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**ORIGINS AND SOURCES OF
ATMOSPHERIC PRECIPITATION
FROM AUSTRALIA: CHLORINE-36 AND
MAJOR-ELEMENT CHEMISTRY**

By

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The work described in this thesis was carried out while I was a full-time post-graduate research student in the Research School of Earth Sciences at the Australian National University. Except where noted in the text, the research described here is my own and to my knowledge original. This thesis, or any part thereof, has not been submitted to any other university or place of higher learning for the purpose of accreditation.

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October 1995

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ABSTRACT

Temporal and spatial variations of major-element and ^{36}Cl chemistry in rainfall across Australia have been assessed. Bulk precipitation samples were collected from two arrays over two years at three-monthly intervals: the WE array (10 sites) extended in a west to east direction from the coast of Western Australia south of Geraldton, inland to Warburton in Central Australia, and the SN array (8 sites), extended in a south to north direction from Port Lincoln in South Australia to Kakadu in the Northern Territory.

The major-element chemistry shows that the main influence on the composition of precipitation in remote areas of Australia is mixing between seawater and continental sources. At most sites along the two arrays it is difficult to distinguish between the separate end-members of this source, except at coastal localities where seawater dominates the chemistry of precipitation. However, the influence of seawater is also evident at non-coastal sites in association with favourable synoptic conditions, such as cold frontal activity in south and western Australia during winter, and monsoonal activity in northern Australia during summer. The continentally-derived end-member is most likely composed of resuspended soil/dust material, including salt-lake and calcareous dune components. In the south of the SN array where agriculture is intense this continental source variably includes a fertiliser component. The chemistry of precipitation across Australia is also affected by an acid-base balance factor, the components of which are derived from natural sources such as biogenic emissions, biomass burning and lightning flash production. The nature of the collection program (i.e. samples are exposed to the atmosphere from the time of deposition to the time of sample retrieval) means biodegradation is also evident in the collected sample chemistry.

Chlorine-36 is a cosmogenic isotope with a half-life of 301,000 years. This time frame, combined with the hydrophilic nature of Cl, makes ^{36}Cl useful as a hydrological tracer. The use of ^{36}Cl as a hydrological tracer however, relies on predicted models of ^{36}Cl and stable Cl fallout to calculate $^{36}\text{Cl}/\text{Cl}$ ratios for recharge to hydrological systems. The results from this investigation agree with the general shape of the latitude-dependent theoretical ^{36}Cl fallout curve of Lal and Peters (1967), but suggests that the curve underestimates the rate of fallout. A revised mean fallout for the southern hemisphere of $15.4 \text{ }^{36}\text{Cl} \text{ atoms/m}^2/\text{s}$ is suggested, and long-term average predictions of ^{36}Cl fallout rates used to predict the input ratios of

$^{36}\text{Cl}/\text{Cl}$ in hydrological investigations should be increased by a factor of 1.4 for the southern hemisphere. Further, while stable Cl concentrations in precipitation display a general exponential decrease with distance from the coast, the nature of this relationship is geographically variable, and Cl concentrations in precipitation should be investigated for each study by local direct measurements, a process that is simple and inexpensive.

The mean ^{36}Cl fallout for the southern hemisphere, calculated from this work is three times lower than has been measured for precipitation in the northern hemisphere. The lower southern hemisphere fallout rates reflect the lower rates of transfer of stratospheric air to the troposphere in the southern hemisphere, which results from the less dynamic nature of the lower stratosphere in the southern hemisphere. The mean global ^{36}Cl fallout that incorporates measurements from the northern hemisphere with the results of this work is calculated to be 25-35 atoms/m²/s, 2-3 times greater than predicted by Lal and Peters (1967). This suggests that the cross-section for the cosmic-ray production of ^{36}Cl may be underestimated in their paper.

This work supports the use of ^{36}Cl as a tracer of atmospheric processes. Its production primarily in the stratosphere suggests that it may trace stratospheric-tropospheric exchange. Seasonal variations in ^{36}Cl fallouts and $^{36}\text{Cl}/\text{Cl}$ show high ratios and fallouts during spring, and at some localities, during summer (i.e. the north of the SN array). The increased spring ^{36}Cl fallouts are attributed to increased transfer of stratospheric ^{36}Cl to the troposphere that occurs as the tropopause height increases during the warmer months. High fallouts during summer in the north of the SN array may be attributed to the direct entrainment of stratospheric air into cumulus clouds during the monsoonal convection.

Chlorine-36 exists in the stratosphere predominantly as HCl gas (Wahlen et al 1991). The correlation between ^{36}Cl and NO_3 and the lack of any relationship between ^{36}Cl , stable Cl and Na concentrations (the latter being entrained as aerosols), suggest that ^{36}Cl is scavenged from the atmosphere as a gas rather than an aerosol phase.

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