MD311: Australia-wide network to measure rainfall chemistry and isotopic composition

Final report
Richard Cresswell, John Dighton, Fred Leaney, Jamie Vleeshouwer, Darren Morrow, Maria Harris and Matthew Stenson

June 2010
A report to the Murray-Darling Basin Authority
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Cover Photograph:

Backyard rain, Brisbane, Queensland
Photographer: Richard Cresswell
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MD311: Australia-wide network to measure rainfall chemistry and isotopic composition

Final Report to:
Murray-Darling Basin Authority
(includes: GIS spatial information for rainfall monitoring stations within the Basin and implementation notes on the monitoring program)

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ACKNOWLEDGMENTS

This project has been jointly funded through CSIRO Land and Water (CLW), CRC Landscape Environments and Mineral Exploration (LEME) and Murray-Darling Basin Authority (MD311). The Bureau of Meteorology and CSIRO Marine and Atmospheric Research (CMAR) have provided additional support. This project is also helped through collaborations with the Fitzroy Basin Association, Australian Nuclear Science and Technology Organisation (ANSTO), International Atomic Energy Agency (IAEA) and the Bureau of Rural Sciences (BRS).
EXECUTIVE SUMMARY

A national network for the collection and analysis of rainfall has been established. The aim is to measure the spatial variation and long-term (minimum 5 year) precipitation-weighted mean concentration of the major ion chemistry and stable isotopes in rainfall across Australia. Samples are being collected on a monthly basis to provide more accurate inputs for atmospheric salt flux and stable isotope input to aid salt and water budgeting. Samples have now been collected and analysis for chemistry and stable isotope concentrations continues. Final data assessment and analysis will be undertaken subsequent to the life of this project and the results reported separately to this report.

The net input of salt to the Australian landscape is largely derived from rainfall-precipitation and dry aerosol deposition. There is very little information on the spatial and, particularly, temporal variation of the major ion chemistry of rainfall in Australia, and none for the interior or northeast. This paucity of information has made it difficult to accurately determine catchment scale salt budgets. A technique to estimate the source of ions in rainfall, and hence assess the provenance of salt input to the landscape has been developed and is presented here. We confirm and enhance previous datasets evaluating salt accession to Australia.

Furthermore, one of the most powerful techniques for estimating groundwater recharge in Australia is by chloride mass balance. A more rigorous constraint on the Cl⁻ flux is needed if we are to provide more reliable estimates of groundwater recharge, both from the point of view of salinity management and groundwater sustainability.

There is little information available on both the spatial and temporal variation of the stable isotopes, \( \delta^2H \) and \( \delta^{18}O \), in rainfall for inland Australia. This dataset will augment the coastal data that has been recorded as part of the WMO/IAEA Global Network of Isotopes in Precipitation (GNIP).

Stable isotope data provide very useful information on mechanisms for groundwater recharge as well as information on groundwater/surface water interactions that cannot be obtained by other methods. In addition, the potential for using stable isotope distribution patterns to improve the understanding of continental-scale water vapour sources and changing rainfall patterns in response to climate change is being realised.

To date, 20 sites have been equipped with rainfall sample collectors, with some samples collected since September 2006, though most collectors did not start collection until April-May 2007. A procedure for reporting and displaying the data via the internet has been developed and will be populated with data from the project once full QA/QC has been completed on the samples.

This project has combined with associate projects being run by the Fitzroy Basin Association, Bureau of Rural Sciences, ANSTO and ANU. The 2 latter still continue and will extend the life of this project beyond the close date of 2010. Alternative source of funding to maintain the network are being sought, so that an on-going repository of chemistry of fallout might be achieved, similar to the isopleth maps provided for the United States through the National Atmospheric Deposition Program (<http://nadp.sws.uiuc.edu> ).
1. PROJECT AIM

To measure the spatial variation and long term (5 year) precipitation weighted mean concentration of the major ion chemistry and stable isotopes in rainfall across Australia.

To provide more accurate inputs for atmospheric salt flux and stable isotope input to aid salt and water budgeting.

2. OUTCOMES

Monthly major and minor ion (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, HCO₃⁻) and stable isotope (δ²H and δ¹⁸O) data for rainfall stations covering all climatic and geographic regions of Australia. Due to processing time constraints, the previously proposed 30 sites have been reduced to 20 (Figure 1). Samples will include some collected from the full complement of 30 stations.

Figure 1. CSIRO rainfall collector sites currently active across Australia.
3. PROJECT DELIVERABLES

Under the exchange of letters between MDBC and CSIRO Land and Water, set out in MDBC letter MD311:CD05/145 dated 11 October 2005, and accepted by CSIRO on 9 May 2006, CSIRO will provide deliverables to the Authority as follows:

