

Chlorine-36 measurements in the Murray Basin: preliminary results from the Victorian and South Australian Mallee region

R.F. Davie¹, J.R. Kellett², L.K. Fifield³, W.R. Evans², G.E. Calf⁴, J.R. Bird⁴, S. Topham⁴ & T.R. Ophel³

³⁶Cl analyses of groundwater samples from 18 wells in the Victorian and South Australian Mallee region of the Murray Basin have been carried out using the technique of accelerator mass spectrometry. Results of these analyses are discussed and presented as evidence for significant recharge from rainfall over much of the

study area to the underlying Murray Group limestone aquifer. In addition, results indicate areas where further ³⁶Cl measurements of Murray Mallee groundwater would provide useful hydrological information on both recharge and discharge mechanisms.

Introduction

Chlorine-36 is a naturally occurring radioactive isotope with a half-life of $301\,000 \pm 2000$ years (Browne & Firestone, 1986) and is the only unstable isotope of chlorine with a half-life greater than one hour⁵. Both stable chloride and ³⁶Cl are natural components of recharge waters into underground aquifers. Furthermore, within the aquifer environment the highly soluble chloride ion has simple geochemistry. These attributes, together with variations in the ³⁶Cl content of environmental sources of chloride, make ³⁶Cl an ideal isotope for studying salt and water movement within an aquifer system.

The recent development of methods for measuring ³⁶Cl at environmental levels has resulted in considerable interest in applying ³⁶Cl to hydrological systems. For example, ³⁶Cl has been used to study the hydrodynamics of the Great Artesian Basin (Bentley & others, 1986b) by tracing the decay of ³⁶Cl along a flow line. In contrast, the pulse of ³⁶Cl produced in atmospheric nuclear weapons tests has been used to monitor modern recharge rates in arid soils (Phillips & others, 1984, 1988). Early studies of environmental ³⁶Cl have been reviewed by Bentley & others (1986a). However, there has been little in the way of detailed systematic studies, or in the use of ³⁶Cl in conjunction with other isotopes (Bird & others, 1988), and the full potential of ³⁶Cl as a hydrological tracer has yet to be realised. The measurements presented here emphasise the usefulness of ³⁶Cl as a natural tracer in environmental systems. The measurements are used to indicate sources of recharge into the groundwater system, and also show that a combination of ³⁶Cl and chloride measurements can provide information about the complicated salinity features exhibited by discharge zones within the study area.

Over the last three years, the ability to measure ³⁶Cl at environmental levels using the technique of accelerator mass spectrometry (AMS) has been developed in Australia, following earlier work in this field at other laboratories (see, for example, Elmore & others (1979) and the review article by Elmore & Phillips (1987)). After a brief discussion of environmental sources of ³⁶Cl, we present details of the ³⁶Cl measurement system based on the 14UD accelerator at the Australian National University, and the results

of a preliminary study of ³⁶Cl levels in some of the Murray Mallee aquifers.

Environmental sources of ³⁶Cl

Chlorine-36 in the atmosphere is produced primarily by cosmic ray spallation reactions on atmospheric ⁴⁰Ar (Lal & Peters, 1962, 1967). Most of this cosmic ray production is in the stratosphere, where the production rate varies with geomagnetic latitude, because of the effect of the earth's magnetic field on the cosmic rays. Cosmic ray production of ³⁶Cl in the troposphere is also significant. However, the integrated column production rate in the troposphere is largely independent of latitude. Most of the ³⁶Cl produced within the stratosphere descends into the troposphere at latitude 35–40°, where a discontinuity in the tropopause allows the transfer of air from stratosphere to troposphere. As a result of this transfer of ³⁶Cl from the stratosphere to the troposphere, the distribution of cosmogenic ³⁶Cl within the troposphere is greatest near 40° latitude. However, distribution is broadened by air mixing and circulation within the troposphere (Lal & Peters, 1962, fig. 15)⁶.

The cosmogenic ³⁶Cl within the troposphere is mixed with atmospheric chlorine salts of marine and terrestrial origin. These salts typically contain only small amounts of ³⁶Cl, relative to the cosmogenic component. Therefore, the ratio of ³⁶Cl ions to Cl ions in precipitation is largely determined by the ratio of cosmogenic ³⁶Cl to the amount of marine and terrestrial salts in the precipitation. In near-coastal regions, there is a large amount of chloride in atmospheric precipitation, as a result of the dominant influence of marine salts in these regions. However, the amount of chloride in precipitation drops markedly with increasing distance from the ocean (Hutton, 1976; Hutton & Leslie, 1958; Blackburn & McLeod, 1983). Therefore, the ratio of ³⁶Cl to total chloride is low for precipitation in coastal regions, and increases with distance from the ocean. This produces a variation in the ³⁶Cl/Cl ratio in atmospheric precipitation, from a few parts in 10¹⁵ on the coast to several hundred parts in 10¹⁵ in continental interiors.

Calculated ³⁶Cl/Cl ratios of modern atmospheric precipitation in and around the Murray Basin are shown in Figure

¹ Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW 2234. Present address: Department of Nuclear Physics, Research School of Physical Sciences, Australian National University, GPO Box 4, Canberra, ACT 2601

² Division of Continental Geology, Bureau of Mineral Resources, GPO Box 378, Canberra, ACT 2601

³ Department of Nuclear Physics, Research School of Physical Sciences, Australian National University, GPO Box 4, Canberra, ACT 2601

⁴ Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW 2234

⁵ Chlorine has two stable isotopes, ³⁵Cl and ³⁷Cl, which are many orders of magnitude more abundant than ³⁶Cl. The natural mixture of these three isotopes makes up environmental Cl.

⁶ In addition to the published works by Lal & Peters (1962, 1967), the authors wish to acknowledge a private communication from D. Lal (October 7, 1988) which clarified some of the points addressed in this paragraph.

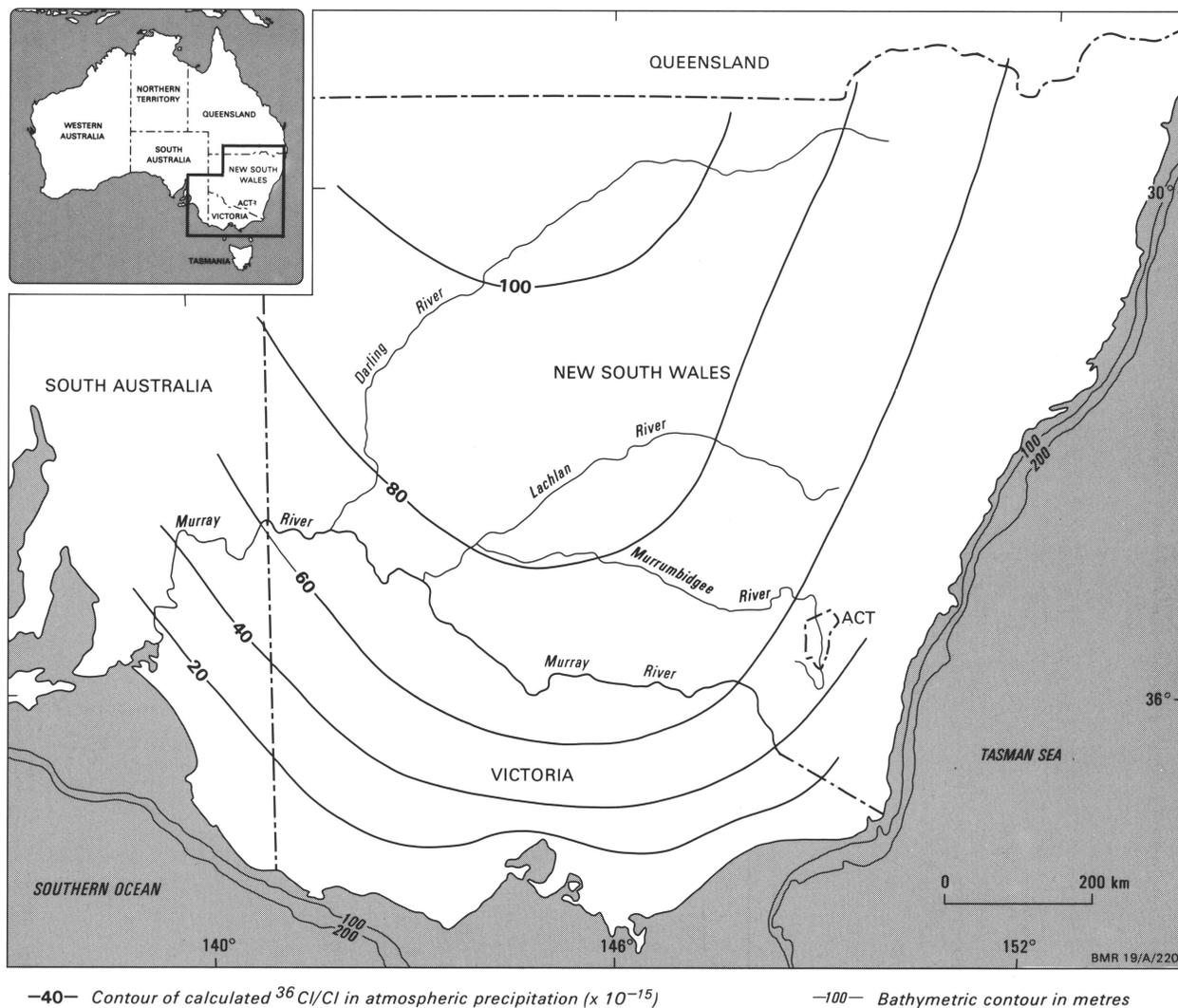


Figure 1. Calculated $^{36}\text{Cl}/\text{Cl}$ ratios of modern atmospheric precipitation in and around the Murray Basin. Contour lines of the $^{36}\text{Cl}/\text{Cl}$ ratio are shown in units of 10^{-15} .

