

A groundwater salinity hotspot and its connection to an intermittent stream identified by environmental tracers (Mt Lofty Ranges, South Australia)

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Abstract High and variable levels of salinity were investigated in an intermittent stream in a high-rainfall area (~800 mm/year) of the Mt. Lofty Ranges of South Australia. The groundwater system was found to have a local, upslope saline lens, referred to here as a groundwater salinity ‘hotspot’. Environmental tracer analyses ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $^{87/86}\text{Sr}$, and major elements) of water from the intermittent stream, a nearby permanent stream, shallow and deep groundwater, and soil-water/runoff demonstrate seasonal groundwater input of very saline composition into the intermittent stream. This input results in large salinity increases of the stream water because the winter wet-season stream flow decreases during spring in this Mediterranean climate. Furthermore, strontium and water isotope analyses demonstrate: (1) the upslope-saline-groundwater zone (hotspot) mixes with the dominant groundwater system, (2) the intermittent-stream water is a mixture of soil-water/runoff and the upslope saline groundwater, and (3) the upslope-saline-groundwater zone results from the flushing of unsaturated-zone salts from the thick clayey regolith and soil which overlie the metamorphosed shale bedrock. The preferred theory on the origin of the upslope-saline-groundwater hotspot is land clearing of native deep-rooted woodland, followed by flushing of accumulated salts from the unsaturated zone due to increased recharge. This cause of elevated groundwater and surface-water salinity, if correct, could be widespread in Mt. Lofty Ranges areas, as well as other climatically and geologically similar areas with comparable hydrogeologic conditions.

Keywords Salinization · Groundwater/surface-water relations · Sr isotopes · Environmental tracers · Australia

Introduction

Understanding the extent and cause of groundwater ‘salinity hotspots’ (>8,000 $\mu\text{S}/\text{cm}$) as well as assessing their impact, both present and future, on associated groundwater and surface-water systems, is of critical concern to overall water quality and resource management in sub-humid to dry areas—for example, saline groundwater input into the Murray River (Australia) has been documented, highlighted, and incorporated into management plans for overall river health (Allison et al. 1990; Jolly et al. 2001; Lamontagne et al. 2005). In the Eastern Mt. Lofty Ranges (MLR) of South Australia, areas of high-salinity surface water and groundwater have been spatially evaluated in terms of climatic and hydrogeologic factors (Poulsen et al. 2006). Poulsen et al. (2006) found groundwater salinity hotspots were associated with geologic units comprising marine shales and generally occurred in the drier eastern parts of the Mt. Lofty Ranges. In the study presented here, this hydrologic association between metamorphosed shale bedrock and high groundwater salinity is extended to a high-rainfall area of the Mt. Lofty Ranges. The example documented here extends Mt. Lofty Ranges groundwater understanding by connecting the hotspot directly to an intermittent stream by identifying seasonal groundwater input to the stream.

The occurrences of upslope-saline-groundwater zones in landscapes with otherwise good quality groundwater and moderate precipitation, as documented here, have not been characterised in detail in the scientific literature. They may be a common occurrence in areas such as the Mount Lofty Ranges (MLR) and elsewhere (Greeff 1994). The hydrogeologic parameters of the Scott Creek site described in this paper are

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representative of significant portions of the MLR (Taylor et al. 1974; Preiss 1987; Poulsen et al. 2006; Bestland et al. 2016). Similar groundwater salinity/chloride profiles (lenses of saline groundwater) have been noted in the Clare Valley, South Australia (Stewart 2005; Love et al. 2002), and the Burra Creek catchment, South Australia (Banks et al. 2007). However, the salinity of the upslope groundwater zone at the Scott Creek site is much greater than these other two examples. It may be the case that the comprehensive shallow-to-moderate depth piezometer nests at the Scott Creek site have allowed for the discovery of very saline water at the top of the aquifer. The documentation of this phenomenon will alert land managers to the existence of groundwater salinity hotspots in high-rainfall areas of the MLR and an understanding of their cause will aid in land management decisions.

The objectives of this study were to: (1) understand the interactions between the intermittent stream and the groundwater system including the salinity hotspot and the dominant groundwater system, and (2) identify the extent of the groundwater salinity hotspot and understand its cause. The study utilises environmental tracer data ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $^{87/86}\text{Sr}$, and major elements) from the intermittent stream, a nearby permanent stream, soil-water/runoff, the shallow saline groundwater lens or hotspot, and the dominant groundwater system.

Study site

The Scott Bottom site in the Scott Creek catchment (SCC; Fig. 1) has been an experimental site for a number of hydrogeologic investigations (Chittleborough et al. 1992; Stevens et al. 1999; James-Smith and Harrington 2002; Harrington 2004a, b; Ranville et al. 2005; Banks et al. 2009; Bestland and Stainer 2013; Bestland et al. 2009, 2016). These studies document the soil hydrology of the dominant Xeralf (red brown earths) soils of the area as well as outlining the site's hydrogeological heterogeneity and geological-geomorphic complexity. A series of soil-water studies (Chittleborough et al. 1992; Stevens et al. 1999; Bestland et al. 2009) documented throughflow hydrochemical characteristics. Banks et al. (2009) and Bestland and Stainer (2013) documented the importance of the fractured bedrock zone and deep clayey regolith for the groundwater/surface-water interactions in relation to the permanent stream Scott Creek. These groundwater studies built upon the investigations of James-Smith and Harrington (2002) and Harrington (2004a, b) that documented the basic hydrology and hydrogeology of the Scott Creek catchment.

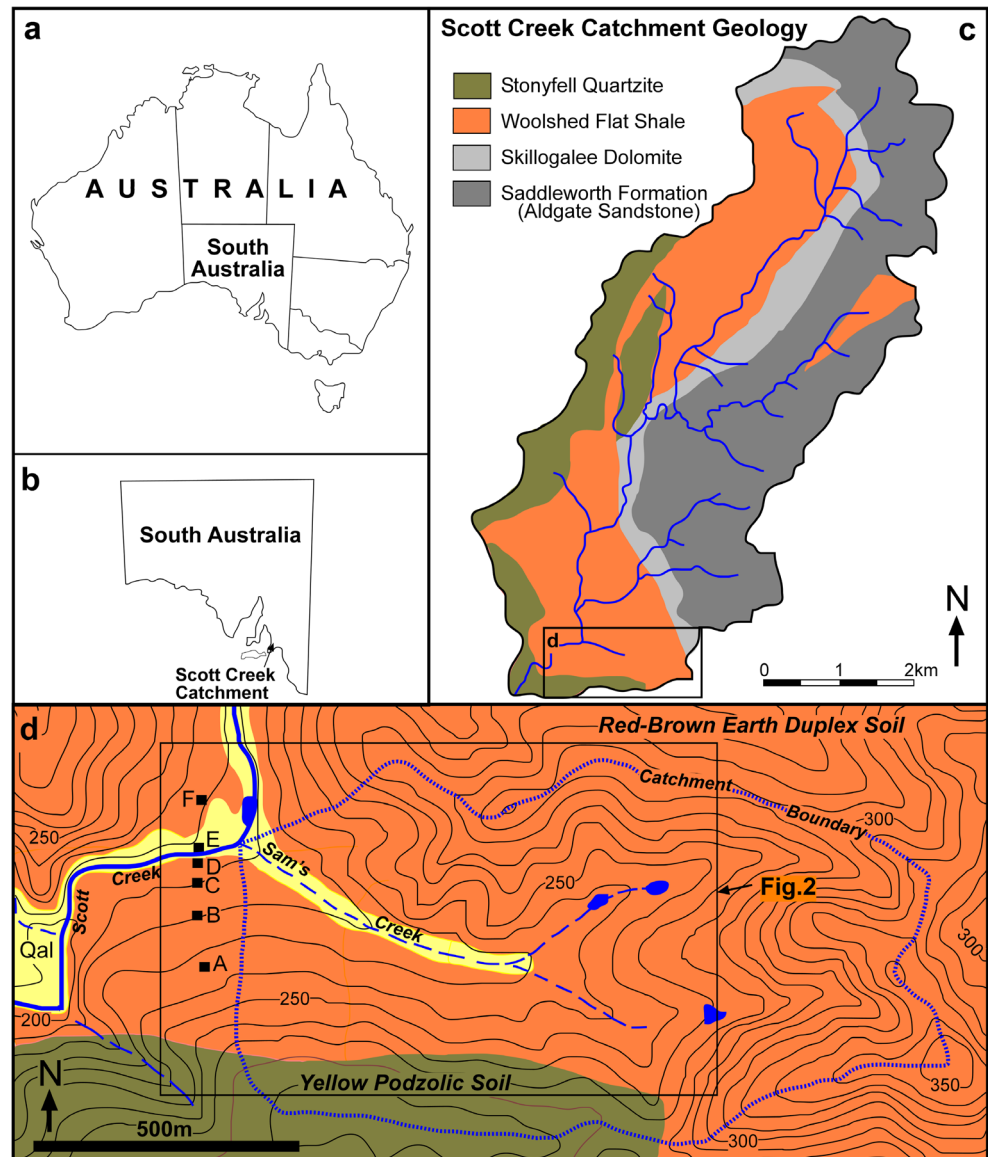
The Scott Creek catchment (Fig. 1) spans an area of 27 km² and is located approximately 30 km south-east of Adelaide. Most of the aforementioned studies on groundwater/surface-water interactions within the Scott Creek catchment were focused on the perennial Scott Creek with the Scott Bottom area as a primary site (Fig. 2). The intermittent stream, which is the

focus of this study and informally named Sam's Creek, is a tributary to Scott Creek entering Scott Creek at the Scott Bottom site. Stream water in Scott Creek is sustained in the creek throughout the hot, dry summers via groundwater discharge. During severe drought conditions (e.g. as occurred in the summer of 2006–2007), however, the stream was reduced to a series of disconnected groundwater-fed pools (Kretchmer 2007). The salinity in Scott Creek during both low flow and high flow regimes, is lower than in Sam's Creek. Salinities in Scott Creek vary from 500 $\mu\text{S}/\text{cm}$ in winter to above 2,000 $\mu\text{S}/\text{cm}$ during the low-flow period from January to April. The seasonal salinity variations were explained by evaporative enrichment and groundwater input during the summer contrasting with runoff dilution during the winter wet season (Harrington 2004b).

Sam's Creek drains a small catchment of 0.9 km² which has 150 m of relief and several small farm dams, only one of which still fills with water (Fig. 1). When the stream flows during the winter wet season, it consists of a series of pools and small streamlets which flow for several months to over half the year depending on the year's rainfall. Sam's Creek was first observed to have substantial salinity variations during its 3-month flow in 2009. Salinity levels of Sam's Creek contrast markedly and are much higher than the nearby ephemeral Mackreath Creek (Milgate 2007; Bestland et al. 2009; Pichler 2009). These investigations revealed Mackreath Creek to only flow after significant Autumn–Winter rainfall. It has very low salinity (200–500 $\mu\text{S}/\text{cm}$) and little salinity variation throughout its flow season. Preliminary data from 2009 suggested that the salinity in Sam's Creek vastly exceeded the general variation of salinity in Scott Creek (Harrington 2004b; Cranswick 2005; Banks et al. 2009; Anderson 2013). This was the initial impetus of this investigation.

