INTRODUCTION
Vertical infiltration of rainwater through sediments in the unsaturated zone commonly recharges groundwater in unconfined aquifers. During recharge, water changes in composition from that of rainwater to one approaching the local groundwater composition. The change is a function of how quickly the water flows through the unsaturated zone and the physical and chemical processes occurring during recharge. Evapotranspiration, mineral dissolution and mixing have often been viewed as limitations to the application of $^{36}$Cl in hydrogeologic studies. However, these mechanisms can be quantified though the combined use of Cl$^{-}$ and $^{36}$Cl, providing a means for understanding solute dynamics and for estimating recharge rates. This application has particular relevance in Australia, where clearing of native vegetation and subsequent alteration to the hydraulic budget has resulted in the mobilization of solutes previously accumulated in the unsaturated zone. However, relatively little is known of past and present arid to semi-arid unsaturated zone dynamics, in particular, solute mobility. This study provides an example of how soil pore water Cl$^{-}$ concentrations and $^{36}$Cl/Cl ratios can be utilized to identify and quantify unsaturated zone Cl$^{-}$ dynamics, estimate groundwater recharge rates, and establish a reliable $^{36}$Cl/Cl input value for age calculations of regional groundwater. The influences of evapotranspiration, mixing and infiltration rates on unsaturated zone pore water chemistry have been investigated to help understand the chemical evolution and timeframes of groundwater recharge to a saline aquifer system in central New South Wales, Australia.

STUDY AREA BACKGROUND
This study focuses on a low-lying alluviated basin in central New South Wales, Australia (Figure 1). Up to 100 m of highly weathered, unconsolidated Cenozoic sediments comprise a heterogeneous hydrogeologic system that hosts brackish to saline groundwater (TDS > 30,000 mg/L). A low hydraulic gradient (< 0.2 m/km) and hydraulic conductivity values of $10^{-5}$ m/s result in an average linear velocity of ~15 cm/yr. Groundwater recharge is likely the result of vertical infiltration of rainwater at outcropping areas along the basin margins and through the near surface sandy-clay sediments present in the southern portion of the basin. Mean annual rainfall is 48 cm/yr. The majority of the study area has been cleared of native Eucalypt forest.

SAMPLING AND ANALYSIS
Pore water was sampled from regolith materials collected proximal (GDH03) and distal (GDH04) to the recharge zone. Laser grain size analyses were performed on regolith materials by Geoscience Australia
Figure 2: Grain size distribution for diamond cores GDH03 and GDH04

Soil pore water was extracted via uniaxial compression at the Australian Bureau of Rural Sciences. Chloride analyses were performed by ion chromatography at The Australian National University (ANU) Department of Earth and Marine Sciences. The analyses of $^{36}$Cl were performed using Accelerator Mass Spectrometry at ANU Department of Nuclear Physics.

RESULTS AND DISCUSSION

High resolution depth profiles of Cl$^-$ and $^{36}$Cl/Cl in the unsaturated zone were compiled at two locations. The two profiles differ in grain size distribution (Figure 2), resulting in two distinct Cl$^-$ and $^{36}$Cl/Cl profiles. Coarser grained materials are present in the near surface at the proximal location, resulting in a greater infiltration rate and lower degree of evapotranspiration. Elevated $^{36}$Cl/Cl ratios were detected in several samples from within the upper root zone (<1.5m) and from 3-5 metres (Figure 3a). These are likely the result of $^{36}$Cl fallout from nuclear weapons testing during the 1950's and 1960's. The deeper "bomb pulse" region corresponds to a region of lower Cl$^-$ concentration in Figure 3b. In combination, the data implies preferential flow along root paths and cracks resulting in less evapotranspiration and mixing during infiltration. Bomb pulse $^{36}$Cl at 5 m indicates a vertical infiltration rate of ~ 14 cm/yr and a high degree of solute mobility. It appears that clearing of native vegetation has resulted in enhanced downward transport of unsaturated zone solutes and represents a significant mechanism of secondary salinization. This contradicts current salinization models which attribute increases in groundwater salinity to the mobilization of solutes in the unsaturated zone by rising groundwater tables.