<table>
<thead>
<tr>
<th>Due date</th>
<th>Description of deliverable</th>
<th>Amount due ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 June 2005</td>
<td>Submission of GIS spatial information for the 10 rainfall monitoring stations within the Basin and a report on the implementation of the monitoring Program</td>
<td>$5,000</td>
</tr>
<tr>
<td>1 December 2005</td>
<td>Progress Report</td>
<td></td>
</tr>
<tr>
<td>1 June 2006</td>
<td>Submission of the monitoring report for 2005-06, including presentation of the data spatially.</td>
<td>$5,000</td>
</tr>
<tr>
<td>1 December 2006</td>
<td>Progress Report</td>
<td></td>
</tr>
<tr>
<td>1 June 2007</td>
<td>Submission of the monitoring report for 2006-07, including presentation of the data spatially.</td>
<td>$5,000</td>
</tr>
<tr>
<td>1 December 2007</td>
<td>Progress Report</td>
<td></td>
</tr>
<tr>
<td>1 June 2008</td>
<td>Submission of the monitoring report for 2007-08, including presentation of the data spatially.</td>
<td>$5,000</td>
</tr>
<tr>
<td>1 December 2008</td>
<td>Progress Report</td>
<td></td>
</tr>
<tr>
<td>1 June 2009</td>
<td>Submission of the monitoring report for 2008-09, including presentation of the data spatially.</td>
<td>$5,000</td>
</tr>
<tr>
<td>31 March 2010</td>
<td>Final report incorporating findings of all monitoring under the Project including a report against the objectives for the whole project in relation to the Murray-Darling Basin</td>
<td>$5,000</td>
</tr>
</tbody>
</table>

This report represents the Final Report for this project and incorporates the GIS spatial information for the sites within and adjacent to the MDB. To date, 5 (reduced from 7) sites within the MDB have been targeted, with a further 5 (reduced from 6) sites adjacent to the Basin, and thereby relevant to the salt accession within the basin. This report also includes information on the Australia-wide network being supported by CSIRO Land and Water, CRC LEME and the Fitzroy Basin Association. Collaboration with BRS will enhance the network within the MDB. The collection network was also used to provide samples to ANU who is investigating the sources and evolution of dust across Australia’s landscape. Examples of the work carried out by two ANU students are provided in Appendix II.
4. WHY DO WE NEED BETTER RAINFALL CHEMISTRY AND ISOTOPE DATA?

4.1. Chemistry

The net input of salt to the Australian landscape is largely derived from rainfall-precipitation and dry aerosol deposition. The two ions that contribute >85% of the salt load, sodium and chloride, are derived from marine aerosols. There is very little information on the spatial and, particularly, temporal variation of the major ion chemistry of rainfall in Australia, and none for the interior or northeast. Comprehensive accession data is reported by Blackburn and McLeod (1983) for 24 stations located in the Murray Darling basin (1974-1975) and by Keywood, et.al. (1997) for 18 sites from the western half of the continent (1992-1994), but only one site has information for NE Australia. This paucity of information has made it difficult to accurately determine catchment scale salt budgets.

Furthermore, one of the most powerful techniques for estimating groundwater recharge in Australia is by chloride mass balance. Although mean annual rainfall records are well known for the past century; the chloride concentration is not. A better constraint on the Cl⁻ flux is needed if we are to provide more reliable estimates of groundwater recharge, both from the point of view of salinity management and groundwater sustainability.

4.2. Stable isotopes

There is little information available on both the spatial and temporal variation of the stable isotopes, δ²H and δ¹⁸O, in rainfall for inland Australia. Modelling has generally been inferred (using corrections for the “rainout effect”), from information derived from the stations at Darwin, Brisbane Melbourne, Alice Springs and Adelaide- all part of the WMO/IAEA global network (GNIP).

Stable isotope data provide very useful information on mechanisms of groundwater recharge as well as information on groundwater/surface water interactions that cannot be obtained by other methods. In addition, the potential for using stable isotope distribution patterns to improve the understanding of continental-scale water vapour sources and changing rainfall patterns in response to climate change is being realised.

Furthermore, it is thought that localised groundwater is derived from recharge occurring during the principal fallout months (summer for the northern part of the basin, and winter to the south). This groundwater is thought to represent the long-term isotopic mean concentration of precipitation. Validation of this anecdotal evidence across the country is essential.
5. NETWORK LOCATIONS

The following stations are located to provide maximum information for the entire continent. Thus, sites are located at increasing distance from the coast, and also span the north-south extents of climate regimes. In addition to accurate rainfall measurements, daily wind direction is required for modelling accession rates. Hence we are siting the collectors at weather stations where possible, but also we have some sites where local agencies (such as CSIRO, Queensland Department of Environmental and Resource Management and ANSTO) have expressed an interest in maintaining a collector. There are currently 20 of the initial 26 sites still collecting monthly samples (Table 1). This number is likely to decrease in the future as the Bureau of Meteorology moves to unmanned stations and telemetered recording of rainfall received with automatic tipping gauges. Remote sites, such as at Giles, could not be used for this reason, and Meekatharra and Halls Creek are likely to move to unmanned stations within the next few years (Paul Smith, Field Operations Group, Bureau of Meteorology, pers. comm.)

Table 1. Current rainfall collection sites, GNIP stations and month of first sampling. Note that all stations are equipped with samplers. Those not recording a sample have yet to record rainfall. Stations that are crossed out ceased supplying samples in 2009. These may be resurrected if further funding becomes available.