These estimates of the $^{36}\text{Cl}/\text{Cl}$ ratio were based on measurements of the salinity of atmospheric precipitation by Hutton & Leslie (1958) and Blackburn & McLeod (1983), and estimates of ^{36}Cl fallout as a function of latitude (Lal & others, 1962, 1967; Bentley & others, 1986b). The shaded area is the study region shown in Figure 2.

1. These estimates of the $^{36}\text{Cl}/\text{Cl}$ ratio were based on measurements of chloride in atmospheric precipitation by Hutton & Leslie (1958) and Blackburn & McLeod (1983), coupled with the deposition rate of cosmogenic ^{36}Cl as a function of latitude (Lal & Peters, 1962, 1967; Bentley & others, 1986a). Similar calculations for the United States have been presented by Bentley & others (1986a). In calculating these ratios, it was assumed that the only source of ^{36}Cl in the precipitation was cosmogenic production. Comparison of the calculated values with measurements of the $^{36}\text{Cl}/\text{Cl}$ ratio in modern recharge waters (G.R. Walker, CSIRO, personal communication) indicates that these calculations are in good agreement with values observed in the Murray mallee region. However, these calculations have yet to be compared with direct measurements of $^{36}\text{Cl}/\text{Cl}$ ratios in samples of atmospheric precipitation. The calculations indicate that the $^{36}\text{Cl}/\text{Cl}$ ratio in atmospheric precipitation varies by approximately one order of magnitude over the basin—this variation is potentially very useful in studies of salt and water movement within the basin.

In addition to atmospheric production, ^{36}Cl can be produced in subsurface chlorine as a result of neutron capture

on ^{35}Cl . The neutron flux for this reaction is produced as a result of natural radioactivity in the aquifer matrix. In such cases, the $^{36}\text{Cl}/\text{Cl}$ ratio will asymptotically approach the secular equilibrium value characteristic of the aquifer environment. This secular equilibrium ratio depends upon local U and Th concentrations, and the chemical composition of the aquifer matrix. Typical secular equilibrium $^{36}\text{Cl}/\text{Cl}$ ratios range from $\sim 4 \times 10^{-15}$ in sandstone to $\sim 30 \times 10^{-15}$ in granite (Bentley & others, 1986a), while ratios in materials with unusually high U or Th content can be very much higher. As with radioactive decay, the time constant affecting the approach to secular equilibrium is the ^{36}Cl half-life. Therefore, subsurface production will usually be important only in salts which are contained within the aquifer environment for times of the order of 300 000 years or longer, unless the secular equilibrium value is very high as a result of unusually large U and Th concentrations.

There are two further major sources of environmental ^{36}Cl . First, ^{36}Cl is produced in the lithosphere by cosmic ray interactions (Yokoyama & others, 1977; Kubik & others, 1984; Nishiizumi & others, 1984). This cosmic ray induced production is greatest near the surface, falling off rapidly

with depth because of the absorption of cosmic rays by overlying rock. However, some components of cosmic radiation have greater penetration, and ^{36}Cl attributed to cosmic ray production has been observed down to depths of 30 m in limestone (Kubik & others, 1984). Secondly, ^{36}Cl was produced in atmospheric nuclear explosions by neutron capture on ^{35}Cl in seawater (Elmore & others, 1982; Bentley & others, 1982). The first such nuclear explosion likely to have produced significant quantities of ^{36}Cl was an underwater explosion at Bikini Atoll in 1946. However, most bomb ^{36}Cl was produced in much larger explosions at Bikini and Enewatak (formerly Eniwetok) Atolls in the 1950s.

Measurement of ^{36}Cl in environmental samples

The ratio of ^{36}Cl to stable chloride in typical environmental samples is of the order of a few parts in 10^{14} . This very low concentration of ^{36}Cl , coupled with the very long half-life of ^{36}Cl , renders the technique of decay counting unsuitable for most environmental applications of ^{36}Cl measurements. Furthermore, conventional mass spectrometry is unable to detect ^{36}Cl at environmental levels, due to interference from the isobar ^{36}S and mass-36 molecules. As a result, although some early attempts were made to apply ^{36}Cl measurements to environmental problems (e.g. Davis & Schaeffer, 1955), little real progress was made before the advent of accelerator mass spectrometry techniques for detecting ^{36}Cl (Elmore & others, 1979).

Accelerator mass spectrometry (AMS) has several advantages over conventional mass spectrometry or decay counting techniques for determining the abundance of rare isotopes. First, the acceleration process used in AMS involves stripping the outer electrons from the accelerated ion. This process essentially dissociates all molecular ions, and thus removes the molecular interference which causes problems in conventional mass spectrometry. Secondly, the high energies used in AMS allow ^{36}Cl to be easily separated from its isobar ^{36}S , and other interfering ions, by their rate of energy loss in a heavy ion detector. This ability to discriminate between ^{36}Cl and other accelerated ions allows very low background levels to be attained. Thirdly, because AMS detects individual ^{36}Cl atoms, rather than radioactive decays, the advent of AMS has allowed measurements to be made on very small samples. For example, ^{36}Cl has been measured by conventional decay counting with 13 g of chloride (Calf & Airey, 1986), whereas AMS requires only ~2 mg of chloride and has a sensitivity 10–100 times greater.

Hydrogeology of the Victorian and South Australian Murray Mallee region

The study area comprises that part of the Mallee region of the western Murray Basin underlain by the Murray Group limestone aquifer (Fig. 2). The region is underlain by up to 600 m of Cainozoic sediments which thicken in a northerly direction towards a centre of sediment deposition in the Renmark area. The sediments are bounded by buried bedrock ridges, which have accumulated thinner sediment covering, along the southwestern margin of the area (Padthaway Ridge).

These sediments can be subdivided into three main aquifer systems (Brown, this issue; Evans & Kellett, this issue). The general setting of the study area within the broader Murray Basin stratigraphic context is shown in Figure 3. The deeper aquifer, the Renmark Group, consists of car-

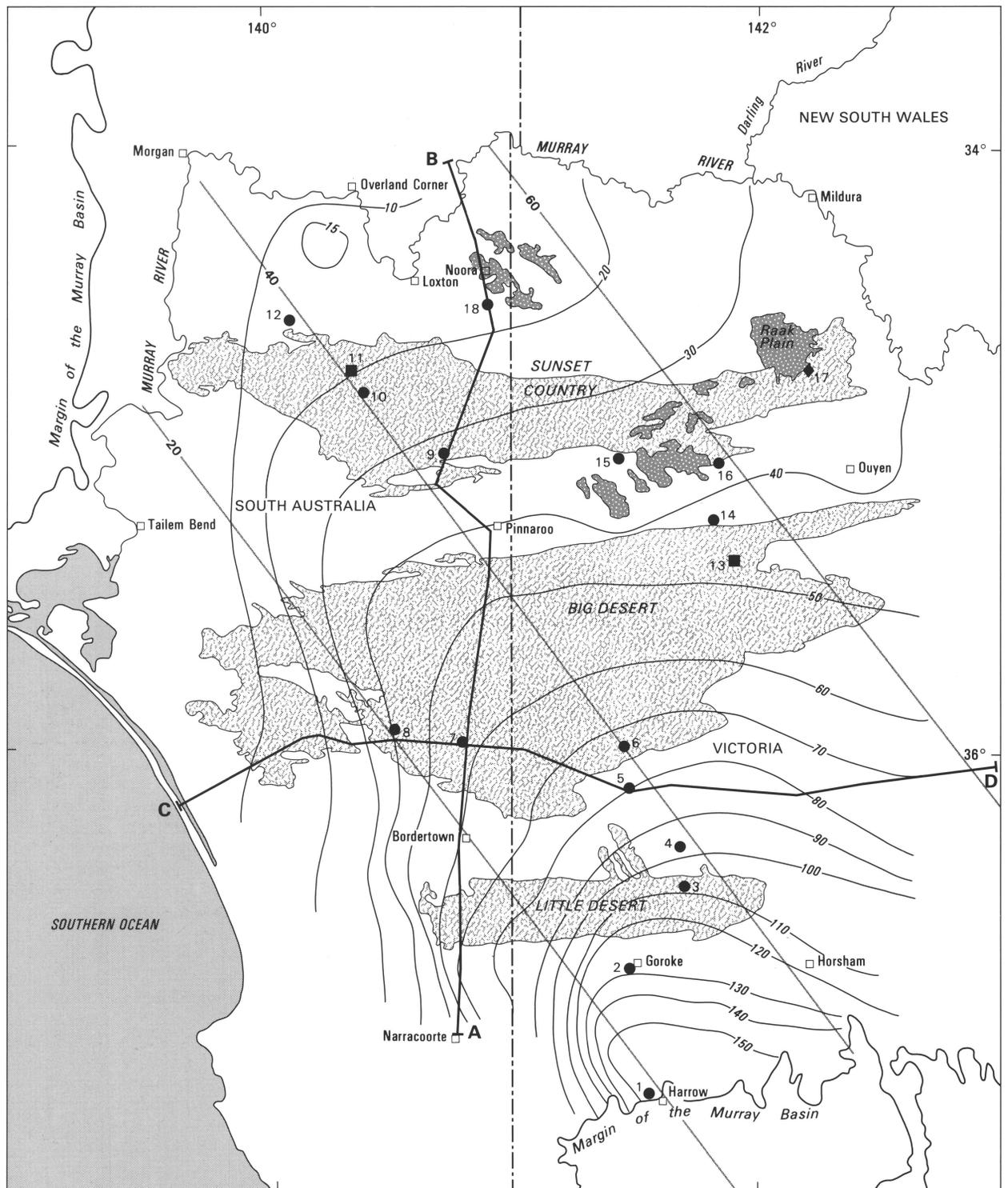
bonaceous clay and silt, with interbedded sand, and locally attains a maximum thickness of 300 m. This aquifer is overlain by the lower confining layer, the Ettrick Formation, a marine clay up to 20 m thick that defines the transgression of the region by the sea, about 30 Ma ago. The marine Murray Group limestone aquifer overlies this confining layer. This, in turn, is overlain, in the centre and east of the region, by the marginal-marine Bookpurnong beds, which form the upper confining layer. East and north of the study region, the Murray Group limestones grade laterally into the finer-grained, lower-permeability marine calcareous sand and clay of the Winnambool Formation and Geera Clay, the mid-Tertiary low-permeability barrier. The youngest marine sediment deposited in the region is the Loxton-Parilla Sand, which overlies the Bookpurnong beds except in the west, where it directly overlies the Murray Group limestone aquifer. The Loxton-Parilla Sand is a component of the regional Pliocene Sands aquifer. Figure 4 shows the regional relationship between aquifers as depicted on cross-sections running along and across the main flow direction.

