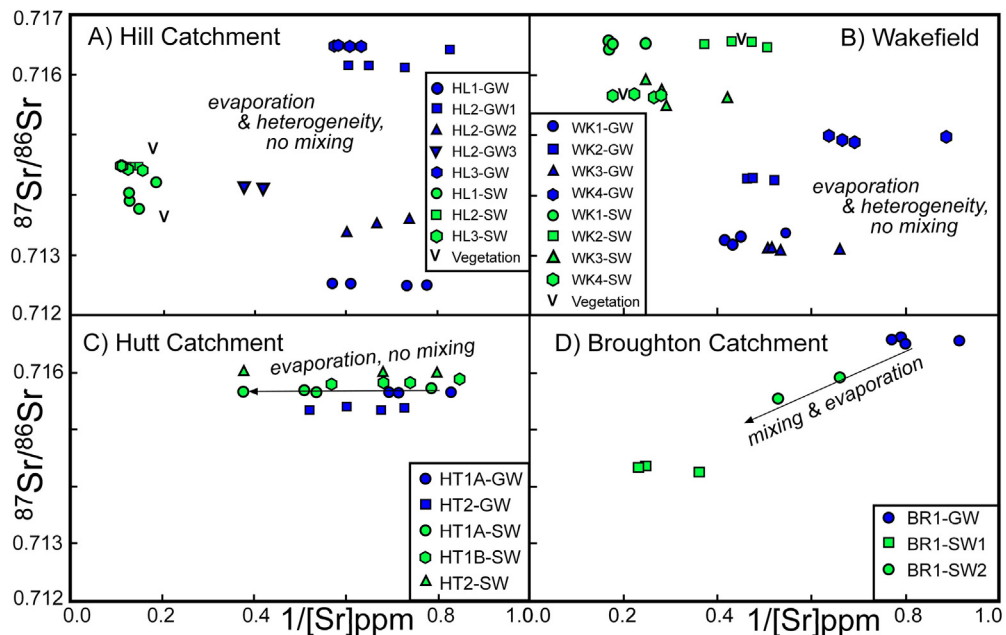
### 3.5. Strontium isotope ratios

The strontium isotope ratio of rainfall is an important end-member to be considered. The single rainfall sample collected for this study has a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7116 (Table 2; Supplementary file) which compares well to eleven rainfall analyses reported by Raiber et al. (2009) from a coast to interior transect in Victoria, Australia (average strontium isotope ratio of  $0.7106 \pm 0.00099$ ). The Clare Valley's rainfall samples' relatively high strontium isotope ratio compared to seawater is justified by comparison to Raiber et al. (2009) transect which found an increase in strontium isotope ratio inland due to mixing of land-derived solutes (from dust) with seawater derived solutes.

The Clare Valley area hydrogeology is dominated by host rocks of Late Precambrian metamorphosed, folded and faulted sedimentary rocks, as mentioned above. The meta-shales and meta-sandstones in the Adelaian sequence have relatively high strontium isotope ratios (Fig. 10A) (Turner et al., 1993; Foden et al., 2001). The carbonate units in this sequence, however,



**Fig. 10.** (a) Composite strontium isotope ratio vs. strontium concentration data for bedrock units (from Turner et al., 1993; Foden et al., 2001), soil solids, soil exchange pool (Bestland and Forbes, 2009; Bestland et al., 2003), surface water and groundwater from this study, and rainfall from Raiber et al. (2009). (b) Groundwater, surface Water, and soil exchange data from the Clare Valley area, and rainfall again from Raiber et al. (2009). Soil exchange data is from representative soil profiles in Red Brown Earth soils and has a lower ratio than all surface water samples and most groundwater samples.



**Fig. 11.** Strontium isotope ratio plotted against  $1/\text{concentration}$  for the four catchments A) Hill, B) Wakefield, C) Hutt, D) Broughton.

have much lower ratios. Soil solids from two representative Red Brown Earth profiles (Bestland et al., 2003) have strontium isotope ratios which overlap with lower ratio silicate bedrock values (Fig. 10A).

All groundwater sites have a narrow range of strontium isotopic ratios of between 0.712 and 0.717 (Figs. 10 A & B and 11 A–D). There was very little seasonal variation at individual groundwater sites of strontium isotope ratios and this pattern persisted across all catchments (Fig. 11A–D). In the Clare Valley area, individual groundwater sites show discrete clustering of strontium isotope ratios; for example the WK1 and WK3 groundwater sites have similar strontium isotope ratios which differ from the ratios of the other two groundwater sites in this catchment (WK4 and WK2). Strontium concentrations varied seasonally at the groundwater sites as did other major ions. One site in the Wakefield (WK4), one site in the Hill (HL2), and the Hutt River sites have very similar strontium isotope values between paired surface water and groundwater samples producing an unchanging trend over a large range in strontium concentration. However, most paired groundwater and surface water sites have somewhat different strontium isotope ratios; this is discussed below in terms of hydrogeologic heterogeneity. Samples of reeds from four different pools (HL3, HL2, WK2, and WK4) were analysed for strontium isotopes in order to evaluate features such as aquatic plants with potentially longer residence time than pool water.