<table>
<thead>
<tr>
<th>Site</th>
<th>GNIP SITE</th>
<th>Region</th>
<th>Collection initiated</th>
</tr>
</thead>
<tbody>
<tr>
<td>COBAR MO</td>
<td>∅</td>
<td>NSW</td>
<td>Sep-06</td>
</tr>
<tr>
<td>SYDNEY AIRPORT AMO</td>
<td>∅</td>
<td>NSW</td>
<td>Sep-06</td>
</tr>
<tr>
<td>WAGGA WAGGA AMO</td>
<td>∅</td>
<td>NSW</td>
<td>Sep-06</td>
</tr>
<tr>
<td>ALICE SPRINGS AIRPORT</td>
<td>∅</td>
<td>NT</td>
<td>Feb-06</td>
</tr>
<tr>
<td>DARWIN AIRPORT</td>
<td>∅</td>
<td>NT</td>
<td>Feb-05</td>
</tr>
<tr>
<td>BRISBANE AERO</td>
<td>∅</td>
<td>QLD</td>
<td>Feb-06</td>
</tr>
<tr>
<td>BRISBANE CSIRO</td>
<td>∅</td>
<td>QLD</td>
<td>Aug-05</td>
</tr>
<tr>
<td>CHARLEVILLE AERO</td>
<td>∅</td>
<td>QLD</td>
<td>Sep-06</td>
</tr>
<tr>
<td>CLERMONT</td>
<td>∅</td>
<td>QLD</td>
<td>May-07</td>
</tr>
<tr>
<td>EMERALD</td>
<td>∅</td>
<td>QLD</td>
<td>May-07</td>
</tr>
<tr>
<td>INJUNE</td>
<td>∅</td>
<td>QLD</td>
<td>May-07</td>
</tr>
<tr>
<td>MOUNT ISA AERO</td>
<td>∅</td>
<td>QLD</td>
<td>May-07</td>
</tr>
<tr>
<td>ROCKHAMPTON</td>
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<td>QLD</td>
<td>Apr-07</td>
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<td>TOOWOOMBA</td>
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<td>QLD</td>
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<td>QLD</td>
<td>Apr-07</td>
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<tr>
<td>ADELAIDE AIRPORT</td>
<td>∅</td>
<td>SA</td>
<td>May-07</td>
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<tr>
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<td>∅</td>
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<td>Oct-04</td>
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<tr>
<td>WOOMERA AERODROME</td>
<td>∅</td>
<td>SA</td>
<td>May-07</td>
</tr>
<tr>
<td>CAPE GRIM BAPS</td>
<td>∅</td>
<td>TAS/ANT</td>
<td>May-07</td>
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<td>MELBOURNE AIRPORT</td>
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<td>VIC</td>
<td>Apr-07</td>
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<tr>
<td>MILDURA AIRPORT</td>
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<td>VIC</td>
<td>May-07</td>
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<tr>
<td>ESPERANCE</td>
<td>∅</td>
<td>WA</td>
<td>Apr-07</td>
</tr>
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<td>HALLS CREEK AIRPORT</td>
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<td>May-07</td>
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<tr>
<td>LEARMONTH AIRPORT</td>
<td>∅</td>
<td>WA</td>
<td>May-07</td>
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<td>MEEKATHARRA AIRPORT</td>
<td>∅</td>
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</tr>
<tr>
<td>PERTH AIRPORT</td>
<td>∅</td>
<td>WA</td>
<td>Apr-07</td>
</tr>
</tbody>
</table>
6. STATION DESIGN

Of the 2 designs initially established, only 5 remain as CSIRO collectors (figure 2); the remaining stations now deploy the BRS collectors (figure 3). While this is a more robust collector, there is increased requirement for cleaning and preparation of these bottles compared to the disposable collectors used in the CSIRO design. This caused backlog in analyses due to insufficient availability of technical staff to then also filter samples for analysis. The limited funding for this project precludes additional support at present.

![Figure 2. CSIRO rainfall collection equipment and installation adjacent to rainfall gauge.](image)

![Figure 3. BRS rainfall collection equipment, mounted on a 1m star picket.](image)
7. GIS ANALYSIS OF CHLORIDE DATA

A compilation of chloride data spanning 40 years has been used to evaluate a possible web-based delivery. This has been accomplished and is published as a conference paper to MODSIM 2009.

This paper is attached as Appendix I.

8. MURRAY-DARLING BASIN

The MDBA contributes directly to the collection and analysis of samples from within and adjacent to the Murray-Darling Basin. These sites include:

Within the Basin:
Charleville, Qld
Toowoomba, Qld (Oakey)
Cobar, NSW
Wagga Wagga, NSW
Mildura, Vic

Adjacent to the Basin:
Brisbane, Qld (including Indooroopilly)
Sydney, NSW (Campbelltown)
Melbourne, Vic
Woomera, SA
Adelaide, SA (including Urrbrae)

The sites adjacent to the Basin will provide valuable data on air masses that cover the Basin and vital parameters to constrain models for salt accession across the Basin.

9. CURRENT STATUS OF THE COLLECTION NETWORK

The first year of sampling has now been analysed for chemistry and some stable isotope analyses have been completed. A further 2 years are currently being analysed and the data checked. The latter samples will be reported separately. Sites within and adjacent to the Murray-Darling Basin are shown in a summary Piper plot below (Figure 4).

The samples form a continuum between sodium-chloride-type waters (to the right on the figure) through to calcium-bicarbonate-type waters (to the left). The former reflects a dominant input from sea-salt; the latter from continental dust sources. Hence, we see that Adelaide waters (blue triangles) are dominated by oceanic sources of ions, reflecting the dominant influence of the south-westerlies. Mildura, by contrast exhibits rainfall with a dominant continental input. Brisbane has a dual personality, with rainfall from both the west and east influencing the chemistry of the waters. Winter rains tend to be from the ocean; summer rains are dominantly from the north (and hence inland), but also from the ocean.

