Cl$^-$ AND ^{36}Cl DISTRIBUTION IN A SALINE AQUIFER SYSTEM: CENTRAL NEW SOUTH WALES, AUSTRALIA

M.J. Lenahan[1], D.M. Kirste[1], D.C. McPhail[1] & L.K. Fifield[2]

[1]CRC LEME, Department of Earth and Marine Sciences, Australian National University, Canberra, ACT, 0200
[2]Department of Nuclear Physics, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT, 0200

INTRODUCTION

A number of studies conducted in semi-arid regions of Australia have utilized Cl$^-$ composition and electrical conductivity of soil pore water and groundwater to evaluate the mechanisms contributing to groundwater salinity (e.g., Johnston 1981, Peck *et al.* 1981). Far fewer studies (e.g., Cook *et al.* 1994, Cresswell *et al.* 1999, Love *et al.* 2000) have applied cosmogenic isotopes, such as ^{3}H, ^{14}C and ^{36}Cl, to better quantify these mechanisms and to determine flow rates and salinization timeframes. This study utilizes Cl$^-$ and ^{36}Cl content of pore water extracted from near-surface (0.25-7 m) unsaturated zone regolith materials and deeper (9-73 m) saturated zone pore water to determine the effects of evapotranspiration, mixing/filtration and ^{36}Cl decay on groundwater ^{36}Cl/Cl in a saline aquifer system of semi-arid central New South Wales.

REGIONAL SETTING AND LOCAL HYDROLOGY

The study focuses on 25x25 km low-lying alluviated basin in central New South Wales (Figure 1). The basin contains up to 100 m of highly weathered, unconsolidated Cenozoic sediments which comprise a heterogeneous hydrogeologic system (Wilford *et al.* 2002) and it hosts highly saline groundwater (TDS > 30,000 mg/L). A low hydraulic gradient (ca. 0.1 m/km) and hydraulic conductivity values of 10^{-4}-10^{-6} m/s result in a specific discharge of ca. 0.3-30 cm/yr. Groundwater recharge to the deeper confined/semiconfined aquifers is likely the result of vertical infiltration of rainwater at outcropping areas along the basin margins, and to the shallow unconfined/semiconfined aquifer through the near surface (< 5 m) clay-rich sediments present throughout the basin.

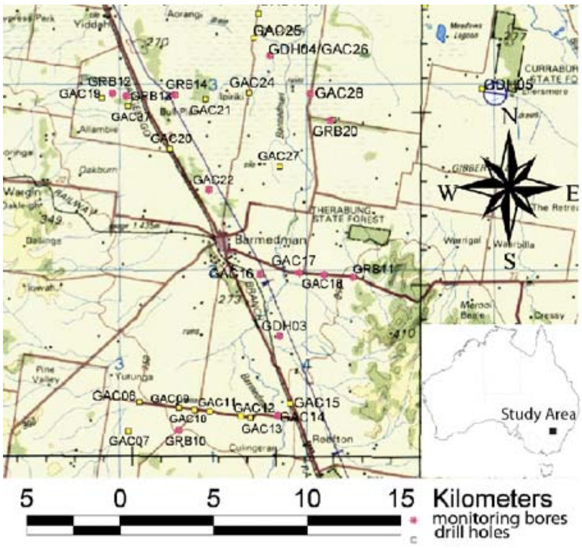


Figure 1: Location of study area on the Cootamundra 1:250,000 topographic sheet.

SAMPLING AND ANALYTICAL TECHNIQUES

Regolith materials were sampled via diamond coring at two locations, GDH03 and GDH04 (Figure 2), to depths of 59 and 80 m, and pore water was extracted via centrifugation and uniaxial compression from a variety of unsaturated- and saturated-zone regolith materials. Groundwater was sampled from permanently installed piezometers (Figure 2). Cl$^-$ content was determined via ion chromatography and ^{36}Cl by accelerator mass spectrometry at The Australian National University Department of Nuclear Physics (Fifield *et al.* 1987). Cl$^-$ measurements were performed for all extracted pore water (2-3 samples/metre) and groundwater while ^{36}Cl measurements were performed on selected samples only. ^{36}Cl measurements were performed on unsaturated and saturated zone pore water samples at GDH04, while ^{36}Cl measurements were performed only on saturated zone pore water samples at GDH03 (Figure 2).

