



Chloride dynamics across Australia

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1 Introduction

The hydrologic cycle neatly describes the dynamics of water on the earth's surface. The simple hydrochemistry, high solubility and conservative behaviour of chloride mean we can incorporate chloride directly into this simple dynamic construct. Further, the natural occurrence of a radioisotope of chlorine (^{36}Cl) in the environment is useful when studying salt, and thus water, dynamics on and within the earth's surface.

2 Chloride dynamics

We now have a good description of chloride accession across Australia (Keywood, et al., 1997; Farrington, et al., 1993; Blackburn and McLoed, 1983; Hutton, 1976; Hingston and Gailitis, 1976). Simply put: chloride entrained in sea-spray is carried up and washes out in rainfall. Chloride concentration in rainfall is therefore dependent on distance from the coast in the direction of the prevailing winds. Keywood, et al. (1997) describe this in terms of the sum of 2 exponential components: rapid fallout of chloride near the coast, presumably as dissolved salts; and a component that is transported further inland, possibly as dissociated chlorine gas. The precise equation (Keywood, et al., 1998) approximates to:

$y = 52.5^{(-d/56)} + 2.95^{(-d/710)}$	(1)
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where: y is in kg/ha.yr and d is the distance from the coast in kilometres.

Equation (1) provides the input to the soil and ground component of chloride in the hydrologic cycle, and we can use chloride concentration through the soil profile to determine recharge and drainage rates through the unsaturated zone, beneath the root-zone (Walker, 1998).

3 Chlorine-36 input to the hydrologic cycle

We now also have a good description of the chlorine-36 distribution across the continent (Keywood, et al., 1998). Chlorine-36 is predominantly created by spallogenic reactions in the stratosphere and is also entrained in rainfall and washed out. It shows a latitudinal dependence on production and has been shown to vary from 10 to 25 $\text{at/m}^2/\text{s}$ from the north to south of Australia (Keywood, et al., 1998).

In the 1960's, nuclear bomb testing in the southern hemisphere had the effect of introducing sufficient neutrons into the atmosphere to neutron-activate ^{35}Cl to ^{36}Cl . Thus, a series of ^{36}Cl spikes were introduced into the hydrologic cycle that then provided convenient time markers for a number of studies into recent processes of recharge and salt mobility (e.g. Walker, 1998; Cresswell, et al., 2002). Two principles are used: The depth to which the bomb spike has moved in the profile gives an estimate of the rate of recharge at that location, provided a basic understanding of the recharge processes is known. Thus, enriched groundwaters of the unconfined aquifers of northern South Australia indicate recharge rates in excess of 30mm/a in the granitic rocks in the vicinity of the Musgrave Ranges, while the alluvial sediments on the flats exhibit recharge rates on the order of 10mm/a (Cresswell, et al., 1999a). Other bores do not contain bomb-pulse ^{36}Cl , suggesting either very slow to zero recharge rates, or extremely fast rates, and the waters containing bomb-pulse ^{36}Cl has passed out of the system. The former is more plausible, so we might expect the enriched waters to appear in the bores in the near future. Rapid recharge down fractures in the granites is likely to indicate a maximum recharge for this area. The generally arid nature of the country (annual precipitation of 300mm; pan evaporation rates in excess of 3000mm) suggests that we are looking at recharge from only the higher rainfall events. This is confirmed by heavy stable isotope results (Cresswell, et al., 2002).

Alternatively, measurement of ^{36}Cl in pore-fluids from cores can give insights into recharge rates if we can make some simple assumptions regarding the dynamics of the system. Thus, in unconfined systems, where vertical recharge dominates, ^{36}Cl concentrations should decrease down profile while chloride concentrations remain constant.

We can thus make 2 independent estimates of recharge: from chloride mass balance and from ^{36}Cl decay considerations. Thus, for cores taken from southern Queensland, chloride mass balance assuming constant chloride accession over time, give recharge rates of 0.1-0.2 mm/a (Kellett and Mullen, 2003). Chlorine-36 analysis of pore fluids (Cresswell, 2003) gave identical estimates of recharge, supporting the conjecture that vertical flux is several orders of magnitude greater than any horizontal component.

If we combine the chloride accession with ^{36}Cl fallout, we can predict the ratio $^{36}\text{Cl}/\text{Cl}$ in rainfall for any location across Australia. While this provides a useful input to studies on the dynamics of recharge and surface mixing of salts prior to infiltration of surface waters to groundwater systems, we find that surface mixing of salts and evaporation strongly modify the rainfall signature, and we must measure the actual input ^{36}Cl values for each site under investigation (Cresswell, et al, 1999b).

4 Chlorine-36 transport through the hydrological cycle

Once the saturated zone of groundwater is reached a lateral as well as vertical component to water movement generally becomes important, adding an additional component to the dynamics. Further, it is generally noted that groundwaters increase in salinity down gradient as salts are remobilised from the formation through which the waters pass. This is illustrated well in the Great Artesian Basin which shows increasing salinity in the direction of the dominant flow directions (Radke, et al., 2000).

Previous studies (Bentley, et al., 1986; Torgersen et al. 1991), have shown the possibilities of groundwater dating of the Great Artesian Basin. We now have sufficient coverage of this basin to compare the ages and flow rates of the groundwaters using ^{36}Cl as a tracer and the similarity to the proposed hydrogeochemical evolution of the basin waters (Radke, et al., 2000).

We may now look at variable flow through the aquifer and the effects of the addition of chloride to evolving groundwaters. In the case of the Great Artesian Basin, we observe the addition of 75 mg/L chloride over each million years the waters are in the system (i.e. from the time of recharge)(Radke, et al., 2000). This also correlates well with the gradual increase in alkalinity from recharge to discharge. This can be taken as a proxy for age as we approach levels of ^{36}Cl that are too low to give meaningful ages.

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