Rainfall samples generally contain low levels of salts (ions), with total soluble salts mostly below 100 mg/L (Figure 5). Further analysis of the data is still required to elucidate the spatial and temporal variability across the Basin. Figure 6 illustrates the range of values for major ions in samples from in and around the Murray-Darling Basin by means of a Schoeller plot. Note that values below 0.01 meq/L are generally below detection limits for cations (Ca, Mg, Na) in these low soluble ion samples, whilst bicarbonate (HCO₃⁻) has been calculated, as alkalinity and pH should be analysed at the time of each rainfall event to be accurate and rapidly change as CO₂ is exsolved over time. All samples represent composite events of about a month’s rainfall each.
Analysis of this data will continue beyond the life of this contract.

Figure 4. Piper plot of a year’s rainfall samples (monthly collections) from in and around the Murray-Darling Basin.

Figure 5. Smoothed histogram of the dissolved ion concentrations of all samples illustrated in Figure 4.
Final Monitoring Report to MDBA June 2010

Figure 6. Schoeller plot of all samples from in and around the Murray-Darling Basin collected through 2008. Samples are mostly sodium and chloride dominant, representing sea-salt contribution, but with little detected sulphate. Calcium and bicarbonate-rich samples represent rain events originating, or travelling, across the interior.

10. ASSOCIATED PROJECTS

10.1. GNIP: Global network of isotopes in precipitation

The GNIP database comprises $^{18}$O, $^2$H and tritium values of monthly composite precipitation samples collected since 1961 from a network of approximately 550 meteorological states around the globe. The data are used for a variety of purposes in the fields of hydrology, oceanography and hydrometeorology and in investigations related to the Earth’s water cycle and climate changes.

In Australia, the Bureau of Meteorology, ANSTO and CSIRO are currently responsible for sample collection (BoM) and analyses (ANSTO & CSIRO) from 7 stations: Adelaide, Alice Springs, Brisbane, Cape Grim, Darwin, Melbourne and Perth. This sampling network has recently (August 2004) seen the resurrection of all 7 stations that were operational through the 1970s and 1980s (Table 1). Currently 2 samples are collected at the tritium stations, with one sent to CSIRO for stable and chemical analysis; the other sample is returned to ANSTO for tritium analysis. In the future, it is envisaged that ANSTO will also run stable isotope measurements, but currently, staff limitations preclude this endeavor, despite the recent acquisition of a new stable isotope mass spectrometer. All results are submitted for inclusion in the GNIP database, which is accessible to the scientific community.
Compiling the stable isotope data previously analysed allows a comparison of different sites and an inference on the characteristics of different rainfall events. Thus, we can plot the ranked rainfall amount estimates over the complete datasets and this gives us an indication of the dominant amount of daily rainfall to a region and the corresponding input stable isotope signature of the bulk of surface and groundwater systems in that region. This is illustrated in Figure 7.

Figure 7. Stable isotope plots for monthly rainfall samples from sites around the Murray-Darling Basin. Blue circles are rainfall amount averages, with increasing intensity (rain per month) from <20mm/month at the bottom left through to >200mm/month towards the top right.

From such estimates, the recharge composition of groundwaters may be estimated, as was demonstrated by Harrington et al (2002) for groundwaters in central Australia. We can also use these values to appreciate the input to waters from different weather systems. Note the distinction between the isotope relationship from the inland site (Alice Springs) and coastal sites and the distinct tail to more depleted isotopic values (to the left) reflecting the greater proportion of low rainfall events and greater proportion of highly evaporated rains (indicated by the low slope of the trend). This is also observed in local sites: Indooroopilly is roughly 30km inland of Brisbane airport, and also shows an evaporated trend in the data. The Cape Grim samples are skewed by the values of a few extreme events and the slope is harder to determine from the tighter clustering of other events, reflecting a consistent, and consistently high, rainfall input to the site.

The slope of the global average of all rainfall approaches 8 (i.e. $\delta^2H = 8 \times \delta^{18}O$) reflecting the equilibrium fractionation of isotopes in a closed system (Rayleigh fractionation). Waters that are evaporated (and the resulting vapour removed) favour the heavy isotopes, hence the slope on these plots reduces to give slopes as low as 3 in highly evaporated systems (i.e. $\delta^2H = 3 \times \delta^{18}O$) such as playa lakes. Recharged groundwaters that reflect near-surface evaporation of rains often have slopes approaching 5. By extrapolating these slopes back to the local rainfall slope gives insights into the rainfall regimes required to initiate recharge.
10.2. BRS chemistry of rainfall in the Murray-Darling Basin

The Bureau of Rural Sciences has joined with the CLW network and will populate spatial gaps in the network where these are deemed necessary. A shared approach to analysis will be undertaken. This collection process has stalled, and further discussions are underway.

10.3. Fitzroy Basin association salinity risk assessment project

The Fitzroy Basin Association (FBA), in collaboration with Queensland Department of Natural Resources Mines and Water (QDNRMW), have undertaken a range of measurements and modelling exercises to improve their understanding of salinity risk at both basin-wide and local scales. As part of this investigation, 5 rainfall collectors were installed across the basin to collect monthly precipitation for chemical and isotopic analysis. Preliminary results for stable isotopes were reported in the 2008 report. These stations have now been decommissioned.

10.4. The dust contribution to salinity and accession

The ANU is undertaking a study of dust transport across the MDB. Dr Richard Greene and his students have taken the remaining rainwater and collection bottles from the collection and have extracted the particulate matter also deposited over the month. This material is then viewed under the SEM, analysed for major element concentration and then analysed for major and minor elements using PIXE at the Ion Beam Facility at ANSTO.

