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

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CHAPTER 1 INTRODUCTION

The Australian continent provides a unique laboratory in which the natural chemistry of the atmosphere may be investigated. The main reason for this is its relatively unpolluted nature. By northern hemisphere standards, the atmosphere of the southern hemisphere is very clean. As an example, the long-term average concentrations of $\text{SO}_4$, $\text{NO}_3$ and Ca in precipitation at Hubbard Brook in North America are elevated by more than 5.5 times relative to Katherine, Australia (Likens et al 1987), despite both sites experiencing similar rainfall. The cleanliness of the atmosphere over Australia may be attributed to its relatively small number of human inhabitants and the relatively short period of time that Australia has been industrialised. In addition, because of the concentration of the majority of Australia's population in the eastern coastal regions, vast areas of the interior of the continent remain little affected by human activity.

In addition to the unpolluted nature of the atmosphere, Australia is an ideal place to investigate precipitation because of the wide range of climatic conditions. These range from tropical to subtropical in the north, to arid in the centre, to temperate along the southeastern coastal areas. This means that rainfall chemistry can be compared with a variety of climate types on a single land mass. Further, the lack of significant topography across the Australian continent minimises orographic effects, thus simplifying the interpretative base. From a practical point of view, there are few places in the world where a comparable investigation sampling over such a vast area would be logistically possible. The inconvenience of crossing international borders was avoided and throughout this investigation, field equipment remained undisturbed by human activity.

This investigation concerns the assessment of the chemistry of precipitation collected across the Australian continent. Samples were collected from 18 sites over two arrays extending in an west to east direction through Western Australia (WE array), and in a south-north direction through South Australia and the Northern Territory (SN array) as shown in Figure 1.1. Precipitation was collected in bulk depositional collectors. The analytical work can be divided into two related sections; an investigation of the major-element chemistry and an investigation of $^{36}\text{Cl}$ composition. Interpretation of the $^{36}\text{Cl}$ data is reliant on an understanding of the
major-element chemistry, while $^{36}\text{Cl}$ can be used to highlight processes affecting the major-element chemistry.

![Map of Australia showing rain gathering sites](image)

**FIGURE 1.1** Location of the WE and SN rain collecting arrays. Small dots are sample sites. Large dots are major cities.

### 1.1 MAJOR ELEMENTS

It is important to understand the chemistry of precipitation from unpolluted areas for two reasons: 1) to understand the processes that control precipitation in the atmosphere of remote areas; 2) to use this understanding as a basis for establishing the effects of industrial, urban and agricultural emissions on precipitation chemistry in populated areas. In particular, the results from this project will expand the sparse data base of precipitation chemistry across Australia both by adding further data to sites that have been measured previously, and by providing the first analysis of precipitation for new sites, in particular in central and northern Australia. This provides fundamental information for other areas of research in the natural environment. For example, information concerning the rates of accession of salts to the Australian landscape is necessary for the understanding of salinisation issues. In
particular, studies using a mass balance approach to the problems of salinisation require data such as the amount of Cl deposited in rainfall.

1.2 CHLORINE-36

Chlorine-36 is a naturally occurring radioactive isotope with a half-life of 301,000 (±200) years (Browne and Firestone 1986). Its production in the atmosphere occurs primarily in the stratosphere (60%) by the cosmic ray spallation of 40Ar. The production of 36Cl in the stratosphere is dependent on latitude due to the influence of the Earth's geomagnetic field on the flux of cosmic rays to the Earth. However, the distribution of 36Cl through the troposphere is dominated by geographically controlled atmospheric conditions and processes.

Lal and Peters (1967) estimated the fallout curve of 36Cl to the Earth's surface by utilising the latitude-dependence and fallout pattern displayed by 90Sr produced during stratospheric bomb tests in the late 1950s.

Chlorine-36 activity in natural samples ranges from 10^{-10} to 10^{-16} atoms 36Cl/Cl, far below the detection limits of conventional (low energy) mass spectrometers. The development of accelerator mass spectrometry (AMS) as an analytical tool means most natural samples are within the range of analysis. Accelerator mass spectrometry allows great sensitivity (down to 5 x 10^{-16} atoms 36Cl/Cl) with small sample size (down to < 200μg Cl as AgCl).

