

HYDROGEOCHEMICAL CONTROLS OF VARIABLE REGOLITH MATERIALS ON THE DISTRIBUTION, MOBILITY AND AGE OF SALTS: BARMEDMAN CREEK CATCHMENT, NSW

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INTRODUCTION

The widespread occurrence of dryland salinity and its ramifications on land management practices are well documented throughout Australia, yet the origin, nature, and mobility of salts are less well understood. Numerous studies (e.g., Macumber 1969, Gunn & Richardson 1979, Johnston *et al.* 1980, Johnston & McArthur 1981, Mazor & George 1992) associate the occurrence of salt affected areas with low-lying, highly weathered landscapes in Australia. In the majority of these areas, the salts tend to be concentrated in low permeability clay-rich units and are considered relatively immobile (e.g., Macumber 1969, Johnston *et al.* 1983, Johnston 1987). However, considering the large timeframes available for accumulation of salts in the landscape, far greater concentrations would be expected if these salts were not continually being exported from basins over time. Simpson & Herczeg (1991) note that Cl⁻ is being exported from the Murray Darling Basin at rates 2.6-4.1 times greater than that contributed from atmospheric precipitation. This imbalance is attributed to the mobilization of unsaturated zone salts by infiltrating irrigation water and rising groundwater tables following land clearance. Less attention has been focused on the mixing of saturated zone salt stores residing in low permeable clay units with "fresher" aquifer water. Ortega-Guerrero *et al.* (1997), Timms *et al.* (2001) and Peck & Hatton (2003) consider isotopic and hydrochemical properties of both aquitard pore fluids and aquifer waters. These results suggest that appreciable degrees of mixing occur between the two. Recent studies in other countries have begun to identify the significance of mixing between aquitard pore fluids and aquifer groundwater in relation to groundwater salinity. Hendry *et al.* (2000) investigated mixing between pore fluids and groundwater within a till aquifer system in Saskatchewan, Canada and noted that saline groundwater is diffusing into near surface freshwater bearing till aquitards. Ortega-Guerrero *et al.* (1997) studied the interaction between saline pore fluids in a clay-rich lacustrine aquitard and a freshwater alluvial aquifer supplying Mexico City, Mexico. The authors concluded that under natural conditions the hydraulic gradient is sufficiently high enough for fresh groundwater to flow upward through the saline aquitard. However, in areas where over-pumping of the aquifer has occurred, a downward vertical hydraulic gradient has formed and saline pore fluids are leaking into the aquifer, thereby compromising the potable water supply for 20 million people. In Australia, alteration of the hydrologic budget due to clearing of native vegetation has caused groundwater levels to rise and mobilize salts formerly residing in the unsaturated zone (e.g., Salama *et al.* 1999). This process, known as secondary salinization, has been attributed to the widespread degradation of soil and water quality throughout Australia. Starr (1999) estimates that up to 1,500,000 hectares of land within the Murray-Darling Basin will be affected by secondary salinization by 2010. The widespread presence of significant salt stores in low permeability, highly weathered regolith materials may have a greater impact than previously assumed on the quality of surface water and groundwater throughout the Murray Darling Basin. A detailed assessment of pore fluid and groundwater properties is therefore fundamental for addressing the salt balances within catchments. This study is part of an evaluation of the origins, nature and mobility of salt stores in the Barmedman Creek catchment of the Bland Basin and will be useful for understanding the nature of other salt affected landscapes in the Murray Darling Basin.

AIMS AND OBJECTIVES

This study focuses on a 25 x 20 km area within the Barmedman Creek catchment, located south of West Wyalong, NSW (Figure 1). Barmedman Creek is a sub-catchment of the Bland Basin, which is a low-lying alluviated palaeo-tributary of the Lachlan River. The Bland basin is chosen because it is representative of low-lying, salinized landscapes in the Murray-Darling Basin, and because of an extensive physical and chemical database as a result of previous studies of the GILMORE project (Phillips *et al.* 2002). The aims of this study are to understand the mechanisms driving the evolution of groundwater from a fresh rainwater source to salinity values approaching that of seawater, and to assess the mobility of salts in a highly variable regolith stratigraphy. The study will first consider differences in the chemical composition of rainwater, pore fluids, groundwater, and the physical characteristics of the regolith. Then it will assess the mobility of solutes in the regolith by considering spatial variations in groundwater salinity and by interpreting pore fluid compositions from two diamond core holes. The origin, age and mobility of salts will then be further

considered via stable and cosmogenic isotope composition of pore fluids and groundwater.