Results from this study are included in Appendix II.
REFERENCES


APPENDIX I


Architecture and Processes for National Ion Coverage Maps

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Abstract: Salt accumulates on the land’s surface via rainfall washout of dissolved ions and via dry deposition of salts attached to suspended dust particles. Local and regional studies, based on point data have provided an understanding of accession processes, but have not been compiled as a coherent spatial coverage for Australia, nor assessed in a temporal context, as is routinely carried out for northern America. This paper describes an information system which couples spatial analysis of salt accession modelling with GIS, to deliver national accession maps over the World Wide Web (WWW).

We illustrate this system through examination of chloride accession data across Australia. As ion accession is a spatially contiguous process, it is important to place the site-specific information into a surface. Expanding from a point-based representation to a surface provides a richer means of visualisation, and hence analysis, of the geographic variation of chloride.

The key components of this system (Figure 1) are: a relational database to store site observations for modelling; the modelling application; a geospatial database to store spatial layers; and a web map application for visualisation.

We use an empirical model to estimate the deposition of chloride (kg/ha) across Australia. This follows previous research which related chloride accession to rainfall, wind direction and distance from the coast. The model was developed using The Invisible Modelling Environment (TIME) in the C#.NET programming language. It also exploits the Surfer application to assist with interpolation of site observations from the relational database.

To account for the natural variability of the atmosphere, Australia was subdivided into Uniform Geographical Units (UGUs) characterised by Australia’s climatic zones. Grid cells within each UGU were parameterised based on chloride concentrations measured in rainfall at sites within each UGU. A base chloride accession map was generated from the aggregate of ~200 chloride observations across Australia. The approach was tested by comparing observed values to the modelled base accession map. Correlation gave an $r^2$ of 0.72.

Chloride accession grids were stored within an ESRI geospatial database. The OpenGIS Web Map Service (WMS) standard was used to request the geo-referenced maps from the database, allowing them to be delivered over the internet to WMS compatible clients. An interactive web map application was developed using ArcGIS Server to view the maps via a WWW browser.

Ongoing work focuses on extending the system to produce temporal chloride accession coverage maps. This spatio-temporal data will provide a mechanism to produce coverage animations, based on the on-going collection of point-based accession data. Emphasis will be placed on the automatic generation of these maps on a regular basis.
1. INTRODUCTION

Knowledge of salt accession to the landscape aids the spatial and temporal understanding of salinity processes and groundwater recharge and provides information that can help unravel groundwater movement through aquifers. Chemistry of rainfall at a number of sites across Australia has been collected by a number of researchers (e.g. Hutton, 1976; Hingston & Gailitis, 1976; Keywood, 1995), and continues through a network of rainfall collectors across the continent. We require a desktop delivery system which will allow this data to be delivered electronically over the internet, and easily and quickly updated as further information is acquired. The objective of the system described here is to deliver time series coverage maps of various ions such as chloride, sodium, calcium, magnesium, potassium, sulphate and nitrate via the web. The coverage maps are generated from rainfall chemistry data collected from field sites across Australia. Due to the limited number of field locations, relationships between the ion data and climate data must be modelled and used to interpolate accession rates where data are sparse.

Previous work (e.g. Hutton, 1976; Keywood, et al., 1997) has shown that distance from the coast, wind, and rainfall are all factors which contribute to the amount of salt accession, hence all need to be considered in the models. The approach we use here uses the distance from the coast via the prevailing wind trajectory, only considering wind direction data if rainfall was also recorded for the same period. This distance value is then used as an input to our chloride accession model. Comparisons of chloride accession relationships and their spatial distribution suggest accession rates vary due to climatic variability across Australia. Hence, Australia is divided into Uniform Geographic Units (UGUs) representing Australia’s climatic zones, whereby each UGU is modelled individually and re-assembled to form a complete coverage map.

Whilst the system described here is applied to generation of a base chloride accession map for Australia, the principles apply to accession of any atmospherically-derived ion. The base map is generated using historic chloride concentration observations from numerous sources, and uses aggregated climate data retrieved from the Bureau of Meteorology (BOM) to develop the wind patterns.

2. METHODOLOGY

The system used for the generation of ion coverage maps is illustrated in Figure 2. The system is based on a 3-tier architectural model consisting of 2 stages (or steps); the temporal point data, and the temporal grid data. The database layer handles persistency of the data, the business logic layer captures the core of the system, and the application layer defines how the user interacts with the system. The structure of this section will be based upon this model.

![Figure 2. Model of system architecture used to produce national ion coverage maps.](image-url)
2.1. Stage 1 (Temporal Point Data)

2.1.1 Database Layer
Hourly wind direction and daily rainfall data are sourced from 1682 monitoring stations maintained by the BOM, and supplied via an annual subscription to their FTP site. These stations are shown in Figure 3. The data are imported into a SQL Server relational database which uses the Observations Data Model (ODM) Schema (Horsburgh, et al., 2008). Several SQL Server Integration Service (SSIS) packages retrieve the data, and perform the data integration which is scheduled to run on a monthly basis. From the wind direction and rainfall data, the most frequent (mode) wind direction at each site is derived when it is raining. Because of different temporal resolutions between the wind and rainfall datasets, all wind direction values for the 24 hours prior to the rainfall data record are used to calculate the mode, except when the wind is calm. Wind direction is a continuous data type, so wind direction data are reclassified to 16 cardinal directions before calculating the mode. This process is executed via SQL Server Stored Procedures at the database layer and has been configured to derive the following modal datasets:
- Monthly modal wind direction at each station (continually updating)
- Seasonal modal wind direction at each station (continually updating)
- Annual modal wind direction at each station (continually updating)
- Modal wind direction of all historic data at each station (Run once, Ending: 30/4/2007)
- Modal wind direction of all historic data for each of the four seasons at each station (Run once, Ending: 30/4/2007)

The relational database also serves to store the chemistry data derived from the rainfall samples. This data can be imported from a spreadsheet using the ODM Streaming Data Loader, and analysed using ODM Tools.