The Scott Creek catchment as well as most of the Mt. Lofty Ranges (MLR) has a Mediterranean climate with cool, moist winters and warm, dry summers. Average daily temperature ranges from 8 to 14 °C in winter, and 14 to 27 °C in summer. The MLR receives varying seasonal precipitation (almost all as rainfall) with yearly averages ranging from 400 to over 1,000 mm/year and with 85% of the rainfall occurring between May and September (BOM 2007). The large annual variability in rainfall in this area impacts the groundwater/surface-water systems as evidenced by the before-mentioned very low flow and disconnected flow during droughts in Scott Creek. Winter wet season recharge causes the water table to rise between 1 and 2 m (Banks et al. 2009). The Scott Bottom site has a rainfall collector at an elevation of 210 m above Australian Height Datum and an average annual rainfall of 804 mm/year (Bestland et al. 2009). The site's closest Class A evaporation pan, Mt. Bold, has an average evaporation of 1,555 mm/year and therefore evaporation exceeds rainfall from October to May (spring, summer and autumn).

Fig. 1 **a–b** Maps showing the location of South Australia and the Scott Creek catchment. **c** Scott Creek catchment geology (the box outlines the Scott Bottom study site shown in **d**). **d** Location of the nested piezometers sites A–F, Scott Creek and Sam's Creek, and the distribution of soil types which follow closely the bedrock geology. Scott Creek in **d** and other streams in the Scott Creek catchment are depicted by *solid blue lines*. Intermittent streams in **d** are depicted with *dashed blue line*. The catchment boundary of Sam's Creek is depicted with *blue dashed line and is labelled*. Blue areas are farm dams and a pond at the weir on Scott Creek. Elevation contour lines are in meters AHD



Geology and hydrogeology

Due to the geology of the Adelaide Geosyncline and the folding and faulting in the area, the geology of the catchment is complex but well understood (Preiss 1987; Banks et al. 2009; Bestland et al. 2016). It consists of various metamorphosed sedimentary formations of Late Precambrian age, including the Woolshed Flat Shale, Stonyfell Quartzite, Skillogalee Dolomite, Saddleworth Formation (including Glen Osmond Slate) and Emeroo Subgroup (including Aldgate Sandstone and Bungaree Quartzite), as well as the recent alluvial deposits (Drexel et al. 1993). Woolshed Flat Shale dominates the lithology of the Scott Bottom site (Banks et al. 2009).

A set of shallow to moderate depth piezometer nests were drilled in 2005 and their locations are shown in Fig. 2. The piezometer nests A–F enabled an analysis of the

hydrogeological structure and flow dynamics of the site (Banks et al. 2009); details of the drilling are available in Cranswick (2005). In addition, six 2–3-m-deep backhoe trenches were excavated and sampled for soil and regolith hydrochemical properties (Bestland and Stainer 2013). The regolith is categorised by a soil zone and a deep saprolite (weathered bedrock) zone of up to 10–15 m (Cranswick 2005). Spatially variable fractured bedrock underlies this zone. The degree and depth of weathering of the saprolite is important in controlling groundwater flow and recharge. Banks et al. (2009) described groundwater flow in the catchment as occurring in three zones: the soil zone, saprolite zone and fractured bedrock zone. The vastly different hydraulic conductivities of each zone has resulted in large heterogeneity of the groundwater system (Harrington 2004a; Banks et al. 2009). The soil zone is characterised as a duplex soil with a

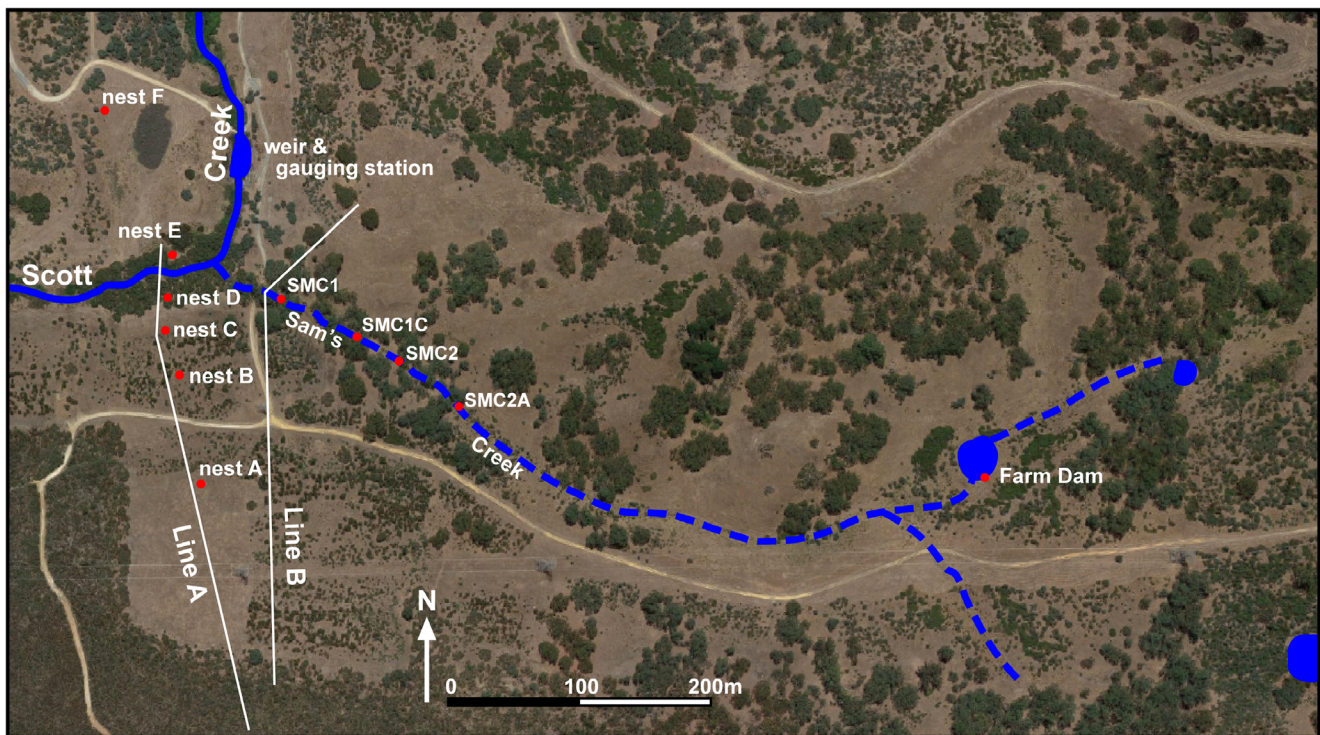


Fig. 2 Aerial image from Google Earth (2015) of the Scott Bottom area showing surface-water sampling sites and piezometer nest locations, as well as cross-sections lines A and B which are shown in Fig. 10

sandy-silty A horizon (10–20 cm depth) over a clayey B horizon (Chittleborough et al. 1992).

The saprolite zone changes progressively from a very clayey poorly structured material to the composition of the unweathered bedrock (Cranswick 2005; Bestland and Stainer 2013). Banks et al. (2009) found that the hydraulic conductivity of this zone ranged from 0.04 to 2.5 m/day and was generally less than the hydraulic conductivity of the fractured bedrock zone. The unweathered bedrock (Woolshed Flat Shale) was a grey siliceous slate. Hydraulic conductivity here ranged from 1.5 to 14 m/day. Banks et al. (2009) also found the fracture density to be on average 0.21 m. The fractured-rock aquifer was determined to be the most active part of the dominant groundwater system with some valley-bottom deep bores being artesian.

Methods

At the Scott Bottom site, six shallow to moderate depth piezometer nests were installed in July 2005 in order to monitor the groundwater processes in the soil, saprolite and fractured-bedrock zones (Figs. 1 and 2; Banks et al. 2009). In addition, water samples were obtained from eight open pre-existing bores, installed in March–April 2002 and reaching up to 96 m in depth (James-Smith and Harrington 2002). The six nests are positioned along a transect perpendicular to the creek valley, on an inferred groundwater flow path covering a

distance of about 330 m (Figs. 1 and 2). Nests A to F have depths varying from 1.5 to 28.5 m. The construction details of each piezometer are depicted in Banks et al. (2009). The ground elevation and piezometers were surveyed and the water table elevations were corrected to a standing water level relative to the Australian Height Datum (Cranswick 2005).

Stream and groundwater sampling

Water samples of Sam's Creek at two locations (SMC1 and SMC 2) and the two piezometers from nest A (A1 and A2) were collected on a weekly basis for environmental tracer analysis (Fig. 2). Weekly sampling was undertaken to document the gradual salinity change in the creek during the change from winter wet season to spring and early summer (Fig. 3). The sampling period occurred from early August to late October 2012 when surface flow ceased in Sam's Creek. A sample was taken, where possible, from each site. Grab samples of water were taken from the creek and farm dam, whereas a submersible 12 V battery pump was used to collect the groundwater samples.

A handheld YSI multi-parameter meter was used at each sample location to measure the pH, electrical conductivity (EC), dissolved oxygen (DO%), redox and temperature. A flow-through cell was utilised during groundwater measurements. Water samples were placed into clean, plastic and airtight sample bottles and filtered through a 0.45- μ m filter in the laboratory a few hours after sampling. Samples for ICP

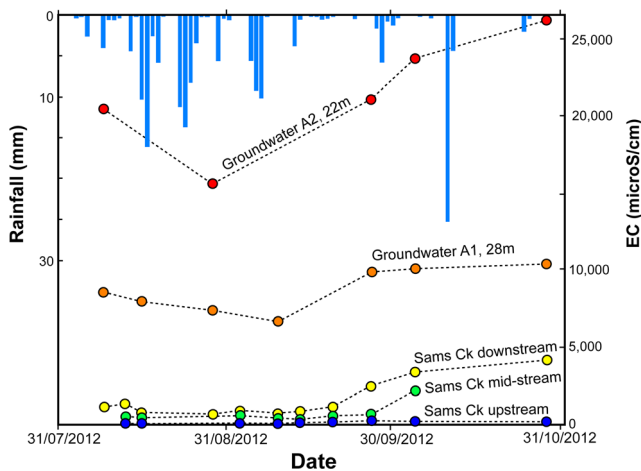


Fig. 3 Time series hydrograph showing salinity variation at sample sites on Sam's Creek, A1 and A2 piezometers, and corresponding rainfall from 3 August to 29 October 2012

analysis were acidified to a pH less than 2 using nitric acid (HNO_3). Water samples were transferred the same day as sampling and stored in a 30-ml McCartney bottle for water isotope ($^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$) analysis. To prevent exchange of water vapour with the air, McCartney bottles were filled with no headspace and sealed with electrical tape.

