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

By

Melita Keywood

A thesis submitted for the
degree of Doctor of Philosophy
of the
Australian National University

October 1995

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.

Melita Keywood

Melita Keywood
October 1995

ACKNOWLEDGMENTS

There are many people to thank for the completion of this thesis. Firstly I wish to thank my supervisor Allan Chivas for initiating the rainfall collection program and for giving me the opportunity to work on this project. It's been a lot of fun and it goes without saying that I've learnt a great deal. I'd also like to thank my adviser Greg Ayers from the CSIRO who knows so much about atmospheric chemistry and has always been very encouraging. Keith Fifield from RSPhySE has given me excellent supervision and advice with respect to the ^{36}Cl section of the work, and has provided me with an insight into how differently geologists and nuclear physicists think.

Richard Cresswell was a great support, and has given me a lot of advice about all parts of several versions of the thesis. The overall structure of the thesis is in part thanks to Richard. Michael Bird, Mike Gagan, John Cram, Edward Linacre and Adam Kent also read various sections. I have also had many useful conversations with John Stone and Geoff Monighan, and correspondence with Mike Manton. I'd like to thank Paul Johnston, Dan Zwartz and Tony Purcell who wrote several programs for me.

I'd like to acknowledge the financial support of RSES to attend ICOG-8 in Berkeley, California and the Fifth Conference on Isotopes in the Australian Environment in Brisbane.

Collecting rainfall over two years each three months from 18 sites almost as far away from Canberra as you can get without using a passport, required the help of many people. Thanks to Dieter Burman, Joe Cali, Mike Gagan, Micnael Bird, Marcella, Lisa Hill, Elmer Kiss, Dusan Dammer, Joan Cowley and especially Leesa Carson, who managed to remain calm even under the most trying circumstances (40^{o} temperatures and bogged above the axel and she was still cool calm and collected). I'd also like to thank all the owners of the properties on which the rain collectors were located. Bob Egan from the CSIRO Kapalga Research Station was especially helpful.

I thank Elmer Kiss, Audrey Chapman, Mike Shelley, Joe Cali and Les Kingsley for their help with analytical work at RSES, John Stone for showing me the Cl precipitation technique, and the members of the AMS group in Nuclear Physics (Keith Fifield, Richard Cresswell, Jodi Evans and Gary Allan, and all the people that keep the accelerator running) for ^{36}Cl measurements. I also thank Penelope Fenley for all her help with library matters.

None of this would have been any fun without the people I have known in the last four years. Friends I'd like to thank are Paul, Richard, Monica, Sue, Jurgen, Deb, Geoff Batt (I'll get you back), Warwick, Gabrielle, Travis, Jennifer Delhaize, (Dirty) Phil, Sammy, Jeppo, Linda, Karen, Alusha, George, Mark, Darryl, Corine and Kevin. I'd also like to thank Paula, Sandra and Gary for staying in touch. Thank you Claudine for being so 'supportive', Geoff Fraser for often having a refreshingly alternative outlook, Dave John Brown (PhD almost) for being so talkative and such a stayer, Tony and Alfredo for stopping me from getting the Pink Slippers, and Stephen Pell for being an inspiration. Thanks to all the people I've shared houses with, in particular Steve Hill whom I wish good luck in his search (for the ultimate snow dome that is, I'll never be able to walk past a souvenir shop again). I'd also like to thank Adam Kent for always knowing the right thing to say. And thanks to Dan Zwartz for never being anything but himself. Thanks to Leah for giving me the mountain-biking bug, and Gill, Pete, Amanda, Dan and Dylan for the subsequent epics. And thanks to Steve Barry for the climbing. I had a great trip around the southwest of the USA with Leesa and Adam, who were just the right company in such a strange place.

Dylan Harrison deserves a medal for suffering not one, but three of his close friends writing up at the same time. We have yet to see if this experience has left any deep-rooted physcological scars. Thanks Dylan. Finally, I'd like to thank my family. They have always been very encouraging and will be very proud.

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 $^{36}Cl/Cl$ 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 ^{36}Cl atoms/m^2/s is suggested, and long-term average predictions of ^{36}Cl fallout rates used to predict the input ratios of

$^{36}Cl/Cl$ 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/m^2/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 $^{36}Cl/Cl$ 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.

CONTENTS