RESULTS

Groundwater samples exhibit Cl$^-$ contents ranging from 5,800-16,000 mg/L and ^{36}Cl/Cl of 79-126x10^{-15}, which are related to proximity to recharge areas, depth and position along the flow path. Local meteoric water exhibits a Cl$^-$ content of 2.5 mg/L and ^{36}Cl/Cl of 374x10^{-15}. Pore water Cl$^-$ concentrations and ^{36}Cl/Cl are unique to each diamond core location, and results are presented separately below.

GDH04

In the unsaturated zone, pore water Cl$^-$ concentration increases from approximately 1,000 mg/L at 0.25 m to 9,000 mg/L at 1.5 m (Figure 3a). Below a depth of 1.5 m, pore water Cl$^-$ concentrations are relatively constant throughout the remainder of the unsaturated zone (0-9 m), followed by a marked increase in the saturated zone. ^{36}Cl/Cl of pore water in the upper 1.5 m decreases from 157x10^{-15} at 0.25 m to 130x10^{-15} at

1.5 m (Figure 3b). Below 1.5 m, ^{36}Cl/Cl decrease throughout the remainder of the unsaturated zone to a value of 94x10^{-15} at 7.5 m. Saturated zone pore waters exhibit highly variable Cl$^-$ content (6,000-20,000 mg/L) yet more consistent ^{36}Cl/Cl (69-87x10^{-15}).

GDH03

In the unsaturated zone, pore water Cl$^-$ concentrations increase steadily from approximately 100 mg/L at 0.35 m to 6,800 mg/L at 8.0 m (Figure 3a). Saturated zone pore water Cl$^-$ concentrations continue to increase with increasing depth to the lower semi-confined aquifer unit (19 m). Below this depth, pore water Cl$^-$ concentrations are relatively constant (ca. 10,000 mg/L) throughout the remainder of the saturated zone profile. Saturated zone pore water ^{36}Cl/Cl is highly variable (115-67x10^{-15}), yet similar within each hydrogeologic unit (Figure 3b). Pore fluids collected from aquifer materials within the screened interval exhibit greater Cl$^-$ and lower ^{36}Cl/Cl than associated groundwater.

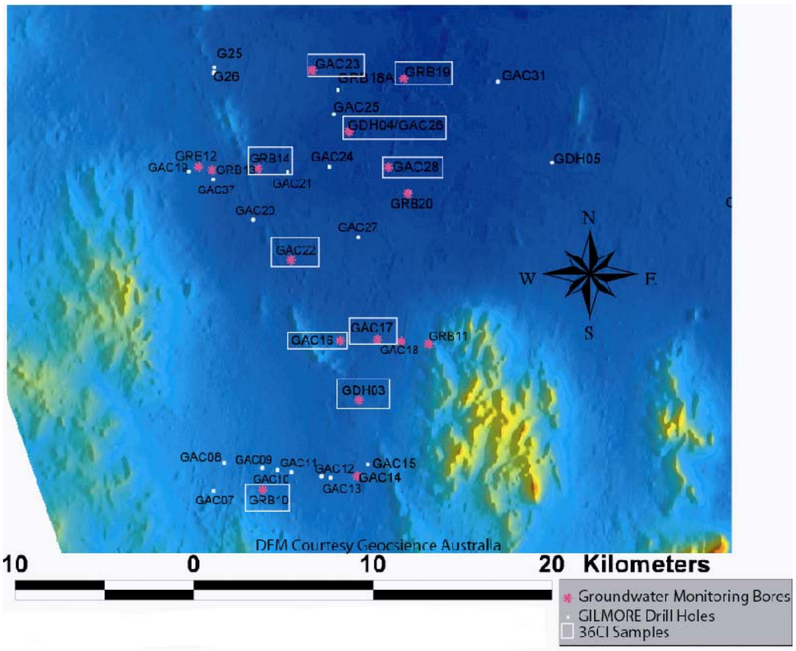
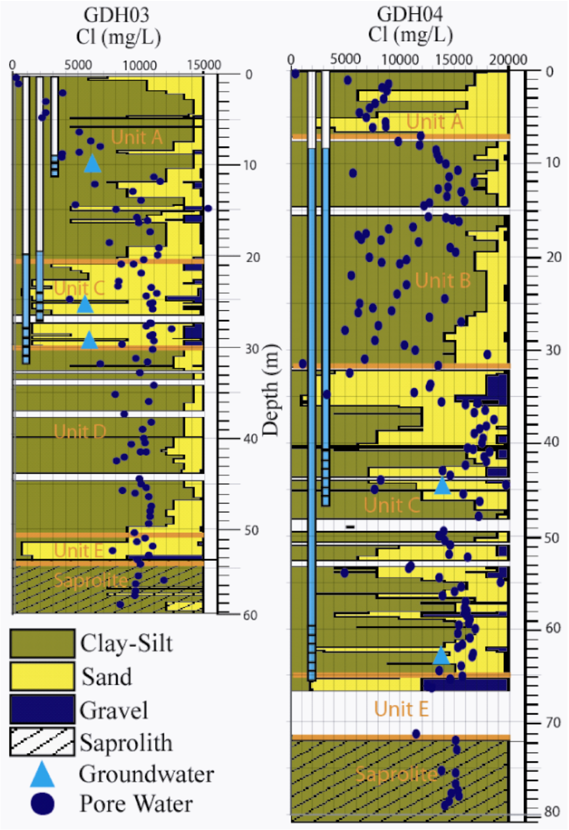