The sea retreated from the region about 2 Ma ago, leaving a landscape composed of a series of linear beach ridge sand dunes with intervening low areas, or swales. This complex landscape was further modified by the action of successive periods of wind erosion. The first such period reworked the uppermost portions of the Loxton-Parilla Sand into east-west-trending sand dune fields. These dune fields have themselves been reworked at later times into 'blow-out' features represented by the Little and Big Deserts, and the Sunset Country (Fig. 2).

The groundwater flow system in the three aquifers — the Renmark Group, Murray Group and Pliocene Sands — can be divided into regimes either side of the Murray River. The Murray River is effectively a hydrogeological divide. In the south, water enters the aquifers in the southern recharge zones and flows north-northwest towards the Murray River. Figure 2 shows contours of the water table (the water level in the uppermost aquifer, which is the Pliocene Sands in the east and the Murray Group limestone in the west) and groundwater flow lines. The deeper aquifers in this southernmost area receive water by downwards leakage through the overlying aquifers. The Pliocene Sands aquifer is recharged from rainfall over most of its surface. It is thought that there is a significant component of downwards leakage from this upper aquifer into the Murray Group in most areas. To the west, where the Pliocene Sands directly overlie the Murray Group limestone, that is, where the upper-Tertiary confining layer is absent, the limestone is unconfined. This enables relatively unimpeded transmission of infiltrated rainfall into the Murray Group aquifer through the unsaturated Pliocene Sands aquifer.

The salinity distribution of the groundwater of the study area is complex. The fresher water in any of the three aquifers is generally found in the southernmost areas, reflecting recharge conditions of enhanced precipitation and relatively lower evaporation. Outside the recharge zones, the Pliocene Sands aquifer is generally more saline than either the Murray Group limestone aquifer or the Renmark Group aquifer. The latter is marginally less saline than the former at any site. The Geera Clay to the east diffuses connate salts into the underlying Renmark Group aquifer (J.S. Hanor, Louisiana State University, personal communication).

The northern groundwater system, which is not part of the study area, has much shorter flow paths. The water for this aquifer system is recharged around the foothills of the



BMR 19/A/221

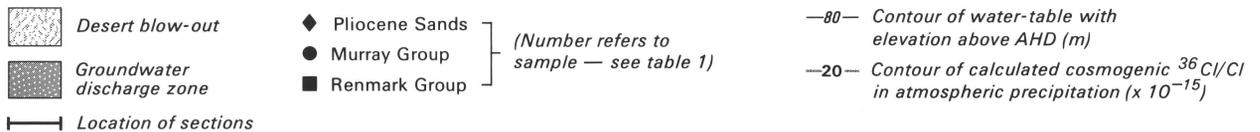


Figure 2. Map of the study area indicating geographic features, potentiometric surface of the Murray Group limestone aquifer, positions of well sites, location of sections shown in Figure 4, and calculated $^{36}\text{Cl}/\text{Cl}$ ratios in modern atmospheric precipitation.

northwestern Murray Basin, and then flows south towards the Murray River. The groundwater is more saline than that in the southern area.

Discharge from both flow systems is into the Murray River,

which incises into the Pliocene Sands aquifer from the eastern margin of the study region to Overland Corner, and into the Murray Group aquifer from Overland Corner to the western margin of the study region. This incision allows direct hydraulic connection between groundwater

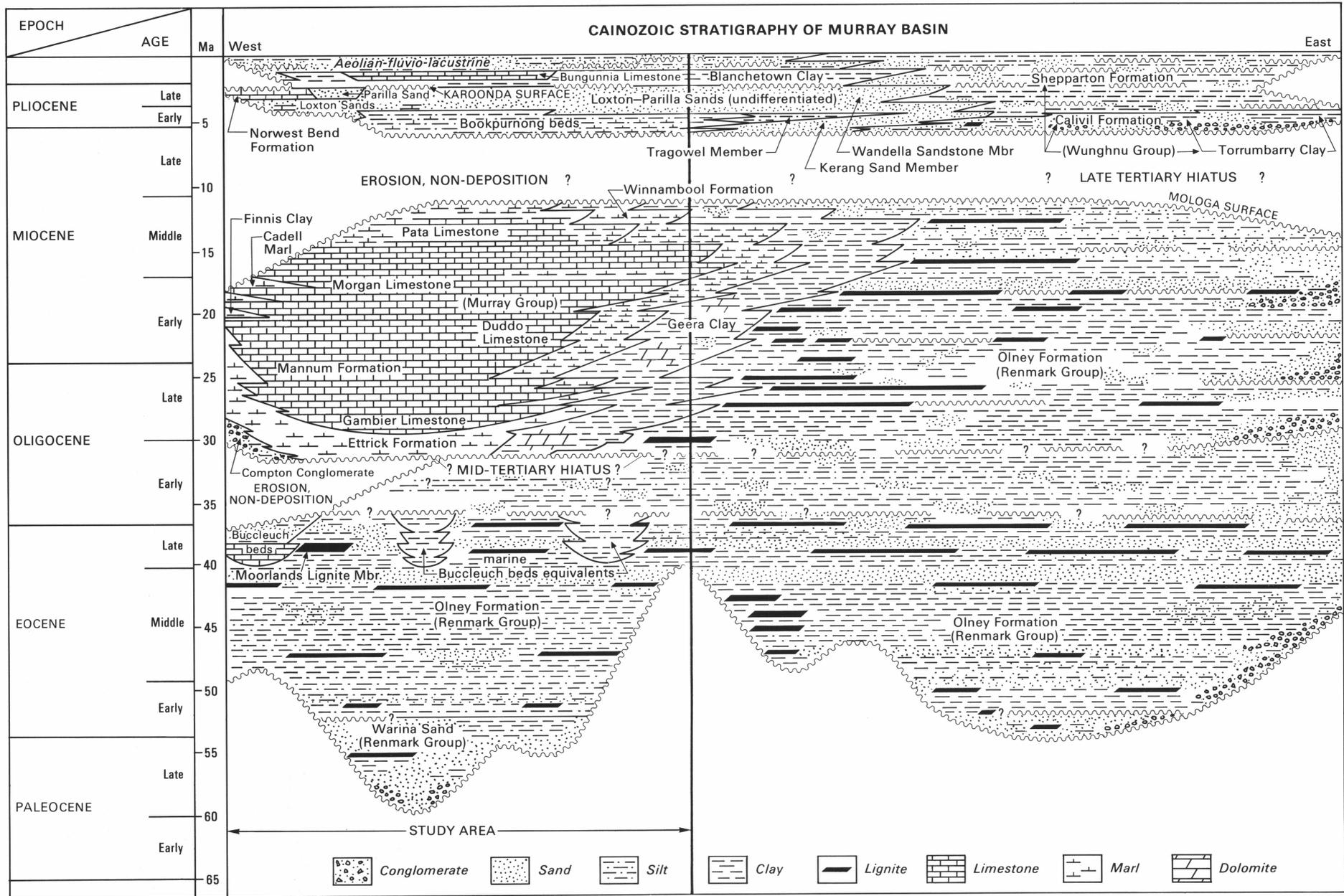
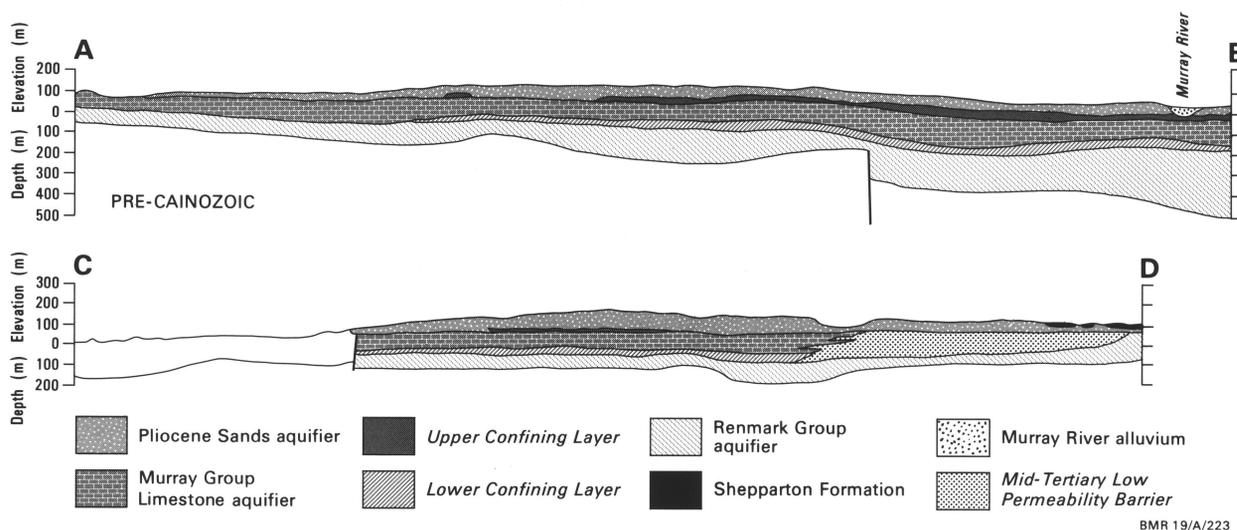


Figure 3. General stratigraphy of the Murray Basin showing study area.