2.1.2 Business Logic Layer & Application Layer
Modal wind direction values for each site are retrieved from the database and interpolated across the whole of Australia to obtain prevailing wind direction grids at the temporal resolution of interest. These grids are calculated using a combination of TIME (Rahman, et al., 2003) and the Surfer® application developed by Golden Software®. Wind vectors are converted into their respective X and Y components, interpolated using the kriging algorithm, and then reassembled back to a directional grid using appropriate trigonometry. This process is achieved by invoking functions within Surfers® Application Programming Interface (API). From the directional grid the mean distance to the coast is calculated to each cell using a modified version of Dijkstra’s shortest distance algorithm (Dijkstra E.W., 1959) which is used as the x variable in the chloride relationship (see below: section 3.1).
The coverage maps are geographically divided into UGUs based on varying climates (see below: section 2.2), and individual relationships are applied directly to each UGU. Data values are then sampled at control points and interpolated once again at a higher resolution (5 km) to produce the final coverage map. Using a Calculate first, Interpolate last (CI) approach, permits field observation data to be incorporated with the sampled control points, as the data becomes available on a regular basis. The locations of the control points varies, with more dense control points being taken near coastal areas, and less dense control point being taken inland, and near the boundaries of each UGU. This allows the higher varying accession rates near the coast to be captured, while also concealing the different relationships between neighbouring UGUs. Figure 4 shows the density of the control points used to generate the coverage grids.

The interface to execute model runs is in the form of a windows console application which accepts parameters as arguments. This allows for easy execution of model runs from a scheduler to assist with automating the process of generating coverage maps. Chloride accession grids, and other data derived in the modelling process are saved to a file server. A user interface has been developed to allow the user to visualise and retrieve datasets (climate and chloride) within the relational database. The time series data values can be viewed in Google Earth (Figure 6) using the ODM2KMZ Gateway\(^2\), and entering the LEME WaterOneFlow Interface URL\(^3\) where required.

![Figure 5. Control point density used for interpolation of chloride accession maps.](image)

2.2. Stage 2 (Temporal Grid Data)

2.2.1 Database Layer
An ESRI ArcSDE geodatabase has been created on the database server. This geodatabase is used to store the time series coverage grids which are generated through stage 1. Coverage grids are currently inserted into the database manually; tools to perform spatial data importing into Geodatabases and compression will be investigated in future studies.

2.2.2 Business Logic Layer & Application Layer
Coverage grids are added as layers to a map using ArcMap and deployed as a Map Service using ArcGIS Server. At present there is no known way to automate this task. Templates can be created and this can serve as a quality control mechanism whereby the maps are required to be reviewed before being made available to the public.

![Figure 6. Google Earth displaying datasets for a site. Upon selection of a site, datasets for various parameters at that site are presented in a bubble. The user may then click on a dataset to view the values in both tabular and chart formats.](image)


\(^3\) WaterOneFlow URL: [http://www.wron.net.au/webservices/odm/leme/cuahsi_1_0.asmx](http://www.wron.net.au/webservices/odm/leme/cuahsi_1_0.asmx)
An interactive web mapping application has been developed which can be used to view the coverage maps via web browser. The application currently supports zooming, panning, controlling visible layers and the ability to identify raw data values from the maps. Figure 7 shows a screenshot of the web mapping application displaying the base chloride accession map. An OpenGIS® Web Map Service (WMS) has also been enabled for the chloride layers to be served from the Geodatabase and rendered in a pictorial format such as PNG, GIF or JPEG. This allows the coverage maps to be visualised in any WMS client such as Google Earth, gvSIG, NASA World Wind, OpenLayers, uDig and Qgis.

3. MODELLING CHLORIDE ACCESSION

Australia has a defined climatic zonation. The analysis of chloride accession, therefore, is undertaken across distinct Uniform Geographic Units (UGUs) which are subsequently integrated to generate a map for Australia. As most of the salt deposited on land falls in rainfall, the UGUs are based upon the major seasonal rainfall zones of Australia (Figure 8).

![Figure 8. Major seasonal rainfall zones of Australia. Locations of chloride observations used to perform the regression analysis for the base accession map are also indicated.](image-url)
3.1. Regression Analysis

Keywood, et al. (1997) demonstrated that chloride accession decreased with increasing distance from the coast and could be described by the sum of two exponentials. Cresswell (2005) showed that a general form of this equation applied across Australia is as follows:

$$y = A_1 e^{-x/\lambda_1} + A_2 e^{-x/\lambda_2}$$

where: $x$ is the distance from the coast, and $A_1$, $\lambda_1$, $A_2$, and $\lambda_2$ are empirical parameters that describe a short-distance relationship, while $A_2$ and $\lambda_2$ describe a far-distance relationship, that vary around the country. Different parameter values typify the different climatic zones (Figure 9; Table 1). This type of relationship has been used for all UGUs to produce the base chloride accession coverage map for Australia.