Chlorine-36 has been used in a range of geological applications, eg. exposure-age dating of impact structures and measurements of weathering rates, and the half-life of 36Cl coupled with the hydrophilic nature of Cl also makes 36Cl an effective hydrological tracer, particularly for dating groundwater and estimating recharge rates. Many such investigations approximate the input rates of 36Cl to groundwater systems by measuring the 36Cl/Cl ratios of recharge to the system, requiring additional 36Cl/Cl ratio measurements. An inexpensive and fast method of approximating input values involves estimations from theoretical calculations of the fallout of 36Cl and stable Cl to the Earth's surface. Hence, this investigation will assess how well the predicted 36Cl fallout values correspond to measured values in precipitation, and its relation to recharge values.

Chlorine-36 also has a number of applications in atmospheric investigations. With the growing interest in the behaviour of Cl in the atmosphere, 36Cl has been used as
a tracer for stratospheric Cl chemistry (Wahlen et al 1991). The use of $^{36}\text{Cl}$ as a tracer for stratosphere-troposphere exchange has been investigated, and it is suggested that enhanced mixing during seasonal shifts in the height of the tropopause is portrayed by increases in the fallout of $^{36}\text{Cl}$ (Hainsworth et al 1994, Knies et al 1994).

Many of the applications mentioned above rely upon an understanding of the processes involved in $^{36}\text{Cl}$ deposition. However there are very few data concerning $^{36}\text{Cl}$ in modern deposition, and the existing measurements are all from the northern hemisphere. This thesis provides data for $^{36}\text{Cl}$ deposition in Australia and hence the southern hemisphere and can be used to address a number of uncertainties existing in our understanding of $^{36}\text{Cl}$ deposition. The SN array spans latitudes $12^\circ$S to $35^\circ$S, and allows an assessment of the latitude-dependent predictions of $^{36}\text{Cl}$ fallout used in many hydrological investigations. The WE array approximates a narrow range of latitudes, and lies equidistant between the northern and southern coasts of Western Australia. It allows an assessment of the change of $^{36}\text{Cl}/\text{Cl}$ ratios with increasing distance from the coast without the added complication of latitude variation. The 2-year seasonal sampling program allows an investigation of the seasonal variations in fallout of $^{36}\text{Cl}$, thus further investigating the use of $^{36}\text{Cl}$ as a tracer of stratosphere-troposphere mixing. The relationship between $^{36}\text{Cl}$ fallout and rainfall amount can be investigated, and correlations between $^{36}\text{Cl}$ concentration and major-element concentrations provide information about the phase of $^{36}\text{Cl}$ in the atmosphere. The data, being the first from the southern hemisphere, allows comparison with northern hemisphere fallout rates.

1.3 OBJECTIVES AND THESIS OUTLINE
This thesis is directed towards an understanding of major-element and $^{36}\text{Cl}$ chemistry in precipitation from remote areas of Australia. This is achieved through the following objectives:
1) The characterisation of the meteorological features that produced rainfall during each season at each site for the sampling program.
2) The characterisation of the major-element chemistry of rainfall from remote areas of Australia and assessment of the flux of ions to the Australian continent.
3) The assessment of the source of material to the continent, and the isolation of the influences of different meteorological patterns on the rainfall chemistry (i.e. seasonal variations).
4) The characterisation of the fallout of $^{36}\text{Cl}$ to the Australian continent.
Chapter 1 Introduction

5) The assessment of the relationship between $^{36}\text{Cl}/\text{Cl}$ ratio with changing distance from the coast.
6) The assessment of the applicability of the latitude-dependent $^{36}\text{Cl}$ fallout model of Lal and Peters (1967).
7) The assessment of processes that perturb $^{36}\text{Cl}$ fallout over time (i.e. seasonal variations).
8) The assessment of the form of $^{36}\text{Cl}$ in the atmosphere before deposition.
9) The comparison of southern hemisphere and northern hemisphere fallout levels.

Point 1 will be the emphasis of Chapter 2 which describes the general features of the atmospheric processes and weather patterns that affect Australia. Chapter 2 also describes a simple classification system of rainfall-producing synoptic processes. This classification is devised to assign the production of rainfall at meteorological stations in the proximity of the sample locations to a particular synoptic process (or combination of processes). From this, the predominant synoptic process that produced rain for each sampling period at each site is determined. Thus, the predominant origin of moisture and movement of airmasses before deposition of precipitation is determined. This is a simple method of tracking the movement of airmasses when back-trajectory information is not available.

