Catchment-scale saline groundwater interactions identified by environmental tracers and high resolution monitoring (Mt Lofty Ranges, South Australia)

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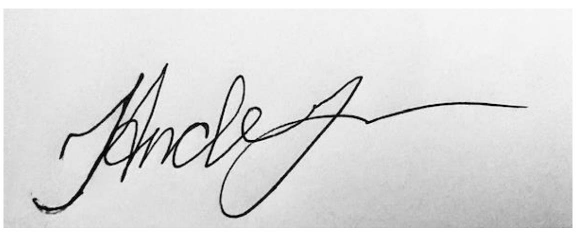
DECLARATION

I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any other university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.



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Thomas Alexander Anderson

19th April 2022

CO–AUTHURSHIP

Tom Anderson is the primary author on this thesis and all the enclosed documents. Chapters 2 to 4 were written as independent manuscripts in which the co–authors provided intellectual supervision and editorial comment. In addition, Dr John Hudson suggested references related to soil chemistry in Chapter 3.

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Summary

The intricacies of hydrological processes at the catchment–scale are still being uncovered, and recognising this is important for water management. This knowledge has emphasised the need for more in–depth investigations of these interactions using multiple lines of evidence, including complimenting environmental tracer data and high resolution salinity and flow data. There has been a significant contribution to the knowledge and understanding of hydrogeological research of groundwater–surface water interactions in the past few decades. There are still specific knowledge gaps in how different systems function and interact at different spatiotemporal scales and in different hydrogeological environments.

This Ph.D. thesis addresses some complexities of groundwater–surface water interactions at the Scott Creek Catchment. This catchment is a hydrogeologically heterogenous, fractured rock catchment two dominant lithologies (sandy and clayey). The complexities addressed involve identifying different spatiotemporal scales and the investigation of number of the dominant controls (e.g., geology, relief, precipitation, land use changes, and vegetation) and how these affect the salinity and water quality of the catchment. Specifically, this work investigates: 1) the origin and extent of groundwater salinity anomalies, 2) the timeframe at which a catchment can reach a new salinity equilibrium after land clearing, and 3) the complexities of different spatiotemporal groundwater–surface water interactions on a catchment–scale during a drought.

The first component of this research investigated the importance of high and variable salinity levels revealed in an intermittent stream in a high–rainfall area of the Mt Lofty Ranges of South Australia. The groundwater system contains a local, upslope saline lens, referred to here as a groundwater salinity 'hotspot.' The study demonstrated seasonal groundwater input of very saline composition into the intermittent stream. This input results in large salinity increases of the stream water. The investigation also revealed: 1) the upslope saline groundwater hotspot mixes with the dominant groundwater system, 2) the intermittent–stream water is a

mixture of soil–water/surface runoff and the up–slope saline groundwater, and 3) the up–slope saline groundwater hotspot results from the flushing of unsaturated–zone salinity from the thick clayey regolith and soil which overlie the metamorphosed shale bedrock. The preferred theory on the origin of the up–slope saline groundwater hotspot is the land clearing of native deep–rooted woodland, followed by flushing of accumulated salinity from the unsaturated zone due to increased recharge.

The second component of this research utilised an analysis of catchment–scale chloride deposition and export to reveal the catchment was returning to a new salinity equilibrium. This analysis found that the catchment exports approximately three times more chloride than inputs from atmospheric sources. Over the time period investigated, salinity load exported to surface water decreased by, on average, 6.4 t annually due to catchment freshening. Groundwater flushes salinity from the catchment via flow into the permanent stream in all years of the record. Deep groundwater is input to the permanent stream, with the mixing of deeper, more saline, and fresher shallow groundwater. Thus, a complex interaction of landscape hydrologic parameters such as relief, precipitation, chloride deposition, and land–use history, determine whether this catchment undergoes salinization or desalinization.

This research's final component determined and quantified stream–flow components (e.g., groundwater, soil water, and surface runoff) during the 'Millennium Drought' (2001-2009). During the drought, base flow could be directly sampled and characterized, as low precipitation rates during the drought resulted in minimal surface water runoff to dilute the hydrochemical signature of the base flow. Run–of–stream hydrochemical parameters were monitored over three seasons from the same experimental catchment as the two previous studies, in order to identify groundwater input to a permanent stream. This analysis revealed a groundwater flow and recharge paradox. A low salinity groundwater type that had approximately seven times the recharge as a high salinity type was evident within the catchment. However, the high salinity type dominates the streams hydrochemistry, and base flow originates predominantly from this groundwater. Given that each groundwater type occupies approximately half of the catchment, it would be expected that base flow would originate from the low salinity type with its much higher recharge. The preferred interpretation is that the low salinity groundwater occupies the meta–sandstone terrane with its sandy regolith drains quickly following wet season recharge and, as a consequence, contributes disproportionately little to dry season base flow. Conversely, the meta–shale terrane (occupied by the high saline groundwater) with its thick clayey regolith drains slowly and therefore continues to provide groundwater to the stream during dry seasons and drought times.

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CHAPTER 1

1. INTRODUCTION

1.1. RESEARCH PROBLEM

Saline groundwater (>10,000μS/cm) occurs across 24 million km^2 of the earth's surface (Van Weert et al. 2009). Groundwater salinity originates from both marine and terrestrial processes and has been linked to various anthropogenic factors. These factors include over–abstraction, clearing of native vegetation, and pollution (Salama et al. 1999; Gordon et al. 2003; Rengasamy 2006; Van Weert et al. 2009; Schwartz and Ibaraki 2011). Globally, the most crucial factor contributing to groundwater salinity is considered to be the dissolution of stored salinity. This includes salinity accumulating in soils due to wetfall and dryfall not washing out during periods of low rainfall. Notably, salinity accumulation causes approximately 26% of shallow to intermediate depth groundwater salinity (Van Weert et al. 2009). Other factors include evaporation of very shallow groundwater (20%), a mixture of dissolution and evaporation (13%), and connate groundwater (14%) (Van Weert et al. 2009). Groundwater salinity is prevalent in many parts of Asia, South America, Europe, North America, and Australia (Salama et al. 1999; Rengasamy 2006; Van Weert et al. 2009). In Australia, salinization is extensive, with 5.7 million km^2 of land identified as 'at–risk' in 2000, projected to increase to 17 million km^2 within 50 years (Webb 2000). In fact, the combination of groundwater salinity and land salinization is amongst the most significant environmental issues in Australia (Harrington and Cook 2014). Therefore, there is a need to dissect and describe the intricate hydrochemical changes in catchment–scale salinity to improve land management decisions.

Dryland salinity has been a significant contributor to the accumulation of stored salinity in the soil and regolith throughout Australia (Pannell 2001). Clearing of native vegetation has contributed to salinity rises in Australian groundwater (Dryland salinity), as documented in various studies (Schofield 1992; Greeff 1994; George et al. 1997; Jolly et al. 2001; Hatton et al. 2003). In agricultural regions, settlers cleared most of the native vegetation and replaced it with annual crop and pasture species, allowing a larger proportion of rainfall to remain unused by plants and enter the groundwater (George et al. 1997; Walker et al. 1999). This process causes recharge rates to increase and is presumed to be the cause of establishing a salinity disequilibrium in various relatively small catchments draining a fractured rock terrain throughout the world (Jayawickreme et al. 2011; Marchesini et al. 2017). Notably, a salinity disequilibrium exists in the Mount Lofty Ranges (MLR) (South Australia) (Cox et al. 1996; Fitzpatrick et al. 1996), the focus area for this research. The mass of salinity that accumulate can indicate the rate at which periods of low rainfall restrict wetfall and dryfall from draining through to the groundwater.

In addition to low rainfall, the concentration of stored salinity increases in shallow saline groundwater, where the soil's geology and porosity restrict drainage (Cartwright et al. 2013). This restriction of drainage can occur where thick clay layer formed from weathered saprolite (e.g., meta–shale bedrock) has a low permeability that slows infiltration rates (Bennetts et al. 2007) and hinders the flushing of salinity (Rengasamy 2006). Recharge of this groundwater is prone to direct evaporation through capillary action (Turner et al. 1987; Salama et al. 1999; Lamontagne et al. 2005). This causes salinity to accumulate in the unsaturated zone, especially near the evaporation front, causing significant increases in salinity (Barnes and Allison 1988). Studying the connection of salinity to the soil, regolith, and the connection between groundwater–surface water (GW–SW) interactions will help understand and manage catchments.

Heterogeneous fractured rock aquifers, caused by the hydrogeology and geology variation, are more difficult than homogenous aquifers to determine movement of stored salinity within a catchment. Currently, knowledge regarding GW–SW interactions in fractured rock aquifers is very limited. Attention has recently been brought to this topic (Hagedorn and Whittier 2015; Padilla et al. 2015; Hale et al. 2016). While research has been undertaken in these types of systems in the last three decades (Berkowitz et al. 1988; Therrien and Sudicky 1996; Manning and Caine 2007), due to hydrogeological heterogeneities and geological complexities, many questions remain. Various methods can be used to understand GW–SW interactions in complex geological regions.

In a review of the Maimai catchment, New Zealand by McGlynn et al. (2002), no single research method has resolved the complexities of streamflow at this site. Mosley (1979) conducted a series of hydrometric and dye tracing experiments. Dye tracers alone have proven to be a limited and often misleading method. Key limitations include varying dye sorption to soil, involving artificial recharge, and remanent dye confounding future investigations (Jones 2019). Hydrochemical analyses by Pearce et al. (1986) and Sklash et al. (1986) have proven a far more successful method of establishing a connection between GW–SW interactions at the Maimai catchment. A flaw in this method is that a mechanistic understanding of the processes that control this groundwater movement cannot be achieved. Further studies at the Maimai catchment (McDonnell 1990b; 1990a; McDonnell et al. 1991a; McDonnell et al. 1991b) combined soil physics techniques with isotopic and chemical tracing in order to provide this understanding. Considering the limitations of these described studies, this investigation will use various methods to achieve the research aims described below.

This research combines multiple environmental tracers with high resolution data on physical parameters (e.g., flow and salinity) to determine whether details of fractured rock aquifer GW–SW interactions can be understood. Environmental tracers can be used to understand various aspects of the signature of water masses at the catchment–scale, including GW–SW interactions, water–rock interactions, as well as the origin, extent, and age of waters (Bertrand et al. 2014; Nordstrom et al. 1989; Vogel 1968). Furthermore, high resolution data sets provide decades and sometimes centuries of physical data for many catchments around the world (Rood et al. 2014; Dixon, 2010), yet these data are often neglected in academic literature. Therefore, analysing the combination of multiple complimentary environmental tracer data with high resolution data sets can significantly improve water resources management**.** For example, 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. Such decisions include planting certain vegetation types in different areas, or the amount of water extraction permitted in different years. Furthermore, 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). Generally, improving land management decisions requires an understanding of the geology, the hydrochemistry, and the historical land use of the site.

While there has been an increasing focus on integrated groundwater and surface water research, several areas require further research and investigation if sustainable management practices are to be achieved. This Ph.D. focuses on three specific knowledge gaps:

Firstly, a local, upslope saline lens in a high rainfall area of the MLR, South Australia, was initially identified as a groundwater salinity 'hotspot'. The impact of such hotspots on associated groundwater and surface water systems is critical to the overall water quality and resource management in sub–humid to dry areas. For example, saline groundwater input documentation into the Murray River (Australia) has been incorporated into management plans for overall river health (Allison et al. 1990; Jolly et al. 2001; Lamontagne et al. 2005). The spatial distribution of groundwater and surface–water salinity were analysed with respect to hydrogeological and climatic influences in the Eastern Mt Lofty Ranges (MLR) of South Australia (Poulsen et al. 2006). Groundwater salinity hotspots are associated with geologic units comprising marine shales and generally occur in the drier eastern parts of the Mt Lofty Ranges. However, further understanding of these salinity hotspots' extent and origin is needed for land management decisions.

Secondly, many studies have determined that catchments are returning to a new salinity equilibrium after the effects of land clearing have taken place (Jolly et al. 2001; Guan et al. 2010a). Studies have identified that changes in the ‘Output/Input’ chloride ratio provide useful information to determine whether a catchment has reached this new salinity equilibrium. Other studies have modelled the timespan required for reaching a new salinity equilibrium (Sivapalan et al. 1996; Smitt et al. 2003; Dawes et al. 2004; Gilfedder et al. 2009). However, a timespan and statistically significant evidence of reaching this equilibrium requires a continuous monitoring history of the physical and chemical parameters.

Finally, during high flow conditions, stream waters become hydrochemically more homogenised due to the dominance of inputs to the stream from surface runoff and shallow soil flow–paths, which tend to dilute groundwater inputs, masking subsurface origins of stream discharge. However, during extreme low–flow conditions, it is possible to identify and characterize local groundwater inputs. This is specifically true when streams cease to have longitudinal flow leading to the formation of disconnected pools. The longitudinal variability of groundwater input can be characterised during these times. Catchment studies rarely consider how individual river reaches function in the context of the overall catchment–scale hydrogeological system and what implications this can have on water quantity and quality.

1.2. PROJECT SETTING

An appropriate catchment was required to achieve the research aims for this project described above. The Scott Creek Catchment of the MLR, was utilised for all three studies of this Ph.D. and the site is further characterized in sections **2.1.1.**, **2.1.2.**, **3.1.1.**, **4.1.1.**, and **4.1.2.** This catchment was chosen for several reasons. For example, the catchment is hydrologically and geologically complex due to the Adelaide Geosyncline’s faulting and folding (Preiss 1987; Banks et al. 2009). These complexities allow an opportunity to study novel catchment processes and elucidate new insights into poorly studied settings. However, the Scott Bottom site of the catchment is well studied (Chittleborough et al. 1992; Stevens et al. 1999; James–Smith and Harrington 2002; Harrington 2004a; 2004b; Ranville et al. 2005; Banks et al. 2009; Bestland et al. 2009; Bestland and Stainer 2013; Bestland et al. 2016), and large datasets of its hydrochemical signature and high resolution physical characteristics exist (Milgate 2007; Banks et al. 2009; Bestland et al. 2009). These data provide the hydrogeological and hydrochemical knowledge base to describe the knowledge gaps of the catchment's complex setting. Several soil–water studies (Chittleborough et al. 1992; Stevens et al. 1999; Bestland et al. 2009) recognized throughflow hydrochemical characteristics. Banks et al. (2009) and Bestland and Stainer (2013) described the importance of the fractured bedrock zone and deep clayey regolith for the groundwater/surface–water interactions concerning the permanent stream Scott Creek. These groundwater studies were built upon the investigations of James–Smith and Harrington (2002) and Harrington (2004a and 2004b) that documented the basic hydrology and hydrogeology of the Scott Creek catchment. Furthermore, the hydrological and geological setting of the Scott Creek Catchment is representative of catchments throughout the MLR and around the world. Additionally, the precipitation and climate of the catchment are characteristic of a Mediterranean climate, with its cool, moist winters and warm, dry summers. Thus, resolving the complexities of this catchment could help resolve misunderstandings and shortcomings of hydrological and geological data elsewhere.

The Scott Creek Catchment experiences precipation variation causing stream water to vary in salinity, in addition to the complex geological setting. The Mediterranean climate of the catchment means it experiences great salinity variation (low salinity during its cool, wet winters (June–August) and high salinity during its warm, dry summers). Additionally, land–use patterns have changed over the years in the Scott Creek Catchment, resulting in further salinity variation. European settlers first occupied the Scott Creek Catchment in 1838 and cleared the Eucalyptus woodland to farm adjacent to Scott Creek. Timber cutters removed much of the original red, blue, and manna gum and stringybark for use in the building industry in Adelaide (EPA

2013). In 1850 the site was mined for copper and later silver (DEHAA 1999). In recent years, however, the native vegetation of the area has been restored to some extent. The vegetation is now 47% native vegetation, 29% residential living, and 16% grazing modified pastures (EPA 2013). Thus, the catchment could have been experiencing dryland salinity (described above), and it could now be returning to a new chloride equilibrium (Peck and Hurle 1973). Despite the salinity variation, the MLR, which includes the Scott Creek Catchment, is a vital water resource for Adelaide, South Australia. The Scott Creek Catchment drains into the Mt Bold Reservoir, the largest reservoir in South Australia, which can annually account for approximately 50% of the annual water supply for the city of Adelaide (Hill and Wright 2005; Pound 2006). In recent years Adelaide has faced significant challenges concerning water supply management, which has become a critical point for the future sustainability and growth of South Australia (Hill and Wright 2005). Besides concerns about water availability, salinity levels of water resources have also become scrutinized in many parts of Australia and the MLR (Hart et al. 1990). Rising stream salinity trends have been determined for various locations throughout the MLR (WDS 2013; DEWNR 2015). Understanding the details of the salinity variations caused within the catchment could resolve the issues they produce.

1.3. RESEARCH AIMS

This research body aimed to combine high resolution salinity and flow data with multiple, complimenting environmental tracers (radiocarbon, strontium and water isotopes, major and trace elements) to develop a more comprehensive understanding of catchment–scale water and solute dynamics. Specifically, this body of work aims to:

1. Understand the interactions between the intermittent stream and the groundwater system, including the salinity hotspot and the dominant groundwater system at the Scott Bottom site within the Scott

Creek Catchment, and identify the origin and extent of the groundwater salinity hotspot and understand its cause on–site.

2. Provide the high resolution data required to thoroughly evaluate salinity input and export at the catchment–scale, including the duration of salinization or desalinization, saturated vs. unsaturated salinity storage, and influence of chloride content of wet–fall and dry–fall. Furthermore, determine whether reforestation can actually increase salinity and decrease surface water flows. Moreover, quantifying the catchment salinity balance, resulting in monthly totals of chloride input and export for a permanent and an intermittent stream. Finally, investigate a hypothesis that catchment–scale salinity is decreasing, through evaluation of the atmospheric chloride deposition and the stored chloride export (or accumulation) at monthly time intervals.
3. Address the paradox as to why the hydrochemistry of the Scott Bottom site is dominated by the Woolshed Flat Shale groundwater and not the Sandstone Bedrock groundwater (with its higher recharge rates and higher percentage of the catchment). Characterize an experimental catchment in terms of changes in the proportion of different water sources contributing stream flow during different periods. Specifically, determining how stream chemistry during a period of extreme drought differs from periods where stream chemistry is more influenced by the atmospheric signature. Additionally, characterise the groundwater flow system to quantify its inputs to the stream (atmospheric, soil moisture, and groundwater from different geological units). Finally, divide the groundwater flow system, where appropriate, into water types according to hydrochemical parameters.

The specific research areas of surface water–groundwater interactions are addressed in three manuscripts and are contained in chapters 2, 3, and 4 of this thesis. The three manuscripts have now been published in international hydrogeological journals. Presented and published conference proceedings as part of this Ph.D. are shown in Appendix A.

[Chapter 2]

Anderson, T.A., Bestland, E.A., Soloninka, L., Wallis, I., Banks, E.W. and Pichler, M., 2017. A groundwater salinity hotspot and its connection to an intermittent stream identified by environmental tracers (Mt Lofty Ranges, South Australia). *Hydrogeology Journal*, *25*(8), pp.2435-2451.

[Chapter 3]

Anderson, T.A., Bestland, E.A., Wallis, I. and Guan, H.D., 2019. Salinity balance and historical flushing quantified in a high–rainfall catchment (Mount Lofty Ranges, South Australia). *Hydrogeology Journal*, *27*(4), pp.1229-1244.

[Chapter 4]

Anderson T.A., Bestland, E.A., Kretchmer, P., Soloninka, L., Wallis, I., Banks, E.W., Werner, A., Pichler, M., 2021. Catchment–scale groundwater–flow and recharge paradox revealed from base flow analysis during the Australian Millennium Drought (Mt Lofty Ranges, South Australia). *Hydrogeology Journal*, pp. 1-21.

1.4. CONTRIBUTION OF THIS PH.D.

This research body addresses the complexities of GW–SW interactions in a hydrologically and geologically complex catchment at different spatiotemporal scales. It investigates many dominant controls (e.g., geology, relief, precipitation, land–use changes, and vegetation). This Ph.D. focuses on how the complexities of the catchment affect salinity and water quality.

The first investigation (chapter 2) explores the origin and extent of a groundwater salinity anomaly. An upslope saline groundwater lens (hotspot) was observed to be mixing with the dominant groundwater system of the Scott Creek Catchment, where this investigation took place. 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 MLR. 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 MLR. In addition, the example documented here extends MLR groundwater understanding by connecting the hotspot directly to an intermittent stream by identifying seasonal groundwater input to the stream. Such salinity hotspots are not described extensively in academic literature. However, they could be widespread in the MLR and other climatically and geologically similar areas with comparable hydrogeologic conditions.

The hydrogeologic parameters of the Scott Creek site represent significant portions of the MLR (Taylor et al. 1974; Preiss 1987; Bestland et al. 2016). Similar groundwater salinity/chloride profiles (capping 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 extensive shallow to moderate depth piezometer nests at the Scott Creek site has allowed for the discovery of very saline water at the top of the aquifer. The documentation of this phenomenon will alert land managers to groundwater salinity hotspots in high–rainfall areas of the MLR, and an understanding of their cause will aid in land management decisions. Overall, the first investigation determined the cause of this hotspot and revealed a connection to surface water in the catchment.

The second investigation (chapter 3) determines the timeframe for a catchment to reach a new salinity equilibrium after land clearing. Researchers have hypothesized and disputed the equilibration of catchments after land clearing for decades (Peck and Hurle 1973; Williamson et al. 1987; Daulhaus et al. 2008; Guan et al. 2010a;). Catchment–scale stream salinity data have been analysed for the Murray–Darling Basin (Australia) to develop concepts and methods of evaluating ratios of salinity output to salinity input (O/I ratios) (Jolly et al. 2001). These statistical methods evaluated salinity trends in catchments with limited data. Peck and Hurle (1973) established that the O/I ratio could be used as a key indicator of catchments undergoing salinization. Guan et al. (2010a) further conceptualized catchment types and suggested how the O/I ratio could be applied. Allison et al. (1990) determined the influence that increased recharge due to land clearance had on the Murray River, South Australia, using groundwater modelling. Further studies have conceptualised catchment–scale salinity equilibration due to land clearing (Jolly et al. 2001; Guan et al. 2010a). Many studies have shown that vegetation clearance has been a pivotal driver for hydrological change. For example, Ruprecht and Schofield (1989) determined how land clearance raised groundwater levels and increased streamflow in southwestern Australia. Similarly, (Ruprecht and Schofield 1991) found that land clearance transitioned catchments from salinity accumulating to salinity exporting. Furthermore, Williamson et al. (1987) determined that more salinity had been exported in higher rainfall catchments than in drier catchments eight years after clearance. A new salinity equilibrium is expected sometime in the future. An established salinity equilibrium is required to utilise the chloride mass balance (CMB) method for estimating groundwater recharge (Wood 1999). Thus, if catchment salinity input/export is significantly out of equilibrium, increased error for groundwater recharge estimates will result. For the MLR, Guan et al. (2010a) established that the catchment salinity O/I ratio provides valuable information to determine whether a catchment has reached a new salinity equilibrium and whether CMB methods are valid. Other studies have modelled the timespan required for a new salinity equilibration (Sivapalan et al. 1996; Smitt et al. 2003; Dawes et al. 2004; Gilfedder et al. 2009). However, these studies did not have continuous monitoring history of the physical parameters to verify the theory that there is a decreasing export of stored salinity from the system.

Many catchment salinity balance studies have claimed that insufficient data was a significant cause that limited the key findings (Williamson et al., 1987; Ruprecht and Schofield, 1989). Thus, considering the available literature on salinity balance, it is evident that high resolution data are required to evaluate salinity input and export at the catchment–scale thoroughly. The study presented here indicated that reforestation could increase salinity and decrease surface water flows. This study employed a multiple regression analysis that revealed a decrease in salinity load as a function of both time and flow. These data and quantifications conclusively showed that a decrease in catchment–scale salinity is occurring. Furthermore, this study evaluated the atmospheric chloride deposition and the stored chloride export (or accumulation) at monthly time intervals. Moreover, the methods presented here quantified the flushing of stored salinity for other catchments with significant monitoring data. Finally, they predicted the timespan where the catchment will reach a new salinity equilibrium following land clearance. Overall, this study revealed the first statistically significant evidence of a catchment returning to equilibrium. High resolution salinity and flow data provided this evidence, which is readily available for many catchments worldwide.

The final study (chapter 4), deciphers the complexities of different spatiotemporal GW–SW interactions on a catchment–scale during a drought. Hydrochemical heterogeneity is common in permanent streams due to differing rates and chemical properties of groundwater, soil, and surface water inputs (Bailly–Comte et al. 2009; Cartwright et al. 2014). During high flow conditions, inputs to the stream from surface runoff and through shallow soil flow paths dilute groundwater inputs, masking origins of stream discharge. The final study takes advantage of low–flow conditions, where it is possible to identify local groundwater input characteristics. Thus, the spatial variability of can characterise groundwater input during these times.

Base flow is relatively straightforward to sample and interpret in streams that fragment seasonally into disconnected pools (McMahon and Finlayson 2003; Bunn et al. 2006). For example, the most significant spatial variability in the hydrochemistry of two intermittent ‘dryland rivers’ in Queensland, Australia, occurred during the no–flow period (Sheldon and Fellows 2010). In the intermittent Cressbrook Creek catchment (Australia), characterising hydrochemical changes assessed groundwater–stream interactions during both no–flow and flooding conditions (King et al. 2014). These studies emphasised the importance of no–flow periods to base flow characterisation.

Unlike intermittent and ephemeral streams, most perennial streams do not have no–flow periods. Instead, perennial streams have a continuous surface flow, except in severe drought conditions (Meinzer 1923; Edwards et al. 2015). Therefore, base flow characteristics need to be inferred. For example, groundwater influences on surface water resulted in higher alkalinity waters with stable chloride concentrations in Scotland's Girnock catchment (Soulsby et al. 2007). Stable isotopes of water have also been used extensively for base flow characterisation, as groundwater is usually less enriched than surface water (Coplen et al. 2000; Hinkle et al. 2001). For instance, water isotopes were used to identify the hydrological processes that influenced spatiotemporal isotopic variations in groundwater and surface water in the Barlow–Ojibway Clay Belt, Canada (Rey et al. 2018). Here, precipitation, groundwater inflow, evaporation, and tributary mixing processes caused this variation. Furthermore, environmental tracers determined the discharge of groundwater recharged by rainwater to the Condamine River, Australia (Martinez et al. 2015). This variability indicated two distinct water types and confirmed groundwater discharge in the upper catchment.

James–Smith and Harrington (2002) describe the Scott Creek catchment in the Mount Lofty Ranges (MLR) of South Australia as a perennial stream. However, it ceased to flow during the extreme drought years of 2006-2007, when the stream reduced to a series of disconnected groundwater–fed pools during summer and autumn. Stream water sampling during this time provided a rare opportunity to determine the characteristics and location of groundwater input to the stream through a spatiotemporal analysis using multiple lines of hydrochemical evidence.

Catchment–scale recharge and water balance estimates are commonly made for water resource management (Crosbie et al. 2010). However, few catchments have had these estimates ground–truthed. One confounding aspect is that runoff and soil water inputs commonly occur throughout the year. In this study, the base flow was directly sampled and analysed during a drought year without these inputs. Thus, the intricate details of the hydrochemical characteristics in the study catchment could be observed.

It is hoped that these research findings will expand the understanding of salinity dynamics and ground - surface water interaction in fractured rock settings. Notably, understanding these interactions is critically important in making effective land management decisions.

CHAPTER 2

2. MANUSCRIPT I: A GROUNDWATER SALINITY HOTSPOT AND ITS CONNECTION TO AN INTERMITTENT STREAM IDENTIFIED BY ENVIRONMENTAL TRACERS (MT LOFTY RANGES, SOUTH AUSTRALIA)

Published in Hydrogeology Journal 2017

Thomas A. Anderson, Erick A. Bestland, Lesja Soloninka, Ilka Wallis, Edward W. Banks & Markus M. Pichler

Anderson, T.A., Bestland, E.A., Soloninka, L., Wallis, I., Banks, E.W. and Pichler, M., 2017. A groundwater salinity hotspot and its connection to an intermittent stream identified by environmental tracers (Mt Lofty Ranges, South Australia). *Hydrogeology Journal*, *25*(8), pp.2435-2451.

Abstract: High and variable levels of salinity were investigated in an intermittent stream in a high–rainfall area (>800 mm/yr) of the Mt Lofty Ranges of South Australia. The groundwater system was found to have a local, up–slope saline lens, referred to here as a groundwater salinity 'hotspot'. Environmental tracer analyses ($\delta^{18}O$, $\delta^{2}H$, $^{87/86}Sr$, 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 up–slope saline groundwater lens (hotspot) mixes with the dominant groundwater system, 2) the intermittent–stream water is a mixture of

soil–water/runoff and the up-slope saline groundwater, and 3) the up-slope saline groundwater lens results from the flushing of unsaturated-zone salts from the thick clayey regolith and soil which overlie the metamorphosed shale bedrock. To further this theory, radiocarbon isotopes will be analysed to establish the chronology of the groundwater salinity hotspots as well as the groundwater flow-path. In addition to the qualitative research, quantitative research will be undertaken using hydrochemical modeling. The preferred theory on the origin of the up-slope 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 Range areas, as well as other climatically and geologically similar areas with comparable hydrogeologic conditions.

2.1. INTRODUCTION

Understanding the extent and cause of groundwater 'salinity hotspots' (>8,000µS/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 Range groundwater understanding by connecting the hotspot directly to an intermittent stream by identifying seasonal groundwater input to the stream.

The occurrences of up-slope 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. The hydrogeologic parameters of the Scott Creek site described in this paper are representative of significant portions of the MLR (Taylor et al. 1974; Preiss 1987; Bestland et al. 2016). Similar groundwater salinity/chloride profiles (capping 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 up-slope 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 ($\delta^{18}O$, $\delta^{2}H$, $^{87/86}Sr$, and major elements) from the intermittent stream, a nearby permanent stream, soil-water/runoff, the shallow saline groundwater cap or hotspot, and the dominant groundwater system.

2.1.1. Study Site

The Scott Bottom site in the Scott Creek catchment (SCC) (**Fig. 2.1**) has been an experimental site for a number of hydrogeologic investigations (James-Smith and Harrington 2002; Harrington 2004a; 2004b; Banks et al. 2009; Bestland et al. 2009). 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 and 2004b) that documented the basic hydrology and hydrogeology of the Scott Creek catchment.

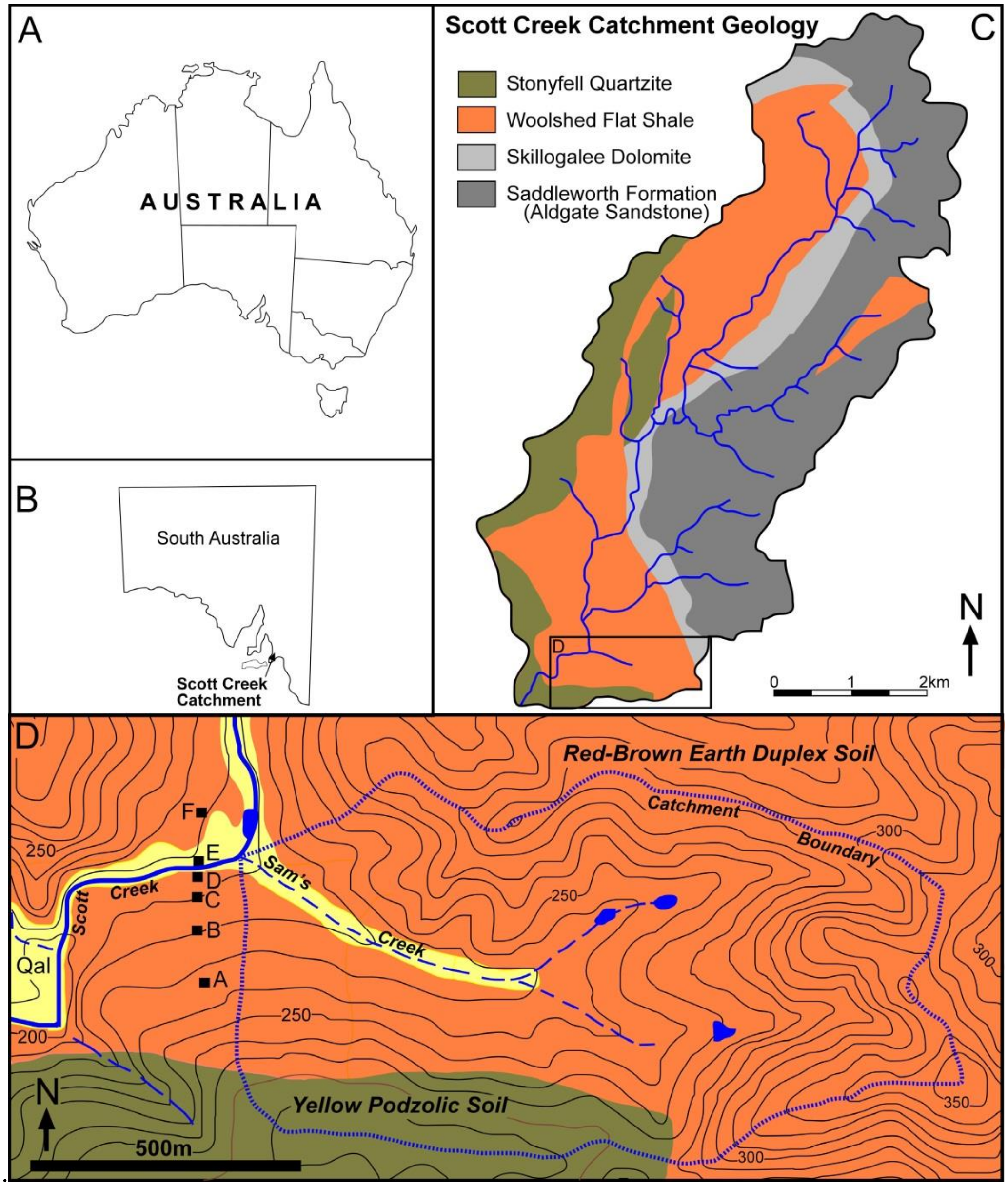

Figure 2.1: Location maps **a**) and **b**) show the location of South Australia and the SCC. **c**) SCC geology is shown with inset map of the Scott Bottom study site. **d**) Location of the nested piezometers sites A-F, Scott Creek and Sam's Creek, are shown as well as distribution of soil types which follow closely the bedrock geology. .