For the analysis of the major and trace elements, 16 samples were sent for a 72-element Group 2C, inductively coupled plasma mass spectrometry analysis at ACME analytical laboratories (ACME Labs 2012), Vancouver, Canada. Analysis of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ isotope ratios from water samples were done at the Stable Isotope Facility, University of California – Davis (UC Davis), USA, using a Laser Water Isotope Analyser V2. Final $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ values were reported relative to Vienna Standard Mean Ocean Water (VSMOW); methods are documented in UC Davis (2012). Four water samples were selected for the strontium isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) analysis. These included a sample from A1 and A2, and two from SMC1. The samples were analysed using a triton thermal ionisation mass spectrometer at the Australian National University. The international standard NBS-987 was used as an internal check for the analyses and values of 0.710249 were obtained with a reproducibility (1σ) of ± 0.000003 ($n = 5$). In addition, an extensive hydrochemical database from the site was also used in this investigation (Milgate 2007; Banks et al. 2009; Bestland et al. 2009).

Results and discussion

Stream salinity hydrograph

The groundwater salinity throughout the extensive groundwater monitoring network located in the SCC is relatively fresh (Table 1); most bores show lower than 1,000 mg/L TDS (total

dissolved solids). Deeper bores (greater than 40 m depth) have higher salinities (up to 3,000 mg/L); however, some bores in metamorphosed sandstone units have lower salinities (down to 200 mg/L; James-Smith and Harrington 2002; Banks et al. 2009). The upslope-saline-groundwater zone represented by piezometers A1 and A2 stand out in stark contrast to the rest of the groundwater system in the area because of their high salinities. Amongst the 50 wells in total at the Scott Bottom site, the A1 and A2 piezometers are the only ones that access the salinity hotspot. Salinity levels in A1 and A2 piezometers exceed 6,000 and 15,000 mg/L TDS respectively (Banks et al. 2009).

Sam's Creek has a large salinity increase during the waning winter wet flow (Fig. 3). There is a corresponding seasonal salinity increase in groundwater from the A1 and A2 piezometers. Surface-water salinities increase to approximately 2,500 mg/L TDS in the spring before flow ceases. The groundwater samples have the highest TDS values averaging 5,587 mg/L (A1) and 13,705 mg/L (A2). The A2 piezometer is 5 m more shallow than piezometer A1 and accesses the more saline upper part of this high-salinity groundwater zone.

There is a large salinity increase from upstream to downstream in Sam's Creek. The farthest upstream sample site (Farm Dam) showed the lowest salinity at 105 mg/L TDS on average, which is 1.4 and 0.6% of the average salinity of the groundwater in the A1 and A2 piezometers respectively.

Early in the winter wet season, soon after commencement of flow within Sam's Creek, water samples collected from midstream and downstream of Sam's Creek had low salinity. Salinity levels remained comparatively low up until the middle of September. Towards the end of the period of flow, the downstream salinity levels increased significantly, while there was no significant change in the salinity of the Farm Dam water. The discovery of this large surface-water salinity increase in what is an otherwise fresh runoff area was the impetus of this study.

Chloride and elemental molar ratios

Major ion to chloride ratios are presented in Fig. 4 and provide a tool to assess the source of salinity within the groundwater and surface waters within the study area. The majority of the lowest salinity groundwater samples exhibit ratios which range from that of local rainfall to ratios of 1, potentially indicating different degrees of dissolution of vadose-zone salts during recharge; nevertheless, all groundwaters remain highly undersaturated with respect to halite. A few fresh groundwater samples show Na^+/Cl^- ratios as high as 1.25, indicating the addition of Na^+ due to water–rock interaction, e.g. silicate weathering reactions; the latter would be consistent with the elevated Si/Cl^- concentrations of these groundwater samples. In contrast, the saline groundwater portions of the aquifer (A1 and A2) show Na^+/Cl^- ratios below that of rainfall and suggest

Table 1 Major and trace ion chemistry for the surface-water and groundwater samples collected from the Scott Bottom experimental site

Site ID	Date sampled	Cl ppm	Br ppm	Na ppm	Ca ppm	Mg ppm	K ppm	Si ppm
A1	16 August 2012	3,570	12.08	1,054	536	432	31	18
A1	29 October 2012	3,550	12.62	1,106	578	527	37	16
A1	3 April 2006	3,337	10.97	1,169	555	444	23	15
A1	24 May 2006	3,325	11.72	1,082	540	420	24	14
A1	1 July 2006	3,052	11.52	1,084	519	419	22	16
A1	3 July 2006	3,087	11.23	1,039	545	426	22	15
A1	15 November 2006	3,190	10.90	1,209	552	434	21	16
A1	13 February 2007	3,166	10.65	1,130	574	435	22	15
A1	2 June 2008	2,481	9.63	941	449	367	21	15
A2	29 August 2012	8,100	28.30	1,898	1,083	1,403	98	16
A2	29 October 2012	9,960	33.72	2,245	1,288	1,706	53	14
B4	3 June 2008	503	1.88	282	121	78	8	12
B5	3 June 2008	506	1.85	281	120	80	8	13
C4	3 April 2006	521	1.72	318	132	86	7	15
C4	24 May 2006	590	2.05	346	148	94	8	15
C4	1 July 2006	577	2.04	346	146	92	8	15
C4	3 July 2006	563	2.07	355	149	91	7	15
C4	15 November 2006	554	1.86	341	139	89	8	13
C4	13 February 2007	543	1.77	320	135	86	7	12
C4	3 June 2008	518	1.91	287	120	80	8	13
C5	3 June 2008	516	1.89	307	122	81	8	12
D1	3 June 2008	790	2.52	382	189	119	16	11
D2	3 April 2006	729	2.41	339	181	127	10	13
D2	24 May 2006	693	2.10	359	113	111	11	13
D2	30 June 2006	701	2.60	410	186	125	9	13
D2	30 June 2006	724	2.67	415	195	130	9	12
D2	1 July 2006	136	0.42	86	12	11	6	14
D2	3 July 2006	750	2.70	415	196	134	9	15
D2	15 November 2006	726	2.65	413	196	134	8	14
D2	13 February 2007	695	2.26	355	172	117	10	15
D2	3 June 2008	716	2.29	358	167	118	10	16
D3	3 June 2008	653	2.13	327	171	112	14	16
D4	3 April 2006	733	2.43	381	213	122	12	15
D4	24 May 2006	723	2.41	400	212	118	12	14
D4	30 June 2006	687	2.60	444	222	121	10	4
D4	1 July 2006	735	2.72	433	221	124	10	15
D4	3 July 2006	747	2.76	447	230	127	10	15
D4	15 November 2006	759	2.85	447	231	127	11	16
D4	13 February 2007	739	2.44	395	208	118	12	17
D4	3 June 2008	767	2.52	415	219	122	12	17
D5	3 June 2008	733	2.43	393	214	120	12	15
D6A	3 June 2008	393	1.32	284	153	93	9	17
D6A	3 June 2008	739	2.64	350	192	117	10	14
D6B	3 June 2008	535	1.75	305	168	110	9	14
E1	4 June 2008	709	2.41	566	190	112	18	13
E2	3 April 2006	971	3.10	438	226	167	13	13
E2	24 May 2006	785	2.47	406	193	135	11	13
E2	30 June 2006	939	3.40	496	238	167	11	13

Table 1 (continued)

Site ID	Date sampled	Cl ppm	Br ppm	Na ppm	Ca ppm	Mg ppm	K ppm	Si ppm
E2	30 June 2006	988	3.48	519	251	175	11	14
E2	1 July 2006	955	3.46	522	242	175	11	15
E2	3 July 2006	938	3.39	513	244	173	10	15
E2	15 November 2006	982	3.50	535	217	182	11	13
E2	13 February 2007	974	3.05	447	220	157	13	15
E2	4 June 2008	968	2.99	448	217	155	13	13
E3	4 June 2008	832	2.64	389	197	134	20	14
E4	3 April 2006	723	2.32	330	172	127	10	13
E4	24 May 2006	538	1.75	287	129	93	7	15
E4	30 June 2006	672	2.52	394	174	121	8	15
E4	1 July 2006	688	2.63	399	188	128	8	15
E4	3 July 2006	687	2.62	404	186	130	8	10
E4	15 November 2006	706	2.54	399	187	131	8	11
E4	13 February 2007	748	2.43	362	174	126	10	15
E4	4 June 2008	676	2.16	327	152	113	8	15
E5	4 June 2008	630	2.05	326	165	111	14	14
E6	4 June 2008	858	2.59	405	185	151	11	15
E6	21 May 2008	803	2.60	365	162	128	11	15
Sam's Creek 1	13 August 2012	386	1.22	151	109	89	10	15
Sam's Creek 1	3 September 2012	234	0.81	96	78	59	7	14
Sam's Creek 1	14 September 2012	217	0.79	73	80	58	7	15
Sam's Creek 1	27 September 2012	692	2.26	222	183	155	12	15
Sam's Creek 1	29 October 2012	1,075	3.36	345	260	225	15	15
Sam's Creek 1C	14 September 2012	170	0.66	75	70	47	7	15
Sam's Creek 2	9 July 2008	422	1.10	134	91	80	14	15
Sam's Creek 2	31 July 2008	575	1.58	180	120	102	12	15
Sam's Creek 2	12 August 2008	68	0.22	32	18	13	8	17
Sam's Creek 2	27 August 2008	270	0.92	95	80	63	11	17
Sam's Creek 2	12 September 2008	466	1.67	146	128	102	14	18
Sam's Creek 2	30 September 2008	1,231	3.59	343	282	248	18	13
Sam's Creek 2	21 October 2008	1,454	4.43	424	344	301	19	15
Sam's Creek 2	13 August 2012	70	0.27	44	53	32	5	18
Sam's Creek 2	14 September 2012	55	0.26	36	44	24	4	17
Sam's Creek 2	5 October 2012	498	1.73	176	146	112	4	18
Farm dam	14 September 2012	33	0.12	17	9	8	1	14
Soil moisture	21 July 2008	100	0.15	48	14	10	7	18
Soil moisture	31 July 2008	84	0.13	45	7	9	7	10
Soil moisture	12 August 2008	77	0.17	45	6	8	7	12
Soil moisture	27 August 2008	58	0.20	42	5	7	6	8
Soil moisture	12 September 2008	50	0.23	40	4	6	6	9
Soil moisture	30 September 2008	57	0.27	44	5	7	7	8
Soil moisture	21 May 2008	11	0.24	10	2	1	8	10
Overland flow	24 September 2006	11	0.07	11	3	2	2	1
Overland flow	24 September 2006	23	0.08	14	5	4	4	2
Overland flow	24 September 2006	66	0.18	48	11	9	2	2
Overland flow	24 September 2006	17	0.42	23	1	1	1	4