### 3.6. Discussion of strontium isotope ratios

Probable sources of strontium to groundwater and surface waters include soil solids, bedrock, and atmospheric sources (rainfall and dust). Strontium in the soil solid samples is a mix of silicate bedrock and atmospheric sources of wetfall and dryfall (Bestland and Forbes, 2009; Bestland et al., 2003). The soil exchange pools from the two soil profiles studied by Bestland et al. (2003) have strontium isotope ratios close to the rainfall range and have much lower ratios than the soil solids, reflecting the dominance of wetfall and dryfall sources in the exchange pool of these soils (Fig 10B). The soil solids are a mix of silicate bedrock material and weathered silicate bedrock material which has lost a fraction of its original strontium and has mixed with strontium from atmospheric sources. Thus, strontium isotope ratios of the soil exchange pools overlaps with the atmospheric end-member represented by the rainfall data.

Similar to the groundwater samples and contrary to expectation, there was very low seasonal variability of strontium isotope ratios in surface water sites (Fig. 11). Surface water sites exhibited very similar strontium isotope ratios despite both the season sampled and the large differences in salinity and thus strontium concentration. Strontium concentration varies directly with salinity, as would be expected (Table 2; Supplementary file). Within all the catchments, the surface water samples had higher strontium concentrations than their paired groundwater samples. Except for the Broughton, there are no obvious mixing lines between surface water and groundwater. Only the Broughton catchment appeared to define a mixing line between groundwater and a lower strontium isotope ratio, higher strontium concentration surface water source. In addition, the Broughton catchment case does not follow the expected mixing between lower concentration, lower ratio surface water input and higher concentration, higher ratio groundwater input. Thus, due to this lack of mixing line at most of the paired sites between two or more end-members, mass balance hydrogeochemical analysis using end-members was not appropriate. Strontium isotopes of reeds from four pools cluster with the surface waters demonstrating strontium isotopic stability in the surface water pools over the growth period of the reeds (Fig. 11).

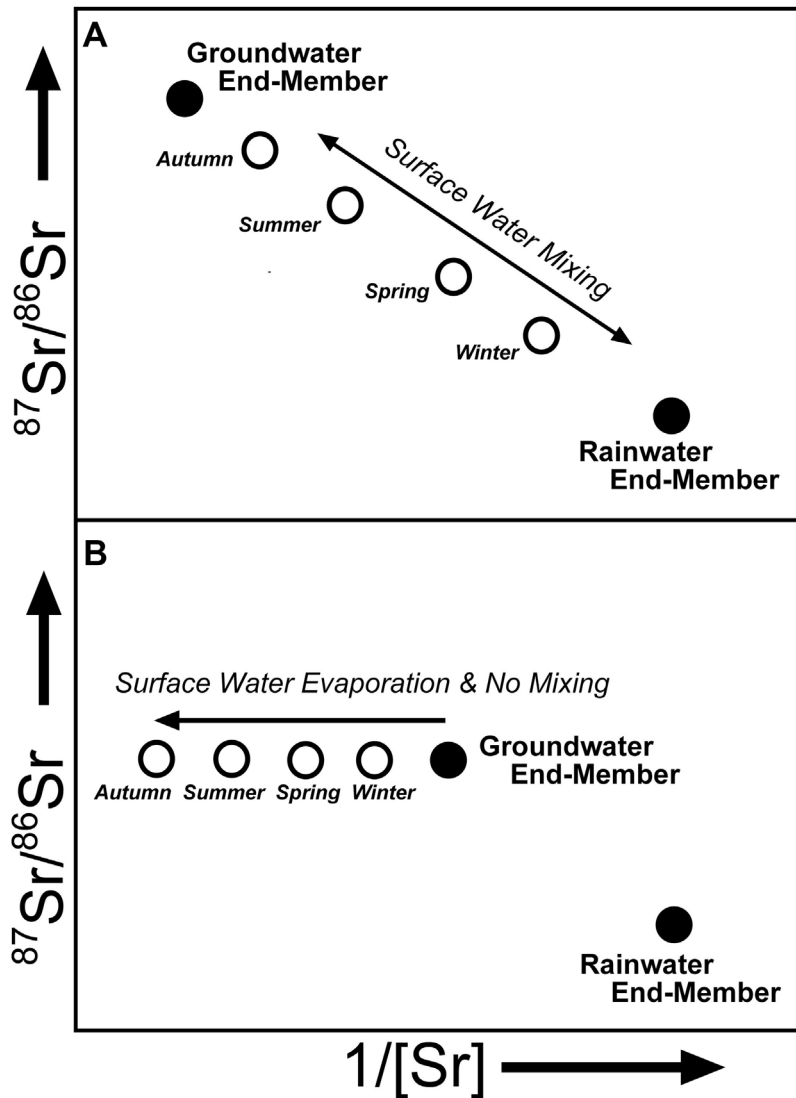
As mentioned above, surface water strontium concentrations are distinctly higher than the associated groundwater sites. Supporting these data are strong evaporation trends for surface water sites observed from water isotopes, chloride concentrations, and most other elemental concentrations, as discussed above. Most paired surface water-groundwater sites have small but significant differences in strontium isotopic ratios between the surface and groundwater sites (Fig. 11). Only the Hutt Catchment paired sites show relatively homogenous  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for both pools and groundwater (Fig. 11C).