LOCAL HYDROLOGY

Up to 80 metres of Cenozoic sediments presently overlie complex saprolith/bedrock (Gibson *et al.* 2002b). Distribution of aquifers and inferred head gradients from standing water levels in piezometers suggest predominantly south-north flow. Low head gradients, high Cl⁻ content, and little to no fluctuation in standing water levels between 2001 and 2004, despite a persistent regional drought, imply a sluggish system and a lack of local, vertical recharge. Extensive bore hole and airborne geophysical data collected as part of the GILMORE study indicate several aquifer horizons contained within a complex hydrogeologic framework. The aquifers appear to be confined to semiconfined, largely dependent on the local bedrock topography, confined by low permeability clay-rich sediments (Wilford *et al.* 2002).

SAMPLE COLLECTION

Groundwater was sampled in 2003 and 2004 from a series of permanent piezometers (Figure 1) at depths ranging from 9–66 m. Three creek water samples were also collected during this period. Cation and anion analyses were performed via Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and ion chromatography at the Australian National University, Department of Earth and Marine Science (ANU EMS). Stable isotopes, δ¹⁸O and δ²H, were analysed via mass spectrometer at Monash University. Selected groundwater samples were analysed for ³⁶Cl via accelerator mass spectrometry at ANU Department of Nuclear Physics (e.g., Fifield *et al.* 1987).

Pore fluids were extracted via a uniaxial compression method from diamond core materials from two nested piezometer locations by The Bureau of Rural Sciences and Geoscience Australia in 2001 as part of the GILMORE project (Tan *et al.* 2002). The pore fluids were analysed for major cations and anions via ICP-OES and ion chromatography. The results were corrected for loss of CO₂ and lack of alkalinity data (Tan *et al.* 2002). Selected pore fluid samples were analysed for ³⁶Cl at the ANU in 2001.

RESULTS AND DISCUSSION

Solute sources

The main solute sources appear to be rainfall and cyclic salts, because groundwater and pore fluid ion ratios are similar to rainwater and seawater. Bromine concentration in rainwater was compared to groundwater concentrations to calculate an evaporation factor, which was then used to evaluate the sources and sinks of major ions in groundwater. The median evaporation factor for all groundwater samples was approximately 2,700, or, modern rainwater evaporated approximately 2700 times would reach the median Br⁻ concentration in groundwater. Although the calculation is based on the assumptions that Br⁻ concentration in rainwater has been consistent throughout time and that there are no terrestrial sources or sinks for Br⁻, it provides a mean for assessing processes affecting groundwater composition. Table 1 displays the difference between the average measured concentration and calculated evaporative concentration of major ions in groundwater.

If evaporation of rainwater was solely responsible for the salinity in this area, the Cl⁻, Na⁺ and Mg²⁺ concentrations would be considerably less than what is present in groundwater. According to this calculation, rainfall accounts for approximately 60% of the Cl⁻, 50% of the Na⁺ and 70% of the Mg²⁺ in the sampled groundwater. Dissolution of cyclic salts, particularly halite, may account for up to 40% of the Na⁺ and Cl⁻ present in groundwater. The remaining excess Na⁺ and the excess Mg²⁺ may reflect mineral weathering and cation exchange mechanisms. The calculated concentration of K⁺ and Ca²⁺ resulting from evaporation alone far exceeds the actual concentrations of sampled groundwater. Sinks for these elements may include nutrient uptake of plants or interaction with clay minerals (Drever 1997). The calculated SO₄²⁻ concentration is also much higher than measured values and may reflect incorporation of aeolian salts into the rainfall (e.g., Blackburn & McLeod 1983, Chivas *et al.* 1991), which would cause an overestimate of the