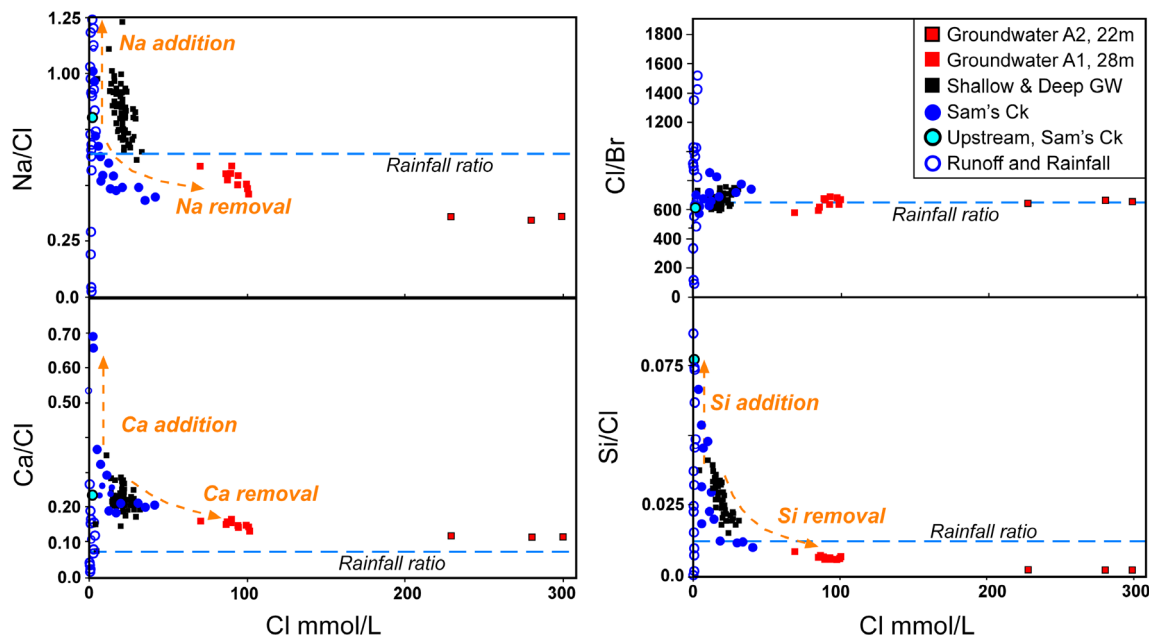


Fig. 4 Composite diagrams of major elements (Ca^{2+} , Na^+ , Si) to chloride ratios versus chloride concentration of surface water and groundwater. Samples were collected between July 2005 and October 2012 at Scott

the preferential removal of Na^+ from solution, whereby the latter is likely to reflect alterations of the groundwater chemistry due to ion exchange, i.e. the adsorption of Na^+ by clays, a common process in salinized areas (Cartwright et al. 2004). Sam's Creek water appears to lie on a mixing line between ratios indicative of rainfall and the saline, upslope groundwater of piezometers A1 and A2.

Dissolution of calcite, along with weathering of feldspars, can explain the elevated $\text{Ca}^{2+}/\text{Cl}^-$ ratios in the fresh groundwater, while a decrease in $\text{Ca}^{2+}/\text{Cl}^-$ ratios with increasing salinity may reflect precipitation of calcite out of the high-ionic-strength waters found up slope. This is consistent with groundwater samples in A1 and A2 being above calcite saturation.

Groundwater samples exhibit homogenous molar Cl^-/Br^- ratios (ranging between 580 and 750) that are consistent with longer residence times that allow extensive groundwater mixing which homogenises the groundwater chemistry. The relative invariance of Cl^-/Br^- ratios with increasing Cl^- concentrations provide evidence of groundwater mixing between the saline groundwater lens and the dominant groundwater system.

Overall, the major ion/ Cl^- ratios and Cl^-/Br^- ratios exhibit distinct contrasts between the compositions of Sam's Creek water, saline groundwater at locations A1 and A2, and that of the dominant groundwater system. These differences were broadly consistent over several years of sampling. However, seasonal differences in ion/ Cl^- ratios for Sam's Creek are observed (Fig. 4). Following initiation of stream flow, the creek water had ratios close to those of the Farm Dam water, which

is rainfall/soil-runoff derived. Major ion ratios (Na^+/Cl^- , $\text{Ca}^{2+}/\text{Cl}^-$, Si/Cl^-) in the creek attained the ratios of the saline groundwater later in the season when the creek had nearly ceased flowing. The stream salinity was still, however, only 33% of A2 in the final sample collected from Sam's Creek. If evapotranspiration played a major role in seasonal changes in stream water chemistry, ion/ Cl^- ratios should have remained constant, opposite to what was observed. Overall, the hydrochemical signatures indicate stream water to be mainly rainfall-runoff derived during high flows. As the water table rises during the wet season, and saline groundwater discharges into the stream, mixing and dilution with runoff occurs. During the waning stream flow, the stream consists predominantly of groundwater.

This investigation supported the findings from Poulsen et al. (2006) who determined that areas of elevated stream salinity were correlated to areas of shallow groundwater where they provide base-flow to the streams in the Eastern MLR. This study was also consistent with that of Banks et al. (2009) on Scott Creek. Scott Creek was shown to be composed of a mixture of groundwater, soil water, and surface-water runoff. The composition of Scott Creek revealed that most dissolved ions were derived from water–rock interactions in the subsurface (especially Ca^{2+} , Mg^{2+} , HCO_3^-) as well as salts deposited in rainfall (i.e. Na^+ and Cl^- ; Banks et al. 2009). The similarity of the concentrations of major ions (Ca^{2+} , Mg^{2+} , Na^+ , Cl^- and HCO_3^-) led Banks et al. (2009) to suggest that the groundwater was relatively well mixed within the fractured bedrock.

Banks et al. (2009) established that the vertical hydraulic gradient between the A1 and A2 piezometers was in a

downward direction. CFC-11 (trichlorofluoromethane, CFCl_3) and CFC-12 (dichlorodifluoromethane, CF_2Cl_2) analyses suggest shorter residence time for the groundwater upslope compared to that of the discharge zone in the valley (Banks et al. 2009). Thus, the salinity variation between upslope down-gradient groundwater and valley-bottom up-gradient groundwater is not due to processes of chemical weathering along a groundwater flow path.

Stable isotopes of water

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition of groundwater samples plot close to the local meteoric water line (LMWL) for Adelaide (Hughes and Crawford 2012; Kayaalp 2001), indicating that these waters are little altered from their meteoric origin and not significantly impacted by unsaturated-zone evaporation or open-water evaporation before infiltration (Figs. 5 and 6; Table 2). Shallow groundwater thereby displays the largest range of $\delta^{18}\text{O}$ values, reflecting the variable extent of local evaporation as well as the local variability of the $\delta^{18}\text{O}$ values of different rainfall. Sam’s Creek water samples also plot close to the LMWLs indicating only minor influence of evaporation. Surface waters are, however, enriched compared to most groundwater samples, with upstream creek waters (Sam’s Creek 2) being more enriched than downstream samples. Sam’s Creek waters cluster near the most saline groundwater samples (piezometer A2). These are enriched in $\delta^{18}\text{O}$ by about 0.5‰ compared to both A1 and other shallow groundwater and up to about 1.5‰ compared to the main groundwater body within the SCC.

A comparison of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in relation to chloride concentrations confirms the subdued role of evaporation in altering the chemistry of surface water and groundwater in the SCC (Fig. 7). An increase in salinity is not accompanied by

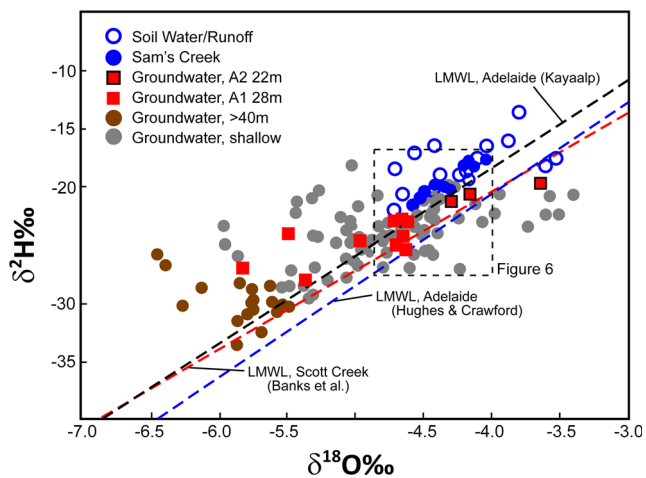


Fig. 5 $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ for runoff, Sam’s Creek water and groundwater sampled over a 7-year period at the Scott Bottom experimental site. The local meteoric water lines (LMWL) are from Kayaalp 2001; Banks et al. 2009; Hughes and Crawford 2012

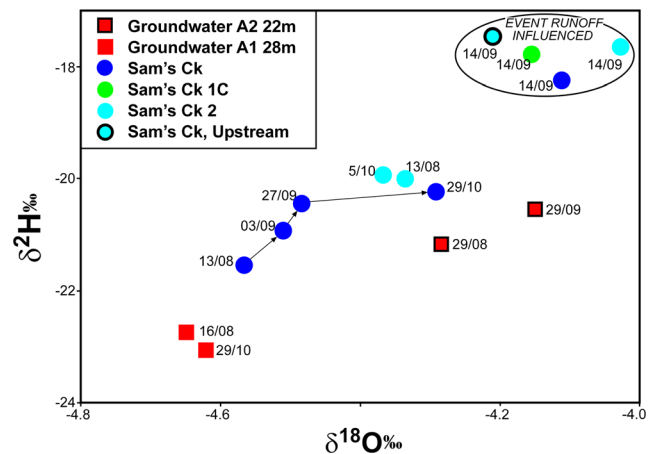


Fig. 6 $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ ‰ for surface water and groundwater sampled from 13 August to 29 October 2012 at the Scott Bottom experimental site

a trend towards heavier isotopic compositions. Instead, as salinity increases, surface-water and groundwater samples show little variation in their isotopic signature.

Age dating by Banks et al. (2009) based on CFC-12 and CFC-13 showed the apparent age of upslope groundwater (A1 and A2) to be less than that of deeper groundwater within the main groundwater body of the SCC. Similarly, Radon-222 data by Cranswick (2005) suggest that water from deeper piezometers, despite lower salinities than the upslope groundwater, have longer residence times.