### 3.7. Strontium isotope end-members

Groundwater and rainwater typically have different sources of strontium and thus differing isotopic ratios. When these end members mix, the expectation is that on a standard strontium isotope ratio vs.  $1/[\text{Sr}]$  plot the mixing will produce a linear trend (if only two sources are contributing) or they will scatter (if more than two sources are contributing). For example, if the strontium in a surface water sample is derived from two different sources, such as groundwater and rainwater, and the groundwater has a relatively high strontium ratio and concentration, and rainfall has a relatively low ratio and low concentration, then the resulting mixed water sample should fall on a line between the two end-members, as conceptually represented in Fig. 12A. The location of the water sample relative to the sources or end-members would then indicate the relative proportion that each of the sources contributes to the sample and can be quantitatively evaluated using simple mass balance equations. Thus, the surface water samples lie between the rainfall signature and that of the groundwater during different seasons due to differences in the mixing proportion of surface and ground water between wet and dry seasons. Alternatively, if there was no direct mixing of waters, then the trend should be horizontal representing no change in isotopic ratios since the dominate hydrologic process would be evaporation.

The initial hypothesis in this study was that groundwater provided as stream and pool base-flow would be dominant during drier times of the year and become diluted with surface water (ultimately from rainwater) during wetter times of the year. Groundwater that had interacted with the fractured rock aquifer host rock of the Precambrian Adelaidean sequence, dominated by strontium with high isotopic ratios, would produce water with relatively high strontium isotope ratios, as observed elsewhere in these rock types in the Mt Lofty Ranges. Bestland and Stainer (2013) report strontium isotope values from groundwater in Burra Group, Adelaidean sequence strata, the same rock types as the Clare Valley, ranging from 0.73 to 0.76. Soil through-flow values from this part of the Mt Lofty Ranges are much lower ranging from 0.715 to 0.717 (Bestland et al., 2010). Green and Stewart (2008) report strontium isotope values from eastern Mt Lofty Ranges groundwater ranging from 0.714 to 0.76. Overall, there is a low level of strontium isotope variation in the groundwater and surface water of this study area compared to other Mt Lofty Range sites and the strontium isotope values of Clare Valley water samples are lower than surface water reported from these other studies.

The strontium isotope data indicates that each groundwater well obtained water from a relatively homogenous source, in terms of strontium isotope ratio, throughout the year regardless of salinity and strontium concentration variations. The strontium concentration changes are probably related to seasonal salinity rise and fall caused by the seasonal water table fluctuations (Love et al., 2002; Stewart, 2005). As water tables rise in response to winter recharge, the salinity in the bore water drops. The constant ratio of the strontium isotopes from the groundwater sites argues against dilution by rainwater in the production bores sampled here. Rainwater dilution would produce a mixing line between lower ratio, low concentration rainwater and the higher ratio, higher concentration aquifer water. The question of how the salinity in the aquifer changes without altering the strontium isotope ratio of the upper part of the fractured rock aquifer is not known. It is probably the



**Fig. 12.** Idealised diagrams of  $1/\text{strontium}$  concentration plotted against strontium isotope ratio of possible water source mixing relationships. Upper diagram (a) illustrates expected mixing between rainwater dominated surface water and groundwater over the seasonal wet-dry cycle. Lower diagram (b) illustrates groundwater dependant pools with no rainwater or runoff contribution and with evaporation changing strontium concentration but not isotopic ratio.

case that there is a salinity increase in the upper few meters of the aquifer, and that the rise and fall of the water table allows the bore access to water of different salinities.