The Scott Creek catchment (**Fig. 2.1**) spans an area of 27 km^2 and is located approximately 30 kilometres 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. 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 μS/cm in winter to above 2000 μS/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 0.9km^2 which has 150m of relief and several small farm dams, only one of which still fills with water (**Fig. 2.1**). 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 three-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 μS/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 400mm/yr to over 1000mm/yr and with 85% of the rainfall occurring between May and September {BOM, 2007 #40}. 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 meters (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/yr (Bestland et al. 2009). The site's closest Class A evaporation pan, Mt. Bold, has an average evaporation of 1555 mm/yr; thus, evaporation exceeds rainfall from October to May (spring, summer and autumn).

2.1.2. 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). 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. 2.2**. 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 meters (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 sandy-silty A horizon (10-20cm depth) over a clayey B horizon (Chittleborough et al. 1992).

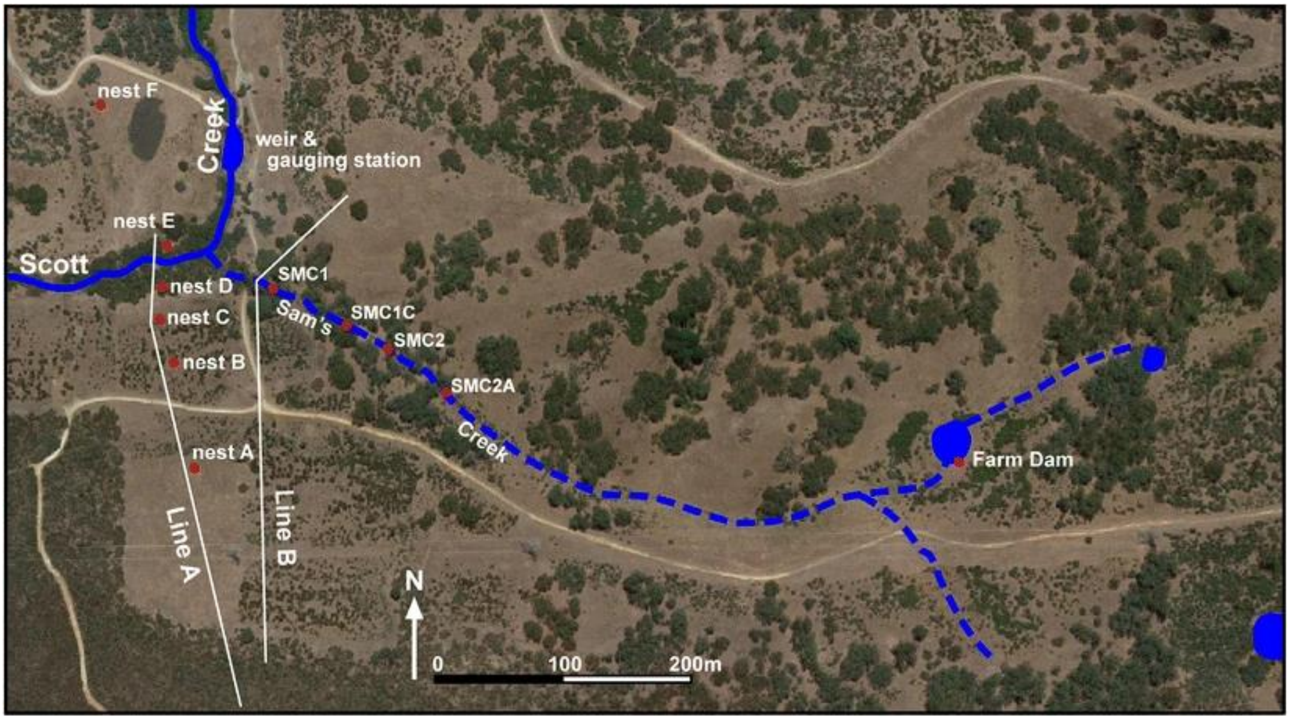

Figure 2.2: Aerial image from Google Earth (2015) of the Scott Bottom area showing surface-water sampling sites and piezometer nest locations, as well as cross-sections lines A and B which are shown in **Fig. 2.10**.

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

y here ranged from 1.5 m/day 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.

2.2. 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. 2.1** and **2.2**) (Banks et al. 2009). In addition, water samples were obtained from 8 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 (**Fig. 2.1** and **2.2**). 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).

2.2.1. 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. 2.2**). 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. 2.3**). 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.

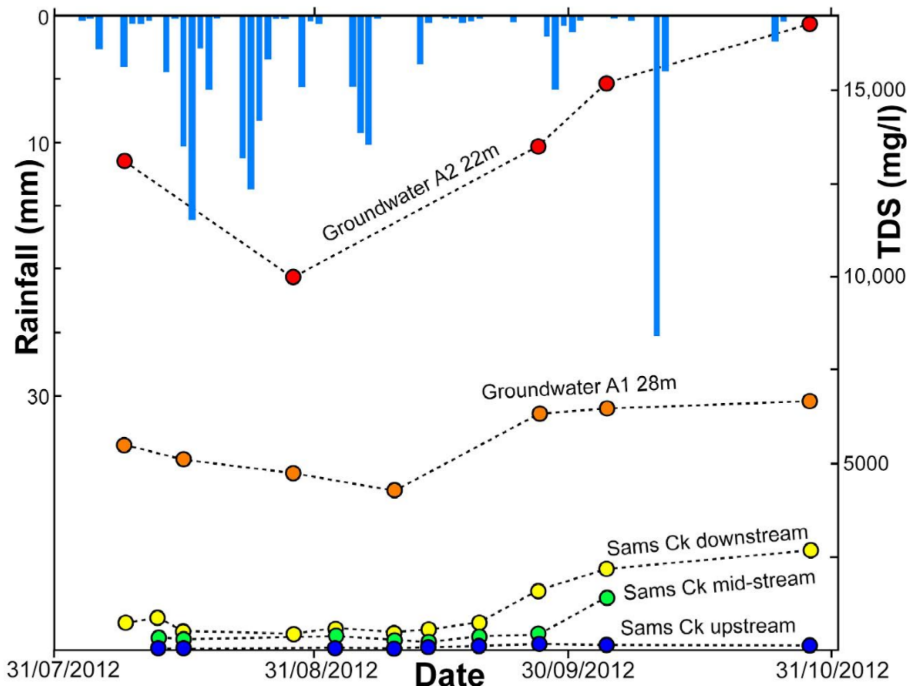

Figure 2.3: Hydrograph of salinity variation at sample sites on Sam's Creek and corresponding rainfall from 3 August–29 October 2012.

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 which ensured that the pH and DO % were maintained as they were within the aquifer. Both groundwater and surface water samples were placed into clean, plastic and airtight sample bottles to avoid contamination and prepared for analysis. Samples were filtered through a 0.45µm filter in the laboratory a few hours after sampling. The samples 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 ($^{2}H/^{1}H$ and $^{18}O/^{16}O$) analysis. To prevent exchange of water vapour with the air, McCartney bottles were filled with no headspace. Electrical tape was also used to seal the lid of the bottle; this ensured that no air could enter the sample.

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 (ACMElabs), Vancouver, Canada. The laboratory methodology is outlined in ACMElabs (2012). Analysis of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ isotope ratios from water samples were done at Stable Isotope Facility, University of California – Davis, USA, using a Laser Water Isotope Analyser V2. Final ^{18}O /^{16}O and $^{2}H/^{1}H$ values were reported relative to Vienna Standard Mean Ocean Water (VSMOW). These methods are documented in (UCDavis 2012). Four water samples were selected for the strontium isotope ratio ($^{87}Sr/^{86}Sr$) analysis. These included a sample from A1 and A2, and two from SMC1. In addition, an extensive database from the site was also used in this investigation (Milgate 2007; Banks et al 2009; Bestland et al. 2009). 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).

2.3. RESULTS AND DISCUSSION

2.3.1. Stream salinity hydrograph

Table 2.1: 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

Site ID	Date sampled	Cl ppm	Br ppm	Na ppm	Ca ppm	Mg ppm	K ppm	Si ppm
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

Site ID	Date sampled	Cl ppm	Br ppm	Na ppm	Ca ppm	Mg ppm	K ppm	Si ppm
E2	24 May 2006	785	2.47	406	193	135	11	13
E2	30 June 2006	939	3.40	496	238	167	11	13
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

Site ID	Date sampled	Cl ppm	Br ppm	Na ppm	Ca ppm	Mg ppm	K ppm	Si ppm
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

Sam’s Creek has a large salinity increase during the waning winter wet flow (**Fig. 2.3**). There is a corresponding seasonal salinity increase in groundwater from the A1 and A2 piezometers. Surface water salinities increase to approximately 2500 mg/L TDS in the spring before the flow ceases. The groundwater samples have the highest TDS values averaging 5587 mg/L (A1) and 13705 mg/L (A2). The A2 piezometer is 5 meters 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. This is 1.4 and 0.6 % of the average salinity of the groundwaters 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.

2.3.2. Chloride and elemental molar ratios

Major ion to chloride ratios are presented in **Fig. 2.4** 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, halite dissolution must be minor and 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 the preferential removal of Na^+ from solution. 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, up-slope groundwaters of piezometers A1 and A2.

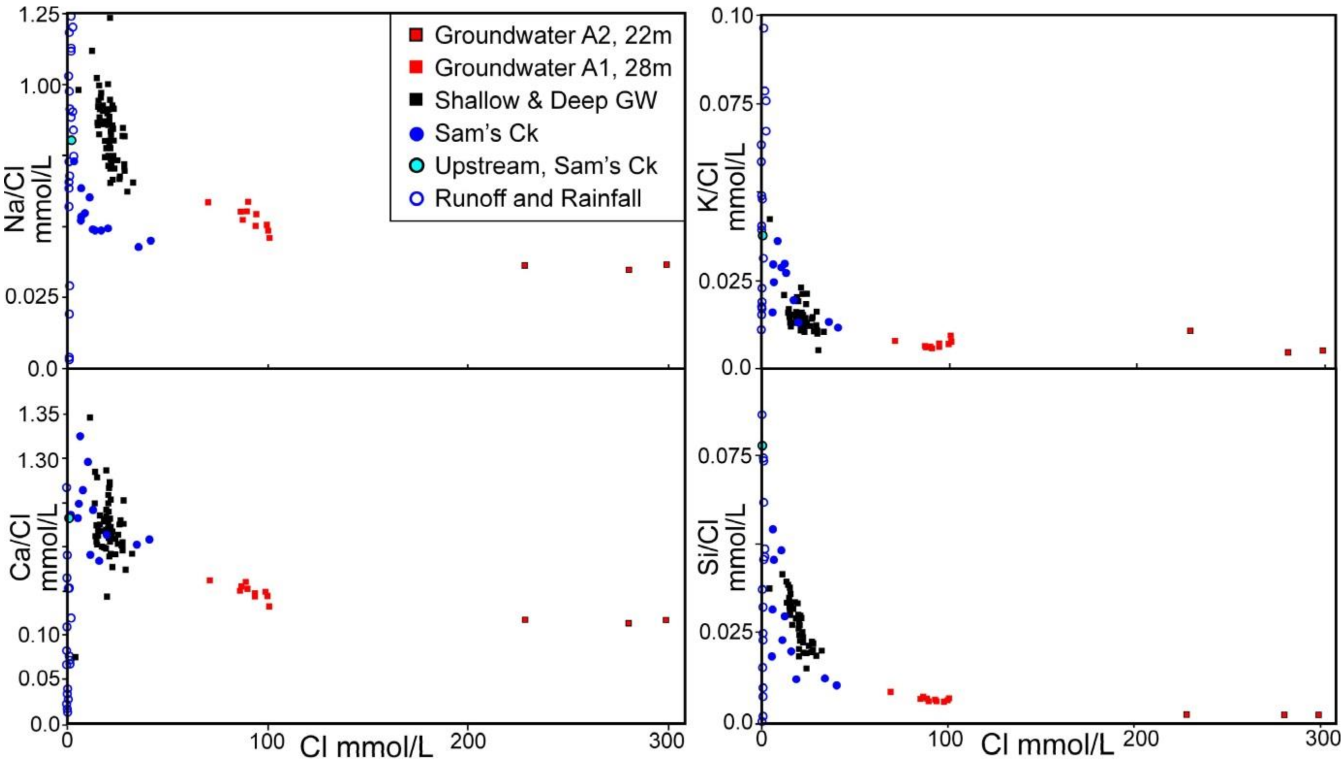

Figure 2.4: Composite diagrams of major elements (Ca, Na, K, and Si) to chloride ratios versus chloride concentration of surface water and groundwater. Samples were collected between July 2005 and October 2012 at Scott Bottom, South Australia. Data sourced from Cranswick (2005); Milgate (2007); Banks et al. (2009); and Anderson (2013).

Dissolution of calcite, along with weathering of feldspars, can explain the elevated Ca^{2+}/Cl^{-} ratios in the fresh groundwater, while a decrease in Ca^{2+}/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 cap 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. 2.4**). 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^-, Ca^{2+}/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, Mg, 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 were undertaken for groundwater samples at this site and a shorter residence time was determined 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.

2.3.3. Stable isotopes of water

The δ^{18}O and δ^{2}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. 2.5**; **2.6**; and **Table 2.2**). Shallow groundwater thereby displays the largest range of δ^{18}O values, reflecting the variable extent of local evaporation as well as the local variability of the δ^{18}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 δ^{18}O by about 0.5‰ compared to both A1 and other shallow groundwaters and up to about 1.5 ‰ compared to the main groundwater body within the SCC.

Table 2.2: Stable isotopes results for the surface-water and groundwater samples collected from the Scott Bottom experimental site

Site ID	Date sampled	δ^{2}H‰ rel VSMOW	δ^{18}O‰ 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

Site ID	Date sampled	δ^2H‰ rel VSMOW	δ^{18}O‰ rel VSMOW
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

Site ID	Date sampled	δ^2H‰ rel VSMOW	δ^{18}O‰ rel VSMOW
D2	15 November 2006	−4.96	−24.3
D2	13 February 2007	−5.13	−24.8
D2	3 June 2008	−4.69	−22.8
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

Site ID	Date sampled	δ^2H‰ rel VSMOW	δ^{18}O‰ rel VSMOW
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
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

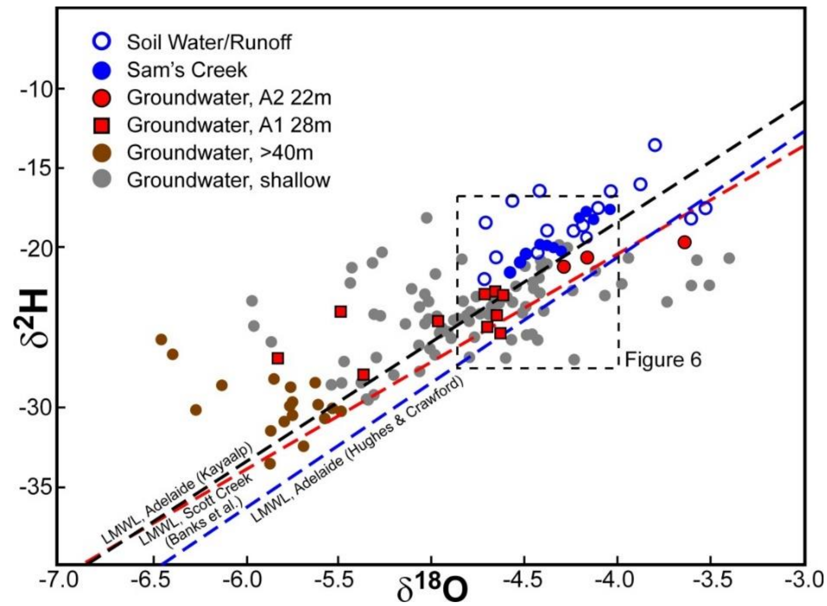

Figure 2.5: δ^2 H versus δ^{18} O for runoff, Sam's Creek and groundwater sampled over a seven year period at the Scott Bottom experimental site. The LMWL's are from (Kayaalp 2001; Banks et al. 2009; Hughes and Crawford 2012).

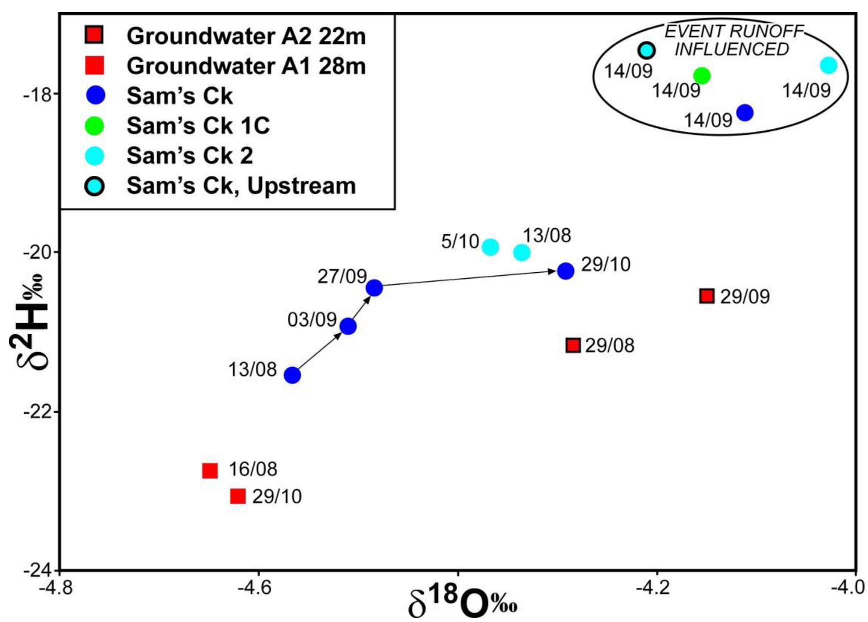

Figure 2.6: δ^2 H versus δ^{18} O ‰ of surface water and groundwater sampled from 13 August–29 October 2012 at the Scott Bottom experimental site.

A comparison of $\delta^{18}O$ and $\delta^{2}H$ in relation to chloride concentrations confirms the subdued role of evaporation in altering the chemistry of surface water and groundwater in the SCC (**Fig. 2.7**). An increase in salinity is not accompanied by a trend towards heavier isotopic compositions. Instead, as salinity increases, surface water and groundwater samples show little variation in their isotopic signature.

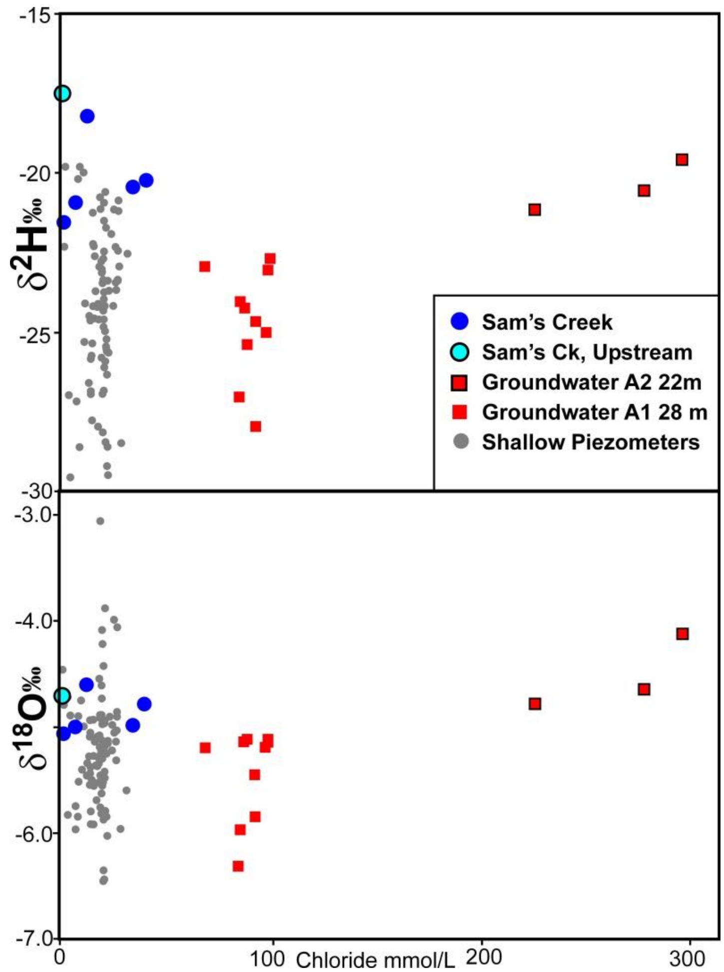

Figure 2.7: δ^2 H versus δ^{18} O ‰ versus chloride of surface water and groundwater sampled over a seven year period at the Scott Bottom experimental site.

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 upslope groundwaters, 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. 2.6**). 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 up-slope saline groundwater (**Fig. 2.6**). This lends further support to the mixing model already outlined, where discharge of saline up-slope 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. 2.6**). 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 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 the surface water in Sam's Creek is a mixture of runoff water and the up-slope saline groundwater zone.

The waters' stable isotopic pattern of up-slope saline groundwater input to Sam's Creek is 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. 2.7**) 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 up-slope 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 up-slope 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 $\delta^{18}O$ ‰ (**Fig. 2.8**). 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 $\delta^{18}O$ ‰.

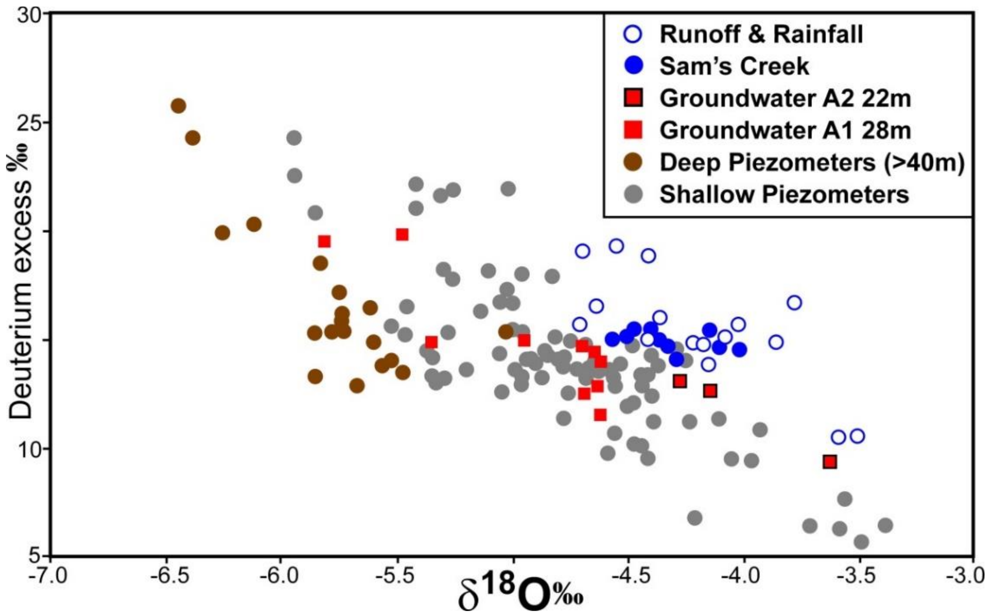

Figure 2.9: Deuterium excess versus $\delta^{18}O$ for runoff, Sam's Creek water and groundwater sampled over a 7-year period at the Scott Bottom experimental site.

Deuterium excess was used to further distinguish major water components (**Fig. 2.8**). 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 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.

2.3.4. 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 deep part of the system (**Fig. 2.9**; **Table 2.3**). Strontium isotopes do not undergo significant mass fractionation during hydrologic processes regardless of temperature, chemical speciation or biological processes, (Capo et al. 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). Atmospheric origins of strontium are dominated by marine sources especially in coastal settings such as the MLR. The $^{87}Sr/^{86}Sr$ 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 nearby State of Victoria coast and then inland (Raiber et al. 2009); four stations, from the coast to 100 km inland, were used to obtain the range shown in **Fig. 2.9**.

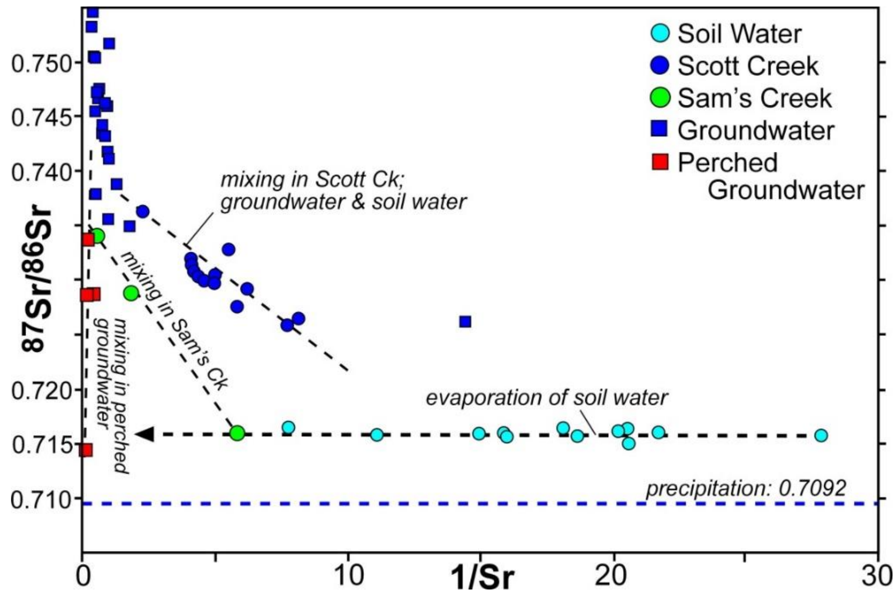

Figure 2.10: Variation of strontium isotope ratios with inverse strontium concentration. Both groundwater and surface water samples at the Scott Bottom experimental site from 2005 to 2012 are depicted. This indicates a mixing of sample sites with distinct Sr isotope ratios. Data sourced from: (Cranswick 2005; Millgate 2007; Banks 2011).

Table 2.3: 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	-

The strontium isotopic ratios of the up-slope 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. 2.9**). The up-slope 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. 2.9**). Three relationships can be concluded from the strontium isotopic data. The mixing lines in **Fig. 2.9** indicate: 1) mixing between the up-slope saline groundwater zone (shallow, more saline piezometer A2) and the dominant groundwater system to produce the compositions from piezometer A1; 2) mixing between the up-slope 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. 2.9**). 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. 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 equation (2) to calculate the fraction of each of the two end members.

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

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

Where $\mathrm{M}_1^{\mathrm{Sr}}$ and $\mathrm{M}_2^{\mathrm{Sr}}$ 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 $(^{87}Sr/^{86}Sr)_{mix}$ is the $^{87}Sr/^{86}Sr$ 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):

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

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 up-slope perched saline groundwater, as previously outlined, can be evaluated with strontium isotopes (**Fig. 2.9**). 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. 2.9** is misleading; strontium concentrations of these samples range from 0.024 ppm to 0.090 ppm. Nonetheless, evaporation of soil water has produced this range of concentrations with no change in isotopic ratio.

2.3.5. Conceptual Model

The conceptual model relies on the specific hydrogeology of this site (**Fig. 2.10**). 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). 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 (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 up-slope saline groundwater zone.

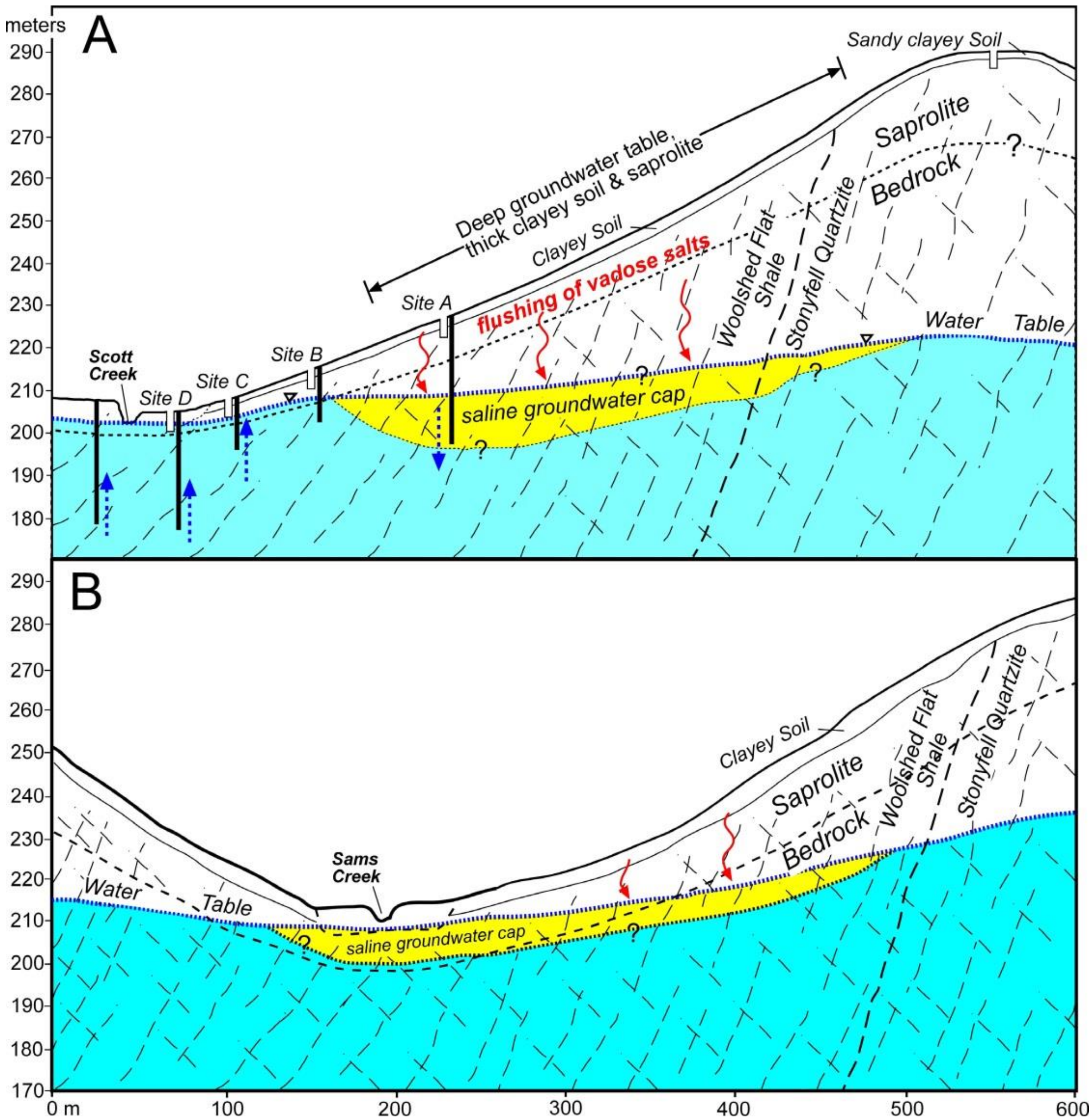

Figure 2.11: Cross-section conceptual models of groundwater salinity at the Scott Bottom experimental site. Location of the cross section is illustrated in **Fig. 2.2**.