Figure 2: Groundwater and pore water sampling locations, shown on a Digital Elevation Model (DEM).



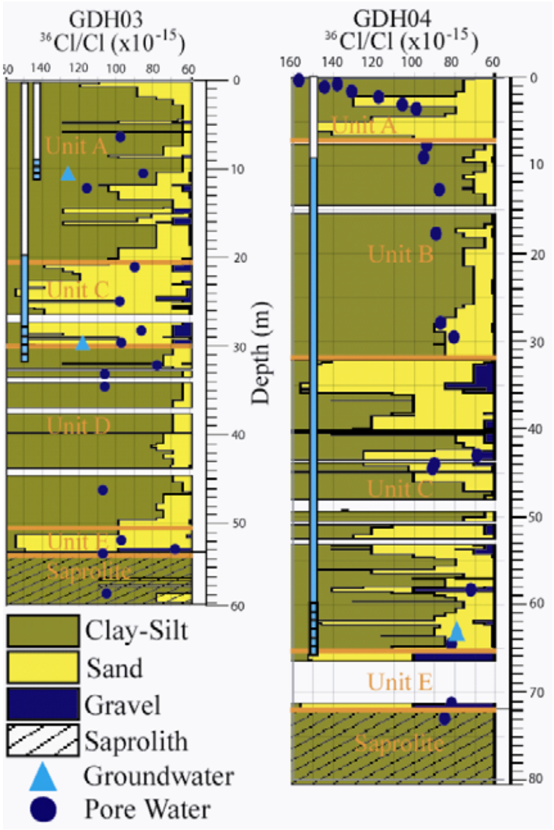


Figure 3a (left): Soil pore water and groundwater Cl$^-$ (mg/L) depth profiles for diamond cores GDH03 and GDH04.

Figure 3b (right): Soil pore water and groundwater ^{36}Cl/Cl (x10^{-15}) depth profiles for diamond cores GDH03 and GDH04.