Instead of a mixing line or scatter of strontium isotope data, an alternative hydrochemical model is presented in Fig. 12B. In this model, groundwater provides the sole source of water and hence strontium isotope ratios are fixed. Strontium concentration changes in surface water are due solely to evaporation of the groundwater flowing into the pool. In such scenarios, the strontium isotope ratio signature of the groundwater is retained but the concentration of strontium in the surface water increases. This type of geochemical trend generates an unchanging strontium isotopic ratio over time. This unchanging strontium isotope ratio is prevalent within the time series of seasonal fluctuations of the surface water sites, thus indicating a single end-member contribution for most of the surface water sites. The data show that one site in the Wakefield (WK4), one site in the Hill (HL2), and all of the Hutt sites display this unchanging trend, with similar strontium isotope values, in both the surface water and paired groundwater samples. In these cases, the surface water-groundwater interaction appears to be limited to groundwater fed pools that are subject to evaporation and are not diluted by rainfall or soil through-flow, irrespective of season. These unchanging isotopic values are thought to be explained by the drought conditions prevalent in the area during sampling. Another mechanism that could explain groundwater fed pools and the unchanging trend is the possibility of local high bedrock fracture density in these areas where pools occur thus allowing for greater groundwater flow.



### 3.8. Strontium isotope heterogeneity

Most of the paired groundwater-surface water sites have different strontium isotope ratios between individual groundwater and surface water sites. In addition there is strontium isotope ratio variation between bores. This heterogeneity is most likely due to hydrochemical differences in the fractured rock aquifer at the spatial scale represented by the distance between groundwater bores. Strontium isotope ratios did not change significantly during seasonal sampling at individual groundwater sites during the 2008–09 period. The small yet significant differences in strontium isotopic ratios in most paired surface water and groundwater sites is most likely due to heterogeneity in the fractured rock aquifer that is at a smaller scale than the distance between the paired surface water-groundwater sites. This apparent mismatch in strontium isotope ratios between many of the paired groundwater and surface water sites implies that the surface water sites are gaining groundwater from the fractured rock aquifer but this exact water was not sampled.

Another viable interpretation for the small differences between strontium isotope ratios of the paired surface water-groundwater sites is that groundwater of variable composition flowed into an alluvial aquifer and then mixed down-gradient. This mixed water would then feed the surface water pools. This scenario is considered unlikely due to the consistency of the strontium isotopic data from the surface water pools over the sampling year.

The lack of evidence of mixing between groundwater and soil-overland flow water in most of the surface water sites is unexpected considering that one of the sampling seasons was during the cool wet season (August–September) when soil through-flow should be a major component to stream pools. The sampling season of 2008–09 was in the midst of a drought cycle and it may be that the soil system did not wet-up sufficiently to generate significant through-flow which would dilute groundwater fed pools. Low recharge rates are inferred for the Clare area over this time period by the lowering of water tables in many bores (Dept. for Water, 2010).

As mentioned above, the seasonal variation in groundwater salinity is difficult to explain in light of the near constant strontium isotope ratio observed from these sites. Water table fluctuations of several meters are common in the Clare Valley area and are due to a combination of low storage capacity in the fractured rock aquifer, wet season recharge and dry season draw-down (Love et al., 2002). Another regional feature of the groundwater is the increase in salinity with depth of about 40 m that is observed in wells of the Clare Valley area (Love et al., 2002). This salinity decrease in the upper part of the fractured rock aquifer is probably related to recent land clearing and the associated increase in recharge and flushing (Love et al., 2002). However, with such seasonal flushing, dilution of the groundwater salinity would be associated with a lowering of the strontium isotope ratio reflecting its meteoric source. This, as has been stated, is not observed. A possible explanation is that the seasonally saturated vadose zone at the top of the aquifer accumulates salts in interstitial pores and exchanges ions with the exchange pool during summer and autumn drying when the groundwater table drops. A rise in the water table during the winter wet season causes the aquifer to intersect this exchange zone and re-mobilises these constituents which must hydrochemically overwhelm the hydrochemistry of the recharge waters. Why the rainfall and recharge do not dilute the upper part of the aquifer in terms of the strontium isotopes is an interesting question that is not completely answered by this research. The strontium isotopes provide no evidence of aquifer dilution during recharge in these groundwater sites, at least during the period sampled and from the bores sampled.