Based on the hydrochemical data presented here and the hydrogeologic context of this site, the following 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 then 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 up-slope saline groundwater zone. The presence and/or extent of an up-slope 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 up-slope 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 dominate water system nor has it caused salt to accumulate in downslope areas where the water table is shallow.

Most Australian native vegetation are efficient in utilising infiltrating rainfall (Allison and Hughes 1983). Following land clearing of native woodland over one hundred 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 increase 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 dryland 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 de-forestation 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 similar groundwater salinity patterns. In that study, it was shown that much of the chloride present within the groundwater represented residual chloride which pre-dated 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 to be 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.

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. Up-slope 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 up-slope 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 water supply of Adelaide.

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. This situation, including the up-slope saline groundwater zone, is thought to be transient. The origin of the upslope saline groundwater zone is thought to be caused by a combination of the thick clayey soil-saprolite zone and 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.

Because of the heterogeneous and geologically complex nature of this site, many questions still remain. And because the thick clayey soil and saprolite zone extends over large areas of the MLR, these up-slope saline groundwater zones could occur on a much broader scale.

2.4. 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. Up-slope 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 up-slope 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 water supply of Adelaide.

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CHAPTER 3

3. MANUSCRIPT II: SALINITY BALANCE AND HISTORICAL FLUSHING QUANTIFIED IN A HIGH-RAINFALL CATCHMENT (MOUNT LOFTY RANGES, SOUTH AUSTRALIA)

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Abstract: Human-induced landscape salinization, including the effects of dryland salinity, is negatively impacting many catchments in southern Australia. Salinization occurs due to increased recharge and water-table rise following land clearing of deep-rooted native vegetation. In low-lying areas with poor drainage, groundwater-level rise can lead to increased evapotranspiration, mobilization of vadose zone salt, and salt scalding. Alternatively, these same processes of increased recharge and groundwater rise can lead to decreased salinization as accumulated salts are flushed into surface waters. This study in a high-rainfall area of the Mount Lofty Ranges of South Australia documents catchment desalinization. A 28-year record (1989-2016) of flow and salinity in Scott Creek was analysed based on monthly data. Analysis of catchment-scale chloride deposition and export determined that approximately three times more chloride is exported than is input to the catchment from atmospheric sources. Over the time period investigated, salinity load exported to

surface water decreased by, on average, 6.4 tonnes annually due to catchment freshening. Analysis of monthly salinity balance of a sub-catchment drained by an intermittent stream demonstrates that accumulation of chloride, rather than export, occurs during drought years. In the catchment as a whole, salts are being flushed via groundwater flow into the permanent stream in all years of the record. Deep groundwater is input to the permanent stream, with mixing of deeper more saline and fresher shallow groundwater. Thus, a complex interaction of landscape hydrologic parameters, such as relief, precipitation, chloride deposition and land-use history, determine whether a catchment undergoes salinization or desalinization.

3.1. INTRODUCTION

Quantifying salinity balance of catchments over time is critical for evaluating overall river and catchment health (Peck and Hurle 1973; Williamson et al. 1987; Williamson and van der Well 1991; Jolly et al. 2001; Guan et al. 2010a; Biggs et al. 2013). Human-induced landscape salinization and catchment salt balances have been the focus of much hydrologic work in southern Australia (Ruprecht and Schofield 1989; 1991; Cox et al. 1996), in the US (Brown et al. 1983; Scanlon et al. 2005) and in South America (Jayawickreme et al. 2011; Marchesini et al. 2017). It is well accepted that in many areas of Australia, increases in soil and stream salinization have resulted from wide-spread land clearing of deep-rooted native vegetation (eucalypt trees) combined with the planting of short-rooted crops and grasses (Schofield 1992; Greeff 1994; George et al. 1997; Walker et al. 1999; Jolly et al. 2000; Jolly et al. 2001; Pannell 2001; Hatton et al. 2003; Poulsen et al. 2006); e.g. in agricultural regions where the native vegetation has been largely cleared and replaced with annual crop and pasture vegetation. In Australia, the eucalypt woodland absorbs substantially more water through root-uptake than the short-rooted pasture/crops and as a consequence, salinity tends to accumulate in the unsaturated zone of uncleared areas. Following land clearing, the decrease in soil water uptake by vegetation increases the groundwater recharge rate, which can mobilise salinity present in the unsaturated zone during water-table rise (Fitzpatrick et al. 1994; Cox et al. 1996). Increases in near-surface evaporation can lead to landscape salinization. These same processes, however, may result in *decreases* in salinization in landscapes that are high in rainfall and well-drained (Norman 1995; Tyagi 2003; Guan et al. 2010a). In such settings, the increase in recharge and rise in water table are thought to have led to increases in stream flow and flushing of stored or historic salinity, i.e. ‘dryland salinity flushing’ (Jolly et al. 2001; Guan et al. 2010a), causing a change in the catchment salt balance over time.

Catchment-scale stream salinity data have been analysed for the Murray–Darling Basin (Australia) with the aim to develop concepts and methods of evaluating ratios of salinity output to salinity input (O/I ratios) (Jolly et al. 2001). These statistical methods were used to evaluate salinity trends in catchments where limited data were available. Peck and Hurle (1973) established that the O/I ratio could be used as a key indicator of catchments undergoing salinization, assuming steady state or salinity equilibrium prior to clearing. Guan et al. (2010a) further conceptualized catchment types and suggested how the O/I ratio could be applied. Allison et al. (1990) determined the influence that increased recharge due to land clearance had on the Murray River, South Australia, using groundwater modelling. Additionally, it has been conceptualised that following a disturbance such as land clearing, the catchment salinity balance would be changed and a new equilibrium or salinity balance would occur with time (Jolly et al. 2001; Guan et al. 2010a). Notably, the study presented here assumes steady state conditions, despite various other factors influencing recharge and salinity balance, including environmental history (Dahlhaus et al. 2008; Cartwright et al. 2013), climate change (Currell et al. 2016) and flow paths through the regolith and aquifers (Ruprecht and Schofield 1989; Cox et al. 1996). However, many studies have shown that vegetation clearance has been a pivotal driver for hydrological change. For example, Ruprecht and Schofield (1989) determined the extent that land clearance had in raising groundwater levels and increasing streamflow in south-western Australia. Similarly (Ruprecht and Schofield 1991) found that land clearance transitioned catchments from salinity accumulating to salinity exporting. Additionally, Williamson et al. (1987) concluded that in higher rainfall catchments more salinity had been exported than in drier catchments eight years after clearance. These catchments are expected to attain a new salinity equilibrium sometime in the future. Having an established salinity equilibrium is required in order to utilise the chloride mass balance (CMB) method for estimating groundwater recharge (Wood 1999). Thus, if catchment salinity input/export is significantly out of equilibrium, increased error for groundwater recharge estimates will result. For the Mount Lofty Ranges of South Australia, Guan et al. (2010a) established that the catchment salinity O/I ratio provides useful information to determine whether a catchment has reached a new salinity equilibrium and therefore whether the application of CMB methods is valid. Other studies have modelled the timespan required for reaching a new salinity equilibrium (Sivapalan et al. 1996; Smitt et al. 2003; Dawes et al. 2004; Gilfedder et al. 2009). However, these studies did not have continuous monitoring history of the physical parameters to verify the theory that there is a decreasing export of stored salinity from the system.

In addition to the estimation of salinity exported from catchments, much research has been undertaken to quantify atmospheric deposition of salinity (Eriksson 1959; 1960; Blackburn and McLeod 1983; Keywood et al. 1997; Biggs 2006; Guan et al. 2010b). Keywood et al. (1997) documented that there was a decrease in chloride deposition with the distance inland from the coast of Australia. Most chloride is deposited within approximately 100 km from the coast (Eriksson 1959; 1960). Biggs (2006) derived equations to estimate annual average rainfall chloride mass deposition as well as total salinity deposition in southern Queensland, Australia. Furthermore, Guan et al. (2010b) created a quantitative map of the bulk chloride deposition in the Mount Lofty Ranges in which distance to the coastline, elevation, and slope orientation were reported as the most significant factors influencing chloride deposition. It is evident from Guan et al. (2010b) that the high resolution data employed were important in influencing these findings, which has been a limiting factor of the aforementioned studies.

Many catchment salinity balance studies have claimed that insufficient data was a major cause that limited the key findings (Williamson et al. 1987; Ruprecht and Schofield 1989). Thus, considering the available literature on salinity balance it is evident that high resolution data are required to thoroughly evaluate salinity input and export at the catchment scale. Necessary data include the duration of salinization or desalinization, saturated vs. unsaturated salinity storage, and influence of chloride content of wet-fall and dry-fall. The study presented here evaluates these factors. Furthermore, the findings of this study should be considered when evaluating reforestation during the process of land management planning; for example, plans made in the Mount Lofty region (AMLRNRM 2013). The study presented here indicates that reforestation can increase salinity and decrease surface water flows. These conclusions are based on high-quality long-term stream and salinity time series data from the Scott Creek catchment (SCC) within the Mount Lofty Ranges. These data quantify the catchment salinity balance, resulting in monthly totals of chloride input and export for a permanent and an intermittent stream. Similar databases, containing river discharge and salinity exist elsewhere, including e.g. the United States Geological Survey 'Water Data for the Nation' program (USGS 2018). Therefore, following the methods outlined in this study, these data can be used to quantify salinity loads in catchments across the globe. This study employs a multiple regression analysis that reveals a decrease in salinity load as a function of both time and flow. These data and quantifications conclusively show that a decrease in catchment-scale salinity is occurring. Furthermore, this study evaluates the atmospheric chloride deposition and the stored chloride export (or accumulation) at monthly time intervals. Moreover, the methods presented here have the potential to quantify the flushing of stored salinity for other catchments with significant monitoring data and allow the timespan in which the catchment will reach a new salinity equilibrium post land clearance to be determined. This paper presents a definition of terms (**Table 3.1**) to assist the reader in understanding frequently used terms and concepts.

Table 3.1: Definition of terms

Annual cumulative mean export	The summation of the mean mass of salinity (or chloride) exported each year, which updates by adding the annual mean export from the previous running total.
Atmospheric deposition	Mass of salinity or chloride deposited from wet-fall and dry-fall processes
Bulk chloride deposition	*As above*
Chloride accumulation	The process by which the mass of chloride deposited to the catchment via bulk chloride deposition is greater than the mass discharged via surface water over a given period
Chloride export	The process by which the mass of chloride deposited to the catchment via bulk chloride deposition is less than the mass discharged via surface water over a given period.
Dryland salinity	Increases in salinization [as] a result of significant clearing of perennial native vegetation and… replacement with annual crops and pastures… reducing the amount of evapo-transpiration and resulting in increased groundwater recharge, *sensu stricto* (Jolly et al., 2001).
Historic salinity	Salinity accumulation in the groundwater and unsaturated zone prior to clearance of native vegetation and subsequent dryland salinity occurring.
Intermittent stream	[A stream] that flows only at certain times when it receives water from springs [or surface water], *sensu stricto* (Meinzer 1923).
Output/input ratio	The proportion of salinity (or chloride) deposited into the catchment via precipitation in relation to that exported out via stream flow.
Salt balance	The output of salinity in stream flow equals the current input of salinity in precipitation [and therefore] a salinity output to input ratio equal to one, *sensu stricto* (Williams et al. 1998).
Salinity load	The mass of salinity exported from a catchment via streamflow.
Weighted salinity concentration	The mass of salinity (salinity load) per volume of water discharged from the catchment (flow).

3.1.1. Site background

3.1.1.1. Hydrology and climate

Numerous hydrogeological studies have been completed at the SCC (**Fig. 3.1**), which includes both the Scott Bottom and Mackreath Creek sites (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 et al. 2016; Anderson et al. 2017). These studies have outlined the hydrogeological heterogeneity and geological complexity of the site as well as the soil hydrology of the dominant Red Brown Earth soils (Xeralfs). Banks et al. (2009) and Bestland and Stainer (2013) documented the importance of the fractured rock and deep clayey regolith for the groundwater/surface-water interactions at the site. In addition, several soil-water studies have recognized the through-flow hydrochemical characteristics on site (Chittleborough et al. 1992; Stevens et al. 1999; Bestland et al. 2009). These studies expanded the investigations of James-Smith and Harrington (2002) and Harrington (2004a, b) that described the basic hydrology and hydrogeology of the SCC.

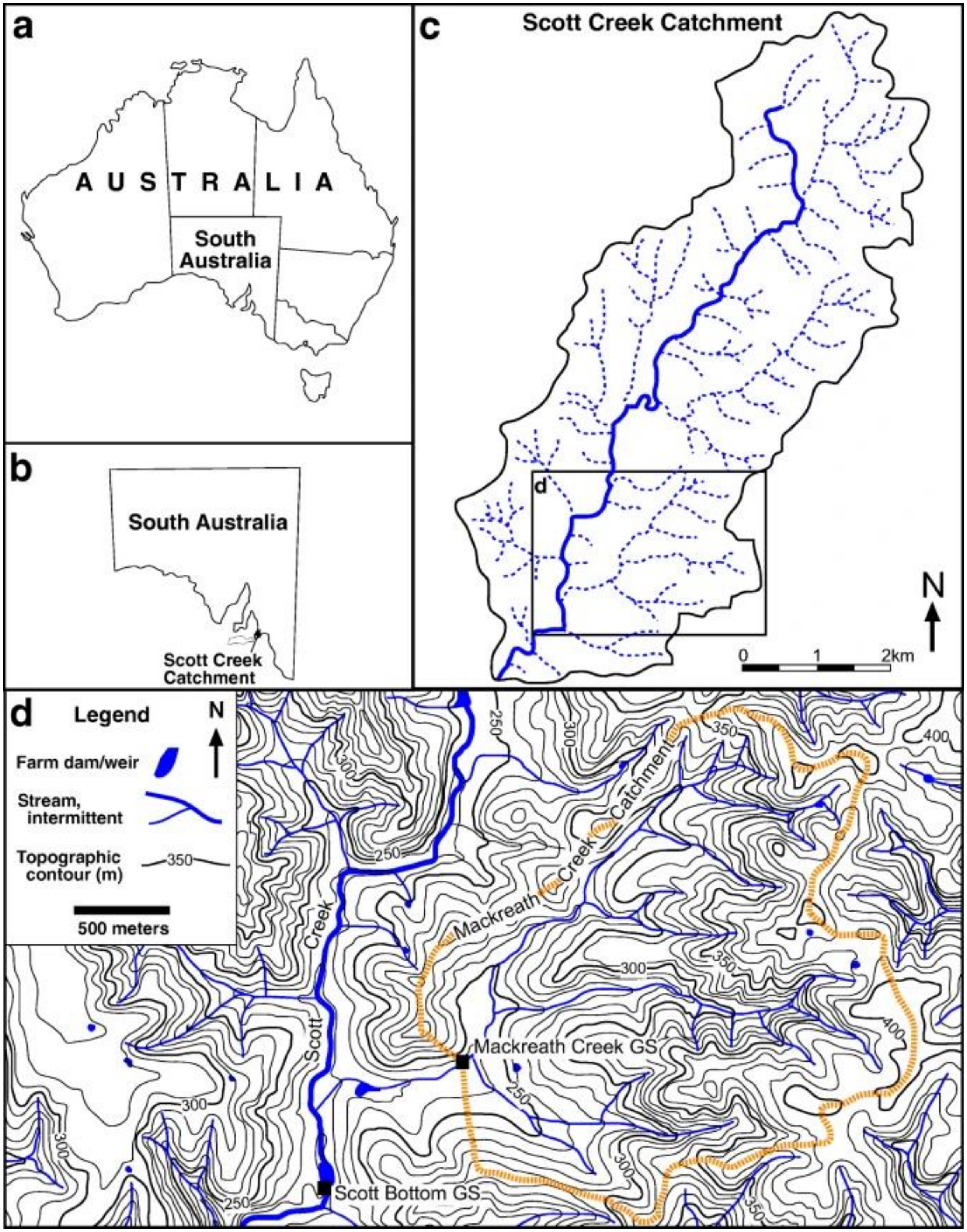

Figure 3.1: Location maps of the Scott Creek Catchment, South Australia, showing location of gauging stations (GS) and Mackreath Creek catchment.

The SCC has an area of 28 km^2 and is located about 30 km southeast of Adelaide. Scott Creek flows into the Onkaparinga River; upstream of Clarendon Weir and downstream of Mount Bold Reservoir. Land-use patterns have changed over the years in the SCC. Following European settlement of the SCC beginning in 1838, farming and logging began in nearby Scott Creek. The building industry in Adelaide made use of the original red, blue and manna gum, as well as stringy bark. In 1850 the site was mined for copper followed by silver (DEHAA 1999). However, since the declaration of the Scott Creek Conservation Reserve in 1985 (as described in Nicholson and Clark (1992)), agricultural use has decreased and the native vegetation of the area has been restored to some extent. At that time, the vegetation was reported to be 47% native vegetation, 29% residential living and 16% grazing modified pastures (EPA 2013).

The SCC has a Mediterranean climate with cool, moist winters and warm, dry summers. Here the mean temperature ranges from 7 to 13 °C in winter, and 14 to 25 °C in summer. The Mount Lofty Ranges receives varying seasonal precipitation (almost all as rainfall) with yearly totals ranging from 400 to over 1,000 mm/year and with 85% of the rainfall occurring between May and September (BOM 2016). The great annual variability in rainfall in this area impacts the groundwater/surface-water systems as demonstrated by the aforementioned 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). A pluviometer in close proximity to the SCC, at the upslope Mount Bold Reservoir weather station, has an average annual rainfall of 801 mm/yr (BOM 2016). Mount Bold also has an average evaporation of 1,555 mm/yr and therefore potential evaporation exceeds rainfall from October to May (spring, summer and autumn) (Bestland et al. 2009).

High salinity levels of Scott Creek at the Scott Bottom site relate to low stream flows and are associated with the groundwater fed base-flow. Conversely, high flows have relatively low salinity that reflects mostly surface water run-off (James-Smith and Harrington 2002). Anderson et al. (2017) provides an understanding of the cause for a high salinity groundwater ‘hotspot’ observed on site and traces it to a tributary stream that flows into Scott Creek. Additionally, Kretchmer (2007) concluded that throughout harsh drought conditions (e.g. as arose in the summer of 2006–2007), Scott Creek diminished to a sequence of disconnected pools sourced from groundwater. Salinities on site fluctuate from 500 μS/cm in winter to above 2,000 μS/cm throughout the low-flow period from January to April. The seasonal salinity variations at Scott Bottom were explained by evaporative enrichment; and groundwater input during the summer contrasting with runoff dilution during the winter wet season (Harrington 2004b). Comparatively, the nearby intermittent Mackreath Creek has much lower salinity than Scott Creek (200–500 μS/cm) and little salinity variation throughout its flow season, as revealed in Milgate (2007); Bestland et al. (2009); and Pichler (2009). This sub-catchment has significant areas of sandy soils. These investigations also disclosed that Mackreath Creek only flowed after significant Autumn–Winter rainfall. However, surface water salinities at both Scott Creek and Mackreath Creek are not believed to be in a state of equilibrium (Banks et al. 2009), reinforcing the theory that stored salts are flushing from the system. Flushing is thought to occur through two mechanisms: 1) during water table rise stored salt is flushed from the unsaturated zone consisting of soil and regolith (Anderson et al. 2017); and 2) the accumulated stored salts from the ambient groundwater is mixed and flushed by fresher recharge (appendix a; Harrington 2004a). These mechanisms are illustrated in a conceptual hydrogeologic model (**Fig. 3.2**).

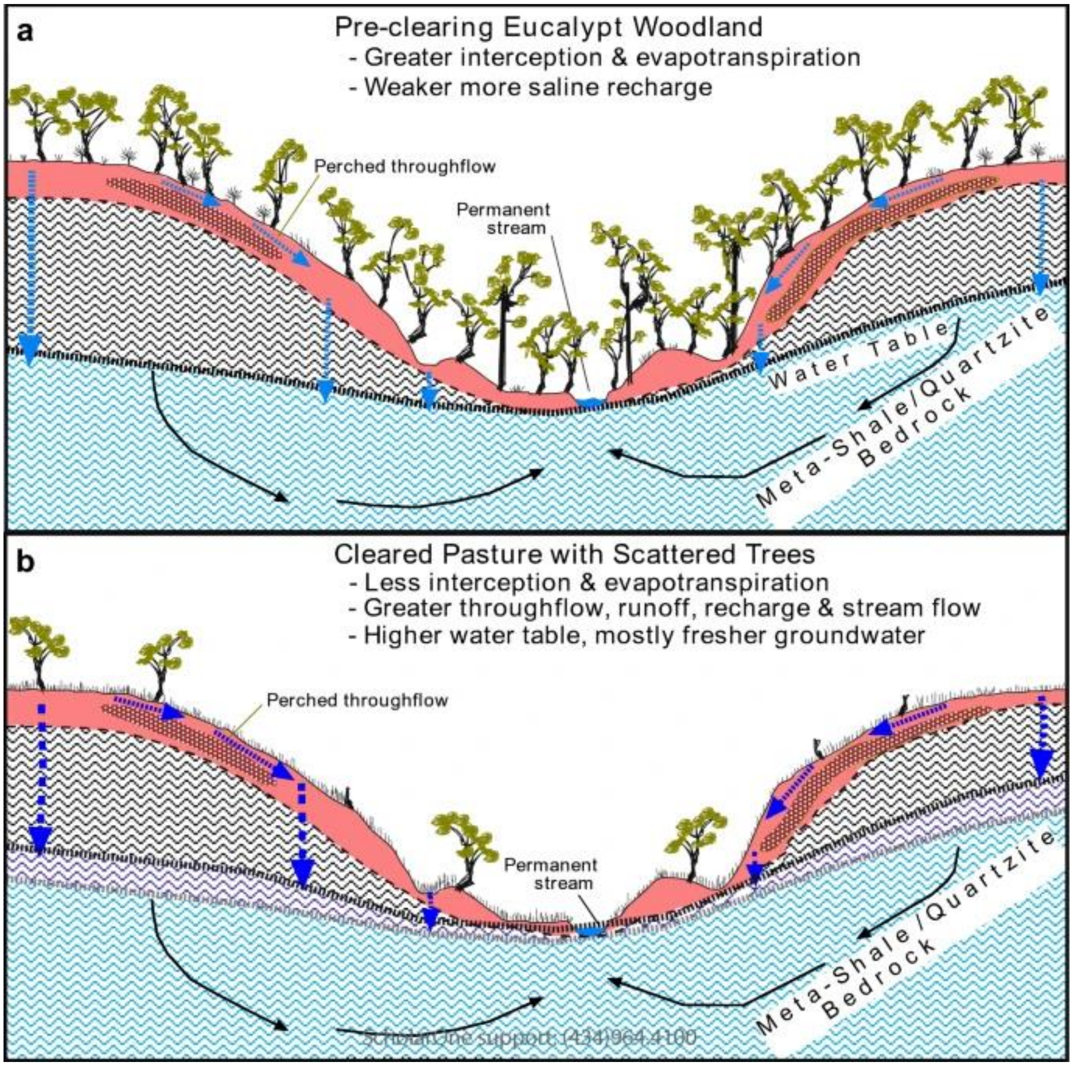

Figure 3.2: Conceptual model of Mount Lofty Ranges catchment groundwater system **a** prior to land-clearing and **b** post land-clearing.

3.1.1.2. Geology and hydrogeology

Despite the relative geological complexity of this area, the geology is well studied and understood (Preiss 1987; Banks et al. 2009; Bestland et al. 2016). The lower one third of the SCC is underlain by the relatively homogenous Woolshed Flat Shale unit. Five 3-m deep backhoe trenches were dug as part of this project (reported in Bestland and Stainer, 2013) from valley bottom to ridge crest in order to characterise the saprolite and soil zone. From this information combined with drill logs (Banks et al., 2009) the thick, clayey nature of the regolith has been determined.

A sequence of shallow to moderate depth piezometer nests were drilled at the Scott Bottom site in 2005 (Cranswick 2005). The piezometer nests allowed an analysis of the hydrogeological structure and flow dynamics of the site (Banks et al. 2009). The drilling logs for these piezometers are documented in Cranswick (2005). This network added to the deeper bores described in James-Smith and Harrington (2002). Piezometer nests adjacent to Scott Creek demonstrate an upward hydraulic gradient, as expected from the presence of artesian deep bores. Piezometer nests on the up-slope from the stream on the mid-slope of the hill demonstrate a downward gradient. Thus, the conceptual model (**Fig. 3.2**), which shows the upward and downward gradient groundwater flow-paths, is supported by this data.

The regolith at the site plays an important role in groundwater flow and recharge and has been separated into zones. The deep, weathered bedrock saprolite zone of up to 15 m depth is generally very clayey with a massive structure (Cranswick 2005). Fractured bedrock underlies this zone. The degree and depth of weathering of the saprolite is vital in directing groundwater flow and recharge. Banks et al. (2009) outlined three zones that control groundwater flow at the site. These are the soil zone, saprolite zone and fractured bedrock zone. The soil zone is characterised as a duplex soil with a sandy-silty A horizon (10–20 cm depth) over thick clayey B and C horizons (Chittleborough et al. 1992).

The saprolite zone changes gradually from poorly structured (massive) clay down to 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 usually less than the hydraulic conductivity of the fractured bedrock zone. The unweathered bedrock (Woolshed Flat Shale) consists of a grey siliceous slate. Hydraulic conductivity here ranged from 1.5 to 14 m/day. The fractured rock aquifer (FRA) is the most active part of the groundwater system with some deep bores being permanently artesian.

The thick clayey character of the saprolite developed from the meta-shale is responsible for the very low hydraulic conductivities found in this material (Banks et al., 2009). In addition, these low permeability zones cause widespread areas of perched through-flow in the Mount Lofty Ranges (Cox et al., 1996). Very low rates of groundwater recharge below these zones are thought to result in local areas of very high groundwater salinity (Anderson et al., 2017). Conversely, areas in the SCC, and elsewhere in the Mount Lofty Ranges, underlain by strata containing sandstones (quartzite) result in rocky and sandy soils, much higher rates of recharge, and much lower groundwater salinities.

The nearby Mackreath Creek study site (**Fig. 3.1**) is underlain by similar geologic units to the Scott Bottom site and includes meta shales, sandstone-quartzite, and minor carbonate units (Priess, 1987). The site has 100–300 m of relief, reasonably steep slopes in many areas and narrow riparian-floodplain zones. The hydraulic head of the FRA is 2 to 3 m lower than the streambed at the gauging station on site, which demonstrates the disconnection between the surface water and the FRA.

The Mackreath Creek area has varying soil types as outlined in Bestland et al. (2016). In addition, three 3-m deep backhoe trenches were excavated and sampled for soil and regolith hydrochemical properties (Bestland and Stainer 2013). To summarise these soil properties, the regolith that occurs over meta shale consists of a stony heavy clay; and where the regolith occurs over quartzite, it is composed of a silty stony sand with some clayey zones. Additionally, minor quartzite outcrops are distributed along steep side slopes and narrow ridge tops.

3.1.1.3. Variation in flow and precipitation

Precipitation and stream flow at the SCC is representative of its Mediterranean climate, exhibiting high annual variability (**Fig. 3.3**). Most years have below 900 mm precipitation and less than 3,000 ML of flow. However, the maximum precipitation and flow over the 28-year period occurred in 2016, which had an annual precipitation above 1,200 mm, and flow that surpassed 9,000 ML. This vastly exceeded the annual mean for the years analysed of 804 mm of precipitation and 3496 ML of flow. By contrast, the lowest annual flow occurred between the years 2002 and 2009 when most years were below 2,000 ML. In particular, 2006 was the driest year in this record with 1,057 ML of flow and 530 mm of precipitation. This was well below the average for the period of analysis. In addition, the standard deviation for flow was 2,000 ML and for precipitation 135 mm; this highlights the extent of the annual climatic variability of the site.

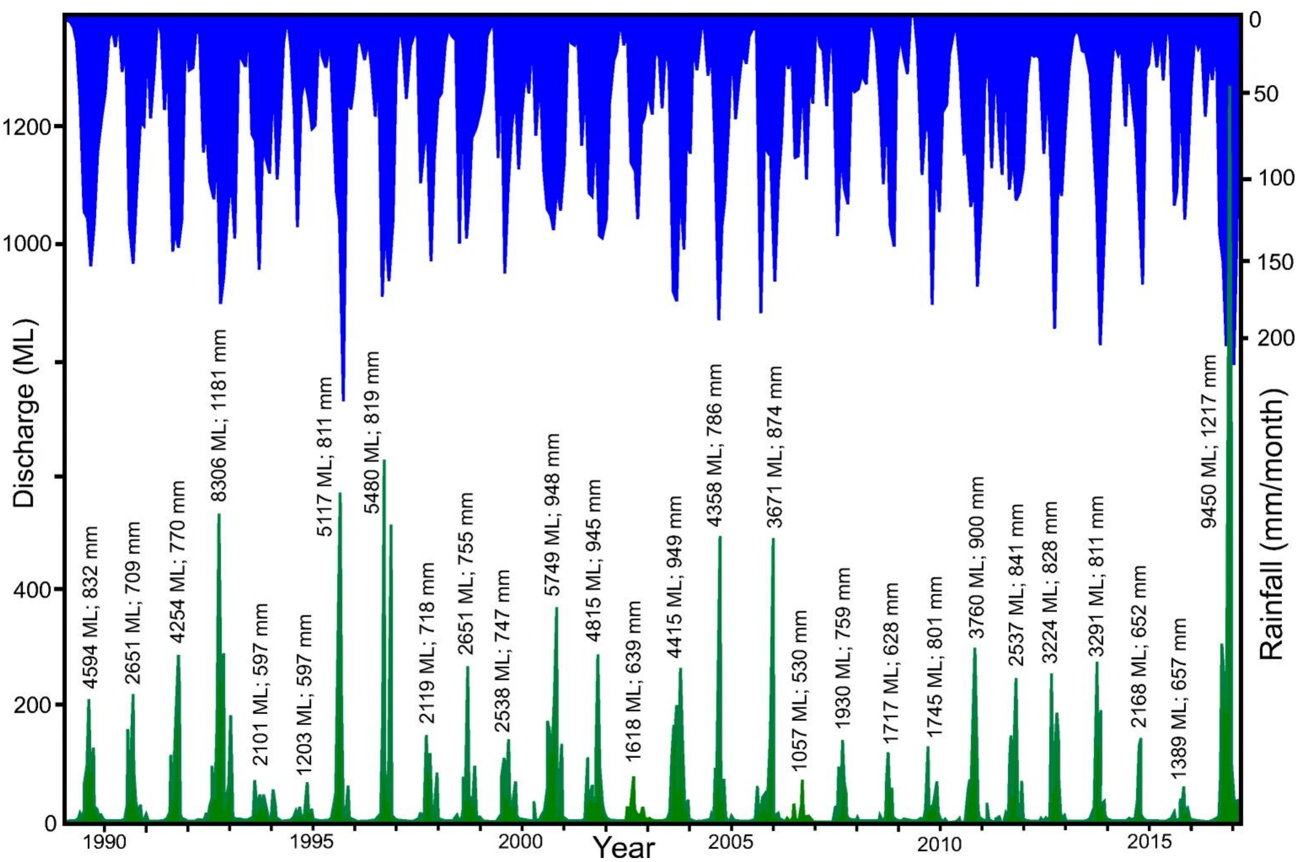

Figure 3.3: Monthly stream flow from Scott Creek and rainfall at Mt. Bold Reservoir station from 1989 to 2017.

The variability in flow strongly correlates with the general climatic conditions for south-eastern Australia (BOM 2016; Murphy and Timbal 2008). Notable, in 2006 during the second worst drought in recorded history (Watkins 2005; Bettio 2006) the lowest flow was recorded at Scott Bottom. Moreover, between 1997 and 2006 (during 'the millennial drought') Southeastern Australia experienced a decade of record breaking drought conditions (Murphy and Timbal 2008). This period also coincides with low flows on site. In contrast, flow on site in 2016 (the highest flow) concurred with the state of South Australia (including the Mount Lofty Ranges) having the highest September rain in recorded history with some sites in the Mount Lofty Ranges having had their highest annual rainfall (BOM 2016). Therefore, observed data from this investigation was consistent with the climatic conditions for the region and was therefore representative of overall climatic conditions of this area.