DISCUSSION

Cl^- contents of near surface (< 2 m) pore waters indicate low infiltration rates and a high degree of evapotranspiration in the upper several metres of the unsaturated zone. Vertical recharge rates to the unconfined/semiconfined aquifers estimated by the chloride-mass balance (CMB) technique (Wood 1999) of unsaturated zone pore waters is $1.5\text{x}10^{-3}$ cm/yr. Low Cl^- and high $^{36}Cl/Cl$ of meteoric water relative to near-surface pore water indicates a significant degree of evapotranspiration and/or mixing occurring during infiltration in the upper 25 cm of the regolith. A rapid increase in pore water Cl^- occurs to a depth of 1.5 m while only a gradual decrease in $^{36}Cl/Cl$ occurs over the same interval. Below 1.5 m, Cl^- content of pore water remains relatively constant while $^{36}Cl/Cl$ decreases steadily throughout the remainder of the unsaturated zone. This suggests that above 1.5 m, rainwater has thoroughly mixed with near-surface pore water, and has reached a steady $^{36}Cl/Cl$ more appropriate for use as an input value in age calculations than the $^{36}Cl/Cl$ of modern precipitation. Below 1.5 m, ^{36}Cl decay appears to be the dominant mechanism influencing the $^{36}Cl/Cl$ of unsaturated zone pore water. If this is the case, the age difference between pore water sampled at 1.5 m and pore water sampled at 3.5 m is 120,000 yr, indicating a vertical flux of 1.7x10-3 cm/yr. This value is nearly an order of magnitude less than the CMB calculated vertical flux. Vertical flow age estimates for the 0-9 m unsaturated zone at GDH04 are 60,000 yr (CMB) and 530,000 yr ($^{36}Cl/Cl$). The discrepancy could be due to palaeoclimatic variability such as fluctuations in annual rainfall rate, and variability in Cl^- and ^{36}Cl concentrations of rainwater. Furthermore, clay rich materials are dominant in the upper 4 m, while the remainder of the unsaturated zone is comprised of sand rich materials. The $^{36}Cl/Cl$ calculated vertical flux is based on results from pore waters sampled from only the near surface clay rich zone and is therefore only representative for the upper 4 m rather than the entire 9 m unsaturated zone.

Within the saturated zone, pore waters exhibit less systematic Cl^- and $^{36}Cl/Cl$ trends with increasing depth, which may reflect varying degrees of mixing between pore water and groundwater. At a sampling site located proximal to a granite rock outcropping area, pore waters exhibit a general decrease in $^{36}Cl/Cl$ with depth and those extracted from aquifer materials exhibit greater Cl^- and lower $^{36}Cl/Cl$ than groundwater sampled from piezometers intersecting the same intervals. This suggests that older, more saline, water is residing in lower permeability pore spaces within the aquifers themselves and is potentially a source of Cl^- to regional groundwater. At a sampling site located distal to the basin margin, saturated zone pore waters exhibit fluctuating Cl^- yet relatively consistent $^{36}Cl/Cl$. The corresponding groundwaters in this area exhibit similar $^{36}Cl/Cl$ values yet slightly greater Cl^- content. Groundwater $^{36}Cl/Cl$ is likely the result of varying degrees of mixing between older pore water and younger, more saline groundwater.

Groundwater Cl^- concentrations increase down-gradient within each hydrogeologic unit, indicating hydraulic connectivity and a semi-confined or confined groundwater flow system. Groundwater $^{36}Cl/Cl$ exhibits two distinct value ranges that correspond to proximity to saprolith outcrop areas located in the southern portion of the study area. Groundwater sampled from the southern portion of the study area exhibits an average $^{36}Cl/Cl$ of $120\text{x}10^{-15}$ compared to groundwater sampled in the northern portion of the study area with an average of approximately $85\text{x}10^{-15}$. This suggests that recharge is occurring predominantly in the southern portion of the study area via infiltration of rainwater through saprolith outcroppings. Calculated flow age from the ^{36}Cl delineated recharge zone in the south to the northern portion of the basin (ca. 10 km) is approximately 150,000 yr. This is within reasonable agreement with the calculated Darcy piston flow age of 135,000 yr B.P.

Determination of actual groundwater ages is complicated by processes occurring in both the unsaturated and saturated zones. Processes such as mixing, filtration and halite dissolution can produce $^{36}Cl/Cl$ not solely attributable to ^{36}Cl decay (e.g., Bethke & Johnson 2002). Furthermore, determining an appropriate input ratio for age calculations is often too difficult and therefore ^{36}Cl age calculations can be unreliable (e.g., Davis *et al*. 1998). In this study, the difference between groundwater age calculations using a $^{36}Cl/Cl$ input value of modern atmospheric precipitation verses near surface, unsaturated zone pore water is ca. 350,000 yr. Several studies in Australia (e.g., Bird *et al*. 1989, Turner *et al*. 1991, Cresswell *et al*. 1999) have used $^{36}Cl/Cl$ of shallow groundwater as input values for assessing flow ages in regional systems. However, when vertical infiltration of rainwater is the dominant recharge mechanism, $^{36}Cl/Cl$ of near surface (< 2 m) pore water may be the most appropriate and practical input value available for determining groundwater ages in regional systems.