BMR 19/A/223

Figure 4. Cross-sections through study area, showing regional aquifer relationships.

For location of sections, see Figure 2.

and the river. For most of the time, groundwater leaks into the river. However, during times of high flow, the river may well locally recharge the aquifer(s) next to its channel. The deeper Renmark Group aquifer discharges groundwater upward into the overlying Murray Group aquifer in these central areas surrounding the river. This area is therefore a mixing zone of groundwater from the northern and southern flow regimes, and possibly minor amounts of river water.

Discharge also occurs from the Pliocene Sands aquifer in discrete areas of the southern flow regime. These groundwater discharge zones, called 'boinkas' (Macumber, 1983), are found in the Walpeup district, at Raak Plain, and at Noora. The boinkas occur where the water table comes within a few metres of the ground surface and water is available for direct evaporation. They are characterised by the precipitation of salts at the ground surface and highly saline groundwater in the upper aquifer underlying the site. Salts from this concentrated groundwater are likely to diffuse downwards into the deeper aquifers, the flux depending upon the concentration gradient between aquifers.

Experimental work

Silver chloride (AgCl) samples were precipitated from groundwater at 18 bore sites, and later purified in a manner similar to that described by Conard & others (1986). Between 20 and 350 mg of AgCl were pressed into copper sample holders before AMS analysis. For the smaller samples, AgBr with a very low sulphur and chlorine content was pressed first, followed by the AgCl.

The ^{36}Cl measurements reported here were carried out using the AMS system based on the 14UD accelerator at the Australian National University, which has been developed over the last 3 years as a collaborative program between the Australian Nuclear Science and Technology Organisation and the Australian National University. Full details of the measurement system have been published elsewhere (Fifield & others, 1987; Davie & others, 1987).

Repeated measurements on standards and blank material have indicated that ^{36}Cl measurements carried out with this system have a long term reproducibility of about 6% and a sensitivity for $^{36}\text{Cl}/\text{Cl}$ of a few parts in 10^{15} (Davie & others, 1988). This performance is sufficient for most en-

vironmental ^{36}Cl studies, and is comparable with that reported by other AMS groups working on ^{36}Cl (see, for example, Leavy & others, 1987).

In addition to ^{36}Cl analyses, major cation and anion analyses were carried out on groundwater samples from each site. The chlorine concentrations for all samples except the Karte 4 and Wanbi Irrigation bores were obtained by wet chemistry and ion chromatography. Chloride concentrations for these two samples were estimated from their total dissolved solids (TDS) using linear regression of Cl against TDS based on data from a large number of sites.

Results and discussion

Results of the ^{36}Cl measurements and chloride concentrations for the various wells are given in Table 1, which also gives names of well sites, and the number used to identify the well in the following text and in Figures 2, 5, 6 and 7. Positions of the wells within the Murray Mallee are shown in Figure 2, with the potentiometric surface¹ in the Murray Group aquifer. This figure also indicates the calculated $^{36}\text{Cl}/\text{Cl}$ ratio in modern atmospheric precipitation within the study region, as discussed earlier.

The $^{36}\text{Cl}/\text{Cl}$ ratios of the samples are plotted in Figure 5 as a function of ^{36}Cl concentration. The inset indicates the effects that different fundamental processes may have upon the ^{36}Cl signal. For example, the addition of ^{36}Cl to a body of water will move the $^{36}\text{Cl}/\text{Cl}$ signal on this diagram radially outwards, as indicated. In contrast, the concentration of salts within a water body by evapotranspiration will change the ^{36}Cl signal by increasing the ^{36}Cl concentration, but leaving the $^{36}\text{Cl}/\text{Cl}$ ratio unaltered. In addition, a mixture of two water bodies will have a ^{36}Cl signal intermediate between that of its two end members. Generally, the processes occurring within the natural environment are a combination of the fundamental processes illustrated, together with the mixing of two water bodies.

Most samples in the present study are from the Murray Group limestone aquifer. The rate of flow of groundwater

¹ The distribution of water level data from which this surface was compiled is not uniform. In particular, the potentiometric surface depicted under the Big and Little Deserts may not reflect the true conditions, because there is sparse water level information.

Table 1. ^{36}Cl and Cl^- measurements of Murray Mallee samples.

#	Well	Aquifer ¹	$^{36}\text{Cl}/\text{Cl}$ 10^{-15}	Cl^- mg l^{-1}	$^{36}\text{Cl}^-$ $(10^6 \text{ atoms L}^{-1})$
1	Harrow	M	19+4	264	85+18
2	Goroke	M	22+4	551	205+37
3	Little Desert 2	M	35+6	361	215+37
4	Nhill	M	32+4	576	315+39
5	Yanac	M	28+6	1067	510+110
6	Willoughby 8015	M	3p17	314	195+37
7	SHG 5	M	31+7	475	250+56
8	MKN 5	M	31+7	468	245+55
9	Karte 4	M	43+7	804	585+95
10	Wanbi Irrigation	M	22+8	747	280+100
11	MND 6	R	32+15	752	410+190
12	Mercunda	M	42+7	2023	1450+240
13	Conga Wonga 17	R	21+6	3191	1140+330
14	Walpeup West 101	M ²	39+7	2573	1710+310
15	Walpeup West 48	M ²	33+6	1607	900+160
16	Walpeup West 89	M ²	22+4	5327	1990+360
17	Walpamunda 3	P ²	13+4	32600	7200+2200
18	BKP 14	M ²	22+6	5566	2080+570
	blank ³		0+2		
	blank ³		3+3		
	blank ³		2+3		
	blank ³		3+3		

¹ P, Pliocene Sands; M, Murray Group; R, Renmark Group

² Within, or close to, groundwater discharge zones.

³ The 'blank' used was Week's Island Halite (Fabryka-Martin & others, 1983; Conard & others, 1986). Samples of halite were prepared, stored and measured alongside groundwater samples.

through this aquifer can be estimated from the pore flow velocity, calculated as

$$v = \frac{-K \times \Delta h}{\mu \times \Delta d} \quad (\text{equation 1})$$

where v is average pore velocity, K is hydraulic conductivity, μ is specific yield for the unconfined Murray Group limestone aquifer, or porosity for the confined case, and $\Delta h/\Delta d$ is hydraulic gradient.

Assuming a constant value of 2 m/day for hydraulic conductivity (Evans & Kellett, this issue), a value of 0.05 for specific yield, and a value of 0.15 for total porosity, this equation yields a flow rate of 2.5–3 m/day for the flow line connecting Harrow and Mercunda. Thus the time taken for groundwater to travel the 330 km from Harrow to Mercunda, for example, is estimated as approximately 120 000 years. This figure should be seen as an order of magnitude estimate only.

The average depth of the top of the Murray Group limestone below the ground surface of the study area is ~65 m; bores used in the present study sampled water which was typically ~30 m below the top of the limestone, although variation within the sample set was considerable. At these depths, ^{36}Cl can be produced within the limestone by two main processes: neutron capture on ^{35}Cl , and disintegration of ^{40}Ca by cosmic ray muons. Detailed chemical analyses of the limestone are not available, therefore we have not been able to calculate the ^{36}Cl production rate in the aquifer. However, calculations by Bentley & others (1986a) show that, below the zone of cosmic ray effects, the $^{36}\text{Cl}/\text{Cl}$ secular equilibrium value in limestone is typically 11×10^{-15} . In addition, the total ^{36}Cl production rate from both cosmic ray muons and neutron capture interactions within the limestone can be estimated from the depth profile of ^{36}Cl in limestone measured by Kubik & others

(1984). Extrapolation of these data gives a $^{36}\text{Cl}/\text{Cl}$ secular equilibrium value of $\sim 58(13) \times 10^{-15}$ in limestone at a depth of 65 m below today's surface in a quarry near Regensburg (Bavaria, West Germany). This value can be used to estimate secular equilibrium in the Murray Group limestone. Following correction for different altitudes and geomagnetic latitudes of the two locations (Yokoyama & others, 1977) and reduction in cosmic ray attenuation (Kubik & others, 1984) caused by the difference between bulk densities in the Regensburg limestone (2.7 g/cm^3) and the sediments overlying the Murray Group (2.1 g/cm^3), the $^{36}\text{Cl}/\text{Cl}$ secular equilibrium ratio at the top of the Murray Group limestone at a depth of 65 m below the surface was estimated to be $39(16) \times 10^{-15}$. This ratio is expected to decrease to $18(8) \times 10^{-15}$ at a depth of 30 m below the top of the Murray Group limestone, falling to the secular equilibrium value of approximately 11×10^{-15} at greater depths, as cosmic ray effects become less important.