3.2. METHODS

3.2.1. Flow and salinity data

Flow and surface water salinity time series data are available from hydrometric monitoring stations located adjacent to weirs at both the Scott Bottom and Mackreath Creek sites (**Fig. 3.1d** and **Fig. 3.4**). In addition, rainfall measurements are available from the nearby Mount Bold Reservoir weather station (**Fig. 3.3**). The Scott Creek data set has accumulated over many decades; whereas, the Mackreath Creek site was only in operation for the years 2001 to 2008. The data recorded for the Scott Bottom site over the last five years are available in SAW (2017) and the full data set available on request from the current custodian, SA Water (Scott Bottom) and DEWNR (Mackreath Creek).

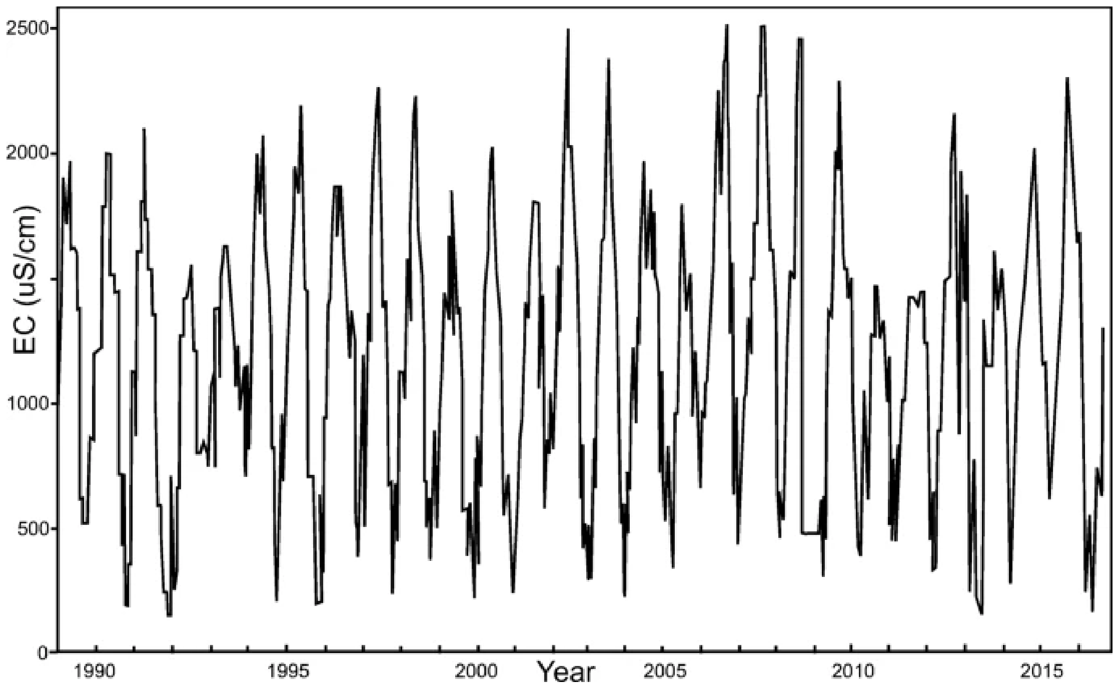

Figure 3.4: Monthly salinity measurements from Scott Creek in 1989–2017.

Measurements of both electrical conductivity (EC; µS/cm) and the total daily volumetric flow (ML) were utilised during this investigation between the periods from 1989 to 2016. In addition to flow data, EC measurements at the Scott Bottom site were collected by acquiring samples of water passing through the site using the flow proportional composite sampling method (Nicholson and Clark 1992). Thus, reported EC values represent the mean flow-weighted concentration for specified sampling periods (**Fig. 3.4**). In 2013, an *in situ* water quality sensor was installed less than five metres upstream of the weir. Henceforth, the sensor recorded EC measurements every five minutes and data from this sensor were utilised instead of the composite sampling method for this study.

Despite these variations in EC sample frequency over the last 28 years, readings were usually taken on at least a fortnightly basis (approximately 90%). In the case measurements were missing in a month (less than 5%), a power regression between flow and EC (**Fig. 3.5b**) was used to estimate EC in cases where flow data existed but EC data were missing. In general, where *in situ* water quality data were available, this was used in preference to composite samples. However, limitations of the sensor method included equipment malfunction. EC of less than 150 μS/cm were assumed to be due to faulty equipment or low flow and in this case, data from the composite sample method were employed instead.

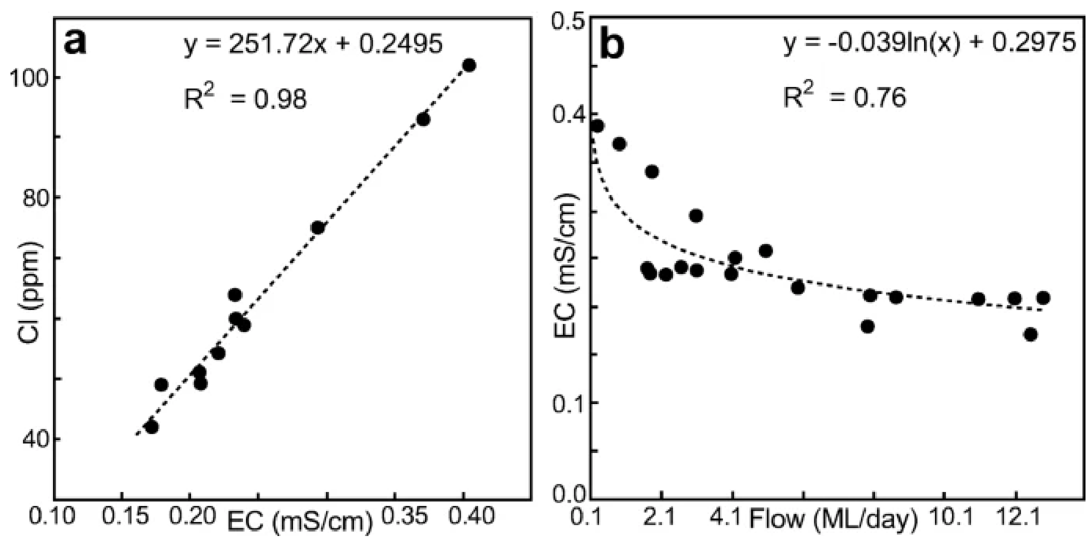

Figure 3.5: a) Mackreath Creek chloride (Cl) measurements correlated to electrical conductivity (EC) measurements using a linear equation. **b**) EC correlated to flow measurements using a logarithmic equation.

3.2.2. Salinity and chloride budget calculation

Based on EC measurements, a salinity load was calculated for Scott Creek at the Scott Bottom site (**Fig. 3.6a**). Salinity or total dissolved solids concentration (TDS, mg/L) of Scott Creek was thereby estimated from EC (in μS cm) measurements multiplied by a conversion factor of 0.64 (Mackay et al. 1988; Ali et al. 2012). Daily salinity loads were quantified by multiplying salinity concentration by the total daily stream flow. These were then summed to provide monthly and annual salinity loads from the two stream systems. Additionally, chloride concentration data for Scott Creek and Mackreath Creek were correlated with EC in order to generate time series of chloride concentration (**Figs. 3.5a**, **b**). The monthly totals for atmospheric deposition of chloride were based on average chloride concentrations (4.45 mg/l) in bulk rainfall for the area

(Guan et al. 2010b), the rainfall from Mount Bold station and the area of each catchment (28.4 and 3.3km^2 respectively). The monthly totals of chloride load in Scott Creek were based on flow measurements from the gauging station and estimated using an exponential relationship with EC for the Mount Lofty Ranges (Guan et al. 2010a). At the Makcreath Creek site, chloride load was calculated by multiplying flow with the concentration correlation equations shown in **Figs. 3.5a** and **3.5b**. Two different sets of correlation equations for the two streams were necessary because of the very different character of the streams: one is permanent, fed by groundwater and higher in salinity, and one is intermittent, fed by runoff and soil water through-flow, and lower salinity.

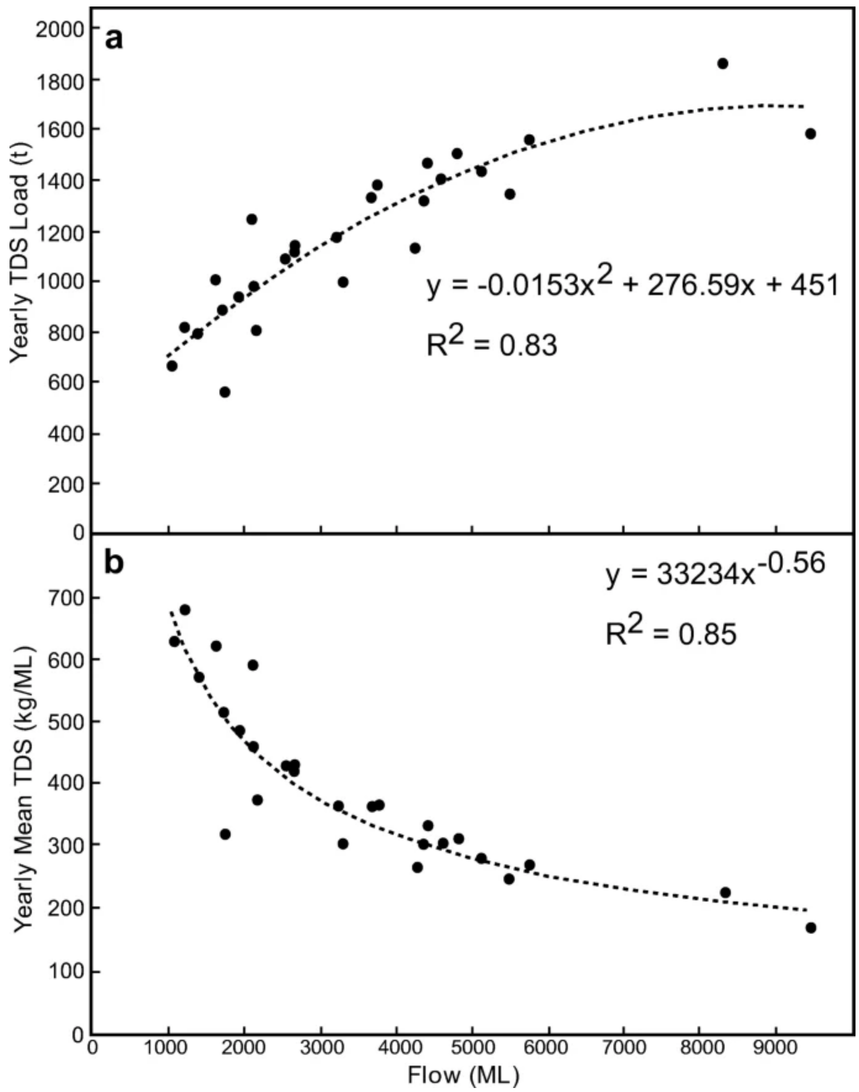

Figure 3.6: a) Yearly salinity load (total dissolved solids, TDS, in tonnes) and **b**) yearly mean salinity concentration (kg/ML), plotted against flow from Scott Creek

3.3. RESULTS AND DISCUSSION

3.3.1. Stream salinity hydrograph and trends

In this strongly Mediterranean climate there is a good seasonal correlation between rainfall, stream flow, and stream salinity (**Figs. 3.3** and **3.4**). There are however times when groundwater input to surface flows has had a delayed response to rainfall on a year to year basis. This interpretation is supported by the contrast in flow that occurred between 1993 and 1994, both low rainfall years. The year 1993 followed the anomalously wet year 1992 and had considerably more flow (>40%) with the same rainfall totals. This lag time in flow response to rainfall is assumed to be reflective of significant groundwater recharge during wet years. Such pulses of recharge generating stream flow is the mechanism envisioned to cause more saline groundwater to flush. Loh and Stokes (1981) found similar variations in flow and salinity following changes in flow in south-western Australia.

Similar to the aforementioned flow data, the EC data at the Scott Bottom site are highly variable (**Fig. 3.4**), with a standard deviation of 503 μS/cm over the 28-year period. In addition, seasonal variation during this sampling period ranges from above 1500 μS/cm in the summer months (Dec-Feb) to below 400 μS/cm during the winter months (June-Aug). Furthermore, the wettest years (e.g. 1992; 1995; 1996; 2000; and 2016) had much lower than average salinity minimums (below 220 μS/cm). Conversely, during the millennial drought (during the years 1997-2006) there is a visually obvious trend of higher salinities, with maximums reaching over 2000 μS/cm. Therefore, it has been well established that there is strong correlation between flow and salinity. The variability in annual flow and salinity of Scott Creek is of critical importance to concepts of salinity flushing from the groundwater system. The seasonal salinity variation is caused by mixing of precipitation-induced runoff and groundwater input. During the drier summer months groundwater contribution to stream-flow is dominant (Kretchmer 2007), which dramatically increases the EC. During wetter winter months there is freshwater dilution from precipitation and runoff lowering the EC (Banks et al. (2009).

As anticipated, both the highest salinity load and flow occurred in winter (Jun-Aug) followed by spring (Sep-Nov) (**Fig. 3.7**). The lowest flow and salinity load occurred in summer (Dec-Feb) and autumn (March-May), which are, approximately equivalent. The highest flow occurred in spring, however, even with similar flow, a higher salinity load is flushed in winter compared to the spring period. Flushing of salinity however, continues during the spring, but then declines by summer. By this time, flows have dropped off and the water table has lowered, unless during years when tropical moisture is present in South Australia (BOM 2016) as in the case of the September 2016 period. During these periods, transient flows can be high. Thus, the change in season plays an important role in the amount of historical salinity flushed from the catchment.

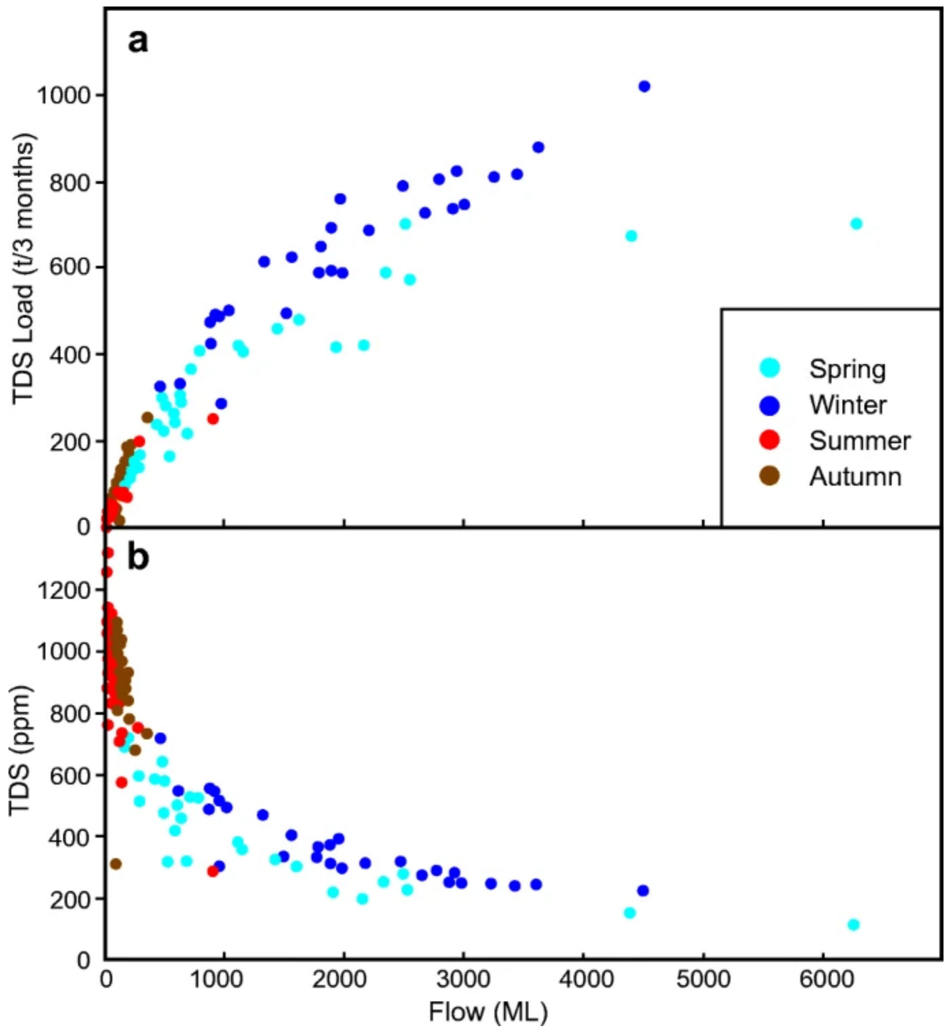

Figure 3.7: Total dissolved solids **a**) load and **b**) concentration, calculated for each season (spring, winter, summer, and autumn) over the time span of 1989–2017.

3.3.2. Deep groundwater salinity flushing

Critical to the discussion of catchment-scale salinity mass balance is the consideration and description of the groundwater flow system. As mentioned, the Scott Creek experimental site has numerous nested piezometers as well as several deep open bores from which groundwater salinity profiles have been obtained (**Fig. 3.8**). Groundwater salinity measurements surrounding the streambed (piezometer nests D and E; Banks et al. 2009) are similar to the summer time stream salinity (between approximately 2000 and 3000 μS/cm; Banks et al 2009). However, in this upward hydraulic gradient area in the valley bottom there is good evidence of groundwater mixing of fresher soil water with more saline deep groundwater (Banks et al, 2009; Bestland and Stainer 2013); this is thought to be the path for considerable salinity flushing from the groundwater system.

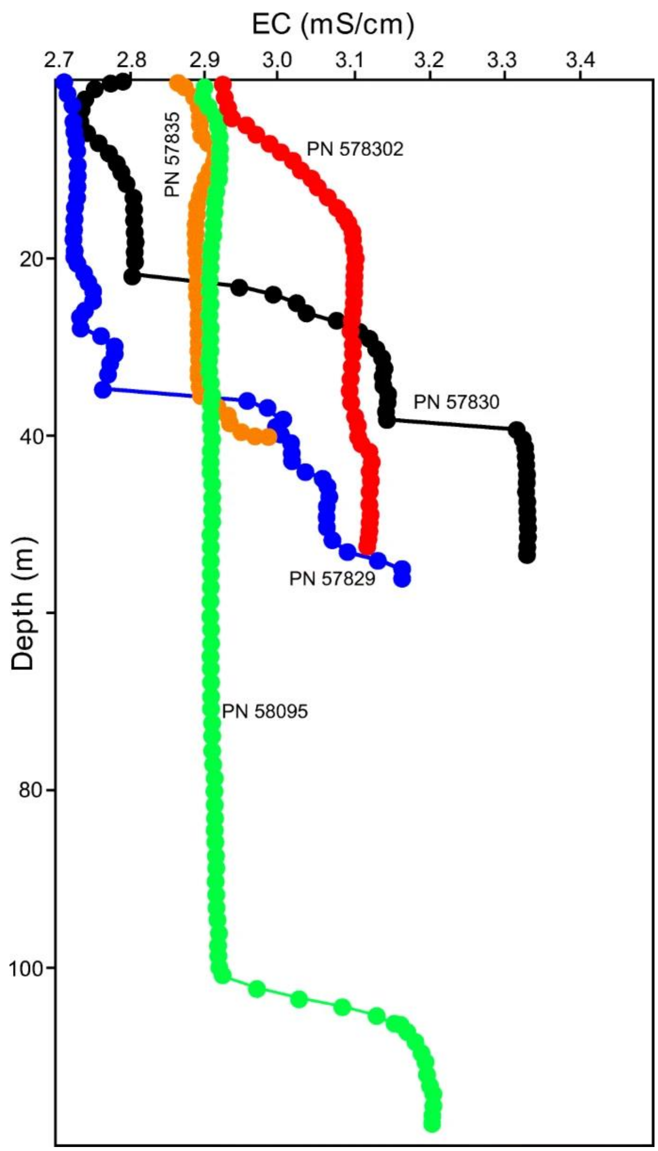

Figure 3.8: Electrical conductivity (EC) depth profiles from open bores at the Scott Bottom site (data from Harrington 2004a).

Deep open bores (up to 120 m) with groundwater EC profiles reveal an increase in salinity with depth (**Fig. 3.8**). There are obvious steps in the salinity increase with depth in most bores (Harrington 2004b). Bore PN 57830 (*black profile* in **Fig 3.8**), which has a step in salinity at about 20 m and again at approximately 40 m; also bore PN 57830 (*blue profile*) has a salinity step increase at 40 m. Additionally, bore PN 57830 (*red profile*) shares this step at 20 m. Similarly, bore PN 57835 reveals a step but not to the extent of the other bores. The bore PN 58095 (*green profile*) does have an increasing step, but at 100 m, much deeper than the other bores.

The salinity rise observed at 20 – 60 m below the ground surface is interpreted as historic groundwater salinity that is flushing due to increase and freshening of recharge. The groundwater system in this valley has a strong upward gradient with several deep bores being artesian (Cranswick 2005; Banks et al., 2009). Banks (2009) describes how the fractured bedrock zone at this site plays an important role in groundwater flow. Variation in the depths of these salinity steps are probably due to the locations of fractures that both access deeper more saline water as well as provide pathways for fresh recharging groundwater. Therefore, the steps in salinity found in most of these bores are interpreted as the result of historic salinity flushing.

The salinity increase in bore PN 58095 at over 100 m presumably represents the deep, unflushed ambient groundwater system. Carbon 14 dating of deep bores within close proximately to the Scott Bottom site (within 8 km) by Harrington (2004b) reveal the apparent age was over 1000 years. Similarly, Radon-222 data by Cranswick (2005) suggest that water from deeper piezometers has considerably longer residence times. In addition, age dating by Banks et al. (2009) based on CFC-12 and CFC-13 found the shallower groundwater (< 30 m) to be a few decades old, considerably younger than that of the deeper bores. Therefore, as land clearing initiated in the 1840 and 1850s, the stored salinity discharging into the stream would have commenced post this era.

3.3.3. The export and accumulation of chloride

For the Scott Creek catchment, defined from the Scott Bottom gauging station, analysis of the monthly chloride deposition and load reveals periods of both export and accumulation (**Fig. 3.9**). Overall, during most years, there is over two times more chloride exported from the system than deposited by atmospheric chloride deposition; i.e. on average per month 8.5 tonnes (t) of atmospheric chloride is deposited and 19.6 tonnes of chloride is exported. It should be noted, however, that any groundwater export from the catchment that does not involve measured surface water flow has been omitted from this analysis. More stored chloride is generally exported during periods of higher flow; this supports the regression in **Fig. 3.6a**. For example, the month with the highest amount of chloride export is July 1995, with over 110 tonnes exported. This occurred during a monthly flow of approximately 3000 ML, which is about 10 times higher than the average monthly flow of 291 ML. Conversely, accumulation of chloride occurs during some summer months that have low stream flow but significant rainfall. For example, for the month of January 2007, 4.2 tonnes of chloride were deposited while flow was only 6 ML. In such an extreme Mediterranean climate with large summer moisture deficit even moderate summer precipitation events can result in little runoff, therefore these calculations and trends are consistent. Furthermore, January 2016 had the highest chloride accumulation of the years under investigation. Eight tonnes of chloride accumulated during this month, following two of the driest years on record (2014 and 2015). Overall, the data illustrate that the amount of chloride exported is highly variable with a standard deviation per year of 22.7 tonnes. The variance was thereby dependent on both time and flow with more stored salinity accessed and exported when water tables rise during periods of high precipitation and flow. During these periods more historical salinity discharged into the surface waters. However, during dry, summer and autumn months (Dec-April) chloride accumulation occurred during rainfall events, expressed as negative values in chloride load (**Fig. 3.9, Table 3.2**). Remarkably, there are higher, longer periods of chloride accumulation in more recent years, probably due to drought years with low flow accompanied by some summer rainfall. Overall, however, the data suggest that the highest contributions to surface water salinity are stored historical salinity rather than salinity recently deposited from precipitation.

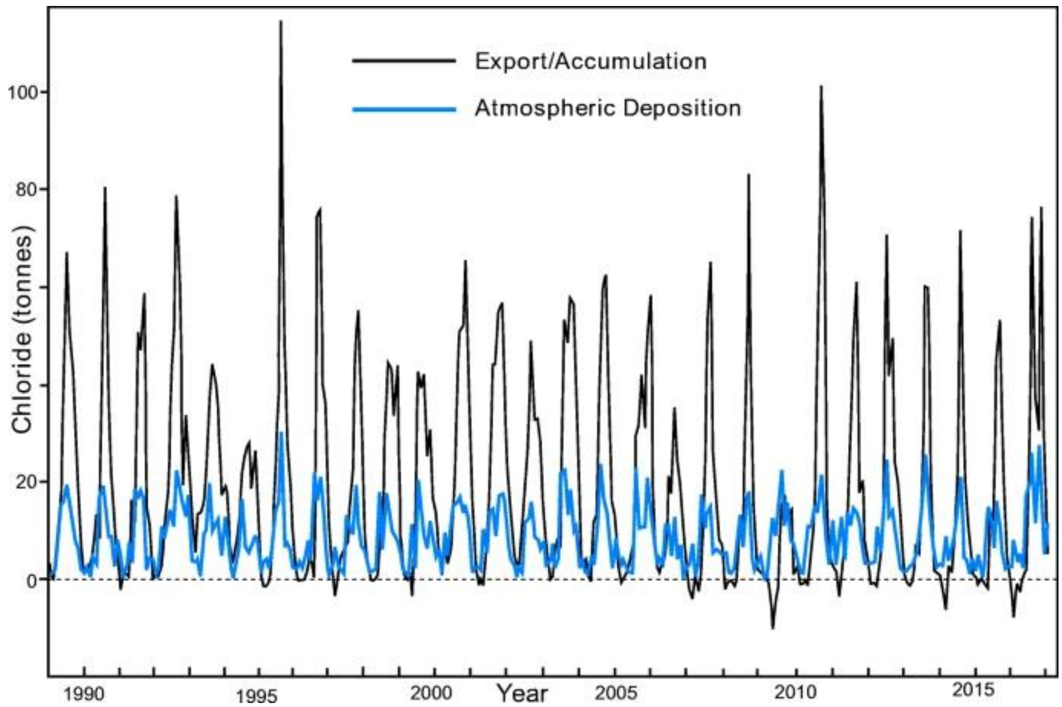

Figure 3.9: Catchment-scale chloride export or accumulation data (black line) calculated from monthly atmospheric chloride deposition (blue line) subtracted from monthly averaged stream chloride load (not shown).

Table 3.2: Chloride load regression statistics. *SE* standard error

					95% confidence interval	
	Coefficient	**SE**	***t*-stat**	***p* value**	**Lower**	**Upper**
Chloride load	−229.9 t	96.7 t	−2.377	0.0254	−429.1 t	−30.7 t
Reduction in chloride load per year since 1989	−1.8 t	0.8 t	−2.254	0.0331	−3.45 t	−0.16 t
Logarithmic flow	140.7 ML	27 ML	5.202	2.21×10^{-5}	84.97 ML	196.3 ML

Importantly however, higher rates of salinity export are not only related to flow, but also related to time. For instance, 30.6 tonnes of chloride were exported during September 2016, the month exhibiting the highest flow (approximately 4600 ML; **Fig. 3.3**) during the 28-year time series. However, this was significantly less than the chloride exported during the next highest flow month. This was July 1995, with 114.9 tonnes of chloride exported despite less flow.

Given the strong correlation between salinity and flow within the SCC, there is an obvious and expected correspondence between the amount of the annual salinity load and the flow volume (**Fig. 3.6a**). An increase in salinity load is observed with a logarithmic increase in flow. Additionally, this relationship has a confidence level of nearly 100% (p value = 4.7×10^{-11}) and a significant coefficient of determination (R^2) of 0.83 (**Table 3.3**). Similarly, salinity concentration in mg/L exhibits a high correlation with flow in which lower salinities are correlated to higher flow (**Fig. 3.6b**; $R^2 = 0.85$).

In addition to correlations between salinity and flow, statistical trends are also apparent between time and flow. While there is no significant correlation regarding a decrease in salinity with time alone, a logarithmic regression with salinity load as a function of both time and flow exhibits a strong correlation (**Table 3.3**). This had an R^2 value of 0.85 with < 1% likelihood that it occurred by chance (significance of F = 6.89E-11). This regression reveals that 6.4 tonnes less salinity was exported each year from the 110 tonnes being exported annually on average (p value = 0.04). This strong relationship of a decrease in salinity exported from the system each year is consistent with the theory that this site is reaching a new salinity balance. The gradual freshening of the catchment over the 28 years of record, expressed through a reduction of 6.4 tonnes of discharging salinity annually, indicates a decrease in salinity flowing into the stream presumably from increased recharge and freshening of the groundwater.

Table 3.3: Salinity load regression statistics.

					95% confidence interval	
	Coefficient	**SE**	***t*-stat**	***p* value**	**Lower**	**Upper**
Salinity load	-2589 t	360 t	-7.191	1.550×10^{-7}	-3330 t	-1847 t
Reduction in salinity load per year since 1989	-6.38 t	2.98 t	-2.145	0.042	-12.51 t	-0.253 t
Logarithmic flow	1105 ML	100.637 ML	10.980	4.702×10^{-11}	898 ML	1312 ML

Analogous to the trend in annual salinity load, the annual chloride load for SCC also shows a decreasing trend with time (**Fig. 3.10a**). Chloride is not being exported consistently at the average observed rate (approximately 22 tonnes per year), as depicted in **Fig. 3.10** and summarised in **Table 3.4.** The observed cumulative load is estimated by regression to decrease over time with chloride export declining by 1.8 tons of chloride per year (**Fig. 3.10b**). Unlike the historic chloride exported from the stream, the trend in atmospheric chloride deposition remains relatively linear throughout the analysed period. Therefore, whilst there is a relatively long-term steady value for chloride deposition, the amount exported is decreasing and indicates the site is attaining a new salinity balance, consistent with the study by Guan et al. (2010a).

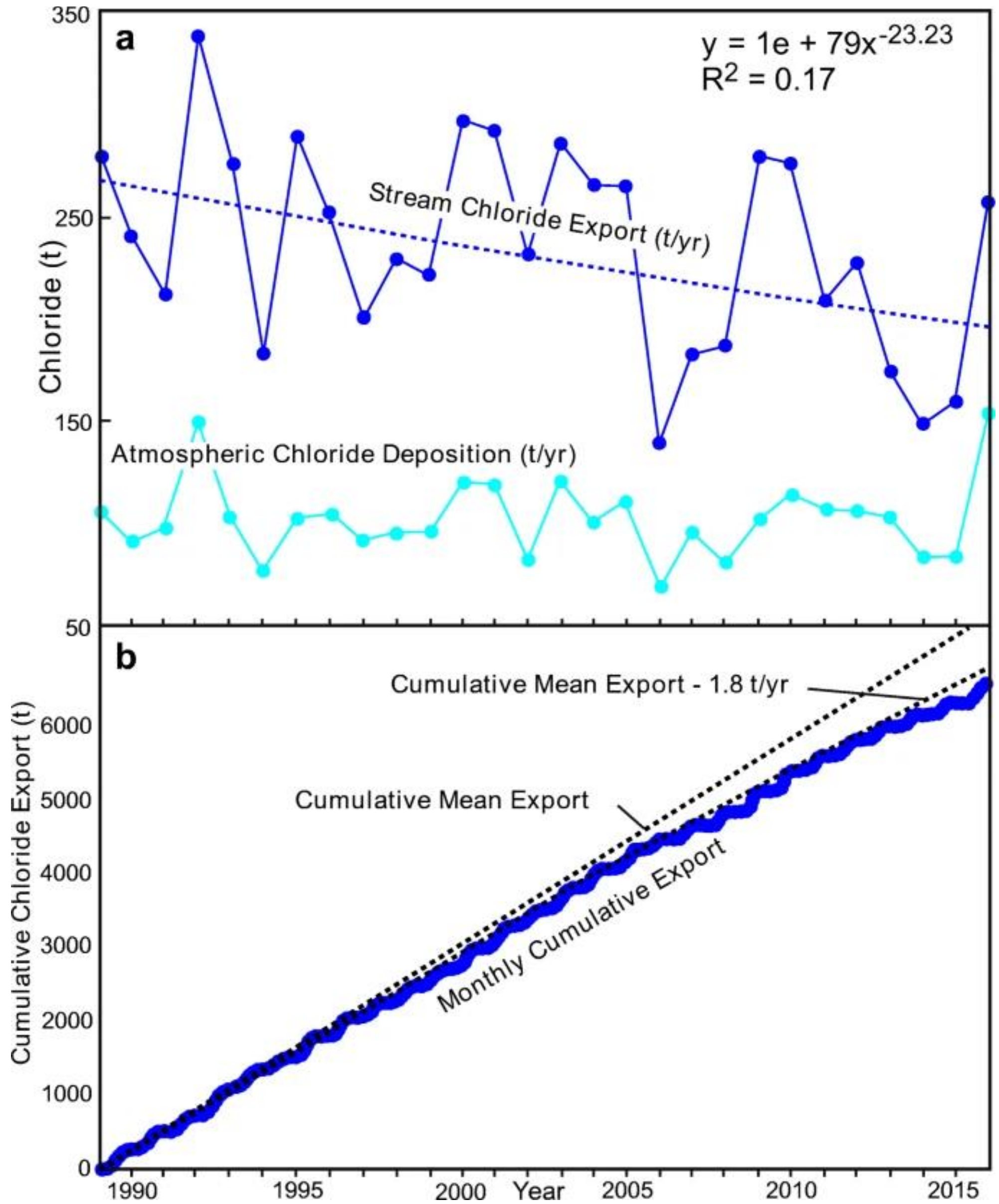

Figure 3.10: a) Yearly chloride export from Scott Creek catchment from 1989 to 2017 showing trend line of decreasing chloride export (1.8 t/yr). **b**) Monthly cumulative chloride export (blue line) compared to cumulative mean chloride export (averaged over years 1989–2016) and cumulative mean chloride export minus observed chloride export decrease of 1.8 t/yr

Table 3.4: Descriptive statistics of chloride load at the Mackreath and Scott Bottom catchments.