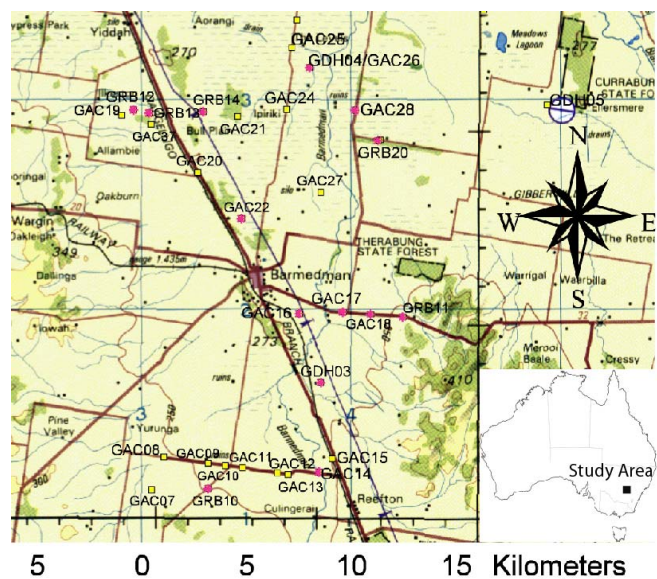


Figure 1: Location of the study area on the Cootamundra 1:250,000 topographic map.

calculated effect of evaporation. Precipitation of gypsum in the unsaturated zone may also contribute to lower than anticipated SO_4 and Ca^{2+} concentration in groundwater. Calcite precipitation could account for the observed Ca^{2+} deficiency.

In conjunction with cyclic salt input, evapotranspiration of rainfall appears to be an important mechanism contributing to groundwater salinity. Based on stable isotope compositions, transpiration rather than evaporation appears to be the primary salt concentrating mechanism (Figure 2).

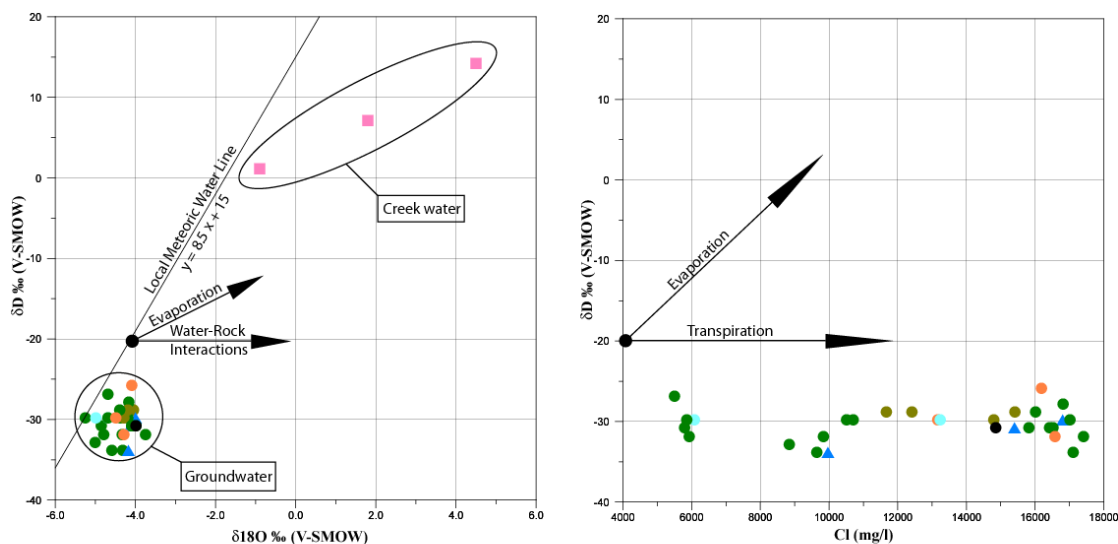


Figure 2: Stable isotope composition of groundwater and surface water.