Chapter 3 describes the methods used in this investigation, including sampling and analytical procedures, methods of data analysis and checks of quality control. Chapter 4 provides an introduction to the formation and chemistry of precipitation and a summary of previous precipitation investigations in Australia. Points 2 and 3 are the emphasis of Chapter 5, which uses multivariate analysis to determine the sources of chemical constituents to the precipitation collectors. Simple analysis of different element ratios allows the determination of seasonal variations in the supply by the sources of material, and these variations are tied into the results from Chapter 2. Points 4 to 9 are covered in Chapter 6 whose emphasis is on $^{36}\text{Cl}$. The conclusions of this thesis are summarised in Chapter 7.
CHAPTER 2 WEATHER PATTERNS OF AUSTRALIA

An understanding of the sources and movement of airmasses and moisture that produce rainfall is necessary to aid the successful interpretation of the chemical and isotopic composition of precipitation collected in the sampling vessels. It was impractical to make detailed meteorological observations at each site given their remoteness. This chapter combines the available meteorological observations with information on average weather patterns, to create a system of assigning rainfall during each sampling period to a particular synoptic process or combination of processes. Note that this system of classifying synoptic processes only includes rainfall-forming events and therefore does not take into account the effects of dry deposition. This system will be used subsequently in the interpretation of major-element and $^{36}$Cl data.

2.1 CONTROLS ON AUSTRALIA'S CLIMATE PATTERNS

An assessment of the accession of material to the Australian continent by rainfall requires knowledge of the sources and movement of air before deposition occurs. This requires an understanding of air circulation over Australia, the airmasses that influence the Australian continent and rainfall distribution over Australia.

Air Circulation

General Circulation

A simplified picture of general global atmospheric circulation is shown in Figure 2.1. The interior of the circle in Figure 2.1 represents circulation at the Earth's surface. In the tropical regions ($30^\circ$N to $30^\circ$S) the trade winds are present flowing from southeast to northwest in the southern hemisphere. The interaction of the northern and southern hemisphere trade winds creates an area of low surface pressure known as the intertropical convergence zone (ITCZ). In the middle latitudes, the westerlies are present. Between the westerlies and trade winds are the zone of high pressure known as the Subtropical High Pressure Belt. In the polar regions, the winds are on average easterly.

The exterior of the circle in Figure 2.1 represents circulation in the upper troposphere. Hadley cells involve air rising in tropical regions and subsiding at middle latitudes. This circulation gives rise to the trade winds and the subtropical
high-pressure belt. Hadley circulation makes up the main component of meridional circulation at low latitudes which maintains the heat flux required to balance the global energy budget. The ITCZ forms a barrier of exchange between the Hadley cells, dividing the troposphere into northern and southern hemispheres. The ITCZ oscillates northwards and southwards about an average position near the equator. Thus the exchange of airmasses between the two hemispheres is due to the seasonal relocation of the ITCZ (Figure 2.2). Other circulation cells shown in Figure 2.1 include Ferrel cells (or indirect circulation), which govern meridional circulation in the opposite direction to that required for thermally driven motion. The polar cells are weak systems that produce the polar easterlies.

**FIGURE 2.1** Simplified schematic diagram of the features of atmospheric circulation. The interior circle represents the lower troposphere, the exterior of the circle represents the upper troposphere. J = Jet streams, H = highs, L = lows. After Neiburger, Edinger and Bonner 1982.

