

# High resolution Cl<sup>-</sup> and <sup>36</sup>Cl profiles: Physiochemical mechanisms in the unsaturated zone

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Vertical infiltration of rainwater through sediments in the unsaturated zone commonly recharges groundwater in unconfined aquifers. Understanding vertical flow rates and physiochemical processes during infiltration is critical for assessing groundwater solute origins and mobility. Concentrations of Cl<sup>-</sup> and its radioisotope <sup>36</sup>Cl, can be used to understand the processes and rates. Evapotranspiration, mineral dissolution and mixing have often been viewed as limitations to the application of <sup>36</sup>Cl in hydrogeologic studies. However, these mechanisms can be quantified through the use of Cl<sup>-</sup> and <sup>36</sup>Cl in combination, providing both a means for understanding solute dynamics and for estimating groundwater ages.

High resolution depth profiles of Cl<sup>-</sup> and <sup>36</sup>Cl/Cl in the unsaturated zone were compiled at two locations within a saline aquifer system in central New South Wales, Australia. The two profiles differ in grain size distribution, resulting in two distinct Cl<sup>-</sup> and <sup>36</sup>Cl/Cl profiles. Coarser grained materials are present in the near surface at one location, resulting in a greater infiltration rate and lower degree of evapotranspiration. Bomb pulse <sup>36</sup>Cl was detected in several samples from within the upper root zone (<1.5m). Preferential flow is also evident from 3-5 metres, highlighted by lower Cl<sup>-</sup> concentrations and greater <sup>36</sup>Cl/Cl ratios than in the near surface. Below 5 metres, mixing is the dominant mechanism contributing to increased Cl<sup>-</sup> concentrations. At this location, soil pore water at the base of the unsaturated zone may represent an appropriate input value for <sup>36</sup>Cl dating of groundwater. At the second location, finer grained sediments result in a greater degree of evapotranspiration, although mixing is still dominant. Decreasing <sup>36</sup>Cl/Cl ratios and constant Cl<sup>-</sup> concentrations with increasing depth indicate a lack of vertical infiltration below a depth of 1.5 metres.

Our results show how Cl<sup>-</sup> and <sup>36</sup>Cl contents of soil pore water can be utilized to determine and quantify unsaturated zone Cl<sup>-</sup> dynamics, estimate groundwater recharge rates and to establish a <sup>36</sup>Cl/Cl input value for age calculations of regional groundwater.