Water-rock interactions may also be influencing the stable isotopic signature of groundwater. Evaporative isotopic enrichment appears evident in creek water samples (Figure 2), which also exhibit similar ion ratios to rainwater. Considering the ephemeral nature of Barmedman Creek and its tributaries, surface water in this study area is most likely evaporated meteoric water collected in stream channels following major rain events. Groundwater does not exhibit an evaporative enrichment in ^{18}O and ^2H , therefore creek water is not regarded as a source of recharge to groundwater.

Subsurface distribution of salts

Pore fluids were extracted from diamond cored regolith materials as part of the GILMORE study. Due to preferential flow paths and a lack of connectivity between pore spaces, the extracted pore fluids may represent water, which under natural conditions, may or may not be mobile. As such, the following discussion considers pore fluids and groundwater separately.

Pore fluid vertical salinity profiles reveal increasing concentration with depth in the unsaturated zone (Figure 3). This is likely the combined effect of infiltrating water mixing with unsaturated zone pore fluids exposed to varying degrees of evapotranspiration, and the dissolution of cyclic salts. Ion exchange and dissolution/precipitation reactions are important mechanisms influencing solute composition within the unsaturated zone but have less affect on overall salinity. Distribution of salts within the saturated zone is dependent on the vertical and horizontal hydraulic gradient and permeability. Where a downward hydraulic gradient is present, combined with the absence of a thick (> 20 m) confining unit, a uniform distribution of salts within the saturated zone is present (Figure 3; GDH03). This indicates a well mixed system where dispersion transport has been slow enough (< 1 m/yr) for diffusion to smooth out concentration gradients between higher and lower permeability units (Appelo & Willemssen 1987).

The lateral distribution of salinity appears dependent on groundwater flow rates and proximity to recharge areas. The presence of a confined/semi-confined system, a low horizontal hydraulic gradient (< 1 m/km) and low hydraulic conductivity aquifers result in a sluggish hydraulic regime. A lack of vertical recharge and low lateral flow rates prevents solutes from being flushed from the unsaturated and saturated zones which allows for a gradual accumulation of salts over time and a general increase in salinity along the flow path (e.g., Peck & Hurle 1973, Salama *et al.* 1999).

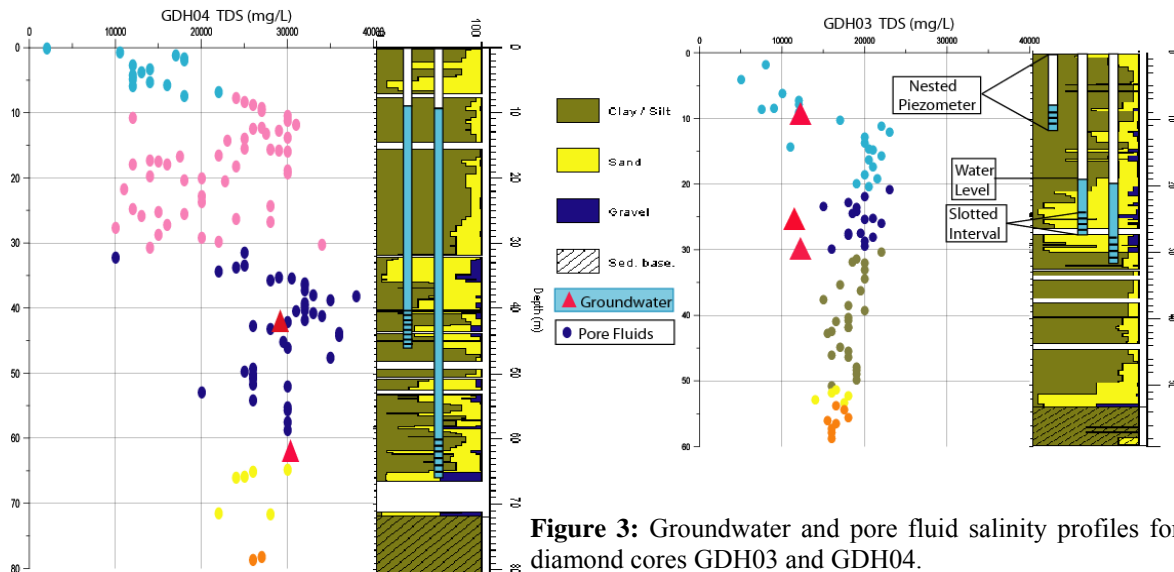


Figure 3: Groundwater and pore fluid salinity profiles for diamond cores GDH03 and GDH04.

