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THE ROLE OF ^{36}Cl AND ^{14}C MEASUREMENTS IN AUSTRALIAN GROUNDWATER STUDIES

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ABSTRACT. An Accelerator Mass Spectrometry system has been developed using the 14UD tandem accelerator at the Australian National University. It has been used for ^{36}Cl measurements on groundwater samples from the Murray Basin in southeastern Australia. Measurements of ^{14}C have also been made on the same groundwaters. The information can be combined with stable isotope ratios and other data to illustrate the occurrence of processes such as radioactive decay and local recharge in different aquifers.

INTRODUCTION

Groundwaters are widely used throughout much of inland Australia and have been the subject of many studies. The Great Artesian Basin (Fig 1) was chosen for one of the first applications of ^{36}Cl measurements by Accelerator Mass Spectrometry (AMS) and the results confirmed indications from ^{14}C data and flow calculations that the groundwater is very old (>1Myr) (Airey *et al*, 1979; Calf & Habermehl, 1984; Bentley *et al,* 1986). However, ^{36}Cl (half-life 301,000 yr) can only be used for dating groundwater in a confined system which is not subject to gain or loss of chloride except in the recharge area. The Great Artesian Basin provides the best example approximating this requirement.

Another economically very important area of Australia is the Murray-Darling Basin (Fig 1), but it is hydrogeologically very complex with numerous separate and linked aquifers. In such a system, ^{36}Cl can only be expected to serve as an additional parameter for studying flow rates, mixing, etc, and this has been one of the subjects tackled with measurements using the new AMS system at the Australian National University (Fifield *et al,* 1987). Initial results have been obtained for groundwater samples from the Lachlan Fan and Murray Mallee aquifers (shaded areas in Fig 1). A detailed discussion of Murray-Mallee samples and the interpretation of individual results is given by Davie *et al* (1988). Although further measurements are needed to establish the best interpretation, systematic trends are observed which are quite different to those for the Great Artesian Basin. The purpose of this paper is to consider the various processes which affect ^{36}Cl levels in groundwater and their use together with ^{14}C results to assist in explaining the observed trends.

^{36}Cl MEASUREMENTS

The AMS system, using the 14UD tandem accelerator, at the Australian National University has been described by Fifield *et al* (1987). Precipitated AgCl is purified to reduce the S content as much as possible

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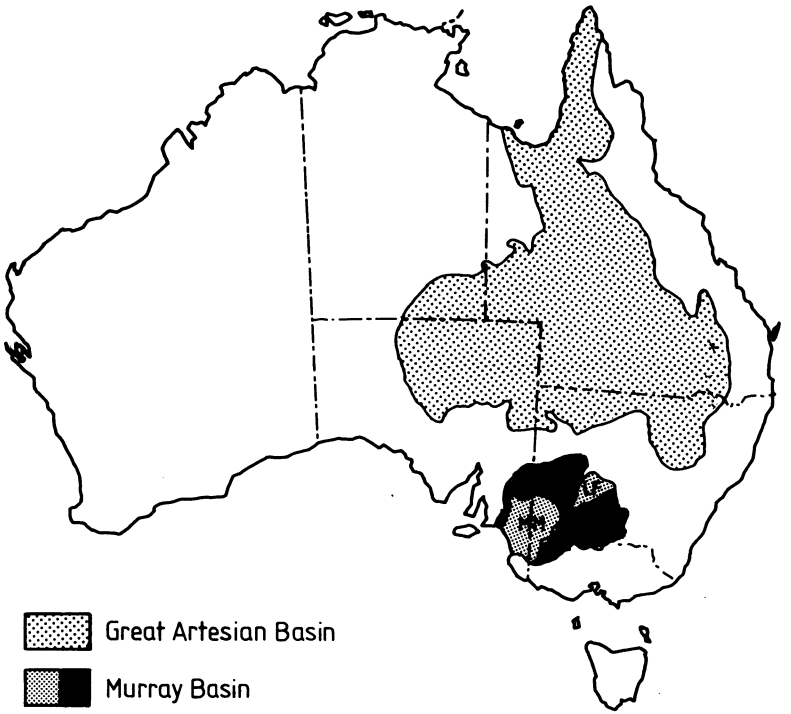