Large-scale eddies (cyclones, anticyclones, waves in zonal currents) act to reduce instability in the global circulation that would result if Hadley circulation was the only method of meridional transport of energy and momentum. Large-scale eddies are in fact responsible for most of the transport of energy and momentum, except at low latitudes where Hadley cell circulation plays an equally important role. The transfer of momentum by eddy motions gives rise to the westerlies in the middle latitudes and upper troposphere, and surface friction in the westerlies gives rise to the weak reverse meridional circulations, forming the Ferrel cells.
FIGURE 2.2 Mean meridional circulation. Mass streamlines in units of $10^{12}$ g/s. Dashed line is the mean tropopause height. The dark shaded area represents streamlines $<-5 \times 10^{12}$ g/s. Light shaded areas represent streamlines $>5 \times 10^{12}$ g/s. In spring (September to November) and autumn (March to May), there are 3 meridional circulation cells in each hemisphere. In summer (December to February) and winter (June to August) this pattern is distorted. After Warneck 1988.
Winds in the upper troposphere are westerly in all latitudes except at the equator. The westerlies encircle the globe in a wave like pattern (Rossby waves). The west wind maxima mark the jet streams (represented by J in Figure 2.1). The dimensions of the jet streams are of the order of 1000 km long, 100 km wide and 1 km deep. Australia is affected by two jet streams, the polar front jet stream being less significant than the subtropical jet stream. The polar jet stream occurs between 50-60° and lies above the boundary between warm air of the tropics and cold air of the pole. The subtropical jet stream is situated above the Subtropical High Pressure Belt at 32°S in February and 26°S between May and November (Figure 2.3) Its speed is greatest in July. A gap in the tropopause at 35-40°S occurs in association with the jet stream allowing maximum transfer of material from the stratosphere to the troposphere at this latitude (Reiter 1975). This is particularly important for the 36Cl discussions of Chapter 6.

Circulation over Australia

Figure 2.3 displays a simplified picture of air circulation over Australia during summer and winter. Australia is influenced by the ITCZ during summer and during winter the ITCZ lies north of Australia. The Subtropical High Pressure Belt influences Australia throughout the year, during summer lying over the southern part of the continent, and during winter moving northwards to lie over the centre of Australia. Trade winds affect Australia northwards of the high-pressure belt.

During summer, when the high-pressure belt lies to the south of Australia, much of the continent is influenced by the steady easterly trade winds. During winter, the north of Australia becomes increasingly influenced by the easterly trade winds, as the high-pressure belt moves northwards. Areas south of the high-pressure belt become influenced by westerly winds, which often have low-pressure cells embedded in them. In the north of Australia, during summer, northwesterly winds associated with the monsoon dominate.

Airmasses

The atmosphere consists of a large number of regions in which conditions of temperature, humidity and stability are relatively uniform. These regions, or airmasses may have a diameter of 500-5000 km and an internal temperature gradient of less than 1°C per 100 km (Linacre and Hobbs 1982). Airmasses attain certain characteristics after prolonged contact with regions of the Earth's surface (source area) having a particular temperature and humidity (Gentilli 1971). Therefore, the
Chapter 2 Weather Patterns of Australia

a) January (Summer)

- Monsoon northwesterlies
- ITCZ (Intertropical Convergence Zone)
- Weak trade winds
- Subtropical Jet Stream
- Westerly winds

b) July (Winter)

- ITCZ
- Trade winds
- Subtropical Jet Stream
- Westerly winds

FIGURE 2.3 Air circulation in a) January and b) July. These diagrams are highly simplified. L = lows, H = highs, arrows represent wind direction, dashed line represents the position of the ITCZ (Intertropical Convergence Zone). The dotted line represents the approximate position of the Subtropical Jet Stream position. After Tapper and Hurry 1994.
characteristics of the airmass reflect the area from which it is sourced. Thus, understanding the movement of airmasses may lead to an identification of the source of the airmass, and ultimately the sources of material measured in precipitation.

The airmasses that affect Australia have a limited range of characteristics so their classification is simpler than for complex systems elsewhere in the world (Gentilli 1971). The source areas of airmasses that affect Australia are shown in Figure 2.4. The characteristics of these airmasses are shown in Table 2.1.

The tropical airmasses (Tc and Tm) dominate over Australia. They originate equatorwards from a ridge of high pressure where sinking and convergence occur in a belt (Gentilli 1971). Subtropical airmasses (sTc and sTm) originate polewards of this ridge. Subtropical maritime airmasses (sTm) originate from the west Indian
### TABLE 2.1 Characteristics of the airmasses that affect Australia (after Gentilli 1971 and Tapper and Hurry 1993).