<table>
<thead>
<tr>
<th>Climate Zone</th>
<th>Parameters</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Rainfall</td>
<td>$A_1$</td>
<td>$\lambda_1$</td>
</tr>
<tr>
<td>Low Rainfall</td>
<td>1.01E-09</td>
<td>14,968</td>
</tr>
</tbody>
</table>

Figure 9. Chloride accession rates plotted against distance from coast (in the direction of prevalent wind direction) for the 6 climate zones shown in Figure 8.

<table>
<thead>
<tr>
<th>Climate Zone</th>
<th>Chloride (kg/ha)</th>
<th>Distance (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Summer, Low Winter Rainfall</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet Winter, Low Summer Rainfall</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet Winter, Dry Summer</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Parameterisation of individual UGUs
Our approach was validated by extracting modelled values from the base map at the locations of the chloride observations and comparing to the observed data. Modelled chloride accession provides a reasonable approximation of the observed values (Figure 10), with an overall $r^2$ of 0.72. This result provides confidence our approach will work adequately for generating coverage maps where observed data is sparse.

![Figure 10. Modelled versus measured values of chloride accession across Australia.](image)

4. DISCUSSION AND CONCLUSIONS

An accession modelling system has been built to electronically deliver time series maps for various ions measured in rainfall chemistry. The system was used to generate a base chloride accession map which used the aggregate of all historic climate observations (wind and rainfall) from the BOM as inputs to the chloride modelling process. The results demonstrate the rapid decrease in accession away from the coast, and influence of climatic zones (Keywood, et al., 1997) on the concentration of salts deposited on the land’s surface. Complete automation of the accession modelling system has not been achieved, but is possible with further development. It is preferable, however, to maintain a level of manual intervention to permit quality checks on the data and outputs.

Rainfall chemistry sampling varies from single events to combined quarterly samples; hence the chloride-distance relationship is driven by modal wind patterns that may not be indicative of the prevalent wind direction during the period of maximum accession. Records indicate the major rainfall events and more detailed analyses could be carried out with further resources and time. To support this, collection of rainfall chemistry data from twenty sites across the country continues. The study has demonstrated that near real time analysis and display of the chloride accession to Australia can be achieved. Interpolating both; measured observations; and modelled discrete data where observations are sparse, will provide a realistic impression of the spatial variability in chloride accession.

ACKNOWLEDGMENTS

This work has been funded through the Cooperative Research Centre for Landscapes, Environment and Minerals Exploration (CRC LEME) and the Murray-Darling Basin Authority.

REFERENCES


APPENDIX II

Papers presented by ANU students on the dust component of fallout, collected in the rainfall collectors used in this study.


4.1. Dust and terrestrial salt (NaCl) in SE Australia: Implications for aeolian co-transportation and co-deposition

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Aeolian dust exerts major effects across the Australian continent in terms of soil-landscape processes and impacts on human society [1]. It not only has serious health implications, but is also thought to be an insidious carrier of terrestrial salts, which when deposited cause salinisation and/or sodification of the soil [2]. However, this argument is still controversial and lacks objective data regarding co-transportation and co-deposition of terrestrial soil and terrestrial salt (NaCl) from their potential source areas such as the enclosed inland drainage systems in South Australia [3]. This research addresses this lack of information, with a special focus on the potential role of aeolian dust to co-transport and co-deposit terrestrial salt (NaCl) in SE Australia.

One hundred and fifteen monthly dust samples were collected from 16 depositional samplers across SE Australia. Both chemical (ion beam analysis) and morphological (SEM) analyses were conducted on these samples. Subsequently, a set of equations and principal component analysis was applied to the initial chemistry results to reveal the contributions from terrestrial salt. The results of these analyses, along with weather records, suggested the existence of terrestrial salt dispersion associated with aeolian dust from the potential source areas.

4.2. Application of IBA and Refined Sample Preparation Techniques to the study of Aeolian Dust Samples from Northwest Australia

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\textsuperscript{d} CSIRO Land and Water, Long Pocket Laboratories, 120 Meiers Rd, Indooroopilly QLD 4068, Australia.

Ion beam analysis (IBA) using the STAR Accelerator at ANSTO was applied to 200 rainwater-derived aeolian dust samples from locations west of the Lake Eyre Basin. The IBA results varied considerably depending on the particle concentration on the filters, and the chemistry of particles remained relatively uniform across particle size fractions. It was recommended that a syringe filtering method using 25mm filters be used for sample preparation to attain reliable IBA results with filtered rainwater.

1. Introduction

IBA can provide extremely accurate data on the elemental composition of dust samples [1]. However, recent analysis of dust samples collected from SE Australia using a range of sample collectors have demonstrated that considerable uncertainty may exist in the interpretation of results because of uncertainties associated with the sample preparation methods [2]. This current study builds on previous work by Shiga (2008) and focuses on refining the methods used for preparing dust samples for analysis.