Since flow time across the study area, as estimated above, is short compared with the ^{36}Cl half-life of 301 000 years, and the production rate of ^{36}Cl in the aquifer environment by neutron capture on ^{35}Cl is low, neither decay nor subsurface production of ^{36}Cl within the groundwater will significantly affect $^{36}\text{Cl}/\text{Cl}$ ratios. However, we should also consider the possible leaching from the limestone of cosmic ray produced ^{36}Cl by the groundwater. Assuming that the system has reached a steady state, we can calculate the *maximum* effect of such a process by assuming that all ^{36}Cl produced in the limestone is leached by the groundwater. Using the ^{36}Cl concentrations in limestone given by Kubik & others (1984), extrapolated to a depth of 65 m, together with the correction factors discussed above, the equilibrium ratio of ^{36}Cl to ^{40}Ca at the top of the Murray Group limestone is estimated to be $2.5 \pm 1.2 \times 10^{-18}$. Using this value we can estimate the ^{36}Cl production rate at the top of the limestone to be

$$P_{36} = \frac{^{36}\text{Cl}}{^{40}\text{Ca}} \times \frac{\rho}{MW} \times N_A \times \frac{\log_e 2}{t_{1/2}} \quad (\text{equation 2})$$

where P_{36} is ^{36}Cl production rate, ρ is density of the limestone (2.7 g/cm^3), MW is molecular weight of limestone, N_A is Avogadro's number (6.02×10^{23} per mole), and $t_{1/2}$ is the ^{36}Cl half-life of 301 000 years.

This calculation yields a ^{36}Cl production rate of 0.09(4) atoms/cm³/year at the top of the Murray Group limestone. Assuming a porosity (or specific yield) of 0.10 ± 0.05 , the production rate of ^{36}Cl within the volume of limestone occupied by 1 L of groundwater is 900(600) atoms/L/year. Hence, using flow times calculated from equation 1, and assuming that all of the ^{36}Cl is leached by the groundwater, the *maximum* increase in ^{36}Cl between Harrow (sample 1) and Mercunda (sample 12) would be $110(80) \times 10^6$ atoms/L. Similarly, the maximum increase between Harrow and Little Desert (sample 3) would be $26(17) \times 10^6$ atoms/L. These maximum calculated effects are considerably less than the observed increases, and are of the same order as uncertainties in the experimental measurements. Furthermore, these effects would decrease by approximately a factor of two within the top 30 m of the Murray Group limestone. Hence, the effects of ^{36}Cl decay and production in both groundwater and limestone on the ^{36}Cl content of the groundwater are expected to be negligible.

The northwestern flow line, Harrow to Mercunda

The Murray Group wells which stretch northwest from Harrow to Mercunda, with the exception of site 10 which is discussed separately below, may be considered an ap-

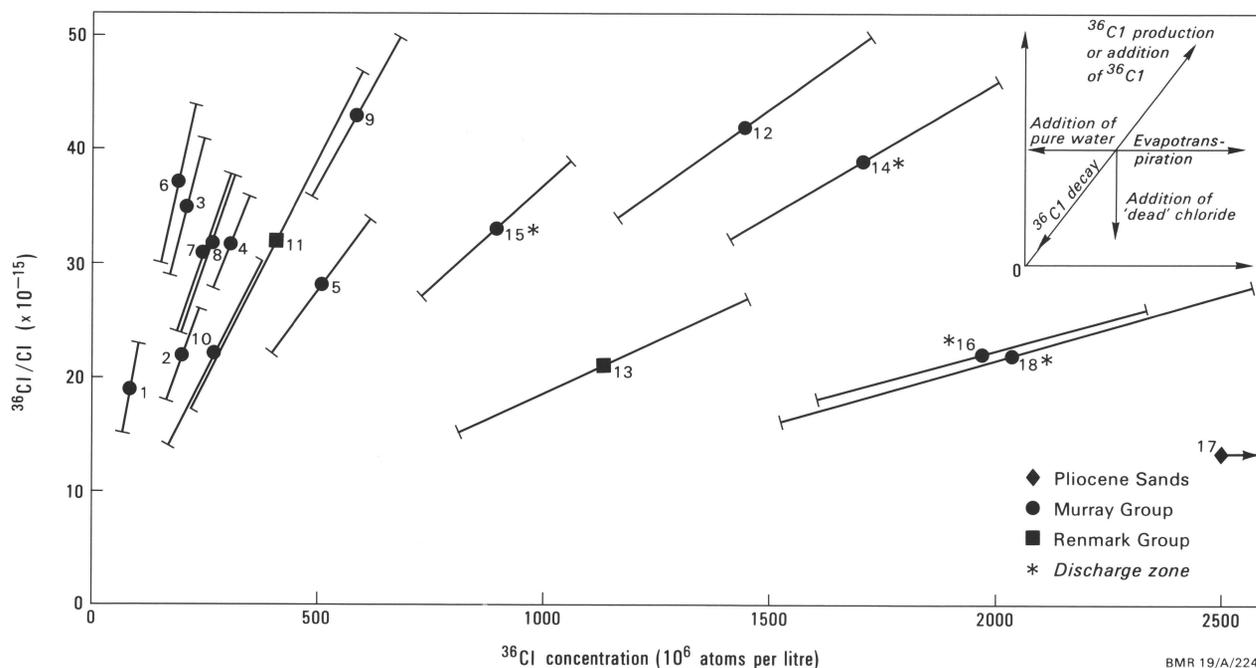


Figure 5. Plot of experimental data, with $^{36}\text{Cl}/\text{Cl}$ ratio against ^{36}Cl concentration. Error bars indicate uncertainties in ^{36}Cl measurements.

Inset shows effects of various fundamental environmental processes on the ^{36}Cl signal.

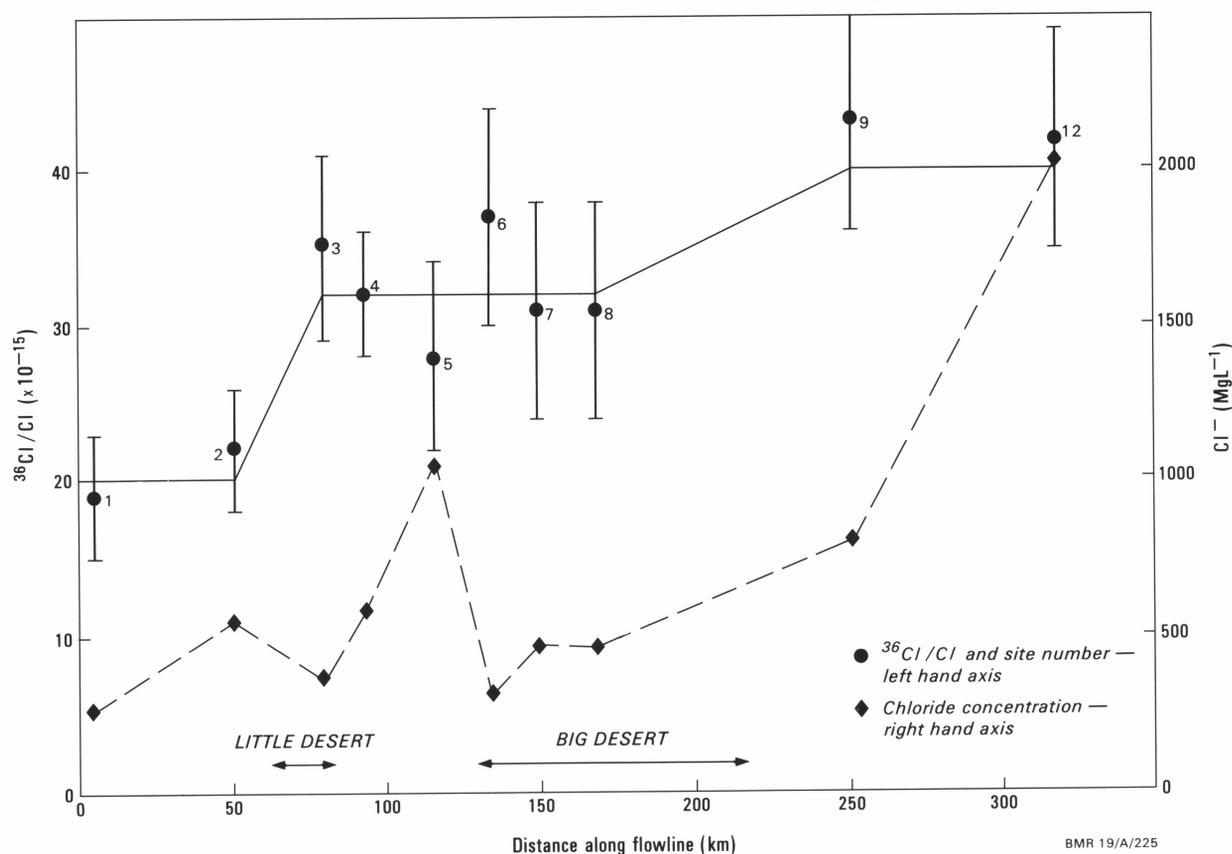
proximation to a flow line, as indicated by the potentiometric surface in Figure 2 (sites 1–9, 12). If the aquifer was a simple closed system then, in the absence of either production or decay of ^{36}Cl , we would expect the ^{36}Cl signal to be unaltered with increasing distance from recharge. However, the ^{36}Cl signal changes significantly along the flow line (Figs 5, 6).