Descriptive statistic	Mackreath Creek	Scott Creek
Minimum chloride load (t/yr/km^2)	-2.2	4.9
Maximum chloride load (t/yr/km^2)	3.7	10.3
Mean chloride load (t/yr/km^2)	0.21	8.1

3.3.4. Intermittent stream export and accumulation of chloride

Having established the overall salinity trend in the SCC, it is noteworthy that significant differences in the mass of chloride accumulated or exported are evident from the intermittent Mackreath Creek (**Fig. 3.11**). The Mackreath Creek catchment with its intermittent surface water flow has no winter flushing in the years 2002 and 2006. Chloride accumulated during these years according to the mass balance based on chloride deposition and stream flow (**Fig. 3.11**). These differences between the annual chloride masses exported or accumulated for these two catchments is expressed as a mass per time per area (t/yr/km^2) (**Table 3.4**). Markedly, Mackreath Creek exported 0.21 tonnes of stored chloride per km^2 per year averaged over the eight-year monitoring period. In comparison, perennial Scott Creek exported 8.1 tonnes per km^2 per year averaged over the same eight-year period indicating that far more of this historical salinity is exported each year through the perennial steam. Additionally, the amount of chloride exported at Mackreath Creek only exceeded accumulation in three of the eight years monitored. In contrast, the mass of chloride exported from Scott Creek was greater than the amount accumulated every year throughout the 28-year monitoring period. Furthermore, over the eight-year period Mackreath Creek had a maximum annual export of 3.7 tonnes per km^2 in 2003 compared to Scott Creek which has a maximum of 10.3 tonnes per km^2 in 2001. Over this eight-year period, the most extreme year in terms of chloride mass balance for Mackreath Creek was 2002 when 2.2 tonnes per km^2 of chloride accumulated (no export occurred). The most extreme year in terms of chloride mass balance for Scott Creek was 2006 with a minimum chloride export of 4.9 tonne per km^2. Furthermore, the amount of chloride exported per km^2 from Mackreath Creek is only 2.6% of that from Scott Creek. Overall, this study revealed that there were vast differences when comparing the amount of chloride discharging from the intermittent stream compared to the perennial stream.

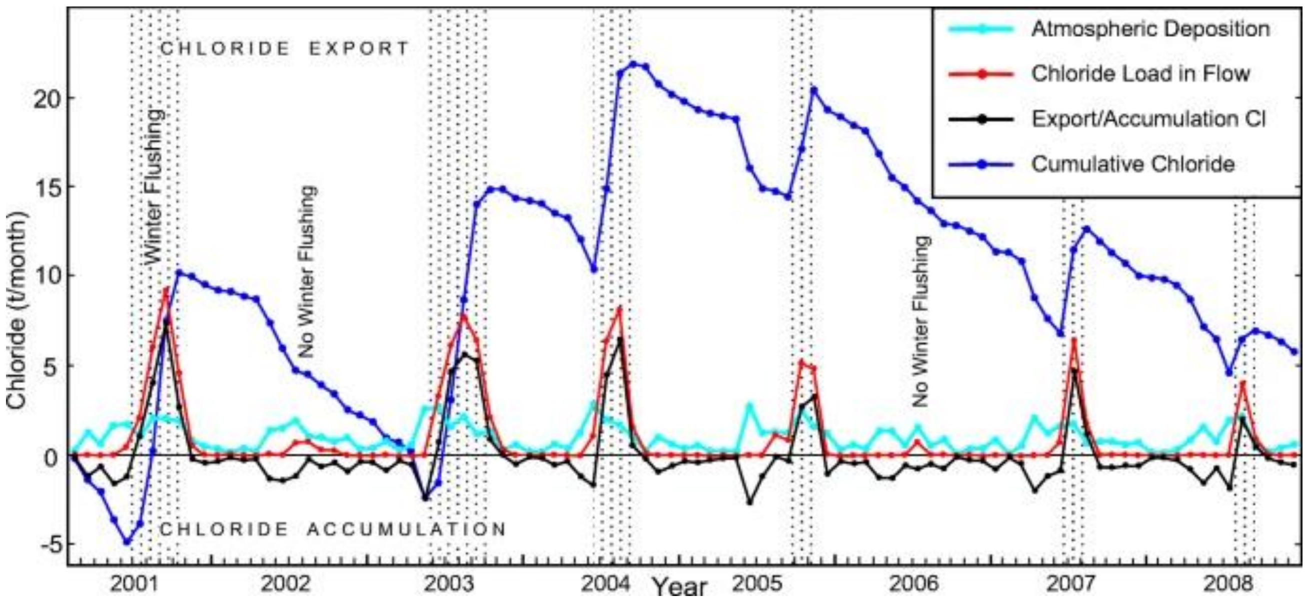

Figure 3.11: Time series of chloride data from Mackreath Creek catchment for years 2001–2008. Export or accumulation of chloride is calculated from monthly atmospheric deposition subtracted from monthly chloride load in stream flow.

It is evident that the intermittent Mackreath Creek catchment, which is representative of most of the landscape of the SCC, has a low rate of chloride export compared to the SCC as a whole. This is due to the fact that most intermittent streams are losing streams where the groundwater does not rise enough to flush the stored salinity into the stream. During drier years there are extended periods of chloride accumulation with no apparent winter flushing. Specifically, this occurs during drought when the low rainfall causes low stream flow.

The considerably lower rate of historical chloride exporting into the surface water at Mackreath Creek is emphasised by the significantly lower salinity in the stream (Milgate 2007; Bestland et al. 2009; Pichler 2009). Presumably, recharge is moving salinity to the water table where flow toward the permanent stream allows this salinity to be flushed. Another consideration is the significant areal extent of sandy soil present in the Mackreath Creek catchment (Bestland et al. 2009) compared to the thick, clayey soil of much of the SCC (Banks et al. 2009; Bestland et al. 2016). Anderson et al. (2017) observed that the soil at Scott Bottom can retain high salinity due to low rates of infiltration and recharge. When geology and porosity of the soil restrict drainage, shallow saline groundwater can occur (Cartwright et al. 2013). Therefore, as more salinity has been historically stored, there is more salinity available to flush. Considering the variation in salinity load exported between the perennial and intermittent streams within the sub-catchment, the perennial stream proves to be by far the more important means of exporting these historical salts.

3.3.5. Timeframe to reach new chloride equilibrium

The quantification of flushed salinity loads over a time interval can be used to approximate the timeframe for the catchment's restoration to a new salinity equilibrium (**Fig. 3.12**). Results from this investigation allowed the development of a conceptual model similar to that of Guan (2010a) and Jolly (2001). However, the model in this study has a plethora of data to support the theory of reaching a new salinity equilibrium. To do this, an approximate period was calculated on a linear scale. Remarkably, this determined that the site would reach equilibrium by 2090.

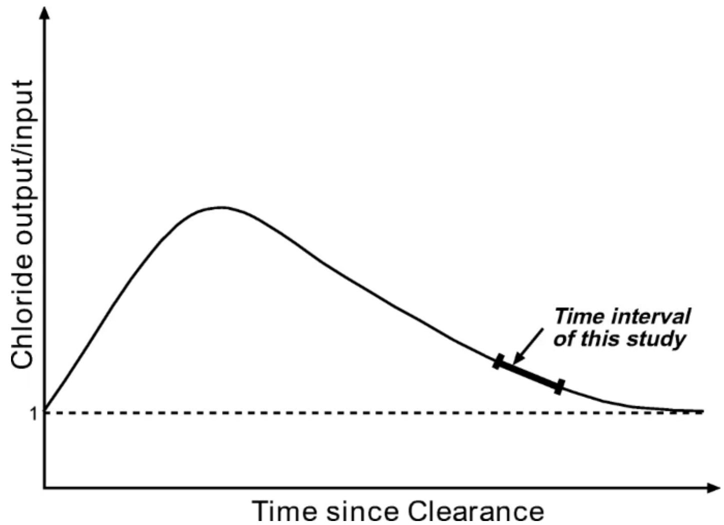

Figure 3.12: Conceptual model of chloride output/input ratio change following land clearing (modified from Jolly et al. 2001 and Guan et al. 2010a).

Findings from this investigation support findings by Guan et al. (2010a) who reported that catchments in the Mount Lofty Ranges with an annual rainfall of > 900 mm would have already reached equilibrium by the year 2008. Therefore, it is understandable that a catchment such as the SCC, with an average annual rainfall of 800 mm, would be approaching equilibrium by the year 2090. Although, Jolly et al. (2001) found that catchments in the Murray Darling Basin with annual rainfall of above 800 mm revealed minimal changes in their salinity balance. Furthermore, in the Murray Darling Basin, catchments with an annual rainfall of 500 – 800 mm displayed a rising trend in the salinity balance. However, these catchments were only analysed over a ten-year period from data collected 20 years prior to the last values in this current investigation. Furthermore, clearing began in the Murray Darling Basin several decades prior to clearing in the SCC (Walker et al. 1993). Therefore, various factors would come into effect causing this variation and for these reasons, the Murray Darling Basin of similar annual precipitation would understandably precede the SCC in the achievement of salinity equilibrium.

This study has determined that the SCC is returning to equilibrium in terms of salinity input/output following clearing of the native vegetation over one hundred years ago. Following clearing, increased recharge and water table rise has flushed stored salinity. Eventually, an equilibrium will be reached between salinity export and salinity deposition (Jolly et al. 2001). Then, as the salinity is leached from the system, the salinity drops until a new equilibrium is achieved.

3.4. CONCLUSIONS

Human-induced salinization, in particular dryland salinity, has had devastating impact on the hydrology of catchments in southern Australia and elsewhere. Notably, cases of salinity imbalance occurred following clearances of native vegetation. However, this study has focused on a catchment that is returning to a new salinity equilibrium. Following the land clearance at the SCC, evidence indicates that stored salinity is flushing into the surface water, driving the catchment to a new equilibrium. Two flushing mechanisms are envisioned: 1) the rising water table flushes salinity stored in the unsaturated zone and also flushes ambient groundwater, 2) increased recharge flushes salinity from the soil-regolith. Additionally, there is a considerable difference between the perennial and intermittent stream on site in the amount of salinity exported. Whilst the perennial Scott Creek had periods of salinity accumulation during dry months of certain years, the intermittent Mackreath Creek had entire drought years of salinity accumulation. Ultimately, this study reveals trends in salinity for this cleared catchment, using methods that are transferable to other catchments within the Mount Lofty Ranges and elsewhere.

The results presented here give conclusive evidence that the SCC is returning to a new salinity balance. Furthermore, it has revealed that despite the long-term variability in flow, salinity, and rainfall, significant trends were able to be determined. Thus, this study has exposed a decreasing trend in salinity with time, achieved through a multiple regression of a 28-year data set. Additionally, the amount of surface water salinity that originates from atmospheric deposition and that from stored sources was able to be determined. Three times more salinity derives from stored sources as affirmed by the chloride analyses. In fact, at the rate the salinity load is decreasing, an estimated new salinity equilibrium will occur by approximately 2090.

CHAPTER 4

4. MANUSCRIPT III: GROUNDWATER FLOW AND RECHARGE PARADOX REVEALED FROM BASE FLOW ANALYSIS OF PERMANENT STREAM DURING THE AUSTRALIAN MILLENNIUM DROUGHT (MT LOFTY RANGES, SOUTH AUSTRALIA)

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Anderson TA[1], Bestland EA[1], Wallis I[1,2,3], Kretchmer P[4], Soloninka L, Banks EW[1,2], Werner AD[1,2], Cendón DI[5], Pichler M, Guan, H[1,2].

Abstract: Catchment-scale recharge and water balance estimates are commonly made for the purposes of water resource management. Few catchments have had these estimates ground-truthed. One confounding aspect is that runoff and soil water inputs commonly occur throughout the year. However, in climates with strong dry seasons, base flow can be directly sampled. In an experimental catchment in the Mt. Lofty Ranges of South Australia, run-of stream hydrochemical parameters were monitored. In this Mediterranean climate during the Millennium Drought (2001-2009), the stream was reduced to disconnected groundwater fed pools. Two groundwater types were identified: 1) high salinity type from meta-shale bedrock with thick, clayey regolith and 2) low salinity type from meta-sandstone bedrock with sandy regolith. End-member mixing using silica and chloride concentrations and robust $^{87}Sr/^{86}Sr$ ratios reveal an apparent groundwater flow paradox as follows: According to chloride mass balance and spatial distribution of hydrogeological units, the low salinity groundwater type has seven times more recharge than the high salinity type. Over the 28-year record, low salinity groundwater contributed 25% of stream water, whereas high salinity groundwater contributed 2-5%. During the drought year, however, annual stream flow from the high salinity groundwater

contributed 50% whereas low salinity groundwater contributed 18%. High salinity groundwater dominated dry-season base flow during all years. The paradox can be resolved as follows: The meta sandstone terrane drains quickly following wet season recharge and therefore contributes little to dry season base flow. Conversely, the meta-shale terrane drains slowly and therefore provides stream-flow during dry seasons and drought years.

4.1. INTRODUCTION

Hydrochemical heterogeneity is common in permanent streams due to differing rates and chemical properties of groundwater, soil and surface water inputs (Bailly-Comte et al. 2009; Cartwright et al. 2014). During high flow conditions, stream waters become hydrochemically more homogenised due to the dominance of inputs to the stream from surface runoff and through shallow soil flow-paths, which tends to dilute groundwater inputs, masking subsurface origins of stream discharge. However, during low-flow conditions, it is possible to identify local groundwater input characteristics, especially when streams cease to flow leading to the formation of disconnected pools. The spatial variability of groundwater input can be characterised during these times.

In Mediterranean climates with their long, dry, hot summers, base flow generally sustains river flow during summer and autumn (Chen et al. 2006; Smerdon et al. 2012). Base flow is relatively straight-forward to sample and interpret in streams that fragment seasonally into disconnected pools (McMahon and Finlayson 2003; Bunn et al. 2006). For example, the greatest spatial variability in the hydrochemistry of two intermittent ‘dryland rivers' in Queensland, Australia, occurred during the no-flow period (Sheldon and Fellows 2010). In the intermittent Cressbrook Creek catchment (Australia), groundwater-stream interactions during both no-flow and flooding conditions were assessed by characterizing hydrochemical changes (King et al. 2014). These studies showed the importance of flooding for both recharge and maintaining groundwater quality.

Perennial streams are defined as having continuous surface flow, except in severe drought conditions (Meinzer 1923; Edwards et al. 2015). Most perennial streams do not have no-flow periods and thus base flow characteristics need to be inferred. Consequently, various methods have been utilised for the analysis of base flow. For example, groundwater influences on surface water resulted in higher alkalinity waters with stable chloride concentrations in the Girnock catchment, Scotland (Soulsby et al. 2007). Stable isotopes of water have also been used extensively for base flow characterisation, as groundwater is usually less enriched than surface water (Coplen et al. 2000; Hinkle et al. 2001). For instance, water isotopes were used to identify the hydrological processes that influenced spatiotemporal isotopic variations in groundwater and surface water in the Barlow-Ojibway Clay Belt, Canada (Rey et al. 2018). Here, precipitation, groundwater inflow, evaporation, and tributary mixing processes caused this variation. Furthermore, environmental tracers determined the discharge of groundwater recharged by rainwater to the Condamine River, Australia (Martinez et al. 2015). This variability indicated two distinct water types and confirmed groundwater discharge in the upper catchment.

Southern Australia experiences highly variable climatic conditions, including prolonged and intense droughts (Nicholls et al. 1997; BOM 2016; Freund et al. 2017). An example is the low rainfall period between 2001 and 2009, termed the "Millennium Drought", when south-eastern Australia experienced one of the worst droughts since European settlement (Murphy and Timbal 2008). In the years 2005-2006 in particular, numerous records were broken. For instance, inflows into the Murray Darling Basin (MDB) were the lowest on record (Murray Darling Basin Commission 2006) and extreme lowflows to reservoirs in the Australian states of Victoria and South Australia were reported (Murphy and Timbal 2008). The "Millennium Drought" provided a unique opportunity to investigate groundwater input processes to perennial streams.

The Scott Creek catchment in the Mount Lofty Ranges of South Australia is described as a perennial stream (James-Smith and Harrington 2002), although it ceased to flow during the extreme drought years of 2006-2007, when the stream was reduced to a series of disconnected groundwater-fed pools during summer and autumn. Stream water sampling during this time provided a rare opportunity to determine the characteristics and location of groundwater input to the stream through a spatiotemporal analysis using multiple lines of hydrochemical evidence.

In this study, groundwater contributions to Scott Creek are investigated using environmental tracers ($\delta^{18}O$, $\delta^{2}H$, $^{87/86}Sr$ and ^{14}C), major element concentrations and high temporal resolution flow, rainfall and evapotranspiration (ET) data. This study presents a novel application of stream and groundwater hydrochemical analysis under drought conditions. The current investigation builds on previous studies by combining high resolution flow and salinity data with multiple lines of evidence from various environment tracers. Furthermore, it combines the characterisation of seasonal hydrochemical and special variability in Scott Creek to catchment-scale recharge and groundwater types.

4.1.1. Study site

The Scott Creek Catchment (**Fig. 4.1**) has been the focus of numerous hydrogeological investigations. James-Smith and Harrington (2002); Harrington (2004a) and Harrington (2004b) investigated the hydrology and hydrogeology of the Scott Creek Catchment and found that there was considerable variation in the contribution of base flow and surface runoff to the stream. However, Werner et al. (2008) found that there was little groundwater recession on site. Bestland et al. (2009) documented the through-flow and lag-time characteristics of the contrasting soil types. This study found that the sandy soil overlying the sandstone-quartzite bedrock had a greater storage and longer lag time of through flow than clayey terrain overlying the shale of the catchment. Banks et al. (2009) and Bestland and Stainer (2013) recognized that flow through the fractured bedrock zone and deep clayey regolith of the shale terrain was an important contribution to groundwater/surface-water interactions within the catchment. Building upon these studies, Anderson et al. (2017) provided an understanding of a groundwater salinity hotspot originating in the clayey terrain and revealed the hotspot was discharging into the stream. Additionally, the study revealed that such hotspots could be a common occurrence within the region. Anderson et al. (2019) determined the origin and extent of salinity in water draining the catchment. The study determined that three times more water originated from stored sources than atmospheric sources.

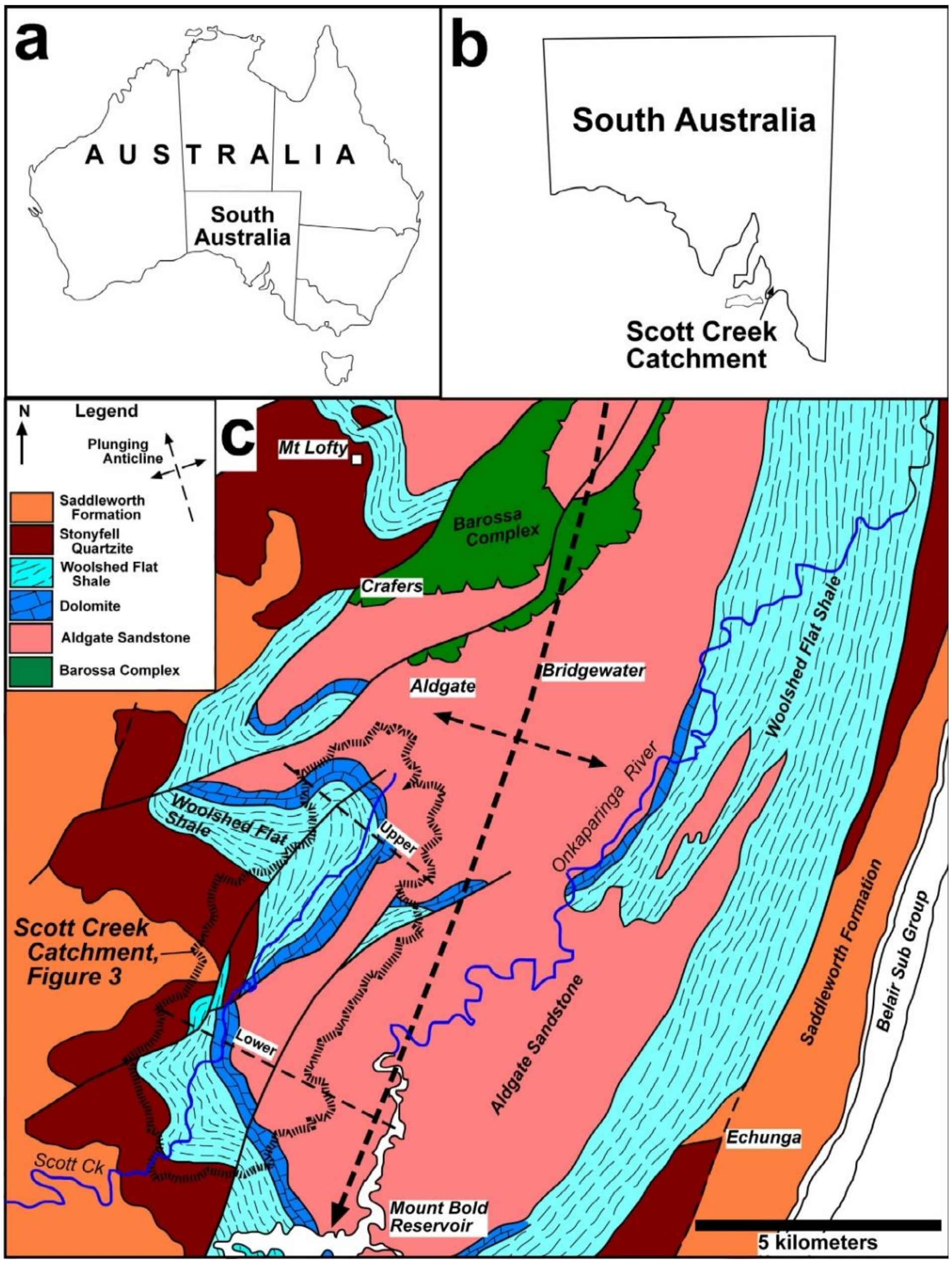

Figure 4.1: Location and geology of the Scott Creek Catchment.

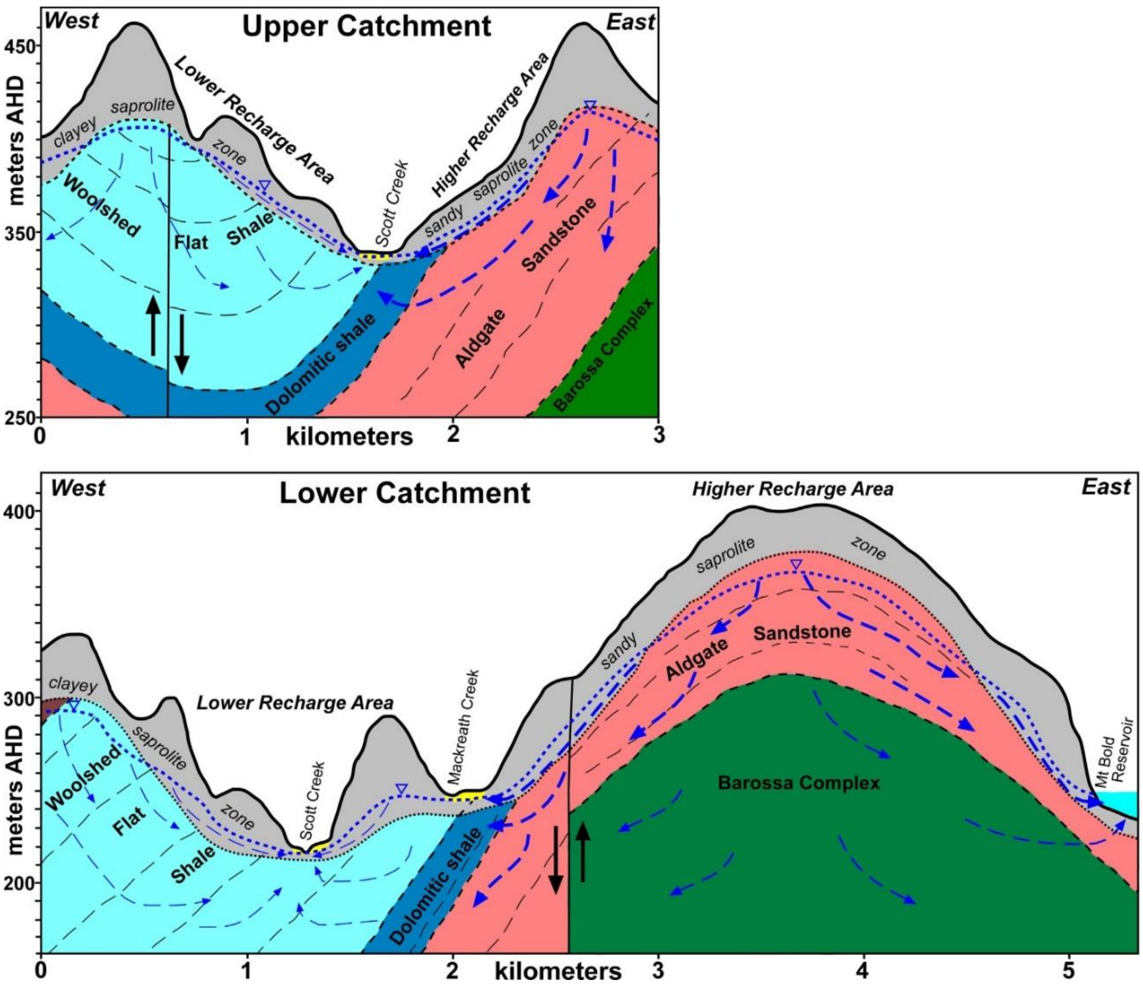

Figure 4.2: Hydrogeological cross-sections and conceptual groundwater flow model. Elevation is given in m AHD (Australian Height Datum), where 0 m AHD is approximately sea level.

The Scott Creek Catchment spans an area of 28 km^2 and is located approximately 30 km southeast of Adelaide, South Australia (**Fig. 4.1**) Scott Creek is approximately 10 km in length and flows in a southern direction, discharging into the Onkaparinga River. The lowest point of the catchment is at Scott Bottom (approximately 220 m AHD). At this location, six piezometer nests were installed in 2005 to monitor the groundwater processes in the soil, saprolite and fractured bedrock zones (Banks et al. 2009). Piezometers range in depth from 1.5 to 28.5 m below ground level. The six nests are positioned along a transect perpendicular to the creek, on an inferred groundwater flow path covering a distance of about 330 m. The construction details of each piezometer are depicted in Banks et al. (2009). A hydrometric monitoring station located at Scott Bottom reveals 8500 ML of annual flow on average over the years 1989-2016. Flow is highly seasonal, with 93% occurring between June and November, reflecting the Mediterranean climate of cool, wet winters and warm, dry summers.

Average daily temperature ranges from 8 to 14 °C in winter and 14 to 27 °C in summer. The catchment is in one of the highest rainfall zones in South Australia, receiving 1190 mm/y of rainfall on average at the top of the catchment in Stirling and 780 mm/y at the bottom at Mt Bold (BOM 2016). However, large intra-annual variability in rainfall in this area is common and influences catchment hydrology (Anderson et al. 2019). Typically, groundwater discharge sustains flow during the drier months (Harrington 2004b; Anderson et al. 2019) with winter wet season recharge causing the water table to rise between 1 and 2 m (Banks et al. 2009). However, during the extreme drought in South Australia of 2006, the catchment received less than 50% of the average annual rainfall (BOM 2016).

4.1.2. Geology

The geology of the Scott Creek Catchment and the Mt Lofty Ranges has been studied in detail (Preiss 1987; Banks et al. 2009; Bestland et al. 2016). The catchment is comprised of several metamorphosed sedimentary formations of Late Precambrian age belonging to the Adelaide Geosyncline. Stratigraphic units include the Woolshed Flat Shale, Stonyfell Quartzite, Skillogalee Dolomite, the Saddleworth Formation (including Glen Osmond Slate) and the Emeroo Subgroup (including Aldgate Sandstone and Bungaree Quartzite), in addition to recent alluvial deposits (Drexel et al. 1993). The Adelaide Geosyncline is a thick sedimentary basin that was folded and metamorphosed about 500 million years ago and later faulted and uplifted to its present elevation. Large-scale folds are evident from geologic mapping (**Figs. 4.1** and **4.2**). A series of much younger faults trending approximately north-south offset many geologic units (**Figs. 4.1** and **4.2**). For example, a fault separates the Aldgate Sandstone ridge line in the eastern half of the catchment with Woolshed Flat Shale on the western side of the catchment and forms an important hydrogeological boundary.

The western side of the catchment is predominantly comprised of Woolshed Flat Shale (**Fig. 4.1**). Banks et al. (2009) outlined three hydrogeologic zones that control groundwater flow at the Scott Bottom site. These are the soil zone (1.3 to 2.4 m thick), saprolite zone with weathered relict bedrock textures (1.3-2.4 to 6-18 m thick), and fractured bedrock zone deeper than 6-18 m). These three zone have very different hydraulic conductivities (0.045, 1.5, and 5 m/day on average respectively, (Banks et al. 2009) which results in large heterogeneity of the groundwater system (Harrington 2004a; Banks et al. 2009). Rock cores of the Woolshed Flat Shale at Scott Bottom reveal a grey laminated meta-siltstone with frequent pyrite and quartz veining to a depth of at least 165 m (James-Smith and Harrington 2002; Harrington 2004b). The regolith of the Scott Bottom site has been described as a deep, weathered bedrock saprolite zone of 15 m thickness (Cranswick 2005). The soils have reasonably distinct A, B and C horizons in the shale-dominated areas, with increasing clay content and decreasing organic content with depth (Banks et al. 2009).

Underlying the Woolshed Flat Shale is a relatively thin dolomitic shale unit (Skillogalee Dolomite) which extends in a generally north-south direction; roughly parallel with the stream. This band separates the Woolshed Flat Shale in the west from the Aldgate Sandstone in the east.

The eastern side of the catchment is predominantly Aldgate Sandstone, and the higher topography on the western side is Stonyfell Quartzite (Preiss 1987). These quartzite-dominated areas have deeply weathered profiles of sandstone with quartz-rich saprolite (Bestland et al. 2016). Macro-pores have been observed in the B horizon to depths of 2 m in quartzite areas, and rapid flow has been observed passing through them in a research trench following a large rainfall event (Milgate 2007). A sandy soil/saprolite zone overlays the sandstone-quartzite bedrock in most areas. However, areas with exposed rocky saprolite are common in the sandstone-quartzite areas (Bestland et al. 2009).