The distribution of salts relative to the hydraulic properties of the regolith materials indicates lower permeability materials are hosting the most saline water. The exception is a clay-rich lacustrine unit present at GDH04 from approximately 8 to 32 m (Gibson *et al.* 2002a), which hosts the least saline pore fluids in the profile (Figure 3). This trend may represent connate water trapped during deposition of sediments, which has not entirely mixed with underlying saline aquifer groundwater despite an upward hydraulic gradient. Pore fluids and groundwater from within the aquifer exhibit similar TDS values and ion ratios indicating complete mixing between fluids residing in lower permeability and higher permeability aquifer materials. Pore fluids extracted from diamond cored materials sampled near a likely recharge area exhibit TDS values up to 12,000 mg/L greater than groundwater (Figure 3; GDH03), yet similar ion ratios indicate mixing. This suggests that a significant quantity of solutes in groundwater may be sourced from saline pore fluids.

Chlorine 36

The presence of greater salinity waters in lower permeability materials may reflect relict salts accumulated under different hydrogeologic and climatic conditions. To test this hypothesis, groundwater samples were analysed for ^{36}Cl content and compared to previously collected ^{36}Cl data for pore fluids. Selected groundwater samples were analysed for ^{36}Cl in July 2004. Sample selection was based on flow path position, depth, Cl^- concentration and hydrogeologic properties of aquifer materials. Groundwater sample depths range from 9 to 66 m and Cl^- content ranges from 6,000-16,000 ppm. Creek water was sampled in 2004 and analysed for ^{36}Cl with the groundwater samples. As discussed above, the surface water in this area is most likely sourced from heavy rain events, therefore, the creek water sample is considered representative of modern atmospheric ^{36}Cl input. Selected pore fluid samples were analysed for ^{36}Cl at ANU in 2001 as part of the GILMORE project. Pore fluid sampling depths range from 6 to 73 m with Cl^- contents ranging from 5,000-20,000 ppm.

Two distinct $^{36}\text{Cl}/\text{Cl}$ signatures are present for groundwater samples and are attributable to their proximity to recharge areas (Figure 4). Samples proximal to granite and sandstone outcrop areas have higher $^{36}\text{Cl}/\text{Cl}$ ratios whereas lower $^{36}\text{Cl}/\text{Cl}$ values occur in samples located further out into the depositional basin.

Along the flow path, a progressive decrease of $^{36}\text{Cl}/\text{Cl}$ ratios in groundwater is accompanied by an increase in Cl^- content. Vertical pore fluid Cl^- profiles exhibit similar Cl^- content with increasing depth yet $^{36}\text{Cl}/\text{Cl}$ ratios vary with a general decreasing trend (Figure 5). Pore fluids extracted from aquifer materials within the screened interval exhibit similar ion ratios yet greater TDS and lower $^{36}\text{Cl}/\text{Cl}$ than

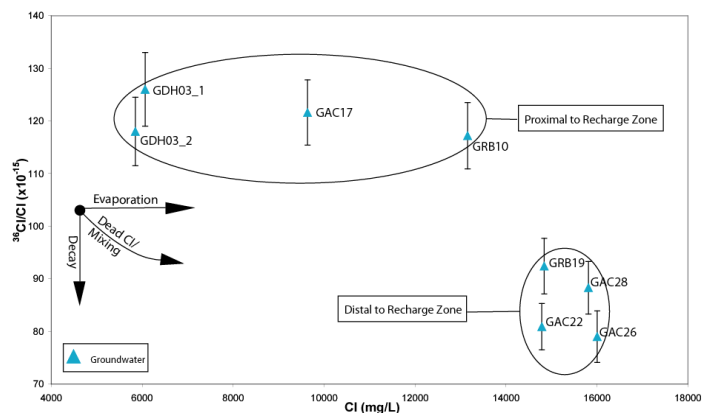


Figure 4: $^{36}\text{Cl}/\text{Cl}$ versus Cl for groundwater samples proximal and distal to likely recharge zones.