Figure 3 (a)-(b): $^{36}$Cl/Cl depth profile (a) and $^{36}$Cl/Cl (b) ratio verses Cl$^-$ concentration for rainwater, creek water and GDH03 pore waters

Water not infiltrating the unsaturated zone via preferential flow is likely moving under steady, piston-like flow conditions and is subjected to a high degree of evapotranspiration in the near surface. This process results in long term solute accumulation in the low permeability regolith materials. Numerical mixing models were constructed to estimate the effects of evapotranspiration, mixing and halite dissolution under one-dimensional piston flow conditions (Figure 3b). Based on meteoric-like Br/Cl ratios at both sampling locations, halite dissolution does not appear to be affecting the Cl$^-$ concentrations or $^{36}$Cl/Cl ratios of unsaturated zone pore water (Lenahan et al., in prep.). Chloride and $^{36}$Cl/Cl trends indicate evapotranspiration of rainwater to 400-500 mg/L Cl$^-$ in the upper 0.5 m. Below this depth, the dominant mechanism appears to be mixing of modern, low salinity pore water with older, saline pore water. At GDH03, soil pore water at the base of the unsaturated zone may represent an appropriate input value for $^{36}$Cl dating of groundwater. At GDH04, finer grained sediments near the surface result in a greater degree of evapotranspiration, although mixing is still dominant. Pore waters in the upper 0.5 m exhibit constant $^{36}$Cl/Cl ratios with increasing Cl$^-$ concentrations (Figures 4a & 4b). This trend is indicative of evapotranspiration and suggests a Cl$^-$
accumulation timeframe of approximately 3,500 yrs. The consistent $^{36}$Cl/Cl ratio observed in the near surface pore waters has also

been observed in modern groundwater from numerous studies within Australia (Bird et al., 1989; Turner et al., 1991; Cresswell et al., 1999a; Cresswell et al., 1999b) and may be representative of an average meteoric input ratio over the last several thousand years. However, this ratio is significantly less than the present meteoric ratio. The results suggest that the present day meteoric values are significantly higher than in the past, and may reflect a short term trend attributable to variation in natural cosmogenic nuclide production rates or due to fallout of anthropogenic $^{36}$Cl from nuclear weapons testing in the 1950’s and 1960’s. This is significant for groundwater dating studies that require establishing an accurate $^{36}$Cl/Cl input value. The data indicate that near surface soil pore water in low permeability regolith materials in arid and semi-arid regions may provide a long term record of $^{36}$Cl fallout and provide a more accurate input value for age calculations of regional groundwaters. Below the near surface zone at GDH04, pore waters exhibit steady Cl$^-$ with decreasing $^{36}$Cl/Cl ratios. This indicates present day meteoric Cl$^-$ or $^{36}$Cl deposition is not occurring below 0.5 m and that isotope decay is responsible for the observed $^{36}$Cl/Cl trend. The calculated age difference between pore water at 0.5 m and 3.5 m is ~ 210,000 years. The large time difference is due to a lack of vertical infiltration and demonstrates the timeframes for solute accumulation in the unsaturated zone. These timeframes correspond well with mass balance calculations based on modern Cl$^-$ deposition.

CONCLUSIONS
Our results show how Cl$^-$ and $^{36}$Cl contents of soil pore water can be utilized to determine and quantify unsaturated zone Cl$^-$ dynamics, estimate groundwater recharge rates and to establish a $^{36}$Cl/Cl input value for age calculations of regional groundwater. Detection of bomb-pulse $^{36}$Cl in saline pore water at a depth of 5 m indicates rapid preferential flow through the unsaturated zone and a high degree of solute mobility. This process is likely responsible for enhanced secondary salinization of the regional groundwater. Measurement of high resolution $^{36}$Cl/Cl profile at one location revealed consistent near surface ratios that are likely indicative of the average $^{36}$Cl/Cl ratio of meteoric water over the past several thousand years. This is significant for age calculations of groundwater in this area, and suggests that $^{36}$Cl analyses of near surface pore waters may provide similar information to groundwater dating studies in other arid and semi-arid regions.

REFERENCES