Groundwater from piezometer A2 (shallowest) was more enriched than groundwater from piezometer A1 and indicates either greater evaporation of A2 groundwater or mixing with the dominant groundwater system resulting in lower salinity for A1. Stream water from the downstream site (Sam’s Creek 1) is more depleted than the upstream site (Sam’s Creek 2) suggesting that there is greater groundwater input downstream in Sam’s Creek.

A seasonal trend of isotopic enrichment in Sam’s Creek is observed (Fig. 6). As the wet season progresses, several samples taken between the start of the wet season and cessation of creek water flow show Sam’s Creek to progressively attain an isotopic composition close to that of the upslope-saline-groundwater (Fig. 6). This lends further support to the mixing model already outlined, where discharge of saline upslope groundwater and soil-water/runoff mix in Sam’s Creek. As rainfall and runoff ceases towards the end of the wet season, the proportion of groundwater input to the creek subsequently rises and creek water attains an isotopically more enriched signature.

Surface-water samples collected on 14 September 2012 had more positive water isotope values than most other surface-water samples (Fig. 6). This enrichment is probably due to a rainfall event of 25 mm on 11 September 2012. The water isotope values in the stream sites after this rainfall were more enriched and, thus, support the interpretation of an

Table 2 Stable isotopes results for the surface-water and groundwater samples collected from the Scott Bottom experimental site

Site ID	Date sampled	$\delta^2\text{H}\text{‰}$ rel VSMOW	$\delta^{18}\text{O}\text{‰}$ rel VSMOW
662,704,233	28 June 2006	-5.68	-32.50
662,704,300	22 July 2006	-6.26	-30.17
662,704,400	29 August 2007	-5.03	-24.9
662,706,869	27 August 2007	-6.44	-25.8
662,707,330	28 August 2007	-5.74	-29.7
662,707,557	28 August 2007	-5.75	-28.8
662,707,802	28 August 2007	-5.52	-30.1
662,707,908	28 June 2006	-6.12	-28.65
662,708,729	28 August 2007	-5.79	-30.9
662,708,783	29 August 2007	-5.74	-30.6
662,709,611	30 August 2007	-5.75	-30.0
662,709,618	28 June 2006	-5.86	-33.57
662,709,708	29 August 2007	-5.57	-30.7
662,709,936	28 August 2007	-5.86	-31.5
662,710,397	30 August 2007	-5.60	-29.9
662,710,414	27 August 2007	-6.38	-26.7
662,711,009	29 August 2007	-5.77	-29.7
A1	3 April 2006	-4.96	-24.7
A1	24 May 2006	-5.35	-27.98
A1	1 July 2006	-5.82	-27.03
A1	3 July 2006	-5.48	-24.04
A1	15 November 2006	-4.62	-25.4
A1	13 February 2007	-4.64	-24.3
A1	2 June 2008	-4.70	-23.0
A1	16 August 2012	-4.65	-22.7
A1	29 October 2012	-4.62	-23.1
a2	29 August 2012	-4.28	-21.2
a2	29 October 2012	-4.15	-20.5
B4	3 June 2008	-4.78	-26.8
B5	3 June 2008	-4.86	-24.6
C4	3 April 2006	-4.94	-25.3
C4	24 May 2006	-5.06	-23.72
C4	1 July 2006	-4.44	-22.61
C4	3 July 2006	-5.42	-22.26
C4	15 November 2006	-5.01	-24.6
C4	13 February 2007	-5.30	-24.2
C4	3 June 2008	-4.59	-26.9
C5	24 May 2006	-4.11	-21.52
C5	3 June 2008	-4.56	-25.8
C6	30 June 2006	-4.23	-27.00
D1	1 July 2006	-3.94	-20.62
D1	3 June 2008	-4.49	-21.1
D2	3 April 2006	-5.27	-24.3
D2	3 July 2006	-4.24	-22.67
D2	15 November 2006	-4.96	-24.3
D2	13 February 2007	-5.13	-24.8
D2	3 June 2008	-4.69	-22.8

Table 2 (continued)

Site ID	Date sampled	$\delta^2\text{H}\text{‰}$ rel VSMOW	$\delta^{18}\text{O}\text{‰}$ rel VSMOW
D3	3 June 2008	-4.60	-22.9
D4	3 April 2006	-5.01	-23.4
D4	24 May 2006	-4.39	-23.94
D4	30 June 2006	-4.06	-22.99
D4	1 July 2006	-3.59	-22.45
d4	3 July 2006	-3.72	-23.40
D4	15 November 2006	-4.96	-21.7
D4	13 February 2007	-4.48	-23.7
D4	3 June 2008	-4.94	-25.4
D5	3 June 2008	-4.80	-24.3
D6A	3 June 2008	-4.90	-25.3
D6B	3 June 2008	-5.05	-27.8
E1	4 June 2008	-5.28	-26.9
E2	3 April 2006	-4.53	-22.4
E2	24 May 2006	-3.39	-20.65
E2	30 June 2006	-3.50	-22.32
E2	1 July 2006	-3.57	-20.86
E2	3 July 2006	-4.56	-23.64
E2	15 November 2006	-4.56	-23.4
E2	13 February 2007	-4.41	-22.9
E2	4 June 2008	-4.82	-23.3
E3	4 June 2008	-5.10	-22.5
E4	3 April 2006	-4.73	-24.2
E4	24 May 2006	-5.32	-20.92
E4	30 June 2006	-5.42	-21.26
E4	1 July 2006	-4.83	-20.77
E4	3 July 2006	-4.40	-21.16
E4	15 November 2006	-4.75	-23.1
E4	13 February 2007	-4.69	-24.2
E4	4 June 2008	-5.03	-23.0
E5	4 June 2008	-4.78	-24.1
E6	4 June 2008	-4.41	-21.9
F2	3 April 2006	-4.42	-25.8
F2	24 May 2006	-5.95	-23.34
F2	1 July 2006	-5.85	-25.90
F2	3 July 2006	-5.94	-24.94
F2	15 November 2006	-4.45	-25.4
F2	13 February 2007	-4.48	-25.6
F2	6 June 2008	-5.37	-28.5
F3	5 June 2008	-2.57	-28.1
F4	5 June 2008	-5.20	-28.0
F5	3 April 2006	-5.34	-29.6
F5	24 May 2006	-4.26	-20.01
F5	1 July 2006	-5.02	-18.20
F5	3 July 2006	-5.26	-20.20
F5	15 November 2006	-5.46	-27.2
F5	13 February 2007	-5.35	-28.6
F5	5 June 2008	-4.50	-24.1

Table 2 (continued)

Site ID	Date sampled	$\delta^2\text{H}\text{‰}$ rel VSMOW	$\delta^{18}\text{O}\text{‰}$ rel VSMOW
F6	5 June 2008	-3.97	-22.3
Farm Dam	14 September 2012	-4.21	-17.5
Sam's Creek 1	3 September 2012	-4.51	-20.9
Sam's Creek 1	14 September 2012	-4.11	-18.2
Sam's Creek 1	27 September 2012	-4.48	-20.4
Sam's Creek 1	29 October 2012	-4.29	-20.2
Sam's Creek 1	13 August 2012	-4.57	-21.5
Sam's Creek 1C	14 September 2012	-4.16	-17.8
Sam's Creek 2	13 August 2012	-4.37	-19.9
Sam's Creek 2	14 September 2012	-4.03	-17.7
Sam's Creek 2	5 October 2012	-4.34	-20.0

enriched rainfall event. In nearby Mackreath Creek catchment, Bestland et al. (2009) documented that lower than normal oxygen and hydrogen isotope ratios (more enriched) of a large precipitation event could be used as a natural tracer. The analysis of stable isotopes of water provides further evidence that

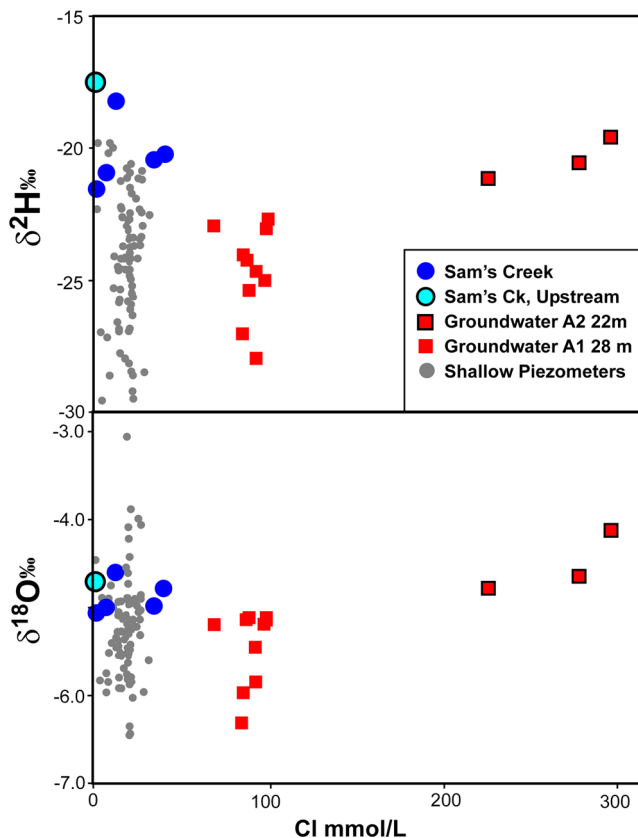


Fig. 7 $\delta^2\text{H}$ versus $\delta^{18}\text{O}\text{‰}$ versus chloride for surface water and groundwater sampled over a 7-year period at the Scott Bottom experimental site

the surface water in Sam's Creek is a mixture of runoff water and the upslope-saline-groundwater zone.

The waters' stable isotopic results depicting upslope-saline-groundwater input to Sam's Creek are comparable to a study by Meredith et al. (2013) albeit on different scales. In their study, the stable isotopes of water were used to determine the influx of saline groundwater to the Darling River, New South Wales, Australia. During times of groundwater discharge, the isotopic signature was depleted and high salinities were evident. This occurred in low to zero flow conditions similar to the conditions where the salinity increase occurred in Sam's Creek.

The results from the water isotopic signature versus chloride (Fig. 7) suggest that there is little if any evaporation that causes the salinity variation in Sam's Creek nor the groundwater in the A1 and A2 piezometers. There were no evaporative trends significant enough to infer that the upslope-saline-groundwater system originated from evaporative enrichment. A much more likely explanation for the increased salinity could, however, be the concentration of salts in the unsaturated zone by transpiration. Transpiration influences the salinity of water; however, it does little to alter the isotopic composition of water (Zimmerman et al. 1967; Forstel 1982). Salt accumulation in the upslope-saline-groundwater zone could therefore be caused by transpiration by plants from the soil and groundwater; during recharge events, salts in the unsaturated zone can be flushed into the groundwater. This would be consistent with a study by Poulsen et al. (2006) who established transpiration to be the primary cause of elevated salinities in the Eastern MLR.