associated groundwater. This suggests that older, more saline waters residing in lower permeability regolith materials are mixing with younger less saline aquifer water. Considering that low permeability regolith materials commonly host the highest TDS waters in semiarid areas of Australia (e.g., Macumber 1969, Johnston *et al.* 1983), a significant source of solutes in aquifer groundwater may be older, more saline pore fluids residing in adjacent aquitard units or within lower permeability aquifer materials. The ^{36}Cl content of pore fluids and groundwater may provide a more definitive method for estimating mixing than ion compositions alone, and may prove valuable in addressing the mobility of solutes in salinity management studies.

CONCLUSION

The sources and distribution of salts within the Barmedman Creek Catchment are well recognized, however, salt mobility and mixing mechanisms are numerous and complex, and require further consideration. Rainwater appears to be the primary source of solutes in groundwater. The rainwater is then concentrated by transpiration in the unsaturated zone. Dissolution of cyclic salts in the unsaturated zone by infiltrating rainwater may constitute up to 30% of the total solutes present in groundwater. The distribution of salts appears to be dependent on the physical properties of the regolith and proximity to recharge areas. Preliminary investigations have revealed higher salinity water residing in the pore spaces of low permeability regolith materials. Water residing in pore spaces within aquifer materials at a bore hole located proximal to a likely area of recharge (GDH03) exhibited salinity values up to 12,000 mg/L—saltier than the groundwater. This suggests that groundwater is moving along preferential flow paths, resulting in a heterogeneous distribution of salts within the saturated aquifer unit. A lack of circulation due to interconnected pore spaces is likely to be the cause for the higher salinity in the pore fluids extracted from aquifer materials. Evidence of mixing between these saline pore fluids and groundwater is manifested through similar ion ratios, despite the variations in salinity. Aquifer pore fluids which exhibit salinity greater than groundwater also exhibit lower $^{36}\text{Cl}/\text{Cl}$ ratios. This suggests that older, more saline water is residing in lower permeability regolith materials and may represent a significant source of solutes for groundwater. The majority of salinity studies in Australia have failed to address this type of mixing, or to recognize pore fluids in low permeability regolith materials as a potential solute source. The interactions between saline pore fluids and groundwater may be a significant process influencing solute concentrations in groundwater. Considering the distribution and mobility of saline pore fluids under various hydrogeologic conditions will increase our understanding of salinization mechanisms in Australia.

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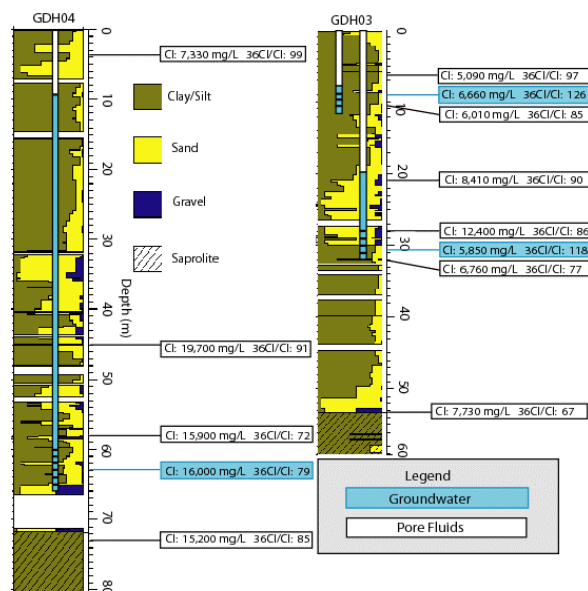


Figure 5: Groundwater and pore fluid $^{36}\text{Cl}/\text{Cl}$ and Cl content and corresponding host regolith materials.

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