The predominant change along this flow line is an increasing $^{36}\text{Cl}/\text{Cl}$ ratio of dissolved chloride (Table 1; Fig. 6). As discussed above, this increase in $^{36}\text{Cl}/\text{Cl}$ ratio is not due to subsurface production of ^{36}Cl . Instead, it suggests that the increase in $^{36}\text{Cl}/\text{Cl}$ results from the mixing of water with a higher $^{36}\text{Cl}/\text{Cl}$ ratio into the aquifer. The $^{36}\text{Cl}/\text{Cl}$ ratios of these Murray Group samples closely follow the $^{36}\text{Cl}/\text{Cl}$ ratios calculated for modern atmospheric precipitation in areas surrounding the well sites (Fig. 7). This strongly suggests that the increase in the $^{36}\text{Cl}/\text{Cl}$ ratio in these groundwater samples is caused by significant recharge of the aquifer with rainwater via downwards leakage. The estimated time taken for such recharge water to reach the Murray Group aquifer in the northwest of the study area is ~20 000 years (Jolly & others, 1988; Allison & others, 1988), a short time compared with the ^{36}Cl half-life. Therefore, we would expect the $^{36}\text{Cl}/\text{Cl}$ ratio of the recharge water to be the same as that in local atmospheric precipitation. Furthermore, correlation of water level fluctuations with rainfall suggest that the recharge rates in the southeast of the study area may be considerably faster (Duran, formerly Victorian Department of Water Resources, personal communication).

In this interpretation of the data, we have assumed that the $^{36}\text{Cl}/\text{Cl}$ ratios in atmospheric precipitation have remained constant with time. This is expected to be a good approximation at the head of the potentiometric surface (near Harrow), as the seashore in this southern part of the study area is fairly insensitive to changes in sea level, as indicated by the sea floor contours (Fig. 1). In addition, the form of major dune fields in the study area (Bowler & Magee, 1978) indicates that predominant wind direction

has been from the west through most of the Quaternary. The combination of these two factors suggests (Hutton, 1976) that the chloride content of atmospheric precipitation has remained fairly constant in the southern part of the study area. Variations in the atmospheric production of radioisotopes by cosmic rays have been constant to within a few per cent over at least the last 13 000 years, as indicated by the ^{14}C record (Stuiver & Kra, 1986). Furthermore, the successful application of ^{36}Cl to dating of groundwater in the Great Artesian Basin of Australia (Bentley & others, 1986b) suggests a fairly constant ^{36}Cl input function on a million-year timescale. Therefore, changes in the $^{36}\text{Cl}/\text{Cl}$ ratio in atmospheric precipitation in the recharge area around Harrow are not the dominant cause of changes in the $^{36}\text{Cl}/\text{Cl}$ ratios along the flow line. The effect of sea-level changes on the shoreline is greater in the northern part of the study area, tending to increase the $^{36}\text{Cl}/\text{Cl}$ ratios at times of low sea level. However, this does not significantly affect the discussion presented here.

Some of the points from these 10 Murray Group wells are displaced to the right in Figure 5, indicating increased chloride concentrations at these sites. This is particularly true of site 12 (Mercunda) and, to a lesser extent, of sites 2, 5 and 9 (Goroke, Yanac and Karte 4, respectively). Such an increase in chloride concentration, without a corresponding reduction in $^{36}\text{Cl}/\text{Cl}$ ratio, is inconsistent with either the addition of connate salts to the groundwater or the dissolution of ancient salt evaporites, both of which would contain negligible ^{36}Cl . Instead, the increased chloride concentration, and the interpretation of the $^{36}\text{Cl}/\text{Cl}$ ratios given above, suggest that chloride concentration of groundwater within the Murray Group aquifer in these areas is being increased by the addition of more-saline recharge, in the form of rainwater concentrated by evapotranspiration in the overlying Pliocene Sands. This hypothesis of evaporation as a dominant process is further supported by Allison & others (1985). They showed that chloride concentrations in groundwater in the northern part of the study area were linearly correlated with ^{18}O stable isotope values. (Evapotranspiration can be ruled out as a



BMR 19/A/225

Figure 6. $^{36}\text{Cl}/\text{Cl}$ ratio of Murray Group samples along the Harrow to Mercunda flow line plotted in order of position along the flow line, illustrating increase in the $^{36}\text{Cl}/\text{Cl}$ ratio in this region of the Murray Group aquifer along the direction of flow. The mechanism proposed for changing $^{36}\text{Cl}/\text{Cl}$ ratio in this region of the Murray Group aquifer suggests that the increase in $^{36}\text{Cl}/\text{Cl}$ ratio should be close to that illustrated schematically by the solid line, in excellent agreement with the data. The figure also illustrates the changes in chloride concentration of groundwater along the flow line.

process within the aquifer itself, as the top of the Murray Group limestone, within this section of the study area, is an average depth of 65 m below the ground surface.) Furthermore, independent evidence based on a variety of techniques including unsaturated zone profiles of environmental chloride, and ^{14}C and tritium measurements (Allison & others, 1988; Jolly & others, 1988) indicates recharge of saline water into the aquifer system by downwards leakage in the northwest of the study area, and also of downward diffusion of salts which have been concentrated by evapotranspiration at a depth of ~ 20 m in the root zone of the native vegetation. If we assume that the salt profile within the soil has reached a steady state, and that all of the salt falling in precipitation enters the soil, then we can calculate the estimated flux of salt into the aquifer system. The deposition rate of chloride within the study area was estimated from the data of Blackburn & McLeod (1983) to be 9 kg/ha/year by taking the average of the measured modern fallout rates at Merbein, Walpeup, Loxton and Wanbi. Thus, assuming that the salt is distributed through 100 m of limestone aquifer with a porosity (or specific yield) of 0.10 and that the transit time of groundwater across the basin is approximately 120 000 years (from above), then the corresponding increase in groundwater chloride concentration across the basin would be ~ 10 g/L $^{-1}$. This is an order of magnitude greater than the increase observed along this northwestern flow line. The discrepancy is not surprising, considering the simplified nature of the calculation. However, the calculation does indicate that downward diffusion of salt and saline recharge from the overlying Pliocene Sands is likely to be an important source of chloride for the Murray Group aquifer, in

good agreement with the interpretation of the data presented here.

The only Murray Group well in the northwestern flow line which is not covered by the discussion above is the Wanbi Irrigation bore (site 10). This well and that at site 11 (MND 6), which taps the underlying Renmark Group aquifer, are discussed below. Some of the other wells in the northwest flow line are also discussed in more detail.

Sites 1 and 2. As indicated by the potentiometric surface in Figure 2, significant recharge into the Murray Group aquifer occurs in the region surrounding site 1 (Harrow) — the southern Wimmera. As would be expected, the $^{36}\text{Cl}/\text{Cl}$ ratio at recharge is equal, within the experimental uncertainty, to the $^{36}\text{Cl}/\text{Cl}$ ratio calculated for modern atmospheric precipitation in this area, and the salinity of the water is low relative to the down-gradient samples. The water at site 2 (Goroke) has similar $^{36}\text{Cl}/\text{Cl}$ to that at site 1. However, the chloride concentration is higher by a factor of 2, suggesting that evapotranspiration may have concentrated the salts between sites 1 and 2. In any case, as discussed above, the ^{36}Cl data indicate that the higher chloride concentration is not due to the addition of connate salts to groundwater or other sources of 'dead' chloride.

Sites 3–8. The $^{36}\text{Cl}/\text{Cl}$ ratios at sites 3–8 are equal within the experimental errors, having a weighted average of $^{36}\text{Cl}/\text{Cl} = 32 \pm 3 \times 10^{-15}$. (Each of the five measurements was weighted inversely as the square of the experimental uncertainty in the measurement.) This value is significantly higher than the $^{36}\text{Cl}/\text{Cl}$ ratio in the primary recharge region around site 1 ($19 \pm 4 \times 10^{-15}$). The change in the ^{36}Cl