The dust samples analysed were collected monthly in “dust traps” from July 2008 – May 2009. Fig. 1 shows the locations of dust traps (given by X) and also the location of source area dust (given by O) that was obtained via researchers at Monash University (Tadhg O’Loingsigh, pers. Comms 2009) to provide a soil fingerprint of potential source areas.
These dust traps are maintained as part of a collaborative project between CSIRO, BoM and ANU researchers looking at precipitation throughout all Australia. The dust samples were analysed using IBA techniques at ANSTO, and interpreted in conjunction with ion chemistry and stable isotope analysis carried out by CSIRO Land and Water at Adelaide [3]. This work has application to studies of air quality and health [4], the aeolian transport of iron and NaCl [5], and also has potential relevance in mineral exploration.

2. Sample preparation

Rainwater samples were decanted to remove paraffin wax used to prevent evaporation, and then filtered into the thoracic size range of 0.2μm – 10μm (referred to here as PM10 samples). Both 47mm and 25mm diameter polycarbonate Nuclepore membranes were used for final filtration, and were weighed using a microbalance before and after filtering. Three different methods of filtration were trialled (Fig. 2) and the exact amount of rainwater in mL was recorded for each run. Both the PM10 and ‘All Particle Size’ portions of each sample were filtered and placed in a sterile Petri dish. 20mL of the <0.2μm filtrate was then poured into a Petri dish containing a blank filter. Each Petri dish was then placed in a drying oven at 40°C until filters were deemed to be dry.

![Diagram of filtration methods]

Fig. 2. Three methods of filtration trialled. Methods 2 and 3 were used for the final samples.

A selection of filters was examined using a Hitachi 4300 (Schottky Field Emission) electron microscope at the ANU Electron Microscopy Unit (EMU). This was done in order to determine the effectiveness of each method of filtration in dispersing a uniform density of particles across the filter; a necessity for accurate IBA. Due to the poor distribution of particles evident to the naked eye using Method 1, only methods 2 and 3 were examined with SEM and subsequently used for IBA.

3. Results and Discussion

3.1 SEM Results

Scanning electron microscope images showed that by using Method 2 the All Particle Size samples tended to be evenly distributed across the 47mm filters (Fig. 3a), and that the samples contained considerable biological material >100μm in length. In the majority of cases the dust in the PM10 samples obtained using Method 2 were quite sparsely dispersed (Fig. 3b). In Method 3 (which increased particle density by a factor of 3.5 relative to the 47mm filters) the SEM images showed consistent densely loaded filters (Fig. 3, c.).
3.2 IBA Results

The results given by IBA in $\mu$g/cm$^2$ were converted to ng/mL by factoring in the amount in mL used during filtration. The results for six elements from the Alice Springs July 2008 sample are presented in Table 1. While these results are only a small portion of the total dataset, they represent the key findings of the study.

Table 1. IBA data given in ng/mL filtered.

<table>
<thead>
<tr>
<th>Element</th>
<th>47mm All Particles (ng/mL)</th>
<th>47mm PM$_{10}$ (ng/mL)</th>
<th>25mm PM$_{10}$ (ng/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>22.902</td>
<td>13.880</td>
<td>2.407</td>
</tr>
<tr>
<td>Si</td>
<td>92.996</td>
<td>10.757</td>
<td>10.144</td>
</tr>
<tr>
<td>K</td>
<td>10.063</td>
<td>1.041</td>
<td>0.344</td>
</tr>
<tr>
<td>Ca</td>
<td>1.041</td>
<td>0.694</td>
<td>1.547</td>
</tr>
<tr>
<td>Ti</td>
<td>1.388</td>
<td>0.694</td>
<td>0.086</td>
</tr>
<tr>
<td>Fe</td>
<td>24.290</td>
<td>2.776</td>
<td>1.633</td>
</tr>
</tbody>
</table>

The oxides of these six major soil elements were added and normalised to 1 using Equation 1. Here, each coefficient is the molecular weight of the oxide divided by the atomic weight of the element. FeO and Fe$_2$O$_3$ were assumed to be present in equal proportions:

$$\text{SOIL} = 1.89\text{Al} + 2.14\text{Si} + 1.2\text{K} + 1.4\text{Ca} + 1.67\text{Ti} + 1.36\text{Fe} = 1$$

A soil fingerprint including calculated O (O was not given by IBA) was then graphed for each sample and used for comparison of soil chemistry. The fingerprints for the Alice Springs July 2008 samples corresponding to the Table 1 data are given below.

Fig. 4. Ratios of major soil components in Alice Springs Jul 08 samples using Methods 2 (47mm) and 3 (25mm).
The fingerprint of the All Particle Size 47mm filter using Method 2, which showed a dense dispersion of particles with SEM (Fig. 3a), is almost identical to the PM$_{10}$ 25mm fingerprint using Method 3. This result was repeated throughout samples at each location, with the major variability being the soluble Ca and K components, and small fluctuations in the Fe values. This demonstrated that a considerably uniform chemical composition exists in the PM$_{10}$ and ‘all particle size’ dust across the sample regions.

The IBA results for the PM$_{10}$ 47mm filters (Method 2) were consistently variable as shown in the middle graph in Fig. 4, even though the size fraction was consistent with the 25mm filters. Coupled with the SEM images of these 47mm Method 2 samples showing a low density of particles on the filter, it has been concluded that these results are unreliable.

3.3 Conclusion

For accurate ion beam analysis of rainwater, it is recommended that a method involving a syringe and filter holder technique (Method 3) be used, as it produces a high concentration and uniform distribution of particles across the filter. This permits detailed SEM examination, and allows the most accurate results to be obtained by IBA techniques.

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