A study of the Eastern MRL by Green and Stewart (2008) revealed comparatively much greater levels of evaporative enrichment, indicating that the level in the study presented here was not substantial. Despite Sam's Creek being constantly exposed to the atmosphere and thus subjected to evaporative processes, evaporative enrichment is insignificant.

Sam's Creek showed little change in deuterium excess with change in $\delta^{18}\text{O}\text{‰}$ (Fig. 8). The average was 14.89‰ with a standard deviation of 0.41. The runoff had a slightly lower excess at 13.82‰ on average with the greatest standard deviation of 5.39‰. The deep groundwater had the highest deuterium excess at 16.65‰ on average. The A1 and A2 piezometers displayed a trend of decreasing deuterium excess with increased $\delta^{18}\text{O}\text{‰}$.

Deuterium excess was used to further distinguish major water components (Fig. 8). Orographic features affect the distribution of the stable isotopes of water in rain (Dansgaard 1964) including deuterium excess, and most likely contribute to the variation in isotopic ratios observed in this study. In hilly terrains such as the MLR, the fractionation of rainfall and that of the associated groundwater vary with altitude (Guan et al. 2013). Rain

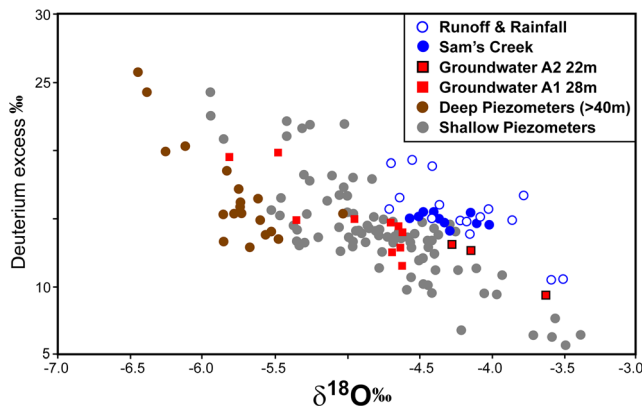


Fig. 8 Deuterium excess versus $\delta^{18}O$ for runoff, Sam’s Creek water and groundwater sampled over a 7-year period at the Scott Bottom experimental site

becomes isotopically lighter with altitude on the windward slope. This was determined to be due to progressive rain-out processes (Guan et al. 2009). At lower elevations, rainfall and corresponding groundwater is isotopically heavier due to sub-cloud evaporation and moisture exchanged with the surrounding air (Guan et al. 2009); therefore, the water from the deep piezometers could have originated from a higher altitude than the dominant groundwater system in the SCC. This also suggested that the saline water that discharged into Sam’s Creek was from a similar altitude to the A1 and A2 piezometers.

Strontium isotopes

Strontium isotopic ratios and concentrations from this site were obtained for soil water, stream water from Sam’s Creek, stream water from Scott Creek, and groundwater from the shallow and

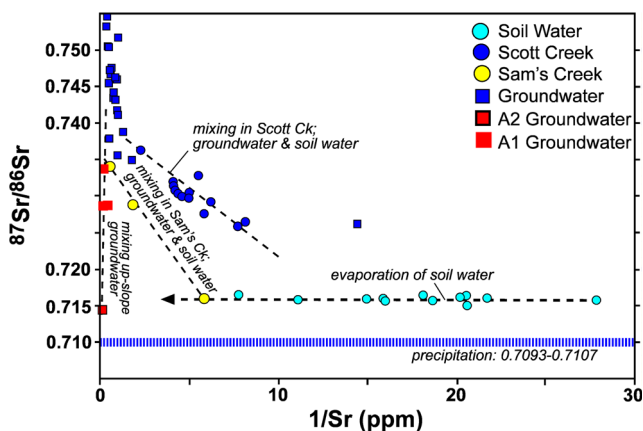


Fig. 9 Variation of strontium isotope ratios with inverse strontium concentration. Both groundwater and surface-water samples at the Scott Bottom experimental site from 2005 to 2012 are plotted. Data sourced from Cranswick (2005); Milgate (2007); Banks (2011). Precipitation range from Raiber et al. (2009) using four stations 100 km or less from the nearby coast of the state of Victoria

Table 3 Strontium isotope results for the surface-water and groundwater samples collected from the Scott Bottom experimental site. *SD* standard deviation

Sample ID	Date sampled	Sr 87/86	SD
A1	29 October 2012	0.728743	0.000005
A2	29 October 2012	0.714402	0.000005
Sam’s Creek	3 September 2012	0.728699	0.000006
Sam’s Creek	29 October 2012	0.734029	0.000004
Scott Creek	30 June 2006	0.725206	0.000072
Scott Creek	1 July 2006	0.731954	0.000077
Scott Creek	1 July 2006	0.731531	0.000078
Scott Creek	1 July 2006	0.730879	0.000076
Scott Creek	1 July 2006	0.730396	0.000084
Scott Creek	1 July 2006	0.729842	0.000095
Scott Creek	1 July 2006	0.730559	0.000069
Scott Creek	1 July 2006	0.727651	0.000091
Scott Creek	1 July 2006	0.725942	0.000091
Scott Creek	2 July 2006	0.726523	0.000072
Scott Creek	5 July 2006	0.729249	0.000062
Scott Creek	14 July 2006	0.730071	0.000078
Scott Creek	29 June 2006	0.731588	0.000071
Scott Creek	1 July 2006	0.722939	0.000071
Scott Creek	5 July 2006	0.723574	0.000266
Scott Creek	29 June 2006	0.716251	0.000068
Scott Creek	1 July 2006	0.715101	0.000063
Scott Creek	5 July 2006	0.715170	0.000068
Scott Creek	29 June 2006	0.716441	0.000081
Scott Creek	1 July 2006	0.716544	0.000099
Scott Creek	5 July 2006	0.716659	0.000069
Soil water	27 June 2007	0.716004	-
Soil water	2 July 2007	0.715991	-
Soil water	6 July 2007	0.715809	-
Soil water	9 July 2007	0.715781	-
Soil water	11 July 2007	0.715780	-
Soil water	15 July 2007	0.715739	-
Soil water	2 July 2007	0.714526	-
Soil water	6 July 2007	0.715137	-
Soil water	9 July 2007	0.715112	-
Soil water	15 July 2007	0.715153	-

deep part of the system (Fig. 9; Table 3). Strontium isotopes do not undergo significant mass fractionation during hydrologic processes regardless of temperature, chemical speciation or biological processes (Capo et al. 1998; Kendall and McDonnell 1998). Strontium originating from mineral weathering reactions has a $^{87}Sr/^{86}Sr$ ratio ranging between the minerals with which it is interacting and the strontium contained in precipitation. In most hydrogeologic settings, the composition of the host rock along the groundwater flow path generally dominates strontium isotopic ratios of groundwater

(Kendall and McDonnell 1998; Harrington and Herczeg 2003). Atmospheric origins of strontium are dominated by marine sources especially in coastal settings such as the MLR. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio range used for precipitation in this study, of 0.7093 to 0.7107, is based on a transect of strontium isotope analyses of precipitation from the coast and then inland in the nearby state of Victoria (Raiber et al. 2009); four stations, from the coast to 100 km inland, were used to obtain the range shown in Fig. 9.

The strontium isotopic ratios of the upslope-saline-groundwater zone are lower than the dominant groundwater system ranging from 0.7144 to 0.7336 compared to the dominant groundwater system which ranges from 0.7355 to 0.7503 (Fig. 9). The upslope-saline-groundwater samples, especially from piezometer A2, are distinguished by their relatively low isotopic ratios and high strontium concentrations. Soil water collected at this site and analysed by Milgate (2007) is characterised by low strontium concentrations and low strontium isotopic ratios (Fig. 9). Three relationships can be concluded from the strontium isotopic data. The mixing lines in Fig. 9 indicate: (1) mixing between the upslope-saline-groundwater zone (shallow, more saline piezometer A2) and the dominant groundwater system to produce the compositions from piezometer A1; (2) mixing between the upslope-saline-groundwater zone and the soil-water/runoff to produce the mixing line of Sam's Creek; and (3) mixing of the dominant groundwater system and soil water to produce the mixing line of Scott Creek.

A simple mixing model was utilised whereby water from the very top of the perched saline groundwater mixed with water from the dominant groundwater system to produce the water in the lower part of the perched groundwater (Fig. 10). Strontium isotope ratios were used to quantify the relative proportions of strontium that contributed to the mixed lower part of the perched saline groundwater represented by water from piezometer A1 (Eq. 1). Strontium isotope ratios from the upper saline groundwater (piezometer A2) and the dominant groundwater system (other piezometers of moderate and deeper depth) were averaged and the three isotope ratios were used in Eq. (2) to calculate the fraction of each of the two end members.

The $^{87}\text{Sr}/^{86}\text{Sr}$ of a mixture of two end members 1 and 2 is:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{mix}} = \frac{M_1^{\text{Sr}} \cdot \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_1 + M_2^{\text{Sr}} \cdot \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_2}{M_1^{\text{Sr}} + M_2^{\text{Sr}}} \quad (1)$$

where M_1^{Sr} and M_2^{Sr} are the masses of strontium from end members 1 and 2. End member 1 is water from piezometer A2 and end member 2 represents the average masses of

strontium of samples from the dominant groundwater system. The term $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{mix}}$ is the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the mixture, which in this case is water from piezometer A1. Rearranged, this formula gives: the fraction of end member 1; (A2) in relation to end member 2; and (dominant groundwater system) in the mixture observed in A1 (modified from Stewart et al. 1998; Green et al. 2004):

$$\frac{M_1^{\text{Sr}}}{M_1^{\text{Sr}} + M_2^{\text{Sr}}} = \frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{mix}} - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_2}{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_1 - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_2} \quad (2)$$

From this equation, the percentage of the dominant groundwater system represented in the mixture of groundwater in A1 was calculated at 46%. The remaining 54% is contributed by the more saline groundwater of A2.

Mixing of soil-water/runoff with upslope perched saline groundwater, as previously outlined, can be evaluated with strontium isotopes (Fig. 9). The three data points form a mixing line, with one data point indicating close to 100% soil water (high-flow sample) and one data point indicating close to 100% groundwater (low-flow sample). The seemingly wide range of strontium concentrations for soil water in Fig. 9 is misleading; strontium concentrations of these samples range from 0.024 to 0.090 ppm. Nonetheless, evaporation of soil water has produced this range of concentrations with no change in isotopic ratio.