### 3.9. Geologic control on strontium isotope ratios

The overall strontium isotope ratios of the groundwater and surface water, as mentioned above, are low compared to other Mt Lofty Range groundwater systems in similar Precambrian rocks (Green and Stewart, 2008; Bestland and Stainer, 2013). Fig. 10 investigates this anomaly by comparing strontium isotope ratios from the surface water-groundwater sites in this study to soil and rock data from previous studies (Bestland et al., 2003; Bestland and Forbes, 2009; Turner et al., 1993; Foden et al., 2001). In Fig. 10A, strontium isotope ratios from soil solids lie on a mixing line between Burra Group shale and local dust, as has been reported previously (Bestland et al., 2003). Strontium isotope ratios of the soil exchange pool (avg.  $0.7128 \pm 0.0004$ ) are slightly higher than local rainfall of 0.7116 and are the same as local dust (0.7128). Surface water and groundwater samples have on average higher strontium isotope ratios than Red Brown Earth soil exchange pool. All of these groups are higher than rainfall, as would be expected due to the contribution of higher ratio strontium from the weathering of Precambrian sedimentary rocks that are dominated by high ratio shale. However, the groundwater ratio mean of  $0.715 \pm 0.00146$  is low compared to Burra Group shales (average ratio of 0.7933) (Foden et al., 2001). One important factor that needs to be taken into account is the abundance of dolomitic strata in the Clare Valley area (Preiss, 1987). Many of the shale units in the Burra Group from this area consist of interbedded siltstone and dolomitic siltstone. In addition, there are dolomite units in the area such as the Blyth Dolomite, Benbouwie Dolomite, Auburn Dolomite, Skillogalee Dolomite and other carbonate units. These Burra Group carbonates have an average strontium isotope ratio of 0.730. Overlying the Burra Group is the Umberatana Group which contains carbonate units that have lower ratios and higher strontium concentrations than Burra Group. Dolomitic units are commonly mixed silicate-carbonate and the analyses reported by Foden et al. (2001) are for bulk rocks. Less impure carbonates in the Umberatana Group have lower ratios and higher strontium concentrations, closely reflecting late Precambrian marine strontium ratios and marine carbonate strontium concentrations. Foden et al. (2001) report that carbonate units in the Burra and Umberatana Groups have strontium isotope values that fall between primary values and that of the clastic basin fill which was apparently re-set to about 0.7183 at around 586 Ma during a metamorphic event (Foden et al., 2001). Thus it is likely that dissolution of low strontium isotope ratio carbonate in the

regolith-saprolite zone and in the basement fractured rock aquifer is a major factor contributing to the low strontium isotope ratio of the groundwater in the Clare Valley area. In addition, it is also clear that the consistently low strontium isotope values of the groundwater indicate that high ratio strontium from Burra Group shale is a minor contributor to the groundwater composition of the wells sampled.

#### 4. Conclusions

This study evaluated the hydrochemical link between stream pools and groundwater with the aim to understand water sources in permanent pools along seasonal stream courses in the Clare Valley area. Because the management of surface water has been conducted independent of groundwater in the Clare Valley and elsewhere this study aimed to investigate these linkages in order to better inform land managers.

The hydrochemical analyses conducted for this study demonstrate that a very limited number of pool sites had mixing of surface water and groundwater. The majority of the evidence indicates that the surface water pools were almost wholly dependent on groundwater for their supply of water. This finding was surprising even considering the level of drought during the sampling period; there was very little evidence of wet season surface water or soil water inflow into the pools. Only the Broughton Catchment pools showed mixing with possible surface water source. Hydrochemical heterogeneity on a spatial scale less than that represented by the paired groundwater-surface sites exists for most of the sites, as evidenced by strontium isotope data. The Hutt River groundwater-surface water sites are hydrochemically homogenous in terms of their strontium isotope ratios.

The strong evaporation observed in many of the pools over the time series of this investigation, especially the up-stream area of the Wakefield, indicates seasonal disconnection or very low input from groundwater sources. These results indicate that groundwater inflows to surface pools cannot be considered a continuous supply as previously believed for this region. The high evaporation in most of the stream pools (up to 50% evaporation calculated) suggests that many of the pools had low levels of groundwater input. Very small inputs of surface water runoff combined with low levels of groundwater input are likely the only water supply sustaining these pools during extended dry periods.

In summary, it is important to note that the pre-conceived model at the start of this study for the water sources of the pools (runoff and groundwater) was largely proved to be wrong. This conclusion however is only valid for the drought period that represented the sampling period of this study. Future investigations of these pools should attempt to assess and sample during a normal or high precipitation period in order to evaluate sources of water during non-drought conditions.

#### Conflict of interest

We are not aware of any conflict of interests with this work.

#### Acknowledgements

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ejrh.2016.12.087>.

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