<table>
<thead>
<tr>
<th>Mass</th>
<th>Source Area</th>
<th>Area Affected</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>tropical continental (Tc)</td>
<td>central Australia</td>
<td>anywhere in Australia</td>
<td>summer, hot dry and unstable (cooler in winter); dew point -4 to +2°C; heat waves</td>
</tr>
<tr>
<td>subtropical continental (sTc)</td>
<td>southern central Australia</td>
<td>inland southern Australia</td>
<td>year round, stable and dry; dew point 2-7°C;</td>
</tr>
<tr>
<td>tropical marine (Tm)</td>
<td>Timor and Coral Seas</td>
<td>northern and western Australia</td>
<td>warm and humid; winter T=22-24°C.; summer T=26-28°C; RH close to saturation; Northwest Cloud Band in winter, tropical cyclones in summer, torrential rains to northeast slopes in summer.</td>
</tr>
<tr>
<td>Indian subtropical marine (IsTm)</td>
<td>Indian Ocean</td>
<td>western and southern coastal areas</td>
<td>winter T=10-12°C, RH= 80-85%, air in the westerly stream; summer T=20-22°C, RH= 70-75%, air in the cool change between two anticyclones</td>
</tr>
<tr>
<td>Pacific subtropical marine (PsTm)</td>
<td>Pacific Ocean</td>
<td>southeast and central coast, Tasmania</td>
<td>winter T=14-16°C, RH near saturation, cyclogenetic belt near Tasmania; summer T=22-24°C, RH saturated, thunderstorms and torrential rains in the presence of orographic barriers</td>
</tr>
<tr>
<td>Equatorial (Eq)</td>
<td>Transequatorial</td>
<td>northwestern Australia in summer</td>
<td>summer only, dew point =21-24°C; monsoon</td>
</tr>
<tr>
<td>subpolar marine (sPm)</td>
<td>Southern Ocean</td>
<td>southern coast</td>
<td>cool and moist; dew point = 7-13°C; cloudy drizzle that may develop into rain in the presence of orographic barriers</td>
</tr>
</tbody>
</table>

Ocean (IsTm) and the east Pacific Ocean (PsTm). Tropical maritime airmasses (Tm) have two major reservoirs, the Timor and Coral Seas. The Gulf of Carpenteria is a minor reservoir of tropical maritime air. The trapezoidal shape of Australia north of the Tropic of Capricorn means that there is very little difference between the influence of Indian Ocean and Pacific Ocean air to the Tm. Tropical continental airmasses (Tc) form over the continent further than 500 km from the coast (Linacre and Hobbs 1982). Equatorial airmasses (Eq) are sourced over the equator. Subpolar
maritime air (sPM) is sourced in the Southern Ocean and only influences southern areas of Australia.

An alternative way of considering the source of material in precipitation is by considering air streams (Figure 2.5). An air stream is the mean airflow averaged over some specific time whose temperature and moisture characteristics are continually changed by the surface over which they pass as well as in response to changes in vertical motion and stability fields (Wedland and McDonald 1985). Airmasses and air streams are not synonymous. However an air stream may become an airmass if it travels over a large homogeneous surface and acquires the temperature and humidity of that surface.

The airstreams that affect Australia have been investigated by Wedland and McDonald (1985), with streamline analysis identifying monthly air stream dominance regions from monthly mean surface winds from more than 30 stations around Australia over 18 years. Two major patterns were observed, a winter pattern of continental airstream dominance and a summer pattern of oceanic airstream dominance: streamlines are less constant in spring and summer than in autumn and winter, which may be due to the presence of confluences that only occur during summer and spring (Figure 2.5). These confluences are caused by the interaction of the northern limit of Southern Ocean maritime air and the south western limit of Pacific maritime air, and the interaction of the Indian Ocean maritime air from the northwest with the easterly trades from the Pacific. Migrating cyclones and fronts are concentrated along these confluences in spring and summer.

Rainfall Patterns of Australia

Figure 2.6 shows the distribution of rainfall across Australia. The highest rainfalls occur in coastal and mountainous terrains (e.g. tropical coast of Queensland, western Tasmania. In contrast, much of the centre of Australia receives very little rainfall, because of the region's isolation from moist oceanic airmasses. The rainfall that the interior of Australia does receive is highly variable.