CONCLUSION

The specific mechanisms influencing $^{36}Cl/Cl$ of pore water and groundwater are dependent on depth below surface, permeability of regolith materials and proximity to recharge areas. The impact of these mechanisms is most apparent in the unsaturated zone where the meteoric $^{36}Cl/Cl$ signature of recharge water is overwhelmed by mixing with near-surface pore water containing greater Cl^- and more depleted ^{36}Cl values.

Knowledge of Cl^- and $^{36}Cl/Cl$ distribution in the unsaturated zone has provided a reliable $^{36}Cl/Cl$ input value for use in age assessments of regional groundwater. Evidence of mixing between pore water and groundwater in the saturated zone is apparent at two sampling locations, yet appears to have more of an impact on the $^{36}Cl/Cl$ content of groundwater located proximal to a recharge area. This demonstrates that groundwater is not in equilibrium with saturated zone pore water, and that $^{36}Cl/Cl$ age calculations for groundwater sampled proximal to recharge areas are reflecting a mixed age. Groundwaters sampled distal to recharge areas appear to be less affected by this type of mixing and exhibit $^{36}Cl/Cl$ values more indicative of aging along the flow path.

REFERENCES

BETHKE C.M. & JOHNSON T.M. 2002. Paradox of groundwater age. *Geological Society of America* **30(2)**, 107-110.

BIRD J.R., CALF G.E., DAVIE R.F., FIFIELD L.K., OPHEL T.R., EVANS W.R., KELLETT J.R. & HABERMEHL M.A. 1989. The Role of 36Cl and 14C Measurements in Australian Groundwater Studies. *Radiocarbon* **31**, 877-883.

COOK P.G., JOLLY I.D., LEANEY F.W., WALKER G.R., ALLAN G.L., FIFIELD L.K. & ALLISON G.B. 1994. Unsaturated zone tritium and chlorine 36 profiles from southern Australia: Their use as tracers of soil water movement. *Water Resources Research* **30(6)**, 1709-1719.

CRESSWELL R., WISCHUESEN J., JACOBSON G. & FIFIELD K. 1999. Assessment of recharge to groundwater systems in arid Southwestern part of Northern Territory, Australia, using chlorine-36. *Hydrogeology Journal* **7**, 393-404.

DAVIS S.N., CECIL D., ZREDA M. & SHARMA P. 1998. Chlorine-36 and the initial value problem. *Hydrogeology Journal* **6**, 104-114.

FIFIELD L.K., OPHEL T.R., BIRD J.R., CALF G.E., ALLISON G.B. & CHIVAS A.R. 1987. The Chlorine-36 Measurement Program At The Australian National University. *Nuclear Instruments and Methods in Physics Research* **B29**, 114-119.

JOHNSTON C.D. 1981. Salt Content of Soil Profiles in Bauxite Mining Areas of the Darling Range, Western Australia. *CSIRO Australian Division of Land Resources Management* **Technical Paper 8**, 1-25.

LOVE A.J., HERCZEG A.L., SAMPSON L., CRESSWELL R.G. & FIFIELD L.K. 2000. Sources of chloride and implications for 36Cl dating of old groundwater, southwestern Great Artesian Basin, Australia. *Water Resources Research* **36(6)**, 1561-1574.

PECK A.J., JOHNSTON C.D. & WILLIAMSON D.R. 1981. Analyses of Solute Distributions in Deeply Weathered Soils. *Agricultural Water Movement* **4**, 83-102.

TURNER J.V., WAITE T.D. & BRADD J.M. 1991. The Conjunctive Use of Isotope Techniques to Elucidate Solute Concentration and Flow Processes in Dryland Salinized Catchments. *International Hydrology & Water Resources Symposium*, Perth, Australia.

WILFORD J., GIBSON D.L., LAWRIE, K.C. & TAN K.P. 2002. Extending regolith-landform maps into the third dimension - unravelling the palaeogeography story for mineral exploration and environmental applications. *In:* G.N PHILLIPS & K.S. ELY eds. *Victoria undercover: Benalla 2002 collaborative geoscience in northern Victoria*. **Conference proceedings and field guide**. CSIRO Publishing, Melbourne, pp. 193-202.

WOOD W.W. 1999. Use and Misuse of the Chloride-Mass Balance Method in Estimating Ground Water Recharge. *Ground Water* **37(1)**, 2-3.