4.2. METHODS

4.2.1. Stream, soil and groundwater sampling

Run-of-stream surface water sampling was conducted along Scott Creek from below the weir at the Scott Bottom site (0 m) to approximately 8400 m upstream (**Fig. 4.3**). Sampling during three seasons: December 2006 (summer), March 2007 (autumn), and June 2007 (winter) was undertaken to characterise the seasonal variability in stream flow and base flow chemistry (**Table 4.1**).

Table 4.1: Scott Creek sampling sites. Electrical conductivity (EC) ranges are based on the three sampling periods between December 2006 and June 2007.

Site No.	Cumulative Distance (m)	Eastings	Northings	Site name	Geology	Location	EC range (μS/cm)
SC 18	8326	290765	6118790	Hale Dam (North)	Aldgate sandstone	Upper Catchment	450 – 990
SC 17	8091	290558	6118091	Hale Dam			580 – 1210
SC 16	7461	290256	6118191	Hale Dam (South)			680 – 1220
SC 15	6416	289713	6117463	Woodlands			770 – 1370
SC 14	5741	289273	6117034	Entry to Rainy's Creek			770 – 1400
SC 13	4226	288862	6116461	Exit of Rainy's Creek			700 – 1520
SC 12	3336	288649	6115667	Woods Dam *	Dolomitic shale	Mid Catchment	740 – 1670
SC 11	2746	288561	6115139	Mackreath Cottage Carpark			720 – 1390
SC 10	2176	288151	6114908	Natural Weir			750 – 2150
SC 9	2089	288079	6114890	Fallen tree			750 – 1630
SC 8	1434	287938	6114318	Almanda Spring Entry	Alluvial; Woolshed Flat Shale	Lower Catchment	760 – 1690
SC 7	744	287923	6113816	Mackreath Creek Entry			810 – 2580
SC 6	719	287982	6113679	Spring fed tributary			840 – 2590
SC 5	667	287970	6113628	Deep piezometer transect			840 – 2670
SC 4	637	287986	6113597	Burnt area			840 – 2600
SC 3	447	288014	6113347	Weir; Sam's Creek entry			850 – 2430
SC 2	340	287955	6113347	Transect			860 – 2430
SC 1	0	287633	6113300	Start of alluvial			870 – 2480

*SC 12 was the only location that reverted to a stagnant pool during the sampling period between December 2006 and June 2007, but was flowing during the June 2007 sampling period.

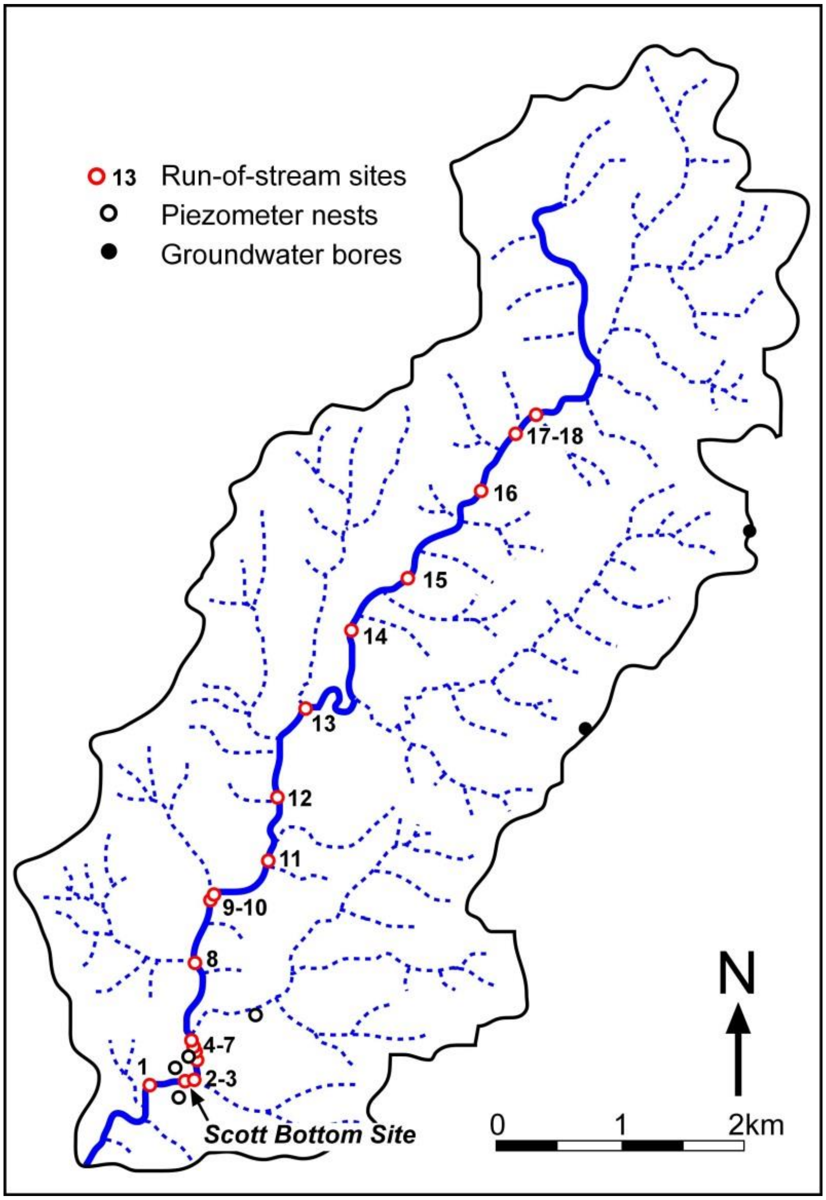

Figure 4.3: Location map of Scott Creek Catchment showing the run-of-stream sampling sites and groundwater bore locations. Hydrogeological cross-sections and conceptual groundwater flow model. Elevation is given in m AHD (Australian Height Datum), where 0 m AHD is approximately sea level.

Besides surface water samples, 18 open hole bores accessing groundwater in different geological units were sampled throughout the catchment, in addition to eight open bores at the Scott Bottom site, installed in

March–April 2002, reaching up to 96 m in depth (James-Smith and Harrington 2002). Shallow groundwater samples were collected from monitoring bores located at the Scott Bottom site.

Soil water was collected from three sites in the Scott Bottom and Mackreath Creek areas two in the sandy soil and two in the clayey soil (Milgate 2007). Each site was equipped with two interflow collectors and one overland flow collector. Overland flow collectors consisted of a 20 m by 20 cm plastic sheeting arranged into a V-shape to funnel water downhill. The sheets were placed 5 cm into the ground surface and were held in position by stakes every 2 m. Polyethylene tubing was attached to the lowest point collect water into a 25 L sample container.

Soil through-flow was collected using 2 to 3 m deep trenches dug at each site by a backhoe (long axis of the trench was downhill). Channels were dug to drain water from each trench as the landscape wetted up during the winter. Additionally, plastic tarpaulins enabled trenches to be covered and prevented direct contact of rainfall with the trench sidewalls. Therefore, these tarpaulins prevented erosion and subsequent contamination of through-flow samples. A ridge of dirt surrounded the upper parts of the trench to divert overland flow. The face of each trench (uphill side) was instrumented with two fibreglass wick through flow collectors with 0.16 m^2 area of soil contact at the two locations (A/B and B/C horizons). Through flow collectors were placed below the A horizons and B horizons at each site and connected directly by 45 mm holes drilled through the lid of the 25 L containers.

The pH, electrical conductivity (EC), dissolved oxygen (DO), redox, and temperature in the creek and during purging of the groundwater bores were measured using a handheld multi-parameter meter. A flow-through cell was utilised during groundwater measurements. After the collection of surface water, soil water and groundwater samples filtration through 0.45 μm membrane filters occurred in the field.

Surface water and groundwater samples were collected for major and trace elements, strontium isotope ratios ($^{87}Sr/^{86}Sr$), and the stable isotopes of water oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$). Water samples were transported for laboratory testing the same day as sampling and stored in glass McCartney bottles for the stable water isotope samples and plastic bottles for other analyses. Bottles were filled with no headspace and sealed with electrical tape.

4.2.2. Sample analysis

In total, 43 surface water and 7 groundwater samples were added to the extensive pre-existing data set as used in Banks et al. (2009), Bestland et al. (2009) and Anderson et al. (2017). Major and trace elements were analysed at Acme Analytical Laboratories, Canada, using Inductively Coupled Plasma Mass Spectrometry (ICPMS). Additionally, stable isotopes of oxygen and hydrogen were analysed at UC Davis Stable Isotope Facility, California using a Los Gatos Research Liquid Water Isotope Analyser. Standards were run every five samples to ensure correct calibration of equipment, which enabled an accuracy of 0.2‰ and 0.6‰ for $^{18}O/^{16}O$ and $^{2}H/^{1}H$ respectively. $^{87}Sr/^{86}Sr$ isotopes 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).

4.2.3. Data analysis

The compositions of water isotopes for samples collected during this investigation were compared with modeled values for water undergoing evaporation at a defined relative humidity in order to refine the estimate of potential evaporation from the surface water of Scott Creek. The chosen relative humidity value was 70%, which was the value that aligned best with the data and correlated with the relative humidity of the area (BOM 2016). A similar method was outlined in Cartwright et al. (2009) and Gonfiantini (1986) and used in Bestland et al. (2017).

Radiocarbon (^{14}C) of dissolved inorganic carbon of groundwater samples was analysed at ANSTO (Australian Nuclear Science and Technology Organisation) following methods in Cendón et al. (2014). Results are reported as de-normalised pmc (percentage modern carbon) values as recommended in Plummer and Glynn (2013), while the Pearson ($\delta^{13}C_{MIX}$) age is based on Skillolagee Dolomitic shale $\delta^{13}C$ values from (Foden et al. 2001).

4.2.3.1. Quantifying proportions of discharge to the stream

Three different methods were utilised and compared in this investigation to quantify the proportions of water types discharging to Scott Creek with the Scott Bottom hydrologic site as the reference point (SC 1-3, **Table 4.1**). These methods are: 1) the end-member mixing method, 2) the catchment-scale water balance method, and 3) the catchment-scale chloride mass balance method (**Fig. 4.4**). All three methods evaluated the contributions of three water types, identified on the basis of their distinct chemistry: 1) soil runoff/overland flow water, 2) high salinity (Woolshed Flat Shale) groundwater, and 3) low salinity groundwater (Aldgate Sandstone, Stoneyfell Quartzite, and Skillogalee Dolomite). These water types comprise the source waters contributing to the stream. All three of these methods have the same set of assumptions as follows: 1) all groundwater recharging in the catchment flows out the stream; i.e. there is assumed to be no groundwater export from the catchment other than via stream flow; 2) the catchment hydrogeology can be represented by two water types, i.e. high salinity (Woolshed Flat Shale) groundwater and the low salinity groundwater described above; and 3) these water types have been representatively sampled and their averaged hydrochemical characteristics are representative of these water types.

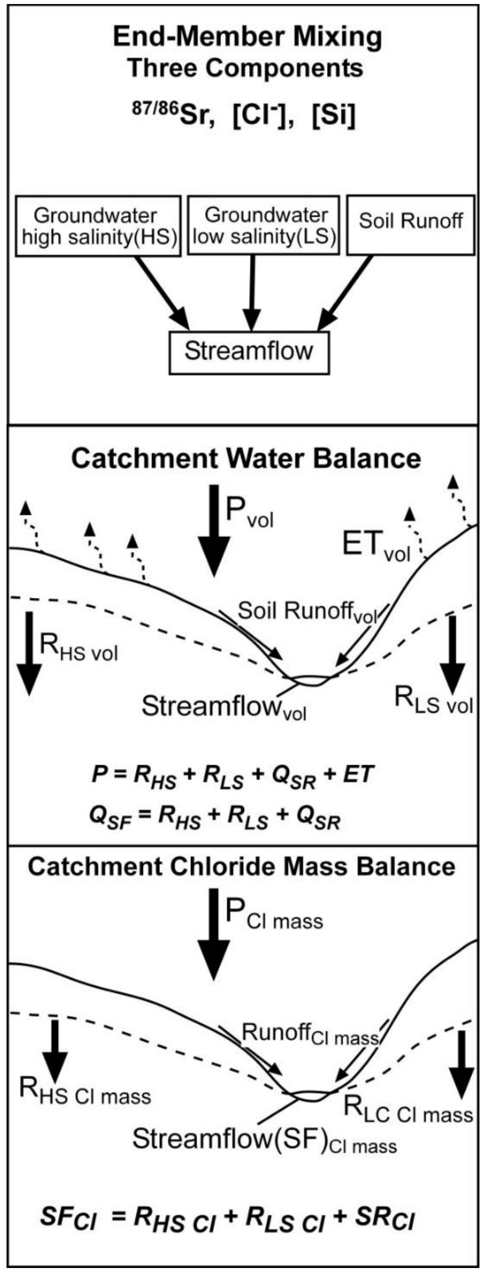

Figure 4.4: Diagrammatic representations of the three methods used to partition stream flow sources where P is precipitation, R is recharge, Q is discharge, SF is stream flow, ET is evapotranspiration, SR is soil runoff, HS is high salinity type groundwater and LS is low salinity type groundwater.

4.2.3.2. The end-member mixing method

The end-member mixing method estimates the proportions of water types contributing to stream flow on the basis of mass balance conservation (**eq. 1**) (Phillips and Gregg 2003; Phillips et al. 2005). IsoSource (EPA 2017) was utilised in this investigation to determine the contribution of the three end-member water sources (given above) which constitute the mix of water in the stream. Equation (1) calculates the three end-member components (isotopic ratio and concentrations) (∂) in order to partition their contributions (*f*) (denoted by subscripts HS, LS, SR) to the resultant stream water mixture (∂_{SF}):

$$\partial_{SF} = f_{HS}\, \partial_{HS} + f_{LS}\, \partial_{LS} + f_{SR}\, \partial_{SR}$$

$$1 = f_{HS} \ + f_{LS} \ + f_{SR} \ = 1 \qquad (1)$$

Equation 1 calculates the possible combination of source water proportions that sum to 100%, rounded to the nearest 1%. ∂_M is predicted based on the multiple combinations possible for f_{HS}, f_{LS}, f_{SR} feasible for ∂_M. Then, the predicted chemical make-up is compared with the observed hydrochemical characteristics and the solution is then optimised until observed and predicted characteristics are approximately equal (within 1%).

Analysis was based on $^{87}Sr/^{86}Sr$ ratios, Cl^- and Si concentrations. These isotopic ratios and elemental concentrations were chosen because they are the most robust parameters to characterise the three water types contributing to stream flow. There is significant variation between each parameter in the different water types at the Scott Creek Catchment. The $^{87}Sr/^{86}Sr$ isotopic composition of groundwater and surface water results from the degree of water-rock interactions combined with dilution from the original precipitation signature (Capo et al. 1998). There are clear and distinguishable $^{87}Sr/^{86}Sr$ isotope signatures in the Scott Creek Catchment (discussed below). Additionally, the conservative behaviour of chloride in the Scott Creek

Catchment (no halite is present in the regolith or bedrock) informs the degree of evapotranspiration. Furthermore, the Si concentration varies significantly between groundwater from different geological units and also between groundwater and surface water, with distinctively higher $^{87}Sr/^{86}Sr$ ratios found in the groundwater from sandstone units. The end-member mixing method was applied to each of the three seasons analysed (summer, autumn, winter) to assess seasonal variability in the discharge of water types to the stream.

In addition to estimating the end-member contributions to stream flow on a seasonal basis, stream water hydrochemical values were averaged on a flow volume basis to give annual mean stream flow values of the source water end-members. These results are compared to the results from the catchment-scale water and chloride mass balance methods. For these annual averaged calculations, the concentrations of Si, chloride, Sr, and the $^{87}Sr/^{86}Sr$ isotope ratios of a wide range of stream flow rates were correlated with the daily stream flow over the available 28-year flow record from the Scott Bottom site. Chloride concentrations were thereby estimated based on EC measurements (Anderson et al. 2019) on the basis of an EC/chloride relationship established for the Mount Lofty Ranges (Guan et al. 2010a). The correlation of hydrochemical concentrations and isotope ratios with daily stream flow revealed the following relationships (r^2 values): Sr concentration vs. $^{87}Sr/^{86}Sr$ isotope ratio (0.90), $^{87}Sr/^{86}Sr$ isotope ratio vs. daily flow (0.83), and Si vs. daily flow (0.67). Using these correlations, annual mean masses of Si and Cl^- were calculated as well as annual mean $^{87}Sr/^{86}Sr$ isotope ratios, which in turn allowed the estimation of the average annual contributions of the three water types to Scott Creek stream flow. Additionally, the Sr concentration vs. $^{87}Sr/^{86}Sr$ isotope ratio and the $^{87}Sr/^{86}Sr$ ratio vs. daily flow were used to estimate a mean ratio for spring 2006. This enabled a comparison between the estimated ratios of water types for spring to the ratios calculated using the end-member mixing method from the other three seasons.

Si and Cl^- concentrations of soil runoff/overland flow varied significantly (mean of 35 mg/L and standard deviation of 21 mg/L). Soil runoff/overland flow samples were weighted according to the area of the catchment underlain by sandy vs. clayey soils in order to produce representative catchment-scale values.

4.2.3.3. The catchment-scale water balance

The catchment-scale water balance method estimates the proportion of water types that contribute to stream flow utilising a water balance equation (Zhang et al. 2001; Zhang et al. 2008)

:

$$P_{L^3/T} = R_{HS} + R_{LC} + Q_{SR} + ET \qquad (2)$$

where $P_{L^3/T}$ = precipitation (L^3/T), R_{HS} = high salinity groundwater recharge (~~mass~~), R_{LS} = low salinity groundwater recharge (~~mass~~), Q_{SR} is overland flow plus soil interflow (soil water discharge to the stream), and *ET* is evapotranspiration.of surface water and interflow (~~mass~~). Long-term changes in soil water storage were assumed zero for this analysis as is reasonable to assume when considering long periods (i.e., decades) (Zhang et al. 2001). This method also assumes that groundwater storage does not change with time.

The volume of groundwater that annually discharges into the stream (*HS*+*LS*)from each water type was determined by calculating the area underlain by each major geological unit from the geological map (SARIG 2019) (**Fig. 4.1**) and multiplying this by the groundwater recharge (R_{HS}+R_{LS}) determined through the chloride mass balance equation:

$$R = \frac{P_{L/T} \cdot Cl_p}{Cl_{gw}} \qquad (3)$$

where *R* is groundwater recharge flux (volume per time per area) for each groundwater type (*HS* and *LS*), $P_{L/T}$ is average annual precipitation (volume per time per area), Cl_p is average chloride concentrations in precipitation and Cl_{gw} is the average chloride concentration in groundwater. Mean chloride concentrations for each groundwater type were based on EC measurements using the relationship between chloride and EC established for the Mount Lofty Ranges by (Guan et al. 2010a). Furthermore, a mean chloride concentration in precipitation for the Scott Creek catchment of 4.45 mg/L was averaged from bulk rainfall estimated for the area (Guan et al. 2010b).

The average annual evapotranspiration for the catchment was calculated using the MODIS global terrestrial evapotranspiration algorithm (Mu et al. 2011), with one ET value used for the entire catchment. It is acknowledged that there is inevitable inter-catchment variability in ET, however, this was neglected, as inherent uncertainty of ET measurements limits point-accurate estimates (i.e. ET estimations can vary by up to 30% within the same site depending on deployed methodology (Mu et al. 2011; Liu et al. 2013).

4.2.3.4. The catchment-scale chloride mass balance method

The catchment-scale chloride mass balance method estimated the proportions of water types that contributed to the stream using an adapted equation from Guan et al. (2010a):

$$P_{L^3/T} \cdot Cl_p = R_{HS} \cdot Cl_{HS} + R_{LS} \cdot Cl_{lS} + Q_{SR} \cdot Cl_{SR} \quad (4)$$

Concentrations of chloride (mg/L) from each source were averaged from the numerous samples collected. Recharge to the two groundwater types and the soil/saprolite zones (clayey and sandy) was calculated using **Eq. 3.** The recharge values for the soil/saprolite zones were based on the mean values of each unit.

Precipitation and evapotranspiration were estimated for use in **Eq. 2** and **4** using the following methods. Average annual precipitation in the Scott Creek Catchment was estimated from the closest pluviometer to the piezometers accessing the groundwater of each geological unit, i.e. the pluviometer from the nearby Mount

Bold Reservoir (801 mm/yr) for the WSF shale and from Aldgate (1062 mm/yr) for the low chloride groundwater area. These calculations were based on measurements over a 28-year period (1989-2016).

By assuming that all rainfall inputs of chloride are discharged via streamflow (SF) and are in steady state, where **Eq. 4** becomes:

$$P_{L^3/T} \cdot Cl_p = R_{HS} \cdot Cl_{HS} + R_{LS} \cdot Cl_{lS} + Q_{SR} \cdot Cl_{SR} = Q_{SF} \cdot Cl_{SF} \quad (4)$$

where $Q_{SF} \cdot Cl_{SF}$ is the chloride mass discharged from the stream at the outlet of the catchment.

4.3. RESULTS

4.3.1. Salinity and Water Isotopes

The summer of 2006-2007 (1st December 2006 to 28th February 2007) had the lowest recorded stream-flow (since 1969; SAW 2017) at approximately 10% of the average summer flow (SAW 2017). With no significant rainfall until late March 2007, the stream was reduced to stagnant evaporative pools well into autumn (1st March to 31st May, 2007) , leading to evaporative signatures in the run-of-stream salinity and water isotope data (δ^2H and δ^{18}O) (**Table 4.2**, **Figs. 4.5** and **4.6**). During March (autumn), salinity ranged from above 2600 μS/cm at SC 5 to approximately 1200 μS/cm at SC 18. Additionally, surface water data from December (summer) and March (autumn) display a large range in spatial variability of δ^{18}O and δ^2H values (**Fig. 4.6**). Stream samples from March (autumn) had the greatest range in spatial variability of isotopic enrichment. Notably, these varied in δ^{18}O from approximately -6‰ to nearly 1‰, and in δ^2H from almost -30‰ to above 2‰ (**Fig. 4.6**). However, June (winter) remained relatively constant and clustered amongst the more depleted samples, between -4‰ and -5 $\delta^{18}O$‰, and -24 and -29 $\delta^{2}H$‰ (**Fig. 4.6**). Also, during the winter wet season, salinity differed only minimally upstream to downstream from between 400 to 900 μS/cm.

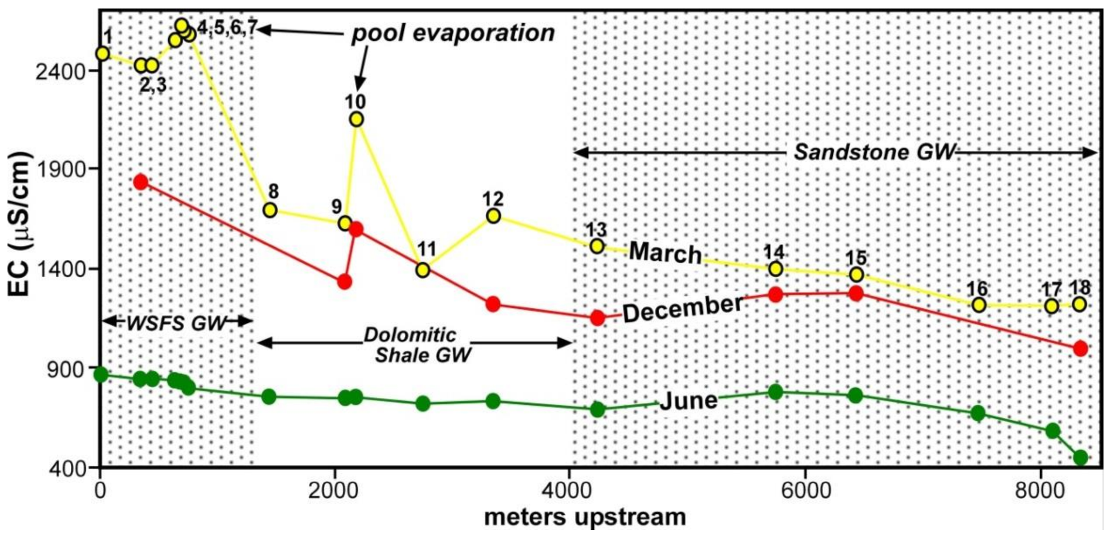

Figure 4.5: Run-of-stream seasonal changes in salinity for Scott Creek stream water sampled during 2006-2007.

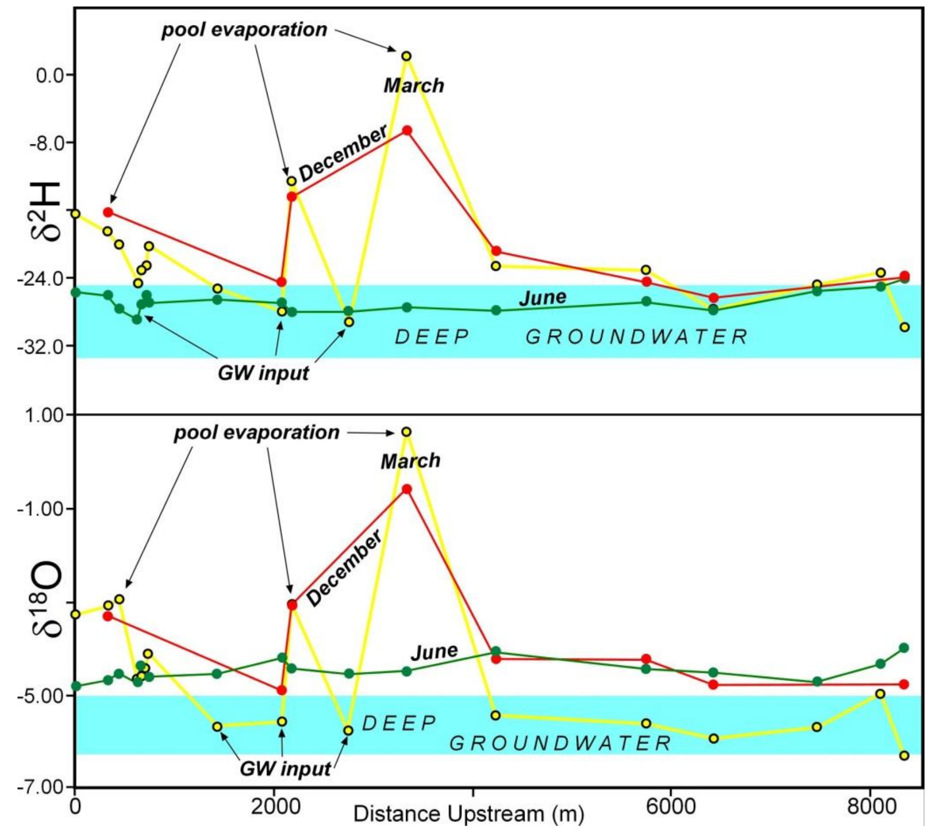

Figure 4.6: Run-of-stream season changes in δ ^{2}H versus δ ^{18}O for Scott Creek stream water sampled during the years 2006-2007.

The evaporative signatures at the Scott Creek Catchment reveal significant temporal variation (**Fig. 4.7**). The variation of δ^{18}O and δ^2H values of surface water and groundwater samples illustrate their relationship to the local meteoric water line (LMWL) for Adelaide (Hollins et al. 2018) and the degree of evaporation that occurs seasonally from surface water. Maximum isotopic enrichment of surface water occurred in one stream pool, which recorded an approximate 50% evaporation in March 2007. Conversely, the June values had negligible evaporation (<5%). The overland flow had a broad range of isotopic values illustrating variations in the isotopic composition of precipitation. Generally, the June stream water isotopes plotted between overland flow and the deep groundwater.

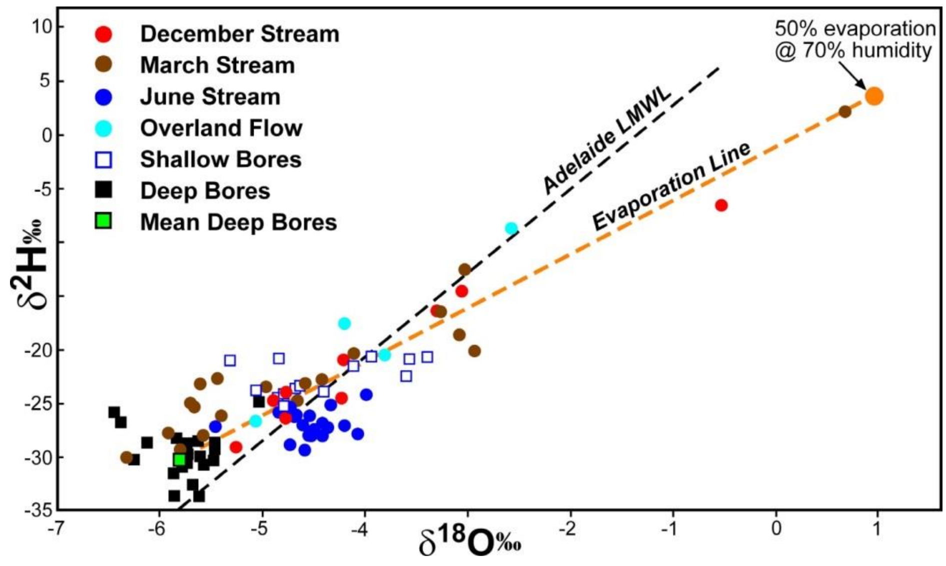

Figure 4.7: δ^2H versus $\delta^{18}O$ for stream-flow at Scott Creek sampled during the 2006-2007 drought and groundwater sampled between 2006 and 2013 at the Scott Bottom experimental site. The local meteoric water line (LMWL) is from (Hollins et al. 2018).

4.3.2. Elemental molar ratios

Major ion-to-chloride molar ratios of stream water through flow, overland flow, and groundwater allow for weathering reactions, ion exchange and biological uptake to be distinguished (Tweed et al. 2006; Currell and Cartwright 2011; Unland et al. 2014). These interactions cause variation spatially (**Fig. 4.8**) and with change in chloride concentration (**Fig. 4.9**). Sodium-to-chloride ratios in the sandy soil water reveal values as high as 4.9, indicating that Na is being added via weathering reactions resulting in ratios far above that of seawater. Likewise, silica-to-chloride ratios in sandy soils are high, again reflecting weathering reactions. In contrast, ratios of sodium-to-chloride and silica-to-chloride in the clayey soil water that are close to and below that of seawater-rainfall mixing suggest the preferential removal of Na from solution, most likely reflecting cation exchange in this thick clayey zone. Furthermore, most groundwater from the high salinity groundwater (Woolshed Flat Shale) indicate the preferential removal of Ca and Mg as chloride and salinity increase.

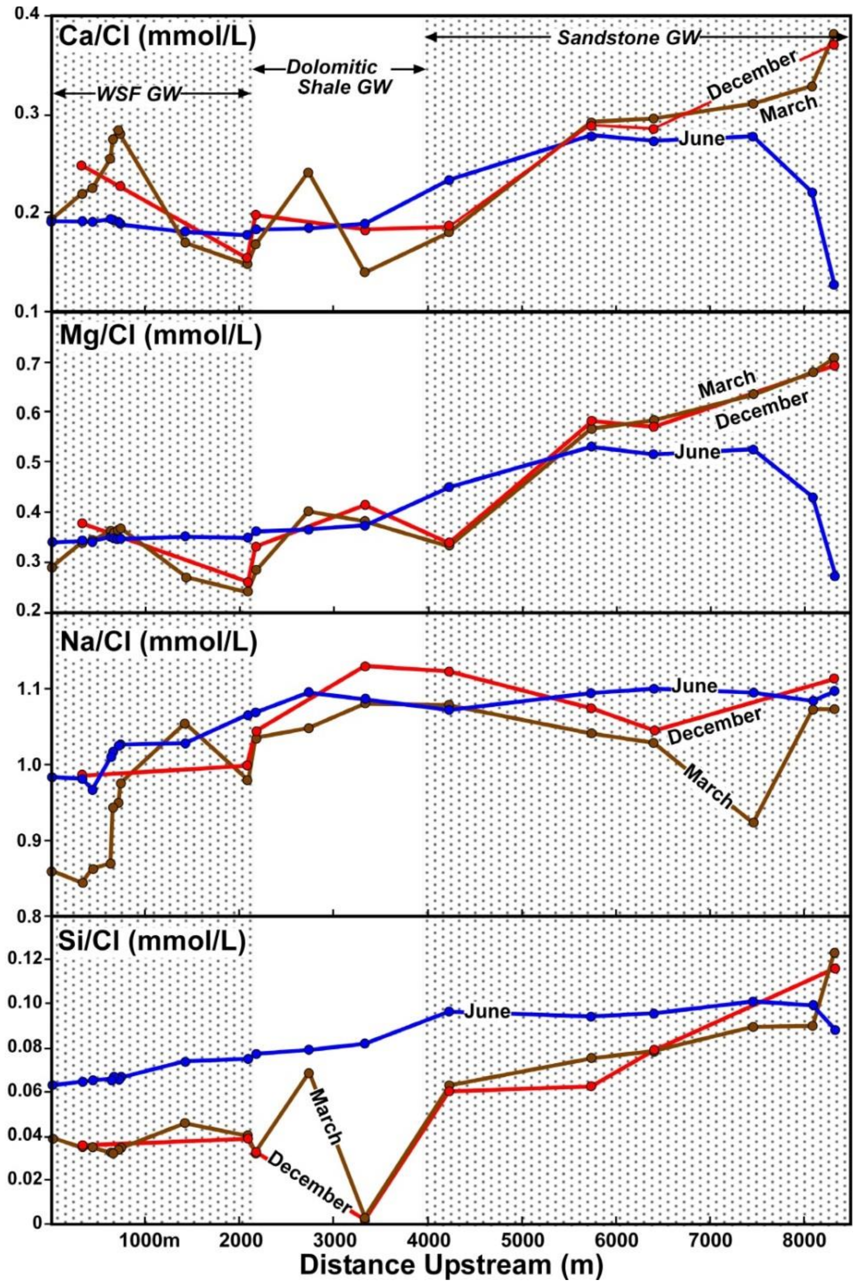

Figure 4.8: Run-of-stream plots of Ca/Cl, Mg /Cl, Na/Cl, and Si/Cl. Stream segments dominated by sandstone groundwater, dolomitic shale groundwater and Woolshed Flat Shale (WSF) groundwater are indicated.