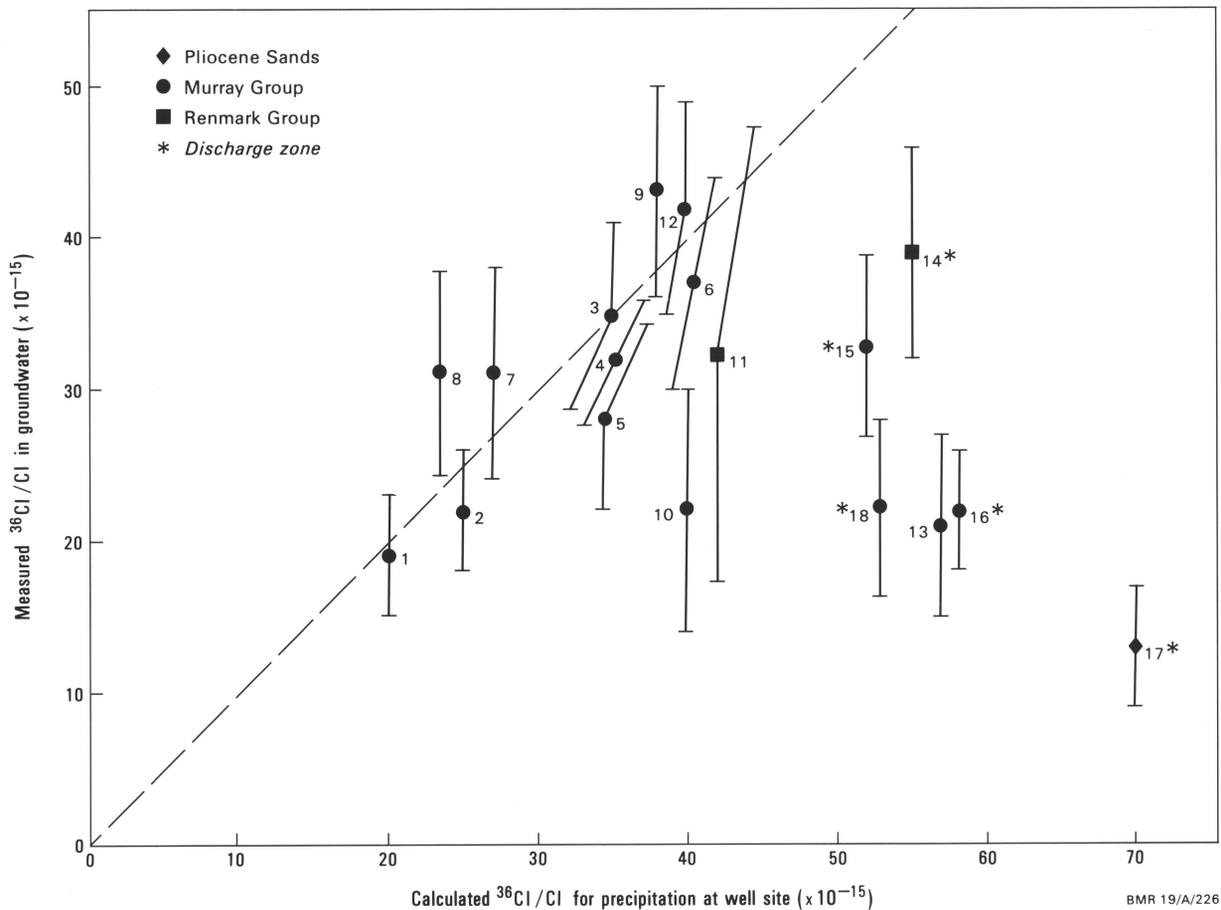


Figure 7. Comparison of measured $^{36}\text{Cl}/\text{Cl}$ ratios with those calculated for modern atmospheric precipitation at well sites.

Error bars are shown for the experimental data.

signal between sites 2 and 3 strongly suggests significant recharge by downwards leakage of rainfall from the Little Desert region between the two sites. Indeed, the fact that the measured $^{36}\text{Cl}/\text{Cl}$ ratio at site 3 is equal, within experimental error, to that calculated for modern atmospheric precipitation in the area around site 3, indicates that the water from this well is predominantly from recharge in the Little Desert region and not from the area surrounding site 1 (southern Wimmera). The drop in chloride concentration between sites 2 and 3 is a further indication of recharge.

The ^{36}Cl signals at sites 4–8 are very similar to that at site 3, with two exceptions. Site 5 (Yanac), which is displaced to the right in Figure 5, shows evidence of the concentration of salts by recharge from more saline water. In contrast, site 6 (Willoughby 8015), which is less saline and has a higher $^{36}\text{Cl}/\text{Cl}$ ratio than the other wells discussed in this section, strongly suggests further recharge by downwards leakage of rainfall in the area around this site on the northern boundary of the Big Desert. In addition, because sites 3–8 run approximately parallel to the lines of equal $^{36}\text{Cl}/\text{Cl}$ in modern atmospheric precipitation, it is not possible to rule out additional recharge by downwards leakage of rainfall in this region on the basis of the data presented here.

Sites 9 and 12. The samples from the Murray Group wells at sites 9 and 12 (Karte 4 and Mercunda, respectively) show further increases in both chloride concentration and $^{36}\text{Cl}/\text{Cl}$ ratio, relative to the samples from further southeast on the flow line. As discussed above, the changes in both chloride concentration and $^{36}\text{Cl}/\text{Cl}$ ratio suggest recharge

with saline water (rainfall concentrated by evapotranspiration) by downwards leakage in the region around these sites, to the northwest of the Big Desert. The measured $^{36}\text{Cl}/\text{Cl}$ ratios of these two groundwater samples are also consistent with this interpretation. The sample from site 12 (Mercunda), in particular, was taken at a fairly shallow depth, near the boundary between the Murray Group and the overlying Pliocene Sands. This is reflected in the high value of salinity found at that site.

Sites 10 and 11. The well at site 10 (Wanbi Irrigation bore) is unusually deep in the Murray Group aquifer, and the pumping of large volumes of water from this well draws water up from the underlying Renmark Group aquifer. Therefore, this sample is not representative of the Murray Group groundwater in this region. Unfortunately, the measurement error on the Renmark Group sample from the nearby site 11 (MND 6) is large, yielding little information about the Renmark Group groundwater in this area. However, both the $^{36}\text{Cl}/\text{Cl}$ ratios and the ^{36}Cl concentrations of these two samples are the same, within experimental uncertainties. This similarity suggests that there might be a significant component of Renmark Group groundwater in the sample from site 10.

Northeastern bores, sites 13–18

All but one of bores 13–18 are situated in or around localised groundwater discharge zones (boinkas). In these areas, salts are brought to the surface by discharging water, concentrated by evaporation, then stored and eventually recycled back into the hydrological system. As one would

expect in such areas, the concentration of salts is highest in the Pliocene Sands (site 17, Walpamunda 3). However, the salts in these discharge zones are concentrated down to at least a depth of 100 m (Evans & Kellett, this issue). This indicates the considerable amount of salt stored in these localised regions.

In addition to high salinity, these discharge zones exhibit $^{36}\text{Cl}/\text{Cl}$ ratios which are low relative to the expected ratio in local rainfall (Figs 2, 7). This indicates that the salts have not accumulated as a result of recent (compared with the 301 000-year half-life of ^{36}Cl) local atmospheric accession, in contrast with the northwestern flow line sites. This low $^{36}\text{Cl}/\text{Cl}$ ratio might reflect that of the water feeding the discharge zones. Alternatively, it might indicate long average residence times ($\sim 500\,000$ years) of salts within the discharge zones. Such a long residence time would have important implications for within-basin salt disposal, and warrants further investigation. Macumber (1983) showed, by an analysis of palaeohydrological, flow net and salt budget information, that a groundwater brine has taken less than 32 000 years to form below Lake Tyrrell, just east of the study area. He also pointed out that brines found below salt lakes of the northeastern parts of the area studied in this paper are in many ways similar to Lake Tyrrell. This estimate of brine age is an order of magnitude lower than the age inferred here from $^{36}\text{Cl}/\text{Cl}$ ratios.

The three Walpeup West wells (sites 14, 15 and 16) are particularly interesting, as they indicate large variations in both chloride concentration and $^{36}\text{Cl}/\text{Cl}$ ratio within this discharge zone (site 16). In particular, the $^{36}\text{Cl}/\text{Cl}$ ratio is lowest, and the chloride concentrations highest, at the centre of the discharge zone. This variation could indicate that salt at the centre of the discharge zone has a greater average residence time than that on the edges of the zone.

The chloride concentration of the Renmark Group sample from site 13 is considerably higher than that at site 11, which is the only other Renmark Group sample covered in this study. This difference is not unexpected, as the two sites are separated by a considerable distance (Fig. 2). Part of the explanation for this high salinity might be diffusion of salts into the aquifer from the Geera Clay (J.S. Hanor, Louisiana State University, personal communication). If the salts in this groundwater were largely derived from the Geera Clay, then the ^{36}Cl signature of both clay and groundwater would be expected to be similar. Unfortunately, pore water from the Geera Clay is not yet available for analysis. Therefore, it was not possible to compare it with the Renmark Group groundwater for this paper.

The large variations in both ^{36}Cl concentrations and $^{36}\text{Cl}/\text{Cl}$ ratios observed in this area indicate that further ^{36}Cl measurements will be able to provide much more information about the history of the groundwater and discharge zones in this region.

Summary and conclusions

Preliminary ^{36}Cl measurements have been presented for the Mallee region of the Murray Basin. These are the first ^{36}Cl measurements reported for the Murray Basin, and constitute both the first application of ^{36}Cl in Australia to a semi-unconfined regional aquifer system and the first use of environmental ^{36}Cl as a tracer within an Australian aquifer system, rather than as a dating tool.

These results indicate significant recharge by downwards leakage of rainfall over much of the study area. Such recharge into the Murray Group aquifer from the Big and

Little Desert regions is relatively fresh (sites 3 and 6, in particular), while that in the region between the Big and Little Deserts (site 5) and northwest of the Big Desert (sites 9 and 12) is more saline. The results also suggest that recharge from the region around Harrow into the Murray Group aquifer is relatively unimportant for regions north of the Little Desert, compared with the recharge mentioned above. Furthermore, the ^{36}Cl results indicate that the major source of salts to the Murray Group groundwater covered in this study, except for the discharge zones, is recent (compared with the half-life of ^{36}Cl) atmospheric accession. In particular, the results are not consistent with the addition of connate salts or ancient salt evaporites to the groundwater.

In addition to the groundwater flow system, $^{36}\text{Cl}/\text{Cl}$ ratios have been measured for several localised discharge zones (boinkas) north of the Big Desert. The $^{36}\text{Cl}/\text{Cl}$ ratios in these samples vary by as much as a factor of 3. This variation indicates that ^{36}Cl has considerable potential as a tool in the study of these features.