The rainfall pattern of Australia is seasonal, with a winter regime in the south and summer rainfall in the north (Figure 2.7). Of interest for this investigation, the wet summer in the tropical north occurs under the influence of the monsoon. The southward movement of the ITCZ brings moist equatorial air to the northern part of
Chapter 2 Weather Patterns of Australia

FIGURE 2.5 Dominant location of major confluences and the months of existence. Confluence regions are marked by dashed lines. IsTm = Indian subtropical maritime, PsTm = Pacific subtropical maritime and sPm = subpolar maritime. From Wedland and McDonald 1985.

the continent from the northwest. The presence of heat lows (eg. Pilbara heat low in WA) also allows the influx of moist air from the humid tropics. The presence of the subtropical high over the south of the continent during summer suppresses rainfall. During the dry season the north is under the influence of the southeasterly trade winds which blow off the continent. The south of Australia experiences winter rainfall with the passage of cold fronts and associated systems. During the winter months the major pressure systems (ITCZ and Subtropical High Pressure Belt) are further north than during summer, increasing the probability of cold fronts reaching southern Australia and bringing rain. Cold fronts may be responsible for generating high winter rainfall in the south of the arid zone (Figure 2.7). The arid zone has a distinct summer rainfall regime in the tropics and subtropics, and uniform seasonal rain to winter rainfall in the south.
2.2 GENERAL WEATHER PATTERNS
Atmospheric pressure, wind and precipitation are changing constantly over Australia. However there are basic patterns of pressure and wind that underlie these changes. Continuous observations of Australia's meteorological conditions over a long period of time allows the generalisation of seasonal weather patterns. These are discussed below for the areas in which the rain collecting arrays are located (i.e. Western Australia, Northern Territory and South Australia). The general weather patterns of each area are described in terms of seasonal changes to coincide with the seasonal sampling program detailed in Chapter 3. The descriptions of the seasonal weather patterns for Western Australia, South Australia and the Northern Territory are summarised from the Monthly Weather Review for each area (Bureau of Meteorology 1992a, Bureau of Meteorology 1993a, Bureau of Meteorology 1993b). Figure 2.8 gives the location of geographical place-names mentioned in this section.

FIGURE 2.6 Median annual rainfall across Australia, and sampling localities from the present investigation. After Tapper and Hurry 1994.
Western Australia (Bureau of Meteorology 1992a) (Figure 2.8a)

Summer (December to February)
In a typical year, the weather in Western Australia during December is controlled by the presence of an anticyclone in the Great Australian Bight and an extensive heat low in the north. The heat low that affects Western Australia (the Pilbara heat low) is an area of low pressure resulting from the anticyclonic transportation of heat from the heart of the continent to the northwest. It remains stationary over the Pilbara area because of the hot land that creates a permanent centre of convection. The southern portion of Western Australia is influenced by dry easterly winds and the north of Western Australia by moist westerlies. As summer progresses, the high-pressure belt becomes centred over the south of Western Australia. In the north the airflow is strongly influenced by the presence of a deepening low pressure over land. Thus a gradient between the tropical and subtropical areas results in the flow of warm to hot continental air over much of Western Australia. January rainfall is therefore usually the result of thunderstorm activity over most of Western Australia. In the tropics, rainfall increases sharply, especially in the Kimberley and is commonly caused by cyclonic activity that originates near the northwest coast. The high-pressure belt remains to the south of the continent during February and West Coast troughs develop. As these troughs deepen northeasterly winds develop and temperatures increase in coastal districts.

The cyclone season in Western Australia spans November to March. Cyclones often develop in the Timor Sea and cyclones that cross the coast tend to decay into tropical depressions that may cause extensive flooding. The probability of Western Australia being affected by a tropical cyclone is highest in February.

Autumn (March to May)
The beginning of Autumn (March) represents the late part of the monsoon in the north of Western Australia so the monsoonal low-pressure area in the tropics is generally weaker. Tropical cyclones tend to develop further westwards and move west or south before decaying. With the impending end of the wet season in the north, there is a decrease in rainfall during March. With the end of the monsoon, the high-pressure belt begins its northwards movement and pressures rise over the state. Westerly winds become more frequent in the southwest, though the incidence of gales and heavy rainfall events remains low. The high-pressure belt continues its northward migration during May and establishes itself over the southern part of the continent. Thus easterly winds are able to move over the northern cooling land
mass, bringing a shift to winter conditions. Over southern parts of the continent westerly winds prevail although periods of calm are common. Incursions of moist middle-level tropical air over the northwest (Northwest Cloud Bands) can sometimes result in heavy rainfall extending from the northwest coast to the Goldfields, and as far east as the eastern states of Australia. Westerly winds in the southern half of Western Australia bring increasing rain over the southwest.