Fig 1. Map of Australia showing the location of the hydrologic basins discussed in this paper

and 300–500 mg is pressed into cones for use in the sputter ion source. Samples as small as 10mg of AgCl can be used if each cone is lined with 500mg of AgBr. The samples are dried in a vacuum oven for 6 hours, in order to minimize the counting rate from $^{18}O^{5+}$ ions. During operation, beams of 5μA or more of Cl^- are obtained from the ion source so that a beam chopper must be used to attenuate the major isotope beams by a factor of 15 or more before injection into the accelerator. An accelerator voltage of 12 MV is used and 10^+ Cl ions are accelerated to 132 MeV before magnetic analysis and detection in a Faraday cup (major isotopes) or a heavy-ion identification system (^{36}Cl). Due to the high vacuum (4×10^{-8} torr) maintained in the 14UD accelerator and beam lines, it has not been necessary to incorporate an electrostatic analyzer in the system.

During a measurement sequence, the inflection magnet, low-energy quadrupoles and terminal voltage are adjusted under computer control to change between ^{35}Cl, ^{37}Cl and ^{36}Cl. The computer also controls the beam chopper, Faraday cups and data collection. A typical measurement sequence consists of 30 sec integrations of both the stable isotope beams and 10 min counting of $^{36}Cl^-$ repeated three or more times as necessary. Provided most of the Cs-irradiated surface of the sample holder is covered with AgCl or AgBr, backgrounds of ^{18}O and ^{36}S are low and, with tails from the ^{35}Cl and ^{37}Cl beams, are adequately resolved by the detector (Fifield *et al,* 1987).

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Source memory effects have been observed at a level of 0.2% for neighboring cones and are only a problem if samples with very high $^{36}Cl/Cl$ ratios are included adjacent to samples with low ratios. Repeat measurements on reference samples show that system parameter and sample variations contribute a standard deviation of, at most, 6% in addition to the counting statistics. Repeat measurements on Weeks Island halite gave a weighted mean of 2×10^{-15} (Davie *et al,* 1988). ^{36}Cl and ^{14}C measurements were made in 36 samples prepared from groundwaters in various aquifers within the Murray-Darling Basin, which occupies a large portion of southeast Australia. Stable isotope ratios were also measured.

INTERPRETATION OF CARBON ISOTOPE RESULTS

Data on ^{14}C and $\delta^{13}C$ have been used extensively to identify processes affecting groundwaters. In the case of the Great Artesian Basin (GAB), a correlation between $\delta^{13}C$ and the reciprocal of bicarbonate concentrations indicates that the carbonate is predominantly of marine origin (Airey *et al,* 1979). The ^{14}C results show significant values (>1% modern) chiefly in limited areas close to recharge (Calf & Habermehl, 1984). These results, together with hydraulic information, lead to the conclusion that the GAB is largely a confined aquifer with low flow rates and progressive aging of water away from the recharge areas.

TABLE 1

^{14}C and Cl measurements for Lachlan Fan groundwater

Sample	^{14}C % mod	^{36}Cl 10^{-6} at/L	Cl^- mg/L	$^{36}Cl/Cl$ $x10^{-15}$	Aquifer*
70	76	150	52	172	P
67	64	100	34	176	P
69	73	115	38	176	P
65	44	185	74	148	UR
68	79	1140	420	160	P
60	27	485	210	136	LR
61	34	395	145	161	UR
66	48	175	65	162	P
64	42	11750	3760	184	UR
59	4	6445	2790	136	UR
58		5300	3120	100	LR
55	0.1	4010	1920	123	LR
62	36	6160	4650	78	P
56		1480	1130	77	LR
57		1250	1390	53	LR
71		585	1110	31	LR