Conceptual model

The conceptual model relies on the specific hydrogeology of this site (Fig. 10). The regolith-saprolite zone of the study site consists of heavy clay that has been weathered from the metamorphosed shale bedrock. This zone forms a thick clay layer over much of the Scott Bottom site (Banks et al. 2009; Bestland et al. 2016). Such clayey zones have been shown to restrict infiltration and cause salinity issues due to poor drainage. Cartwright et al. (2013) demonstrated that shallow saline groundwater can occur where the geology and porosity of the soil restricts drainage. These zones can have very low permeability and slow infiltration rates that hinder the flushing of salts (Bennetts et al. 2007; Rengasamy 2006). Shallow groundwater such as this can be prone to direct evaporation through capillary action (Turner et al. 1987; Salama et al. 1999; Lamontagne et al. 2005). This causes salts to accumulate in the unsaturated zone, especially near the evaporation front, which can cause significant increases in salinity (Barnes and Allison 1988). At the Scott Bottom site, the clayey soil and saprolite along with the thickness of this zone are thought to be a critical factor in the formation of the upslope-saline-groundwater zone.

Based on the hydrochemical data presented here and the hydrogeologic context of this site, the following

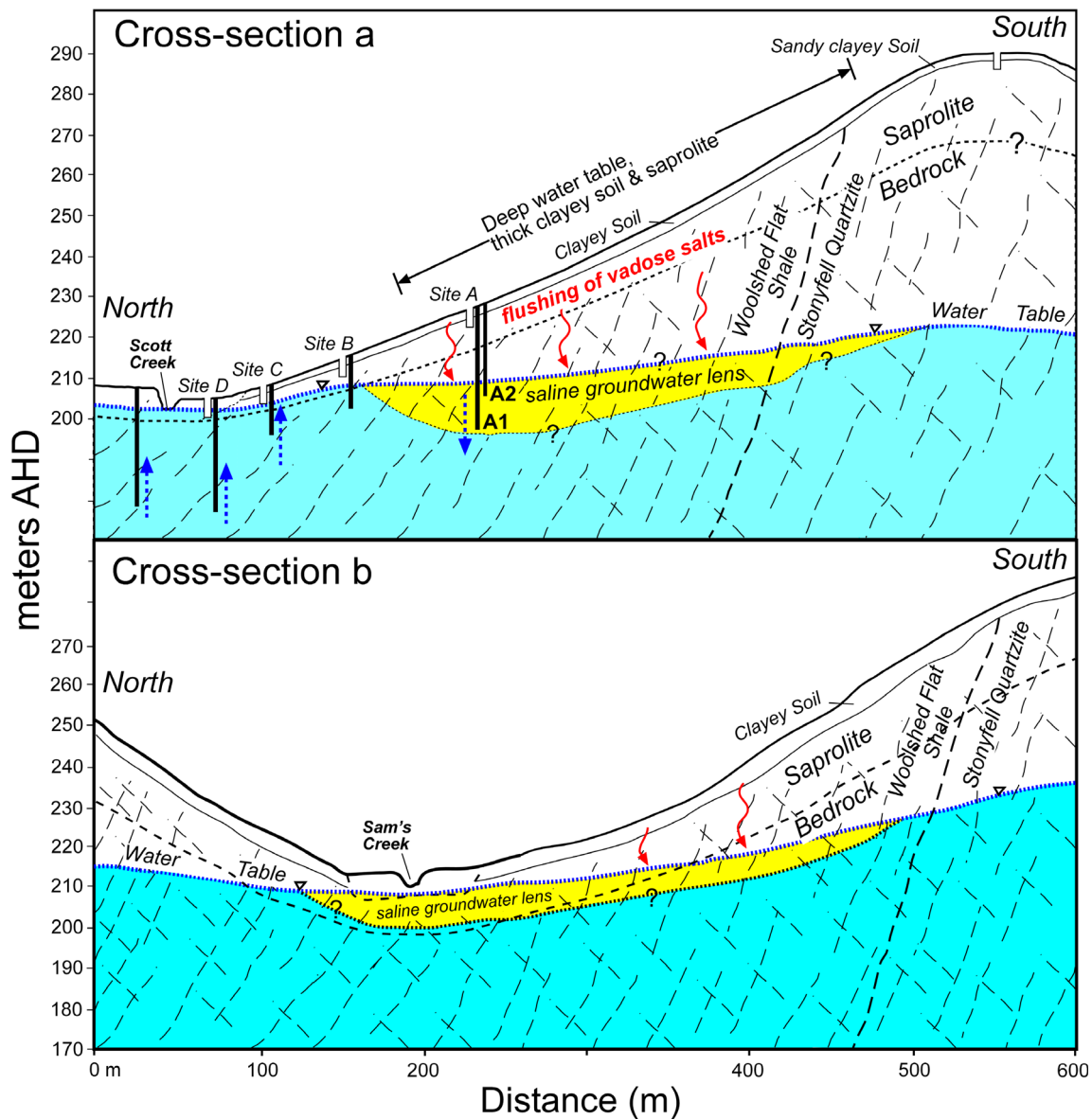


Fig. 10 Cross-section conceptual models of groundwater salinity at the Scott Bottom experimental site. Locations of the cross sections are illustrated in Fig. 2: **a** line A, **b** line B. The blue dashed lines in cross-section A are based on hydraulic heads in the piezometer nests. Transient

flushing of accumulated salts in the thick clayey unsaturated zone, following clearing of woodland, is the preferred interpretation for the cause of the saline groundwater lens

conceptual model is presented. Salts have accumulated in the thick, clayey unsaturated zone due to low rates of infiltration and recharge. These salts (dissolved solids) are sourced primarily from precipitation as indicated by strontium isotopes, but with a component of soil-saprolite weathering input. The salts accumulated over some unknown time span in the unsaturated zone. Evapotranspiration from woodland vegetation combined with the thick low-permeability unsaturated zone would have led to very low rates of recharge. During heavy rainfall events, some recharge would have flushed a portion of the accumulated salts to the water table. Following clearing of much of the woodland vegetation

and its replacement with short-rooted pasture vegetation, an increase in infiltration and recharge is envisioned. The flushing of accumulated salts would then have formed the upslope-saline-groundwater zone. The presence and/or extent of an upslope-saline-groundwater zone prior to land clearing are unknown. It is thought that this flushing of accumulated salts is a transient process. Further, as recharge increased and the water table rose, saline groundwater would have discharged into Sam's Creek. The upslope-saline-groundwater zone and its discharge into Sam's Creek are thought to be transient features because (1) the strong density inversion of the saline groundwater zone above the dominant groundwater

system would not be stable over time, and (2) there is a lack of salt scalds in the valley bottom. Thus, this process has not reached equilibrium with the dominant water system nor has it caused salt to accumulate in downslope areas where the water table is shallow.

Most Australian native vegetation is efficient in utilising infiltrating rainfall (Allison and Hughes 1983; Schofield 1992). Following land clearing of native woodland over 100 years ago and the expansion of short-rooted pasture grasses, increased recharge would be expected and could result in raising the water table and flushing accumulated salts. With increased recharge, steady-state salt movement through soil-regolith should result in a decrease in groundwater salinity. A pronounced shallow-groundwater-salinity decrease, widespread in the Clare Valley area of South Australia, has been interpreted as being caused by land clearing of woodland and increased recharge resulting in freshening of the shallow groundwater (Love et al. 2002; Stewart 2005; Bestland et al. 2017).

The origin of the accumulated salts in the unsaturated zone is analogous to the common Australian feature of dry-land salinity. Prior to European settlement, groundwater salinity concentrations in Australia were in long-term equilibrium. In agricultural regions, settlers cleared most of the native vegetation and replaced it with annual crop and pasture species. This vegetation allowed a larger proportion of rainfall to recharge to the groundwater (George et al. 1997; Walker et al. 1999). As a result, water tables have risen, often to the point where evaporation from shallow groundwater has led to salt accumulation and salt scalds as well as input of salty water into surface waters (Earl 1988; Evans 1994).

At the Scott Bottom site, analysis of the stable isotopes of water indicates that transpiration was the dominant process for the accumulated salts. It is thought that the woodlands that previously dominated the area caused this transpiration. The subsequent removal of this natural transpiration pump due to deforestation could have caused the water table to rise. This conceptual model is supported by a study in the Clare Valley, South Australia (Love et al. 2002), which investigated vertical groundwater salinity variations. In that study, it was shown that much of the chloride present within the groundwater represented residual chloride which predated clearing of the native vegetation. Removal of native vegetation within the last 100 years was postulated to have caused recharge rates to have increased. The leaching of chloride was proposed as being regulated by the rate of diffusion of salts into fractures. If the fractures were widely spaced it would take a considerably long time for the salts to leach. The areal extent of the saline groundwater in the wider area is currently unknown and to answer this question additional bores,

covering a more comprehensive section of the landscape need to be drilled.

Conclusions

Many of the concepts outlined in this paper are scarcely documented in scientific literature. Intermittent streams are not commonly sampled due to their transitory flow. Upslope-saline-groundwater zones in hilly landscapes could be widespread in areas such as the MLR. The study here has documented the connection between an intermittent creek and an upslope-saline-groundwater zone. The probable mechanism for the late season salinity increase in Sam's Creek was determined to be the water-table rise of the underlying saline groundwater during wet season recharge. This study was undertaken to better understand the interactions between stream flow, rainfall, groundwater and land-use changes, with a view to better understanding the sustainability of these water resources.

The results presented here document saline groundwater input into the intermittent Sam's Creek. The saline groundwater, accessed by two piezometers (A1 and A2), is thought to be caused by flushing of accumulated salts following clearing of native woodland and subsequent increased recharge. The origin of the upslope-saline-groundwater zone is thought to be caused by a combination of the thick clayey soil-saprolite zone and the clearing of woodland. The low permeability of the clay soil and saprolite causes low infiltration and recharge and the accumulation of salts from evapotranspiration, as demonstrated by water isotope analysis. This situation, including the upslope-saline-groundwater zone, is thought to be transient. Because the thick clayey soil and saprolite zone extends over large areas of the MLR, these upslope-saline-groundwater zones could occur on a much broader scale.