This paper has concentrated on the Murray Group aquifer, producing new hydrological information about this aquifer. Both the data presented for the Murray Group, and the sparser data presented for the overlying Pliocene Sands and the underlying Renmark Group, indicate that ^{36}Cl will provide additional information about the Murray Mallee system as the study progresses and further samples are analysed.

Acknowledgements

This research was supported in part by the Australian Water Research Advisory Council, under grant number M86/16. Selection of sites in South Australia was done in cooperation with S.R. Barnett, and in Victoria with P.G. Macumber, as part of the Commonwealth-States Murray Basin Groundwater Project. The authors would like to thank J.T. Fabryka-Martin and I.D. Jolly for their useful comments on the manuscript.

References

- Allison, G.B., Stone, W.S., & Hughes, M.W., 1985 — Recharge in karst and dune elements of a semi-arid landscape as indicated by natural isotopes and chloride. *Journal of Hydrology*, 76, 1–25.
- Allison, G.B., Walker, G.R., Hughes, M.W., Cook, P.G., & Jolly, I.D., 1988 — Recharge, salinity and land-use change in the mallee region. *Murray Basin 88 Abstracts. Geology, groundwater and salinity management conference, Canberra, 23–26 May 1988*, 1–2.
- Bentley, H.W., Phillips, F.M., & Davis, S.N., 1986b — Chlorine-36 in the terrestrial environment. In Fritz, P., & Fontes, J.C., (editors), *Handbook of environmental isotope geochemistry*, Vol. 2. The terrestrial environment, *Elsevier, Amsterdam*. 427–480.
- Bentley, H.W., Phillips, F.M., Davis, S.N., Gifford, S., Elmore, D., Tubbs, L.E., & Gove, H.E., 1982 — Thermonuclear ^{36}Cl pulse in natural water. *Nature*, 300, 737–740.
- Bentley, H.W., Phillips, F.M., Davis, S.N., Habermehl, M.A., Airey, P.L., Calf, G.E., Elmore, D., Gove, H.E., & Torgersen, R.T., 1986a — Chlorine-36 dating of very old groundwater 1. The Great Artesian Basin, Australia. *Water Resources Research*, 22, 1991–2001.
- Bird, J.R., Calf, G.E., Davie, R.F., Fifield, L.K., Evans, W.R., Kellett, J.R., & Habermehl, M.A., in press — The role of ^{36}Cl and ^{14}C measurements in Australian groundwater studies. *Radiocarbon*.
- Blackburn, G., & McLeod, S., 1983 — Salinity of atmospheric precipitation in the Murray-Darling drainage division, Australia. *Australian Journal of Soil Research*, 21, 411–434.

- Bowler, J.M., & Magee, J.W., 1978 — Geomorphology of the Mallee region in semi-arid northern Victoria and western New South Wales. *Proceedings of the Royal Society of Victoria*, 90, 5–25.
- Brown, C.M., 1989 — Structural and stratigraphic framework of groundwater occurrence and surface discharge in the Murray Basin, southeastern Australia. *BMR Journal of Australian Geology & Geophysics*, 11, 2/3, (this issue).
- Browne, E., & Firestone, R.B., 1986 — Table of radioactive isotopes. *John Wiley & Sons, Brisbane*.
- Calf, G.E., & Airey, P.L., in press — Hydrological studies using environmental chlorine-36. *Proceedings of the Research Co-ordination Meeting on the Study of Very Old Groundwater, International Atomic Energy Agency, Vienna, 7–11 April 1986*.
- Conard, N.J., Elmore, D., Kubik, P.W., Gove, H.E., Tubbs, L.E., Chrnyk, B.A., & Wahlen, M., 1986 — The chemical preparation of AgCl for measuring ^{36}Cl in polar ice with accelerator mass spectrometry. *Radiocarbon*, 28, 556–560.
- Davie, R.F., Bird, J.R., Calf, G.E., Topham, S., Fifield, L.K., Ophel, T.R., Allison, G.B., & Chivas, A.R., 1987 — The chlorine-36 measurement program at the Australian National University. *Proceedings of the Fifth Australian Conference on Nuclear Techniques of Analysis, AINSE, Lucas Heights, N.S.W., 4–6 November 1987*, 6–9.
- Davie, R.F., Fifield, L.K., Bird, J.R., & Ophel, T.R., 1988 — Systematic and random errors in $^{36}\text{Cl}/\text{Cl}$ ratios measured at the ANU 14UD Accelerator. *Australian National University internal report ANU-P/1017*, 1–18.
- Davis, R., & Schaeffer, O.A., 1955 — Chlorine-36 in Nature. *Annals of the New York Academy of Sciences*, 62, 105–122.
- Elmore, D., Fulton, B.R., Clover, M.R., Marsden, J.R., Gove, H.E., Naylor, H., Purser, K.H., Kilius, L.R., Beukens, R.P., & Litherland, A.E., 1979 — Analysis of ^{36}Cl in environmental water samples using an electrostatic accelerator. *Nature*, 277, 22–25, errata 246.
- Elmore, D., & Phillips, F.M., 1987 — Accelerator mass spectrometry for measurement of long-lived radioisotopes. *Science*, 236, 543–550.
- Elmore, D., Tubbs, L.E., Newman, D., Ma, X.Z., Finkel, R., Nishiizumi, K., Beer, J., Oeschger, H., & Andree, M., 1982 — ^{36}Cl bomb pulse measured in a shallow ice core from Dye 3, Greenland. *Nature*, 300, 735–737.
- Evans, W.R., & Kellett, J.R., (1989) — The hydrogeology of the Murray Basin, southeastern Australia. *BMR Journal of Australian Geology & Geophysics*, 11, 2/3, (this issue).
- Fabryka-Martin, J.T., Bentley, H.W., Davis, H.S., Elmore, D., & Gove, H.E., 1983 — ^{36}Cl measurements in Gulf Coast salt domes. Unpublished manuscript, quoted in Bentley, H.W., Phillips, F.M., & Davis, S.N., 1986 — Chlorine-36 in the terrestrial environment. In Fritz, P., & Fontes, J.C., (editors), *Handbook of environmental isotope geochemistry*, Vol. 2. The terrestrial environment, Elsevier, Amsterdam. 427–480.
- 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.
- Hutton, J.T., 1976 — Chloride in rainfall in relation to distance from ocean. *Search*, 7(5), 207–208.
- Hutton, J.T., & Leslie, T.I., 1958 — Accession of non-nitrogenous ions dissolved in rainwater to soils in Victoria. *Australian Journal of Agricultural Research*, 9, 492–507.
- Jolly, I.D., Walker, G.R., & Cook, P.G., 1988 — Diffuse discharge/recharge under native vegetation in the western Murray Basin, Murray Basin 88 Abstracts. *Geology, groundwater and salinity management conference, Canberra, 23–26 May 1988*, 87–89.
- Kubik, P.W., Korschinek, G., Nolte, E., Ratzinger, U., Ernst, H., Teichmann, S., Morinaga, H., Wild, E., & Hille, P., 1984 — Accelerator mass spectrometry of ^{36}Cl in limestone and some paleontological samples using completely stripped ions. *Nuclear Instruments and Methods in Physics Research*, B5, 326–330.
- Lal, D., & Peters, B., 1962 — Cosmic ray produced isotopes and their application to problems in geophysics. *Progress in Elementary Particle and Cosmic Ray Physics*, 6, 3–74.
- Lal, D., & Peters, B., 1967 — Cosmic ray produced radioactivity on the Earth. In Flugge, S., (general editor), *Handbuch der Physik XLVI*, part 2, Springer-Verlag, Berlin. 551–612.
- Leavy, B.D., Phillips, F.M., Elmore, D., Kubik, P.W., & Gladney, E., 1987 — Measurement of $^{36}\text{Cl}/\text{Cl}$ in young volcanic rocks: an application of accelerator mass spectrometry to geochronology. *Nuclear Instruments and Methods in Physics Research*, B29, 246–250.
- Macumber, P.G., 1983 — Interactions between groundwater and surface systems in northern Victoria. *Ph.D. thesis, University of Melbourne*.
- Nishiizumi, K., Elmore, D., Ma, X.Z., & Arnold, J.R., 1984 — ^{10}Be and ^{36}Cl depth profiles in an Apollo 15 drill core. *Earth and Planetary Science Letters*, 70, 157–163.
- Phillips, F.M., Mattick, J.L., Duval, T.A., Elmore, D., & Kubik, P.W., 1988 — Chlorine-36 and tritium from nuclear-weapons fallout as tracers for long-term liquid and vapour movement in desert soils. *Water Resources Research*, 24, 1877–1891.
- Phillips, F.M., Trotman, K.N., Bentley, H.W., Davis, S.N., & Elmore, D., 1984 — Chlorine-36 from atmospheric nuclear weapons testing as a hydrologic tracer in the zone of aeration in arid climates. In Udluft, P., Merkel, B., & Prosl, K.-H., (editors), *Recent investigations in the zone of aeration (RIZA), Proceedings of the International Symposium, Munich, West Germany, October 1984*. 47–56.
- Stuiver, M., & Kra, R., (editors), 1986 — *Radiocarbon*, 28, number 2b (Calibration issue).
- Yokoyama, Y., Reyss, J.-L., & Guichard, F., 1977 — Production of radionuclides by cosmic rays at mountain altitudes. *Earth and Planetary Science Letters*, 36, 44–50.