* P = Pliocene; LR = Lower Renmark; UR = Upper Renmark

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The Murray-Darling Basin is a relatively complex system which is characterized by relatively small changes in stable isotope ratios. ^{14}C measurements on groundwater samples from the Lachlan Fan are listed in Table 1, together with the aquifer involved in each case. The results are listed in order of distance to the west of the recharge area (near Hillston) and, hence, in order of distance along the main flow line across potentiometric surfaces which lie approximately north-south. The most significant feature of ^{14}C results from this initial sampling is the drop from close to modern at the recharge area to ca 1% modern towards the center of the Basin. The calculated flow rate is 3.6 m yr^{-1} which is in agreement with a flow of 5.2 m yr^{-1} calculated from the Darcy flow equation. The maximum age of the water sampled is, thus, of the order of 30,000 yr. ^{14}C measurements are not yet available for groundwater samples from the Murray-Mallee region.

INTERPRETATION OF CHLORINE RESULTS

The total chloride and ^{36}Cl contents of groundwaters are affected differently by various environmental processes (Fig 2). The central portion of

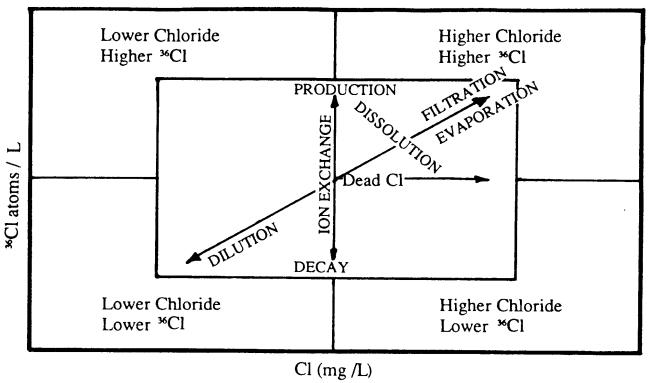

Fig 2. Effect of environmental processes on ^{36}Cl and Cl values; inner section: changes in ^{36}Cl; outer section: mixing of two bodies of water

the figure shows processes affecting Cl atoms in a particular body of water. Decay moves values vertically downwards in the figure and, since decay proceeds independently to other processes, an appropriate vertical vector should be combined with vectors describing any of the other processes. In other words, when water ages significantly on the time scale of the ^{36}Cl half-life (301,000 yr), the coordinates in Figure 2 will move along lines that curve downwards.

Production of ^{36}Cl by neutron capture in ^{35}Cl in groundwater would move values vertically upwards, whereas the dissolution of chloride which has been subject to a variety of sub-surface ^{36}Cl production mechanisms (Fabryka-Martin, 1988), would populate the top right quadrant of the figure. Leaching of dead chloride provides horizontal movement to the right whereas *in-situ* production of ^{36}Cl would result in movement upwards in the

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figure. A number of processes are also shown (Fig 2) which would give rise to movement along a line to or from the origin.

The outer section of Figure 2 illustrates the effects of mixing of two water bodies. The observed coordinates will then move along a straight line joining the points applying to the separate bodies. This linear behavior is not observed when $^{36}Cl/Cl$ is plotted against ^{36}Cl values. It will be clear from Figure 2 that any observed change can be explained on the basis of either changes affecting Cl atoms or the mixing of water bodies. Fortunately, measurements of other parameters provide a basis for rejecting some of the alternative hypotheses.