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References

- ACME Labs (2012) ACME analytical laboratories: pricing brochure. acmelab.com/pdfs/Acme_Price_Brochure.pdf. Accessed 12 July 2012
- Allison G, Hughes M (1983) The use of natural tracers as indicators of soil-water movement in a temperate semi-arid region. *J Hydrol* 60(1–4):157–173
- Allison G, Cook P, Barnett S, Walker G, Jolly I, Hughes M (1990) Land clearance and river salinisation in the western Murray Basin, Australia. *J Hydrol* 119(1–4):1–20

- Anderson TA (2013) Origin of high salinity water in an ephemeral stream, Scott Creek, Mount Lofty Ranges. Honours Thesis, Flinders University, Adelaide, South Australia
- Banks EW (2011) Hydrogeological and hydroclimatic controls on surface water-groundwater interactions. PhD Thesis, Flinders University, Adelaide, South Australia
- Banks EW, Wilson T, Green G, Love A (2007) Groundwater recharge investigations in the Eastern Mount Lofty Ranges, South Australia. DWLBC Rep 20, Dept. of Water, Land and Biodiversity Conservation, Adelaide, South Australia, 105 pp
- Banks EW, Simmons C, Cranswick R, Love A, Werner A, Bestland E, Wood M, Wilson T (2009) Fractured bedrock and saprolite hydrogeologic controls on groundwater/surface-water interaction: a conceptual model (Australia). *J Hydrogeol* 17(8):1969–1989
- Barnes C, Allison G (1988) Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. *J Hydrol* 100(1):143–176
- Bennetts DA, Webb JA, McCaskill M, Zollinger R (2007) Dryland salinity processes within the discharge zone of a local groundwater system, southeastern Australia. *Hydrogeol J* 15(6):1197–1210
- Bestland EA, Stainer G (2013) Down-slope change in soil hydrogeochemistry due to seasonal water table rise: implications for groundwater weathering. *Catena* 111:122–131
- Bestland EA, Milgate S, Chittleborough D, Vanleeuwen J, Pichler M, Soloninka L (2009) The significance and lag-time of deep through flow: an example from a small, ephemeral catchment with contrasting soil types in the Adelaide Hills, South Australia. *Hydrol Earth Syst Sci* 13:1–14
- Bestland EA, Liccioli C, Soloninka L, Chittleborough DJ, Fink D (2016) Catchment-scale denudation and chemical erosion rates determined from 10 be and mass balance geochemistry (Mt. Lofty Ranges of South Australia). *Geomorphology* 270:40–54
- Bestland E, George A, Green G, Olifent V, Mackay D, Whalen M (2017) Groundwater dependent pools in seasonal and permanent streams in the Clare Valley of South Australia. *J Hydrol Reg Stud* 9:216–235
- BOM (2007) Climate statistics for Australian sites Bureau of Meteorology. http://www.bom.gov.au/climate/averages/tables/ca_vic_nos.shtml. Accessed 22 September 2016
- Capo RC, Stewart BW, Chadwick OA (1998) Strontium isotopes as tracers of ecosystem processes: theory and methods. *Geoderma* 82(1):197–225
- Cartwright I, Weaver TR, Fulton S, Nichol C, Reid M, Cheng X (2004) Hydrogeochemical and isotopic constraints on the origins of dryland salinity, Murray Basin, Victoria, Australia. *Appl Geochem* 19(8):233–1254
- Cartwright I, Gilfedder B, Hofmann H (2013) Chloride imbalance in a catchment undergoing hydrological change: Upper Barwon River, southeast Australia. *Appl Geochem* 31:187–198
- Chittleborough D, Smettem K, Cotsaris E, Leaney F (1992) Seasonal changes in pathways of dissolved organic carbon through a hillslope soil (Xeralf) with contrasting texture. *Soil Res* 30(4):465–476
- Cranswick R (2005) Hillslope scale geological controls on surface water-groundwater interaction: evidence of active recharge to a fractured rock aquifer. Honours Thesis, Flinders University, Adelaide, Australia
- Dansgaard W (1964) Stable isotopes in precipitation. *Tellus* 16(4):436–468
- Drexel JF, Preiss WV, Parker A (1993) The geology of South Australia: the Precambrian. Mines and Energy, South Australia, Geological Survey of South Australia, Adelaide, Australia, 54 pp
- Earl G (1988) Stream salinities and salt loads in the Goulburn and Broken River catchments. Rural Water Commission of Victoria, Maffra, Australia
- Evans W (1994) Regional salt balances and implications for dryland salinity management. Water Down Under 94: Groundwater papers; Preprints of papers, Engineers Australia. Barton, Australia, pp 349–354
- Forstel H (1982) 18O/16O ratio of water in plants and in their environment. In: Schmidt H, Forstel H, Heizinger K (eds) Stable isotopes. Elsevier, Amsterdam, pp 503–509
- George R, McFarlane D, Nulsen B (1997) Salinity threatens the viability of agriculture and ecosystems in Western Australia. *Hydrogeol J* 5(1):6–21
- Greeff G (1994) Ground-water contribution to stream salinity in a shale catchment, RSA. *Ground Water* 32(1):63–70
- Green G, Bestland EA, Walker GS (2004) Distinguishing sources of base cations in irrigated and natural soils: evidence from strontium isotopes. *Biogeochemistry* 68:199–225
- Green G, Stewart S (2008) Interactions between groundwater and surface water systems in the Eastern Mount Lofty Ranges. Dept of Water, Land and Biodiversity Conservation, Adelaide, South Australia
- Guan H, Simmons CT, Love AJ (2009) Orographic controls on rain water isotope distribution in the Mount Lofty Ranges of South Australia. *J Hydrol* 374(3):255–264
- Guan H, Zhang X, Skrzypek G, Sun Z, Xu X (2013) Deuterium excess variations of rainfall events in a coastal area of South Australia and its relationship with synoptic weather systems and atmospheric moisture sources. *J Geophys Res Atmos* 118(2):1123–1138
- Harrington G (2004a) Hydrogeological Investigation of the Mount Lofty Ranges, Progress Report 3: borehole water and formation characteristics at the Scott Bottom research site, Scott Creek Catchment. Report DWLBC 2004/03, Dept. of Water, Land and Biodiversity Conservation, Adelaide, South Australia
- Harrington G (2004b) Hydrogeological Investigation of the Mount Lofty Ranges, Progress Report 4: groundwater–surface water interactions in the Scott Creek, Marne River and Tookayerta Creek catchments. Report DWLBC 2004/03, Dept. of Water, Land and Biodiversity Conservation, Adelaide, South Australia
- Harrington GA, Herczeg AL (2003) The importance of silicate weathering of a sedimentary aquifer in arid central Australia indicated by very high 87Sr/86Sr ratios. *Chem Geol* 199:281–292
- Hughes CE, Crawford J (2012) A new precipitation weighted method for determining the meteoric water line for hydrological applications demonstrated using Australian and global GNIP data. *J Hydrol* 464:344–351
- James-Smith J, Harrington G (2002) Hydrogeological Investigation of the Mount Lofty Ranges, Progress Report 1: hydrogeology and drilling phase 1 for Scott Creek Catchment, Dept. for Water, Land and Biodiversity Conservation, Adelaide, South Australia
- Jolly I, Williamson D, Gilfedder M, Walker G, Morton R, Robinson G, Jones H, Zhang L, Dowling T, Dyce P (2001) Historical stream salinity trends and catchment salt balances in the Murray-Darling Basin, Australia. *Mar Freshw Res* 52(1):53–63
- Kayaalp A (2001) Application of rainfall chemistry and isotope data to hydro-meteorological modelling. PhD Thesis, Flinders University, Adelaide, South Australia
- Kendall C, McDonnell J (1998) Isotope tracers in catchment hydrology. Elsevier, Amsterdam
- Kretschmer P (2007) Determining the contribution of groundwater to stream flow in an upland catchment using a combined salinity mixing model and modified curve number approach. Honours Thesis, Flinders University, Adelaide, South Australia
- Lamontagne S, Leaney FW, Herczeg AL (2005) Groundwater–surface water interactions in a large semi-arid floodplain: implications for salinity management. *Hydrol Process* 19(16):3063–3080
- Love A, Cook P, Harrington G, Simmons C (2002) Groundwater flow in the Clare Valley. Report DWR02 3, Dept. for Water Resources, South Australia, 43 pp

- Meredith K, Hollins S, Hughes C, Cendón D, Stone D (2013) The influence of groundwater/surface water exchange on stable water isotopic signatures along the Darling River, NSW, Australia. In: Ribeiro L, Stigter TY, Chambel A, Conesso de Melo M, Medeiros A (eds) *Groundwater and ecosystems*, vol 18. CRC, Boca Raton, FL, pp 57–68
- Milgate SA (2007) Hydrochemical investigation of flow pathways through quartz-sand and duplex soils during a storm event: Mackreath Creek, Mount Lofty Ranges. Honours Thesis, Flinders University, Adelaide, South Australia, Adelaide, South Australia
- Pichler M (2009) Characterization of spatial and seasonal changes of dissolved organic carbon in the soils of a South Australian Catchment, PhD Thesis, Flinders University, Adelaide, South Australia
- Poulsen DL, Simmons CT, Le Galle La Salle C, Cox JW (2006) Assessing catchment-scale spatial and temporal patterns of groundwater and stream salinity. *Hydrogeol J* 14(7):1339–1359. doi:10.1007/s10040-006-0065-9
- Preiss WV (1987) The Adelaide Geosyncline: Late Proterozoic stratigraphy, sedimentation, palaeontology and tectonics. Dept. of Mines and Energy, Adelaide, South Australia
- Raiber M, Webb JA, Bennetts DA (2009) Strontium isotopes as tracers to delineate aquifer interactions and the influence of rainfall in the basalt plains of southeastern Australia. *J Hydrol* 367:188–199
- Ranville JF, Chittleborough DJ, Beckett R (2005) Particle-size and element distributions of soil colloids: implications for colloid transport. *Soil Sci Soc Am J* 69:1173–1184
- Rengasamy P (2006) World salinization with emphasis on Australia. *J Exp Bot* 57(5):1017–1023
- Salama RB, Otto CJ, Fitzpatrick RW (1999) Contributions of groundwater conditions to soil and water salinization. *Hydrogeol J* 7(1):46–64
- Schofield N (1992) Tree planting for dryland salinity control in Australia. *Agrofor Syst* 20(1–2):1–23
- Stevens DP, Cox JW, Chittleborough DJ (1999) Pathways of phosphorous, nitrogen, and carbon movement over and through texturally differentiated soils, South Australia. *Aust J Soil Res* 37:679–693
- Stewart BW, Capo RC, Chadwick OA (1998) Quantitative strontium isotope models for weathering, pedogenesis and biogeochemical cycling. *Geoderma* 82(1):173–195
- Stewart S (2005) Clare prescribed water resources area groundwater monitoring status report 2005. DWLBC 2005/18, Government of South Australia, Adelaide, 43p
- Taylor JK, Thompson B, Shepherd R (1974) The soils and geology of the Adelaide area. Geological Survey of South Australia, Adelaide, South Australia
- Turner J, Arad A, Johnston C (1987) Environmental isotope hydrology of salinized experimental catchments. *J Hydrol* 94(1):89–107
- UC Davis (2012) Stable Isotopes Facility homepage. University of California, Davis, CA. <http://stableisotopefacility.ucdavis.edu/index.html>. Accessed 12 February 2012
- Walker GR, Gilfedder M, Williams J (1999) Effectiveness of current farming systems in the control of dryland salinity. CSIRO Land and Water, Clayton, South Australia
- Zimmerman U, Ehhalt D, Munnich K (1967) Soil water movement and evapotranspiration: changes in the isotopic composition of water. From ‘Isotopes in Hydrology’ conference, IAEA, Vienna