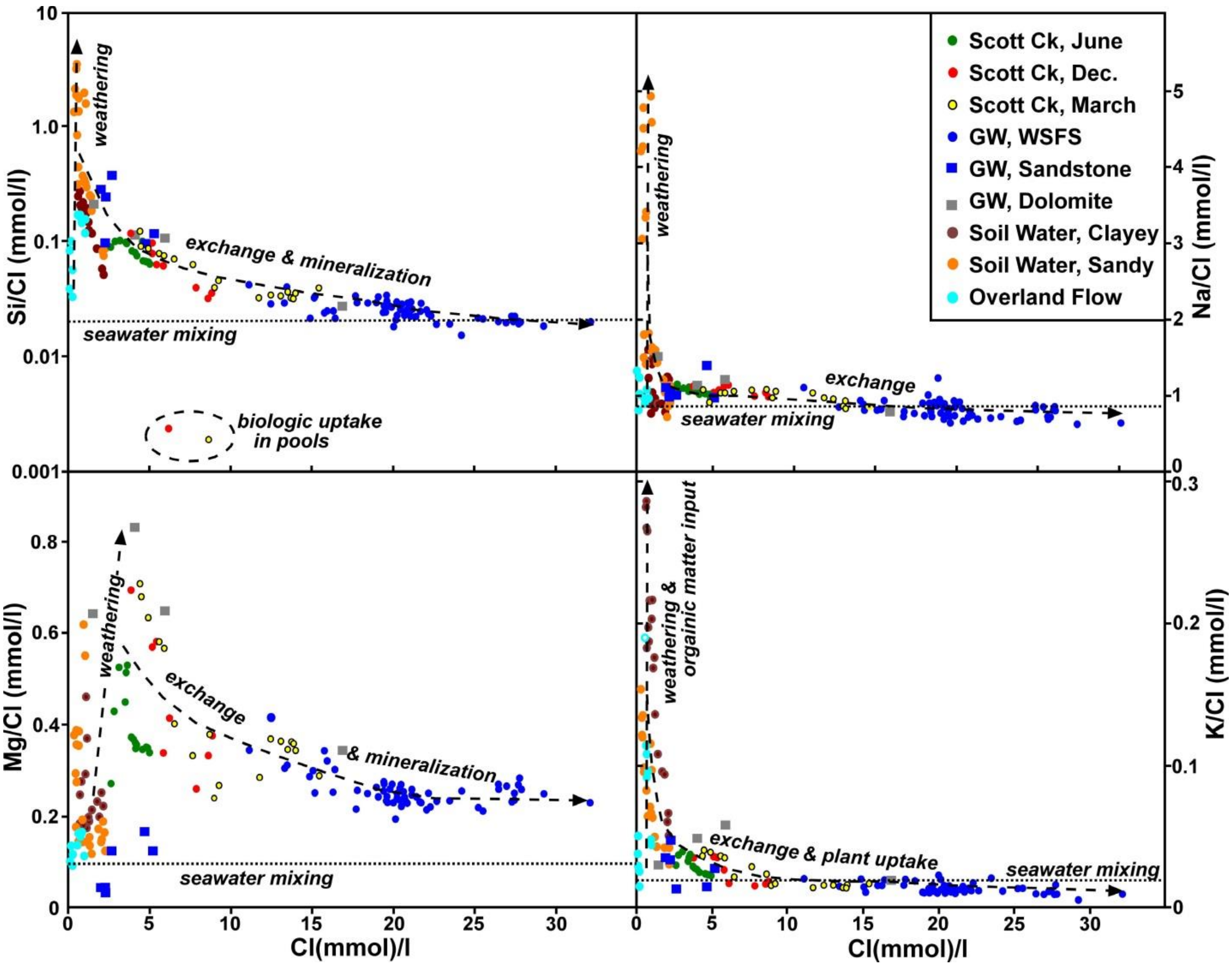

Figure 4.9: Scatter plots of Si/Cl, Mg/Cl, Na/Cl, and K/Cl against chloride concentration.

While stream evaporation will increase stream salinity, it is not expected to significantly change these ionic ratios. Thus, these ratios are useful in differentiating the effects of saline groundwater input to the stream and stream evaporation, both of which increase stream salinity. In this study, elevated Ca/Cl ratios (0.292-0.383 mmol/l) correlate well with locations where dolomitic influenced groundwater input to the surface water occurs (**Fig. 4.8**). This reflects a greater influence of groundwater and is more predominant towards the end of dry season and further into the drought period. In that, March has higher ratios than December (0.372-0.248 and 0.383-0.192 mmol/l, respectively). However, a decrease in Ca/Cl ratios occurs with an increase in salinity during December and March, which may reflect precipitation of calcite in the hyporheic zone, which would take Ca out of the surface waters. This is consistent with most stream samples being above calcite saturation (SI: 0.17-0.84) during these months at this location. Contrastingly, June data from the lower and upper catchment have lower Ca/Cl ratios (0.278 to 0.192 mmol/l) and therefore demonstrate soil runoff and surface water dilution. This is most evident in samples from far upstream sites.

High K/Cl ratios in the stream water of the upper catchment (not shown) can be attributed to a greater proportion of soil water input. Soil water samples have the highest K/Cl ratios (**Fig. 4.9**) with clayey soils having higher ratios than the sandy soils (up to 0.284 mmol/l compared to 0.156 mmol/l), reflecting the greater abundance of soil organic matter and exchange complex in the clayey soils. High K ratios can occur due to bioaccumulation by vegetation and soil organic matter. For example, K enrichment in soil was due to bioaccumulation and biocycling of K in soils in Western Australia (Liu et al. 2002). Furthermore, mineral transformations, which fixes K in the solid soil phase was revealed to be driven by K return to soil via litter decomposition (Tice et al. 1996). Poszwa et al. (2004) have attributed the accumulation of cations under trees to biocycling and depth of root uptake.

The Aldgate Sandstone unit constitutes the predominant geologic unit in the upper catchment, where the increases in K/Cl ratios and soil water input took place. The high Si/Cl ratios in the upper catchment (up to 0.116 mmol/l) are characteristic of the high quartz content of the geologic and soil units. In contrast, the minimal Si/Cl ratio in the evaporative pool, down to 0.00187 mmol/l at approximately 3,300 m in **Fig. 4.8** is hypothesized to be a result of biological (diatoms) influence. Diatoms incorporate Si especially during evaporation phases since additional nutrient loads provide suitable conditions for enhanced bioproductivity (Wolin and Stone 1999). Soil processes can be excluded from causing the Si concentration to decrease, as soil waters have high Si/Cl ratios and the Na and Mg ratios are not impacted (**Fig. 4.9**).

Overall, the major ion/Cl ratios exhibit distinct seasonal and longitudinal variations. Generally, variations in the hydrochemical compositions at each surface water site reflect differing local-scale groundwater and soil water input. Additionally, seasonal differences in observed ion/Cl ratios indicate dilution of groundwater during winter compared to its dominance during the low-flow periods. Thus, March stream water is indicative of high salinity groundwater input at Scott Bottom (**Fig. 4.8**). Conversely, June stream water samples indicate dilution from both soil water and the low salinity groundwater.

4.3.3. Strontium Isotopes

Differences in $^{87}Sr/^{86}Sr$ isotopic ratios of surface water and groundwater are caused by different $^{87}Sr/^{86}Sr$ isotope ratios released from weathering reactions of soil and rock mixing with Sr from atmospheric origins (Graustein 1989; Capo et al. 1998). Atmospheric sources of $^{87}Sr/^{86}Sr$ are dominantly of marine composition especially in coastal settings such as the Mount Lofty Ranges. Based on values of atmospheric $^{87}Sr/^{86}Sr$ isotopes from the nearby state of Victoria (Raiber et al. 2009), the $^{87}Sr/^{86}Sr$ of the Mount Lofty Ranges atmospheric contributions (dry deposition and rain) is assumed to be between 0.7093 and 0.7107. Rocks and minerals of the same age but with different Rb/Sr ratios develop different $^{87}Sr/^{86}Sr$ ratios because of ^{87}Rb decay (half-life = 4.92×10^{10} years) over time. Thus, a stream water's isotopic signature reveals the influence of groundwater interactions reflective of the geological units that it has flowed through. The ratios and concentrations from the Scott Creek Catchment groundwater were obtained from piezometers accessing the Woolshed Flat Shale, dolomitic shale, and Aldgate Sandstone. Notably, the Woolshed Flat Shale is highly weatherable and has high concentrations of Sr (34-139 ppm) and high ratios (0.7285 to 0.8159) (Turner et al. 1993; Foden et al. 2001). Conversely, the minerals constituting marine carbonates (such as the Skillogalee Dolomite) result in rocks with relatively high Sr concentrations and low Rb concentration (Paces et al. 2007). Therefore, the $^{87}Sr/^{86}Sr$ values inherited from ancient seawater will not change appreciably with time due to the lack of ^{87}Rb. As a result, carbonate units from the Adelaide Geosyncline have Sr concentration of 11-55 ppm and a ratio of 0.6814 to 0.7295 (Turner et al., 1993; Foden et al., 2001). Notably, these $^{87}Sr/^{86}Sr$ values constitute a mix of carbonate and silicate, and the silicate (shale) component is more radiogenic increasing this ratio above typical marine carbonate values. Additionally, the weathered sandstone within the catchment has low Sr concentrations and $^{87}Sr/^{86}Sr$ ratios (Bestland and Stainer, 2013).

These variations in Sr concentration and $^{87}Sr/^{86}Sr$ ratios of the geological units enabled groundwater to be identified and traced within the surface water system. The $^{87}Sr/^{86}Sr$ isotopic ratios of the Woolshed Flat Shale groundwater are much higher (0.738 to 0.754) than the groundwater from the Aldgate Sandstone (0.715 to 0.716) (**Figs. 4.10** and **4.11**), with the $^{87}Sr/^{86}Sr$ ratios in the Skillogalee Dolomite groundwater even lower at 0.7148 to 0.7151. These variations are easily distinguishable in the surface water, as the higher values indicate an interaction with the Woolshed Flat Shale groundwater, and lower values indicate an interaction with the Aldgate Sandstone and dolomitic shale groundwater with the exception of higher flow periods when there is dilution of groundwater fed stream water by low ratio surface water. Additionally, low $^{87}Sr/^{86}Sr$ ratios in the upper catchment coincided with high K/Cl, Ca/Cl and Mg/Cl ratios (**Fig. 4.8**), and therefore could be attributed to high rates of soil and saprolite water input in the upper catchment.

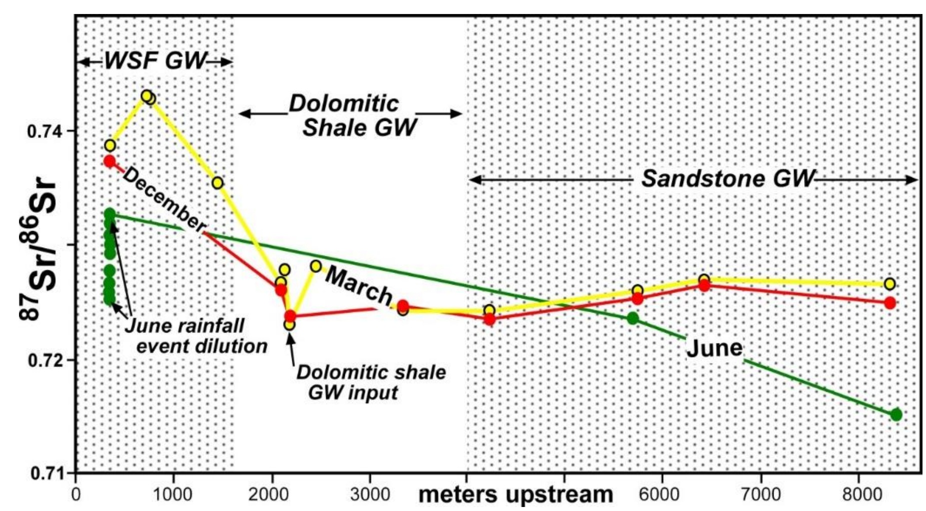

Figure 4.10: Run-of-stream changes in $^{87}Sr/^{86}Sr$ isotope ratios for Scott Creek stream water and groundwater sampled during the 2006-2007 at the Scott Creek Catchment. Data sourced from Anderson et al. (2017).

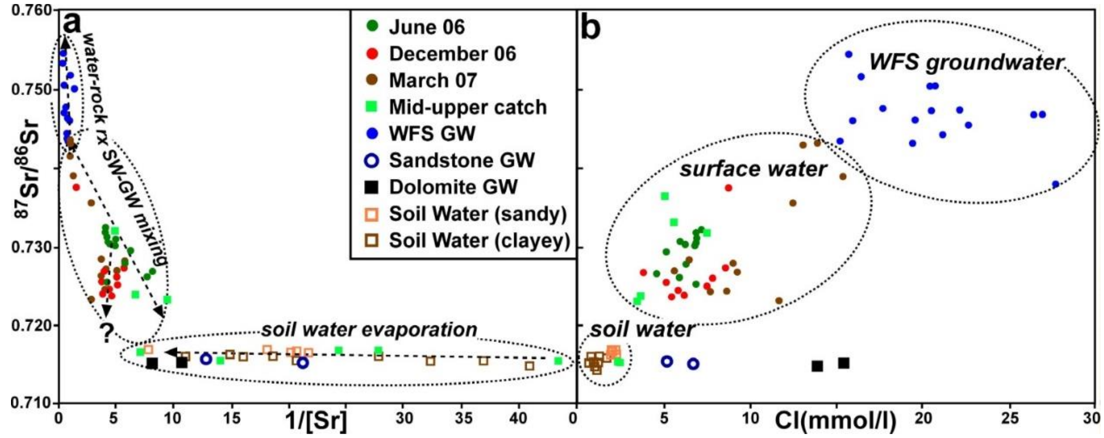

Figure 4.11: a) Variation of $^{87}Sr/^{86}Sr$ isotope ratios with inverse Sr concentration. Groundwater samples from both the Woolshed Flat Shale (WFS) and the Aldgate Sandstone and longitudinal surface-water samples at the Scott Creek Catchment from 2006 to 2007 are plotted. Data sourced from Cranswick (2005); Anderson et al. (2017). **b)** Variation of $^{87}Sr/^{86}Sr$ isotope ratios with chloride concentration. Groundwater samples from both the Woolshed Flat Shale and the Aldgate Sandstone and longitudinal surface-water samples at the Scott Creek Catchment from 2006 to 2007 are plotted. Data sourced from Anderson et al. (2017).

A small but noticeable variation in the $^{87}Sr/^{86}Sr$ isotope ratios is present between the clayey and sandy soil water whereby the sandy soil water has higher $^{87}Sr/^{86}Sr$ isotope ratios (0.7164±0.0002) than the clayey soil water (0.7155±0.0005). The higher clay and organic matter content of the clayey soils compared to the sandy soils creates a reservoir of exchangeable cations with lower $^{87}Sr/^{86}Sr$ isotopic ratios due to bio-cycling of atmospherically derived Sr. The soil organic matter as well as the soil exchange pool is commonly dominated by wet fall-dry fall sources mixed with parent material (Chadwick et al. 2009). In many soil-weathering systems, wet fall sources are dominated by marine sources from sea spray and dry fall sources are dominated by windblown dust (Derry and Chadwick 2007). In this current study, the $^{87}Sr/^{86}Sr$ ratios from vegetation on site ranged from 0.713 to 0.714 (**Table 4.2**). These low values are due to atmospheric sources dominating soil water and thus vegetation and the resulting soil organic matter.

In addition to the longitudinal variation in $^{87}Sr/^{86}Sr$ isotope ratios, seasonal changes were also present. Generally, the ratio of June surface water was lower than in March and December. Additionally, the June stream water plotted closer to soil water (**Figs. 4.10** and **4.11**) caused by dilution from overland flow and soil water during this period. Stream water from the lower catchment had much higher $^{87}Sr/^{86}Sr$ ratios in December and higher still in March. This reflected that the lower catchment almost exclusively sourced water from groundwater in the high salinity groundwater (Woolshed Flat Shale) during the drought. However, the isotopic ratio of the lower catchment in winter is indicative of a mixture between Woolshed Flat Shale groundwater and the low values from the low salinity groundwater and soil water/runoff. Stream waters from the mid to upper catchment have $^{87}Sr/^{86}Sr$ isotope ratios and Sr and chloride concentrations very similar to soil water/runoff. In addition, two groundwater samples from the dolomitic shale and two samples from the low salinity groundwater overlap in terms of $^{87}Sr/^{86}Sr$ isotope ratio and Sr concentration (**Fig. 4.11**). Si concentration was used to differentiate low salinity groundwater from soil water/runoff water types.

Notably, the $^{87}Sr/^{86}Sr$ isotope ratio from Wood's Dam at 3,300 m (a weir on the stream) revealed negligible variation between December and March sampling. Thus, this supports the conclusion that evaporation rather than further groundwater discharge is the major contributor to the salinity rise at the dam during March and December. Evaporation by itself would not change $^{87}Sr/^{86}Sr$ isotope ratios. Seasonal sampling of disconnected stream pools in nearby Clare Valley revealed similar findings (Bestland et al., 2017). Despite a large seasonal change in salinity in the Clare Valley pools, $^{87}Sr/^{86}Sr$ isotope analysis indicated the pools relied almost exclusively on groundwater with virtually no soil water/runoff contribution. Conversely, at the Scott Creek Catchment, $^{87}Sr/^{86}Sr$ isotope analysis demonstrates mixing between soil water/runoff and groundwater except during the late summer of an extreme drought year when the stream and pools approached the composition of the groundwater.

Overall, soil runoff/overland flow water is distinct in regards to its low $^{87}Sr/^{86}Sr$ ratios and low chloride concentrations, similar, but distinct from the groundwater encountered within the Aldgate Sandstone, Stoneyfell Quartzite and Skillogalee Dolomite. Contrastingly, the Woolshed Flat Shale groundwater has much higher chloride concentrations and $^{87}Sr/^{86}Sr$ isotope ratios than both the low salinity groundwater and soil runoff/overland flow.

4.3.4. Hydrogeological division of the catchment

The catchment was divided into three sub terrains based on variations in salinity, elemental hydrochemistry, $\delta^{18}O$ and $\delta^{2}H$ composition, and major geologic divisions. These consisted of 1) the lower catchment influenced by groundwater from the Woolshed Flat Shale accessed by nests of piezometers at the Scott Bottom site; 2) the mid-catchment influenced by the Skillogalee Dolomite and strong evaporation in the natural weir and farm dam; and 3) the upper catchment influenced by low salinity soil-runoff water and the Aldgate Sandstone groundwater. Of these areas, the lower catchment (0-1,500 m) had the highest salinities of above 2600 μS/cm in March at approximately 600 m upstream (**Fig. 4.5**). Additionally, the water isotopes were more depleted to nearly -5 $\delta^{18}O$‰ and below -24 $\delta^{2}H$‰ at 600 m, which coincided with the highest salinity of the stream. Additionally, a permanent seep exists on a hill slope adjacent to the stream at this location, approximately 5-7 m above stream level. This suggests that groundwater input is the main contributor to flow in the stream reach at Scott Bottom during the low-flow season. The seeps as well as the upward hydraulic gradient in the groundwater system in the valley bottom demonstrate that Scott Creek is a gaining stream. Because the groundwater of the Woolshed Flat Shale has moderate salinity, Scott Creek has a sharp increase in salinity between 1,500 to 600 m along the run-of-stream sampling points. The water isotopes from the lower catchment indicate that water in the stream has not undergone significant evaporation. Therefore, it is probable that the increase in salinity is due to groundwater discharge. Moreover, these results indicate that groundwater is the main contributor to increasing salinity in the lower catchment, which is in agreement with previous studies (Harrington 2004a; Banks et al. 2009; Anderson et al. 2017). Indeed, the research presented here further supports this conclusion by showing that $\delta^{2}H$ and $\delta\ ^{18}O$ values generally decrease in areas of significant salinity increase. Thus, these salinity changes are from groundwater input.

Unlike the lower catchment, groundwater input to the mid-catchment (1,500–4,200 m) resulted in lower salinity (**Fig. 4.5**). The mid catchment begins upstream of the Almanda Spring entrance to Scott Creek at 1,500 m. Between these sampling locations, the salinity levels and the water isotope signatures both contrasted markedly (**Figs. 4.5** and **4.6**). Evaporation in weirs and dams, as well as locations dominated by groundwater input cause this variation. Further upstream, groundwater discharge is noticeable at both 1,500 and 2,700 m and represented by low values of salinity and water isotopes. At these locations, salinity decreased to below 1,700 μS/cm and 1,400 μS/cm respectively in March. Additionally, evaporation in a natural weir caused water isotopes to enrich to -3 δ^{18}O‰ and -12.4 δ^{2}H‰ at 2,200 m, compared to as low as -6.8 δ^{18}O‰ and -29.9 δ^{2}H‰ in the upper catchment. Samples from March and December at SC 12 indicate that salinity increases occur due to evapo-concentration, given that the isotopic compositions enriched to the maximum recorded of 0.68 δ^{18}O‰ and 2.2 δ^{2}H‰, coinciding with a minor rise in salinity. This sampling location is downstream of a long and shallow in-stream farm dam (Wood’s Dam). The dam had no visible over-spill during fieldwork throughout these months (Kretchmer 2007), and was therefore assumed to have been a stable evaporative body. The peaks in salinity and water isotopes occurred in March and December but not June, where winter runoff diluted the signatures. Notably, water flowing from this location downstream reflected greater variance in salinity compared to that of the upper catchment.

The upper catchment (4,200 to 8,300 m) revealed relatively stable salinity and water isotope composition. The salinity was highest in March at between 1,200 and 1,600 μS/cm and lower in December ranging from 1,000 to 1,300 μS/cm. This salinity increase is caused by a lack of soil water flow later in the summer and autumn months. The most depleted sample occurred at the highest upstream location in March, and indicated groundwater input. However, in June, there was little variation in both the stream salinity and water isotope values, despite large variations in flow. During this time, the EC was between 400 to 800 μS/cm. This decrease in salinity was determined to be caused by soil water dilution and not a reduction in evaporation as there were minimal changes to the water isotope ratios. Therefore, the extreme low-flow condition during the dry season of the Millennium Drought has allowed the identification of base flow and groundwater inflow.

4.3.5. Carbon Isotopes

Stable and radiogenic carbon isotopes were utilised to evaluate residence time of groundwater flow paths as well as to determine the extent of dolomitic shale hydrochemical impact on the groundwater system (Kehew 2000; Appelo and Postma 2004; Cook and Herczeg 2012). In addition, stable and radiogenic carbon isotopes of dissolved organic carbon (DOC) from soil water and surface water as well as soil organic matter were used to evaluate the carbon isotopic fractionation in the hydrologic system.

The $\delta^{13}C$ values of DOC from soil and surface water reflect the C_3 vegetation that dominate the catchment and which have depleted values of between -24‰ and -29‰ (**Fig. 4.12a**). Using a value of -27‰ as an average, carbon dioxide generated from plant respiration, decomposing soil organic matter, and decomposing DOC in turn disassociates into bicarbonate with a isotopic fractionation to approximately -19‰, reflecting $\delta^{13}C$ values of bicarbonate in equilibrium with CO_2 gas at near neutral pH (Kehew, 2001). There is also an increase in $\delta^{13}C$ values down profiled in most soils and an overall fractionation of about 4‰ that is used in many groundwater studies (Cartwright et al., 2019). Values of groundwater $\delta^{13}C$ of between -11 to -14‰ indicates a further fractionation of carbon species and/or addition of higher ratio carbon derived from marine limestone. In parts of the groundwater system, dissolution of Skillogalee dolomitic shale has occurred resulting in heavier $\delta^{13}C$ signatures and lower pMC of the groundwater. Thus, in order to correct for dead carbon input to the groundwater, two $\delta^{13}C$ values from the Skillogalee Dolomite of +2.5 and +3.1 (Foden et al., 2001) were used for five of the groundwater samples thought to be impacted by dolomitic shale dissolution (**Table 4.2**).

Table 4.2: Radiocarbon and stable carbon isotopes results for groundwater samples collected from the Scott Bottom experimental site. Pearson correction used +2.5 and +3.1 $\delta^{13}C$ values from Skillogolee Dolomite (Foden et al., 2001).

Sample ID	**Date sampled**	**$\delta^{13}C$ per mil, 1σ error**	**pMC, 1σ error**	**Years BP, 1σ error**	**pMC not-normalised**	**Pearson ($\delta^{13}C_{MIX}$) correction**	**Pearson ($\delta^{13}C_{MIX}$) age with dolomite**
A1	13-Oct-17	-13.0+/-0.4	71.06±0.15	2,745±20	72.82	na	
A1	23-Mar-17	-14.0+/-0.1	73.46±0.17	2,480±20	75.13	na	
A2	10-Sep-17	-13.3+/-0.1	85.94±0.22	1,215±20	88.01	na	
A2	23-Mar-17	-11.0+/- 0.1	87.08±0.23	1,110±25	89.60	na	
B4	23-Mar-17	-13.3+/- 0.1	77.31±0.22	2,070±25	79.18	na	
B5	23-Mar-17	-11.4+/- 0.1	79.33±0.25	1,860±30	81.56	na	
C4	19-Mar-17	-13.6+/- 0.1	74.42±0.26	2,375±30	76.17	na	
F6	27-Apr-17	-14.0+/- 0.1	63.83±0.21	3,605±30	65.28	na	
MakA	19-Mar-17	-12.7+/- 0.2	65.92±0.23	3,345±30	67.59	0.76	997 (modern)
MakB	19-Mar-17	-15.4+/- 0.1	86.27±0.30	1,185±30	87.98	0.89	57 (modern)
MakC	19-Mar-17	-17.2+/- 0.2	93.47±0.32	545±30	94.97	0.97	158 (modern)
pn57835	21-May-17	-12.1+/- 0.4	35.84±0.12	8,240±30	36.79	0.74	5722
pn57883	21-May-17	-12.2+/- 0.1	49.01±0.15	5,730±30	50.31	0.74	3188

Piezometer nest Mak A,B,C was drilled into dolomitic shale (unpublished data E. Bestland) and as such has direct input from dissolution of dolomitic shale which results in an increasing trend of $\delta^{13}C$ values with depth and a decreasing trend of pMC with depth (**Fig. 4.12b** and **c**). Piezometer nest A1-A2 were sampled twice during 2017 and have both decreasing $\delta^{13}C$ values and decreasing pMC with depth. This piezometer nest is in a semi-perched, highly saline, locally restricted groundwater body which mixes downward with the ambient groundwater (Anderson et al., 2017). Thus, the decrease in pMC with depth in the A1-A2 piezometer nest is due to mixing of recently recharged water with longer residence time deeper groundwater. The decrease of $\delta^{13}C$ values in the A1-A2 piezometer nest is probably due to carbon isotope fractionation in the thick vadose zone that is widespread across this hilly area. Similar to nest A1-A2, nest B4-B5 has both decreasing pMC and $\delta^{13}C$ values with depth. Both of these piezometer nests have downward gradient flow.

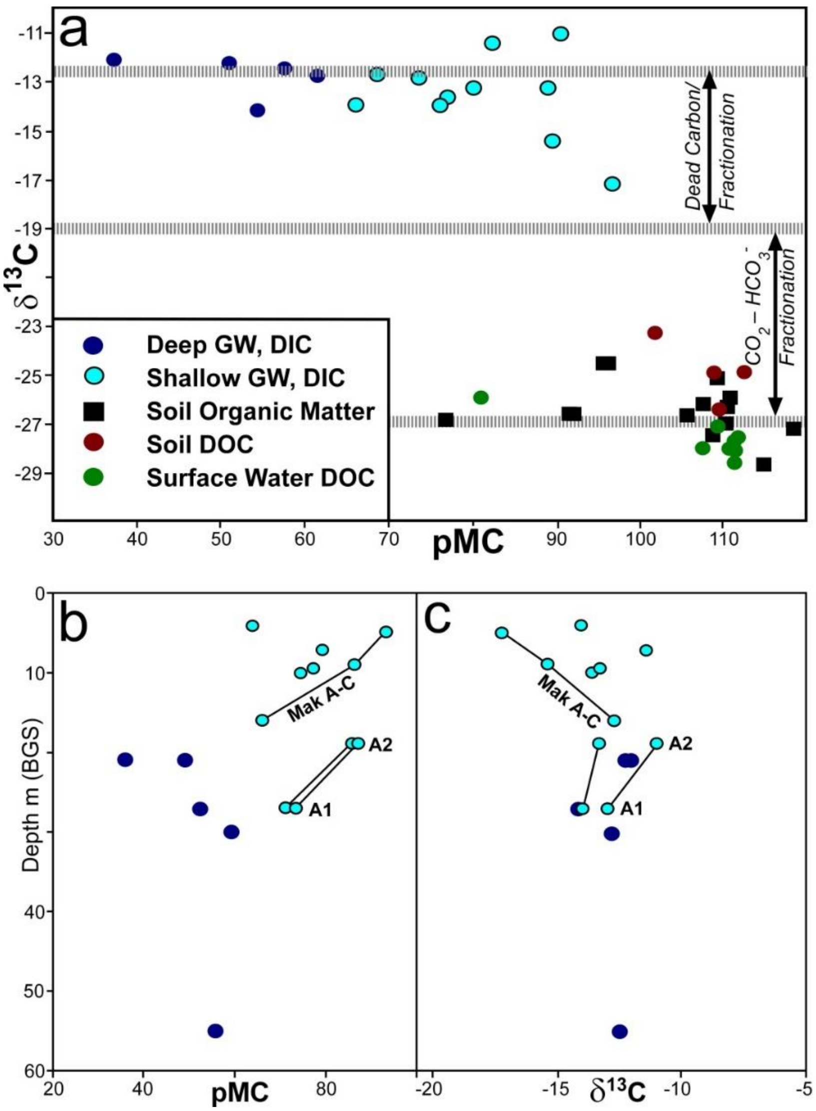

Figure 4.12: a) Percent modern carbon (pMC) versus $\delta^{13}C$ for groundwater and soil water sampled from the Scott Bottom experimental site in the year 2017. Two deep groundwater data points sourced from Harrington (2004b). **b**) Percent modern carbon (pMC) versus depth meters below ground surface. **c**) Stable carbon isotope ratio versus depth meters below ground surface.