Results for ^{36}Cl and Cl in the Australian GAB (Bentley *et al,* 1986) are plotted in Figure 3. A considerable spread of values was observed for

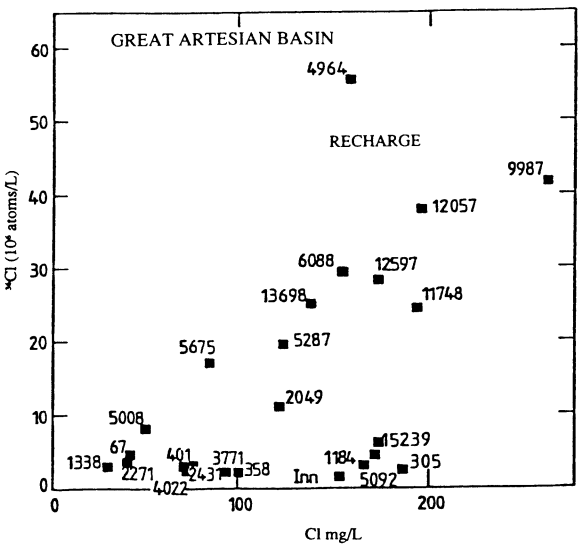

Fig 3. Results of ^{36}Cl and Cl measurements for groundwater samples from the Australian Great Artesian Basin (Bentley *et al,* 1986)

groundwater samples from near the recharge area but much lower ^{36}Cl content was observed as the distance along the flow lines increased. Decay is clearly important and this is supported by the ^{14}C data, which shows significant levels only near the recharge area. The lowest ^{36}Cl value was observed at the furthest distant point (Inn, ca 800km) indicating an age of close to 10^6 yr. Bentley *et al* (1986) interpreted the variation in initial chloride content as evidence for addition of low $^{36}Cl/Cl$ ratio chloride to establish low and high chloride decay lines. Other interpretations are possible but ^{36}Cl decay is undoubtedly a dominant process in the GAB.

Measurements of $^{36}Cl/Cl$ and total chloride have been made on 16 groundwater samples from the Lachlan Fan area of the Murray-Darling Basin (see Fig 1). The ^{36}Cl and Cl concentrations derived from these results are included in Table 1 and plotted in Figure 4. They show a trend opposite

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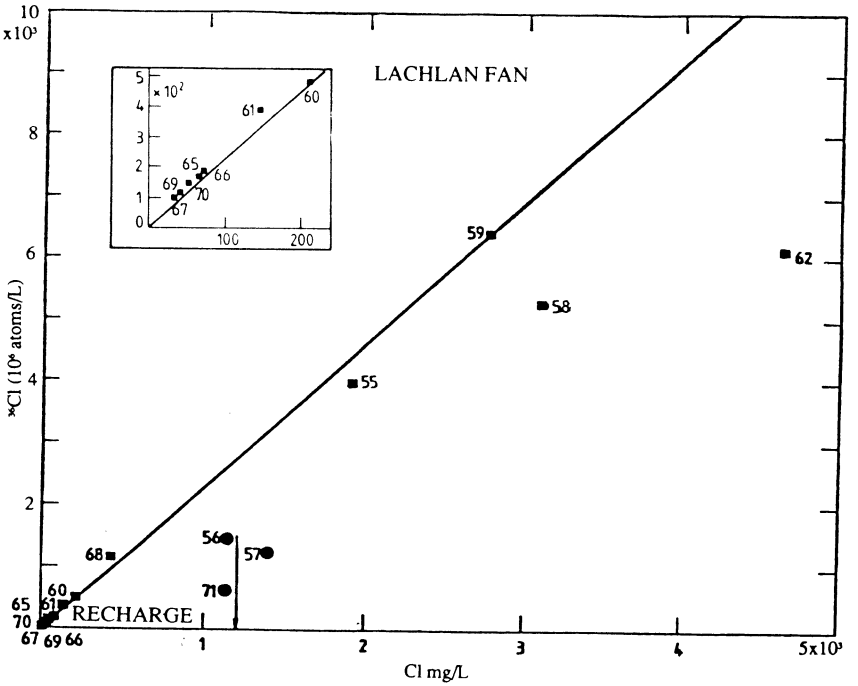

Fig 4. Results of ^{36}Cl and Cl measurements for groundwater samples from the Lachlan Fan area of the Murray-Darling Basin, Australia. The points near the origin are for wells in the recharge area and the lines illustrate schematically some of the possible trends involved.

to that of Figure 3. Low values are observed for samples from sites closest to the recharge area at the eastern end of the Lachlan Fan. A major increase in both ^{36}Cl and Cl is observed down the flow line towards the west with most values lying close to the line in Figure 4 which defines a constant $^{36}Cl/Cl$ ratio (=140). The maximum age of the water is of the order of 30,000 yr, so that ^{36}Cl decay is insignificant in these samples. The nearly linear correlation between ^{36}Cl and total Cl observed for most samples indicates that the dominant processes are most likely to be evaporation and dissolution of constant ratio ($^{36}Cl/Cl$) chloride. Stable isotope data show no evidence for the effects of filtration.

Some of the points in Figure 4 depart from the main line and three of these (nos. 56,57,71) are for groundwater from wells a considerable distance from the flow line connecting the other sites. These three points imply that decay could be important in this area but ^{14}C data are not yet available to confirm this conclusion. Alternatively, mixing with water containing "dead" chloride may explain these results.

Chlorine isotope data for groundwater from the Mallee region of the Murray-Darling Basin (Davie *et al,* 1988) are shown in Figure 5. Again, there is an increase in both ^{36}Cl and Cl values away from the recharge area along several lines leading away from the origin. As flow lines in this region are parallel to the southern Australian coast, the preferred interpretation is

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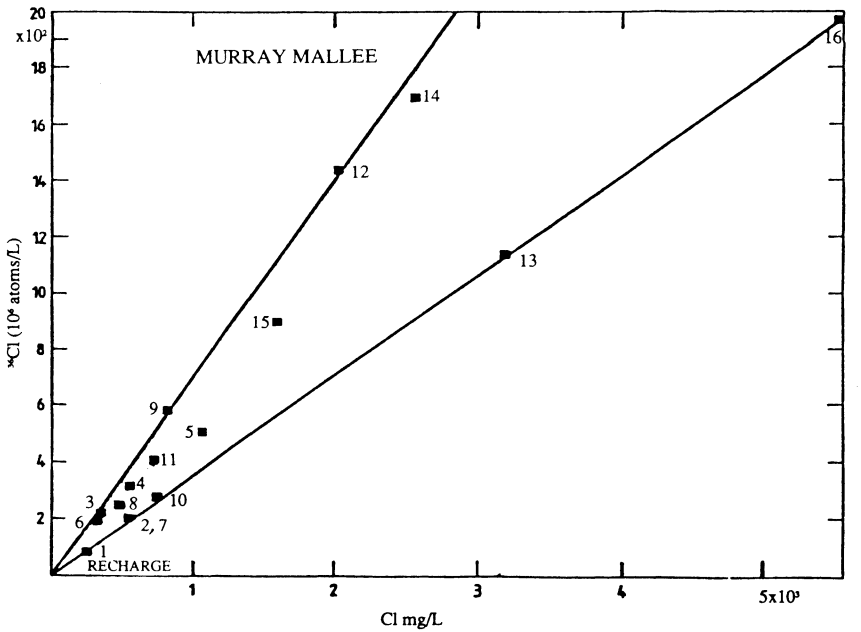

Fig 5. Results of ^{36}Cl and Cl measurements for groundwater samples from the Mallee area of the Murray-Darling Basin, Australia. The lines illustrate schematically some of the possible trends involved.

that the effects of percolation of rainwater with ^{36}Cl/Cl ratios varying by a factor of 2 are controlling the observed results. Further measurements are needed in both regions to confirm the tentative conclusions reached but it is clear that different processes are important in different regions. A number of independent parameters are needed to identify these processes and ^{36}Cl measurements have an important role to play in such work.

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