4.4. DISCUSSION

4.4.1. Drought Impacts

The Millennium Drought inpacted the hydrodynamics and hydrochemistry of Scott Creek very significantly. The low-flow period allowed for groundwater-fed pools to be identified (Kretchmer 2007). The drought impacts are illustrated by run-of-stream salinity and water isotope (δ^2H and $\delta^{18}O$) data (**Figs. 4.5** and **4.6**). Higher water isotopic ratios reflected exposure to evaporation in soil, pools, and weirs; and decreases in water isotopic ratio reflected groundwater input (**Fig. 4.5**). The low variability in isotopic composition and salinity during high flow periods is a result of soil runoff dilution of groundwater input as well as mixing of stream water. The overall increase in salinity downstream during the winter wet season is due to higher salinity groundwater input in the lower half of the catchment. Thus, during the Millennium Drought, greatly reduced soil runoff and increased exposure to evaporation during the dry season caused a large seasonal contrast in the stream salinity. The findings from these years (2006-2007) were supported by the salinity increases displayed at site SC2 during the remainder of the Millennium Drought (Anderson et al. 2019)**.**

4.4.2. Groundwater surface water interactions

In southern Australia, winter rainfall has generally the most depleted water isotopes (Kayaalp 2001; Guan et al. 2010b) giving rise to more negative water isotopes in groundwater that is recharged during large winter and spring recharge events. Evaporation of stream water during the winter-wet period has little effect on the downstream salinity variation in Scott Creek. However, dry season downstream salinity changes are evident (**Fig. 4.5**). Anderson et al. (2017) found that evaporation in the Scott Creek Catchment did not significantly alter the salinity of surface water during wet season flow during the year 2012. Similarly, the findings from this study support this, as the water isotope composition of groundwater samples plot close to the LMWL for Adelaide. Therefore, these waters have altered little from their meteoric origin and are not significantly influenced by unsaturated zone evaporation or open water evaporation before infiltration. This is particularly evident in the June samples. During December (summer) and March (autumn), some data plots closer to the deep groundwater, inferring surface water is being sourced exclusively from groundwater during these months. Furthermore, this investigation supports the findings of Anderson et al. (2019) from Scott Creek. In that the export of historical salts from the groundwater rather than evaporation is a major source of stream salinity based on the differences in chloride values imported to the system via precipitation compared those exported through stream flow. Due to higher groundwater gradients during winter and spring, greater quantity of deep groundwater is being discharged to the stream during winter at the Scott Creek Catchment; however, due to the freshwater dilution salinities remain low (**Fig. 4.5**). By contrast, due to low-flow and low water tables, relatively less groundwater discharges to the stream during summer and autumn. Thus, evaporation increases salinity during these periods.

4.4.3. Groundwater residence time

The $\delta^{13}C$ isotopes in groundwater samples do not change significantly with changing pmc (**Fig. 4.12**). Deep groundwater samples from Scott Bottom site do not have significant dolomitic shale in their groundwater catchment and have pmc values indicating residence times of between 2000 – 8000 years (**Table 4.2**). Thus, as pmc decreases with no variation of $\delta^{13}C$ values, this indicates increased residence time along groundwater flow-path instead of addition of dead marine derived carbon.

4.4.4. Quantifying proportions of discharge to the stream

The proportions of the three different source waters discharging into Scott Creek were calculated based on three different methods of quantification (**Table 4.3**) (see methods section). The end-member mixing method is considered most accurate of the three methods due to directly balancing stream water with mass-balance mixing. During the drought year investigated, the end-member mixing method estimated the highest proportion of high salinity groundwater in the stream for all seasons investigated (winter 2006, summer

2006-2007, and autumn 2007). The most extreme drought season was autumn in which as much as 69% of the stream water had the hydrochemical signature of the high salinity groundwater. The catchment-scale chloride mass balance method estimated 14%, and the catchment-scale water balance estimated 1%. The catchment-scale water balance has no salinity parameter and the chloride mass balance assumes groundwater flow and stream water input result directly form recharge. In summary, the high salinity groundwater contributed more than twice the than the other two sources in autumn, and approximately 40% more in summer.

When the end-member mixing method is applied over the 28 year flow record using annual mean stream flow, elemental concentrations and $^{87}Sr/^{86}Sr$ isotope ratios, the proportion of the high salinity groundwater source is greatly diminished compared to the drought year and accounts for only 2-5%. In contrast, over the 28 year record, the low salinity groundwater contributes 21-30% and the soil runoff/overland flow contributes 68-74%. This 28-year record includes many high flow and very high flow periods when large volumes of dilute, soil runoff dominated water flowed through the catchment. The end-member mixing estimates over the 28 year record are roughly similar to the catchment-scale water balance albeit with greater input from both groundwater types. Both groundwater types have higher salinity than the soil water. Thus, these calculations are consistent with the catchment being out of chloride equilibrium (Anderson et al. 2019). In other words, according to these catchment-scale methods, there is more chloride discharging to the stream each year than is recharging to the groundwater. The overall water mass discharging from the catchment calculated using the catchment-scale water balance method (4302 ML) was comparable to the average annual streamflow calculated from time-series data (3490 ML) (Anderson et al., 2019), supporting the accuracy of the estimation.

Table 4.3: Average proportions of source water discharging into Scott Creek

		Stream Input (%)		
Method	**Period**	**Soil runoff / overland flow**	**Low salinity groundwater**	**High salinity groundwater**
End –member mixing method drought year	Winter (drought)	49-55	8-17	34-37
	Summer (drought)	29-36	21-32	39-44
	Autumn (drought)	5-12	19-30	65-69
	Spring (drought)***	45-47	1-6	47-49
	Annual (drought)	28-35	13-24	48-52
End-member mixing from flow record	Annual (flow record)***	68-74	21-30	2-5
Catchment-scale water balance method	Annual	87	12	1
Catchment-scale chloride mass balance*	Annual	59	30	10
Catchment-scale chloride mass balance (saprolite)**	Annual	26	27	47

*Recharge rates calculated from average groundwater concentrations from each groundwater type
**Recharge rates calculated from average concentrations in the regolith-saprolite zones (clayey and sandy)
*** Proportions of water types include values estimated based on correlations between hydrochemical parameters and daily flow

One cause of the variance in the proportion of water types estimated between the three methods is the flushing of historic salts from deeper groundwater sources (Anderson et al., 2019). The recharge was calculated from deep high salinity groundwater (Woolshed Flat Shale). The recharge estimate of 5.5 mm/yr for the high salinity groundwater and 40.3 mm/yr for the low salinity groundwater (**Table 4.4**) was based on the present salinity of the deep groundwater which contains historic salt, not in equilibrium with present catchment processes. However, the calculated recharge value is probably lower than the actual present day recharge because of land clearing of native eucalypt woodland which absorbs substantially more water through root-uptake than the succeeding short rooted pasture/crops. This occurs due to evapo-transpiration reduction and groundwater recharge increase following clearing of deep-rooted plants (Allison and Hughes 1983). Furthermore, such changes are occurring at the Scott Bottom site (Anderson et al. 2017; Anderson et al. 2019). Therefore, the recharge rates calculated for the regolith-saprolite zone are greater due to the increased recharge since clearing. Thus, the annual recharge rates may be more accurately represented by water with the Cl^- concentration of the regolith-saprolite zone.

Table 4.4: Estimated recharge from hydrogeological units to Scott Creek in the Scott Creek Catchment based on CMB.

Subsurface unit	Recharge (mm)
Woolshed Flat Shale	5.5
Aldgate Sandstone	40.3
Regolith-saprolite (clayey)	46.9
Regolith-saprolite (sandy)	68.8

The proportion of the two hydrogeologic units input to Scott Creek is much different when using recharge values from the regolith-saprolite zone groundwater, rather than the deep groundwater. Using regolith/saprolite values, the high salinity groundwater accounts for 47%, low salinity groundwater 27%, and 26 % from soil runoff/overland flow. Notably, these proportions are close to those based on the hydrochemistry of the stream during the Millennium Drought and the end-member mixing method. This indicates that the regolith-saprolite zone recharge values are much more representative of the source water contributing to the stream. The reason for the similarities is likely to be due to the regolith zone being closer to a chloride equilibrium, which is an assumption of the CMB method for groundwater recharge (Wood 1999).

The CMB method is useful in estimating catchment groundwater recharge in hilly terrains where hydrogeological conditions are complex (Wilson and Guan 2004). Additionally, it has been suggested to be the most reliable technique for determining recharge rates to fractured rock aquifers systems (Cook 2003). However, the applicability of the CMB method for this catchment is questionable as a new chloride equilibrium has not been reached in the Scott Creek Catchment (Anderson et al. 2019). Furthermore, estimated groundwater recharge can vary by an order of magnitude in southern Australia (Scanlon et al. 2006), the western Mount Lofty Ranges (Green and Zulfic 2008) and at the Scott Creek Catchment itself (Banks et al. 2009). Therefore, finding the correct estimate for recharge can be challenging. The deep groundwater would not accurately represent recharge in this catchment because it is not in a new chloride equilibrium and would represent preclearance conditions. Alternatively, the Cl concentrations of regolith-saprolite would more likely to have reached a new equilibrium under the current post clearance conditions.

Thus, it may represent the best estimation of recharge rates and the consequent estimate of the proportions of source water. This current investigation supports the reliability of using the regolith-saprolite zone as it established similar values to the hydrochemical composition of the stream.

The overestimation of salts from the regolith-saprolite zone is a likely explanation for the variation in source groundwater within Scott Creek. Another explanation could be that the water from the Aldgate Sandstone in the upper catchment could be seeping into another catchment through 'groundwater flow piracy' (e.g. Schorghofer et al. 2004; Adel 2012). Groundwater piracy occurs when the largest valleys in a landscape attract groundwater recharged in a neighbouring catchment. Gravity directs groundwater to these valleys, as this is the lowest point of the landscape. The lowest point surrounding the Scott Creek Catchment is the nearby Onkaparinga River valley at 243 m AHD. The Onkaparinga River could be in contention for attaining some of this groundwater, thus could also contribute to the lack of representation of the low salinity groundwater in the Scott Creek Catchment because the eastern side of the Scott Creek catchment is dominated by this rock type (**Figs. 4.2** and **4.3**).

The proportion of stream flow originating from the high salinity groundwater based on the 28 year flow record is 2-5%. During the drought year of 2006-2007 this proportion increased to about 50%. This very large difference between the mean proportion over many years and what was observed during the drought year necessitates an explanation. The following conceptual model is the preferred interpretation. The upper half of the Scott Creek catchment is dominated by quartzite and dolomitic shale whereas the lower half is dominated by the Woolshed Flat Shale, a metamorphosed shale. Overall, the upper catchment has higher recharge, higher permeability and hydraulic conductivity saprolite/regolith zone whereas the lower catchment has much lower recharge and clayey, thick saprolite/regolith zone with very low hydraulic conductivity. During normal rainfall and stream flow years, stream flow is dominated by soil/runoff, with groundwater from the low salinity groundwater (quartzite and dolomitic shale) at 25% and groundwater from high salinity zone at 5%. The groundwater flow system is envisioned as having a deeper slow-flow-path and a shallow, quick response system where groundwater flows through saprolite and regolith into the stream. An important parameter of the quick response system is the increase in water table head of several meters that occurs during the wet season. When the groundwater head decreases later in summer and into autumn, the shallow quick flow system slows down resulting in decreased flow to the stream. This leaves the deeper slow flow-path to dominate the base flow input to the stream. In addition, it is envisioned that groundwater recharged into the deeper system from the quartzite-dolomitic shale terrain, is hydrochemically overprinted during the slow flow through the meta-shale. Because the quartzite is hydrochemically poorly reactive and the meta-shale more reactive, groundwater is overprinted and mixed with higher salinity groundwater type.

4.5. CONCLUSIONS

Perennial streams rarely become exposed to no-flow conditions. Thus, the occurrence of an extreme drought provides a rare opportunity to determine the detailed hydrochemical characteristics of groundwater input to such streams. Additionally, the chemical characteristics of the surrounding geological units and soil types can be identified in the catchment in order to delineate catchment water types. This study has documented the connection between these geological units and the seasonal variation of the stream. Markedly, the Scott Creek Catchment documented here has revealed stark contrasts between sampling locations undergoing groundwater recharge and evaporative processes. These processes were prominent in no-flow conditions, whereas, the usual flow conditions would have otherwise masked them. In undertaking this study, local scale anomalies, such as specific biological influences could be identified. Thus, understanding these factors altering the hydrochemical characteristics of the stream during no-flow periods can assist in better understanding the sustainability of these water resources.

The results presented here examine the intricate details of the vast spatiotemporal variation in the perennial Scott Creek. During the Millennium Drought, the lower part of the catchment was almost exclusively sourced from surrounding groundwater in the Woolshed Flat Shale. However, during the higher flow period this water was diluted to a mixture of the less saline groundwater from Aldgate Sandstone of the upper catchment and dolomitic shale of the mid-catchment. Additionally, evaporative trends and low saline groundwater input were revealed in the mid-catchment when the stream was disconnected into groundwater-fed pools during the drought. The upper catchment revealed a stronger influence from soil water even during the drought. Contrastingly, water tables in the upper catchment had risen during higher flow periods, to a level that the Aldgate Sandstone groundwater-dominated the steam.

This investigation addresses the paradox as to why the hydrochemical signature of the Scott Bottom site is so dominated by the Woolshed Flat Shale groundwater. The higher recharge rates and higher percentage of the catchment represented by the Sandstone bedrock would dictate a greater proportion of water mass within the stream. Notably, the variance is believed to be due to the catchment being in the process of returning to a new chloride equilibrium. In that, historical salts are still flushing from the catchment and therefore the Cl^- mass discharging into the stream would differ from the mass recharging the catchment. Additionally, there would be an overestimation of salts from the regolith-saprolite zone due to increased recharge and reduced evapotranspiration since land clearance within the catchment. This zone proved more representative for recharge of the catchment as it was closer to a state of equilibrium than the deeper groundwater.

CHAPTER 5

5. CONCLUSIONS

5.1. RESEARCH AIMS ADDRESSED

This research body successfully addressed the majority of research aims intended. Analyses of high resolution salinity and flow data and environmental tracers (radiocarbon, strontium, and water isotopes; and major and trace elements) established a thorough understanding of solute dynamics within the Scott Creek catchment, South Australia.

Chapter 2 explained the hydrochemical interactions and solute dynamics between an intermittent stream and groundwater system at the Scott Bottom sub–catchment. Analyses demonstrated a connection between a groundwater salinity hotspot, the intermittent Sam's Creek, and the dominant groundwater system. The cause of a late–season salinity increase in Sam's Creek was interpreted as flushing of stored salinity after a historical eucalypt forest clearance and consequent increased recharge. Additionally, the probable origin of the groundwater salinity hotspot was 1) a restriction of recharge through the thick clayey soil–saprolite zone, 2) the rise in water–table and stored salinity post land clearance, and 3) the accumulation of salinity from transpiration. However, the extent of the hotspot still requires further research, which is discussed in detail in section 5.3.

Increased recharge and flushing of accumulated salinity from land clearing were again deemed a major cause of salinity changes at the Scott Creek catchment in chapter 3. The investigation of this chapter evaluated catchment salinity input/export and determined a trend of decreasing salinity over a 28 year period. Evidence indicated that saturated and unsaturated stored salinity was flushing into the surface water, driving the catchment to a new equilibrium. Salinity accumulation occurred in the catchment during some drier months in the perennial Scott Creek and entire drought years in the intermittent Mackreath Creek. However, an estimated new salinity equilibrium in Scott Creek could occur by approximately 2090.

Furthermore, chapter 3 determined the proportion of surface water salinity originating from atmospheric deposition and stored sources. Markedly, this analysis revealed three times more salinity derived from stored sources. Thus, reforestation could increase salinity and reduce surface water flows because the native vegetation would reduce recharge and salinity flushing.

All chapters related the Scott Creek catchment's hydrochemical interactions and solute dynamics to returning to salinity equilibrium post land clearance. However, only chapter 4 utilised this understanding to interpret the paradox as to why the meta–shale (not sandstone bedrock) groundwater dominates this hydrochemistry. One would expect the sandstone bedrock groundwater to influence the hydrochemical signature more, as it covers nearly twice the area and receives considerably more rainfall. The catchment's salinity disequilibrium explained the contradiction. The discharged instream chloride is more significant than that of chloride recharged to the catchment during the disequilibrium. Thus, increased recharge and reduced evapotranspiration would flush stored salinity from the meta–shale post land clearance. Critically, base flow sustains streamflow in Scott Creek during dry seasons. The meta–shale terrane drains slowly, providing most of this base flow. Conversely, the sandstone bedrock terrane contributes little to base flow as it quickly drains the recharge. Hence, the meta–shale groundwater dominates the stream's hydrochemistry due to this contribution to base flow.

Chemical and structural differences between the geological units draining the catchment were valuable in characterising water types that determined different sources contributing to streamflow during different periods. This study documented the connection between these geological units and the seasonal variation of the stream. Woolshed Flat Shale, Aldgate Sandstone, and Dolomitic Shale characterised the groundwater flow system. Notably, this investigation revealed contrasts between sampling locations undergoing groundwater recharge and evaporative processes.

This investigation determined differences in stream chemistry between a period of extreme drought and regular streamflow periods. Woolshed Flat Shale groundwater almost exclusively sourced the lower part of the catchment during the drought. However, during higher flow periods, this water diluted to a mixture of the less saline groundwater from Aldgate Sandstone of the upper catchment and dolomitic shale of the mid–catchment. Even during the drought, the upper catchment revealed a more substantial influence from soil water. Contrastingly, water tables in the upper catchment rose during higher flow periods, to the extent that the Aldgate Sandstone groundwater–dominated the steam.

5.2. SUCCESS OF METHODS TO ADDRESS RESEARCH AIMS

The various environmental tracers and high resolution parameters utilised in this project provided multiple revelations. To clarify, each method employed throughout the research body offered a different role to address, or complement other methods to address the research aims. Ion to chloride ratios, strontium isotopes, salinity balance, high resolution data, and carbon isotopes all contributed to the success of the research.

Ion to chloride ratio analyses determined the sources of water that contributed to streamflow and influencing factors within these sources (chapters 2 and 4). Specifically, water–rock interaction, cation exchange, and geological and biological characteristics identified and influenced the chemistry of these water sources. In addition, the elemental signatures of these water types are distinctly different, which enabled the identification of mixing between water types. For example, ratios correlated mixing between the upslope saline groundwater lens and the salinity rise in the intermittent Sam's Creek in chapter 2. Additionally, analysis of the ratios indicated which water types contributed to streamflow during each season investigated in chapter 4.

In addition to ion to chloride ratios, strontium isotope analyses helped classify different water types contributing to streamflow and the mixing dynamics within the catchment. Both hydrochemical signatures revealed great contrast between different water types, making them valuable resources in the investigations of chapters 2 and 4. Notably, the upslope saline groundwater hotspot investigated in chapter 2 has low $^{87}Sr/^{86}Sr$ isotope ratios. These ratios indicated that the groundwater in the hotspot is soil–derived, which was critical in determining the origin of the hotspot. In addition to the mixing relationships found using ion/Cl^- ratios, strontium analyses quantified the relative proportions of groundwater types contributing to the streams in chapters 2 and 4. Analyses of strontium isotopes in chapter 4 were integral in identifying and quantifying the discharge proportions from different water types to Scott Creek. The $^{87}Sr/^{86}Sr$ isotope ratios identified significant longitudinal and seasonal variation. For example, stream water from the lower catchment had higher $^{87}Sr/^{86}Sr$ ratios during drier periods and correlated to the groundwater signature of the Woolshed Flat Shale. However, the lower catchment's isotopic ratio in winter indicated mixing with low salinity groundwater and soil water/runoff.

Unlike the previously mentioned environmental tracers, analyses of the stable isotopes of water were instrumental in distinguishing evaporative trends within the catchment. The investigation in chapter 2 suggested groundwater recharge caused salinity variation in Sam's Creek, not evaporative enrichment. Furthermore, salinity in the unsaturated zone concentrated by transpiration (not evaporation) contributed substantially to the high salinity groundwater in the perched groundwater lens. However, water isotope ratios in chapter 4 determined much more significant evaporative trends in Scott Creek during the drought. Water isotope analyses complimented strontium analyses in determining the proportion of water types in the stream during different seasons. However, water isotope ratios were critical for distinguishing how extreme drought differed from periods where the atmospheric signature dominated stream chemistry. More enriched water isotope ratios identified soil, pools, and weirs exposed to evaporation during the drought. In contrast, depleted isotope ratios reflected groundwater input, and low variability in ratios revealed a dominance of precipitation and soil runoff in the stream during winter.

Environmental tracer data addressed many aims of this research. However, high resolution flow and salinity data were crucial in determining the mass of salinity input and export from the site in chapter 3. Markedly, the high resolution data provided the first statistically significant evidence that the catchment is returning to a new salinity equilibrium after land clearing. Furthermore, the data revealed significant trends; despite the long–term variability in flow, salinity, and rainfall. Critically, this method determined a decreasing trend in salinity with time, achieved through a multiple regression of a 28–year data set. Additionally, the data established the mass of stream water salinity originating from atmospheric deposition and stored sources. Furthermore, this method ascertained stored sources contributed three times more salinity to discharge and estimated that the new salinity equilibrium would occur by approximately 2090.

The use of high resolution flow and salinity data produced considerable measurements to attain thorough chloride/salinity budget evidence. This evidence allowed for investigating whether the catchment–scale salinity is decreasing on–site. The data enabled the comparison of atmospheric chloride deposition and stored chloride export, and thus, the confirmation that salinity is decreasing with time. Furthermore, it supported the interpretation that land clearance caused the water table to rise, which flushed the salinity stored in the unsaturated zone and ambient groundwater. Thus, using high resolution data in the chloride budget supported the notion that reforestation could increase salinity and decrease surface water flows.

Chloride budget equations that revealed the salinity disequilibrium in chapter 3 also assisted in answering the research aims of chapter 4. The budget contributed to the interpretation of why Woolshed Flat Shale groundwater dominates the hydrochemistry of the Scott Creek Catchment and not the Sandstone bedrock groundwater. Critically, the budget determined the chloride disequilibrium in the system. Additionally, the CMB equation usually calculates recharge using deep groundwater. However, the method used in chapter 4 compared recharge calculated from the regolith–saprolite zone. This zone was envisioned to be more representative of chloride that recharged this catchment, as it would be closer to equilibrium post land clearance.

5.3. LIMITATIONS OF THE STUDY AND FUTURE RESEARCH

Further research could advance knowledge of catchment–scale solute dynamics and address the limitations of this current research. For example, all investigations (chapters 2–4) focus on the same catchment. However, there is a need to investigate the broader, global implications for understanding the described processes in other catchments. Therefore, this body of research calls for further research across a larger geographical scale with more diverse controls. For instance, future studies could replicate methods from chapters 3 and 4 using catchments with varying geology, precipitation, land–use changes, and vegetation. In addition, previous studies described the salinity hotspots of chapter 2 in other catchments globally. Thus, additional studies could investigate the origin and extent of other salinity hotspots using methods from this current study.

In addition to further research on the origin of groundwater salinity hotspots, the research could also address the geographical extent of these hotspots. An intended aim of this current study was to determine the extent of the hotspots, but it remains unsolved in chapter 2. At present, only two piezometers access the hotspot at Scott Creek. However, installing more piezometers further upslope within the catchment could enable estimation of the hotspot's extent. Furthermore, geophysics could assist in mapping the complex hydrogeology of the Scott Creek catchment and others. For example, the hotspots could be mapped rapidly in three dimensions using airborne electromagnetics, as Dent (2007) investigated. Moreover, the latter method would have further implications on the effective management of water resources by predicting the occurrence of salinity threats.

Future research could also address the limitations recognised in chapter 3. For example, an assumed linear scale and steady–state conditions estimated the approximate period of the catchment's return to salinity equilibrium. However, other factors influence recharge and salinity balance, including environmental history, climate change, and flow paths through the regolith and aquifers. These factors impose transient hydrological conditions, restricting the catchment from equilibrium. To estimate a more accurate time of return would entail including these factors. Additionally, modelling the equilibration times in such catchments would further increase the accuracy of the estimated time. For example, Choo et al. (2009) incorporated a groundwater flow model (MODFLOW) that accounted for factors that caused transient conditions.

This research body made further assumptions in addition to those regarding steady–state conditions of the catchment. Chapters 3 and 4 made assumptions regarding flow paths and the lag time of solute export from the catchment. The assumption was that all groundwater recharging the catchment flows out instream. However, groundwater would also export via other paths (e.g., extraction, groundwater piracy, evaporation, via springs). Additional studies could investigate these factors and their influence on solute transport. Furthermore, the strong upward gradient in the catchment's groundwater system would limit the downward propagation of fresh recharge (following land clearing) and salinity export from such sources. This lag time in flow response to rainfall was assumed to be reflective of significant groundwater recharge during wet years. Such pulses of recharge generating stream flow was the mechanism envisioned to cause more saline groundwater to flush. Thus, further research could be undertaken to understand the key indicators on these time lags.

The residence time and chronology of the complex groundwater system within this catchment are crucial factors that could benefit from more research. Specifically, the comparatively large number of radiocarbon samples to previous studies (Kalin 2000) allows for an in-depth understanding of this chronology. For example, further research could investigate the mixing of old and new groundwater in the upslope salinity hotspot. Reactive transport modelling, developed from the extensive radiocarbon isotope dataset, could give a detailed insight into this chronology. Furthermore, other tracers could more accurately date the groundwater of differing ages; given that different dating techniques are more appropriate for older (e.g., chlorine-36), and more recently recharged groundwater (e.g., tritium-helium-3) (Bethke & Johnson 2008; Aggarwal al. 2010; Cartwright et al. 2017; Howcroft et al. 2019).

There is considerable opportunity for further research due to the Scott Creek catchment's hydrogeological heterogeneities and geological complexities. The investigations presented here, and others indicated that more data analysis coincided with new research questions that emerged. However, nearly all questions addressed contributed to understanding how this groundwater system functions and interacts..

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6. APPENDIX

6. PUBLISHED CONFERENCE PRECEDINGS

6.1. Groundwater salinity hotspot in the Mt Lofty Ranges (South Australia): connection to an intermittent stream and origin from land-clearing

Presented at Australasian Groundwater Conference, Sydney, Australia, 2008

Thomas A. Anderson, Erick A. Bestland, Lesja Soloninka, Ilka Wallis, Edward W. Banks & Markus M. Pichler

Abstract: Clearing of native vegetation for agricultural crops and grazing has been the definitive anthropogenic cause for dryland salinity in Australia and has had a devastating effect on catchment hydrology. In a high rainfall area of the Mt Lofty Ranges, land-clearing has caused a groundwater salinity 'hotspot'to form on a hill-slope producing transient groundwater salinity disequilibrium. The perched saline groundwater is over ten times more saline than the ambient groundwater. This phenomenon is largely unknown in the hydrologic literature. Furthermore, this saline groundwater was observed to discharge into a nearby intermittent stream thereby greatly increasing its salinity. This surface water-groundwater interaction was investigated by weekly sampling and analysis of the physical parameters of the stream and the saline groundwater hotspot. Samples were analyzed for major and trace elements, stable isotopes of water and stable isotopes of strontium. These indicate that the probable mechanism for the salinity increase in the stream is a water-table rise during wet season recharge, which causes the saline groundwater to drain into the creek. Major and trace elements and strontium isotopes indicate the stream water is a mix of runoff and saline groundwater that has discharged into the creek. Strontium isotopes also identified that the source of salinity in the saline groundwater is largely caused by salts concentrated during evapotranspiration in the

clayey unsaturated zone. Stable water isotopes have no relationship to salinity. CFC data indicates that the saline groundwater hotspot has been recently recharged which supports historic land-clearing as the cause of the high salinity. The preferred model for the origin of the groundwater hotspot involves flushing of accumulated salts from the thick clayey unsaturated zone due to increase recharge following land-clearing. Depending on the veracity of this model, this process of groundwater salinization could be much more widespread than presently appreciated.

6.2. Hydrogeological sensitivity to drought conditions in a perennial creek system, Mt Lofty Ranges, South Australia (oral presentation)

Presented at GESSS South Australia - Earth Sciences Student Symposium, Bedford Park, South Australia, 2017

Thomas A. Anderson, Erick A. Bestland, Lesja Soloninka, Ilka Wallis, Edward W. Banks & Markus M. Pichler

Understanding the hydrological sensitivity of perennial streams to drought conditions is essential to prepare for the associated post-drought hardships that are inevitable South Eastern Australia. These types of streams, which are defined as having continuous surface flow throughout the year, except in cases of severe drought, are critically important to the freshwater ecosystem stability. This is because they provide important ecological refuge during periods of low rainfall and surface runoff. The record breaking drought conditions that occurred between 1997 and 2006 has provided a rare opportunity to investigate hydrological sensitivity of perennial streams. Hydrological and hydrogeological data from Scott Creek Catchment, a perennial stream within a heterogeneous fractured rock aquifer in the Mt Lofty ranges of South Australia was reported. A conceptual model was developed to investigate the hydrochemisty in surface water and groundwater at this location. Statistical analysis of flow and salinity data of Scott Creek over a 27 year period, from 1989 to 2016 was undertaken. Surface water samples were collected on a monthly interval before and after the experienced drought conditions at a continuously monitored gauging station at the base of the catchment. Additional samples were collected longitudinally at 19 locations along the river and at 54 groundwater monitoring bores over a 3 year period. These samples were analysed for major and trace elements, stable isotopes of water and stable isotopes of strontium. The results indicated that groundwater from specific geological strata discharged into the creek. The findings determined that the severity of drought conditions imposed a dominant groundwater input signature to the stream's chemical composition. This has enabled contributions to the stream at particular locations within the catchment to be determined. Therefore, compartmentalising the mechanisms responsible for the chemical composition of these types of streams can assist in managing water sources now and into the future.

6.3. Catchment salt balance and historical salinity flushing quantified in a high rainfall stream (Mount Lofty Ranges, South Australia)

Presented at Australian Freshwater Sciences Society Conference, Glenelg, South Australia, 2018

Thomas A. Anderson, Erick A. Bestland, Ilka Wallis, Huade D. Guan

Abstract: Human-induced landscape salinization, including dryland salinity, has had devastating consequences on many catchments in southern Australia. Salinization occurs due to increased recharge and a rise in groundwater tables following land clearing of deep rooted native vegetation. In low lying areas with poor drainage groundwater table rise can lead to evapotranspiration and salt scalding. However, these same processes of increase recharge and groundwater table rise can lead to decreases in salinization as the historic salts are flushed into the surface water. This study in the Mount Lofty Ranges of South Australia documents a case of catchment desalinization. In the Scott Creek catchment, a 28 year record (1989-2016) of flow and salinity data were analysed on a monthly basis. Analysis of catchment-scale chloride deposition and export determined that approximately three times more chloride is being exported than is being input to the catchment from atmospheric sources. Salt load exported in surface water over the time period analysed was calculated to decrease on average by 6.4 tonnes per year. Furthermore, analysis of an intermittent sub-catchment demonstrates accumulation of chloride rather than export during dry years whereas in the permanent stream catchment chloride accumulation greater than export rarely occurs. A significant portion of the stream water is discharging from the deep groundwater, as evidenced by stable isotopes of water.

Considering the available literature on salt balances it is evident that a continuous, high resolution monitoring history is required to thoroughly evaluate salt input and export. This current study provides such data.

6.4 Catchment salt balance and historical salinity flushing quantified in a high rainfall stream (Mount Lofty Ranges, South Australia)

Presented at Australian Geoscience Council Convention, Adelaide, South Australia, 2018

Thomas A. Anderson, Erick A. Bestland, Ilka Wallis, Huade D. Guan

Abstract: Human-induced landscape salinization, including dryland salinity, has had devastating consequences on many catchments in southern Australia. Salinization occurs due to increased recharge and a rise in groundwater tables following land clearing of deep rooted native vegetation. In low lying areas with poor drainage groundwater table rise can lead to evapotranspiration and salt scalding. However, these same processes of increase recharge and groundwater table rise can lead to decreases in salinization as the historic salts are flushed into the surface water. This study in the Mount Lofty Ranges of South Australia documents a case of catchment desalinization. In the Scott Creek catchment, a 28 year record (1989-2016) of flow and salinity data were analysed on a monthly basis. Analysis of catchment-scale chloride deposition and export determined that approximately three times more chloride is being exported than is being input to the catchment from atmospheric sources. Salt load exported in surface water over the time period analysed was calculated to decrease on average by 6.4 tonnes per year. Furthermore, analysis of an intermittent sub-catchment demonstrates accumulation of chloride rather than export during dry years whereas in the permanent stream catchment chloride accumulation greater than export rarely occurs. A significant portion of the stream water is discharging from the deep groundwater, as evidenced by stable isotopes of water. Considering the available literature on salt balances it is evident that a continuous, high resolution monitoring history is required to thoroughly evaluate salt input and export. This current study provides such data.