**Winter (June to October)**

The high-pressure ridge has completed its northward migration by the beginning of winter (June). Winter conditions are characterised by fine clear weather and drops in temperature over much of the state, and intense rainfall in the southwest. In the tropics, fine weather prevails, except when a strong southern front penetrates to the north coast. The sub-tropical ridge intensifies slightly during July so that skies are

![Rainfall Zones](image)

**FIGURE 2.7** Rainfall zones of Australia and sample localities from the present investigation. After Tapper and Hurry 1994.
FIGURE 2.8A Sample localities along the WE array, Met Stations used for meteorological observations, and location of geographical place names discussed in the text.
more frequently clear, and the large net loss of radiation makes July the coolest month in the state. The tropical regions rarely receive rain in July. Again incursions of moist middle-level tropical air may result in widespread rain in the Pilbara, Gascoyne and Eucla. Cold fronts from the southwest Indian Ocean can interact with these disturbances to produce widespread heavy rain over most of the southern half of the state. The high-pressure system begins its southward movement by August, signaling the beginning of a gradual return to summer conditions. The wind patterns remain easterly to the north of the ridge and westerly to the south. In the north, August is the driest month.

Spring (September to November)
The first isolated thunderstorms of the spring season occur during September and may produce rain in the Kimberley. Westerly winds occur more frequently in the Northern Kimberley as the month progresses. Easterlies still prevail over the rest of the north while on the south coast, winds remain westerly. The remainder of the south of Western Australia is dominated by easterly winds as the high-pressure ridge moves southwards. Westerly gales occur with less frequency in the southern areas of the Western Australia. The high-pressure belt continues to move southward during October, so that the south of Western Australia experiences more days with easterly winds. The southward movement of the ridge allows an influx of moist tropical air into the Kimberley from nearby seas, contributing to the increased thunderstorms as the season progresses.

The high-pressure belt is mainly confined to the south of the continent by the end of spring and easterly winds are produced to the south of the belt. The southern areas experience westerly winds and scattered showers when the high-pressure belt is centred over the continent. There is usually no rain further north except over the Kimberley where rain becomes more frequent as the month progresses. Cyclones may cause very high rainfalls along the tropical coast although cyclones are rare during November.

Northern Territory (Bureau of Meteorology 1993a) (Figure 2.8b)

Summer (December to February)
The Northern Territory experiences the third month of the wet season during December. This is characterised by active monsoon bursts (broad areas of rain with sustained northwesterly winds) and break periods (light winds, isolated showers and storms, occasional gusty thunderstorms and squall lines) between the active
FIGURE 2.8B Sample sites along the northern section of the SN array in the Northern Territory, and Met stations used for meteorological observations.
monsoon bursts. Active monsoon bursts occur late in December. January and February represent the height of the wet season, with monsoonal bursts occurring for periods of up to seven days at a time. Active monsoonal bursts favour the development of tropical cyclones. December has a tropical cyclone once in every two years, January twice in every three years and February once in every two years.

East to southeasterly trade winds produce fine conditions over the southern half of the Northern Territory. Thunderstorms may develop during December when tropical moist air extends southwards. January and February rainfall in the southern half of the Territory may also be produced by the inland movement of the monsoonal trough.

**Autumn (March to May)**
Autumn sees the weakening of the wet season during March and the beginning of the dry season in May in the north of the Northern Territory. Active monsoon bursts persist for shorter periods during March, become less common and confined to the north during April, and are absent during May. March is the most likely month for the development of tropical cyclones, with the Territory being affected by tropical cyclones at the rate of one per year.

East to southeasterly winds predominate in the south of the Northern Territory during March and April, bringing fine conditions. These conditions extend over the entire Territory during May, except along the northeast coastal fringes which may experience brief morning thunderstorms. Thunderstorms are uncommon during May and there is a marked decrease in the amount of rainfall from April to May.

**Winter (June to August)**
The dry season is firmly established in the north of the Northern Territory during winter. Fine conditions prevail with the establishment of east to southeasterly winds over the Territory except on the northeast coastal fringes. Occasionally troughs can bring rain and thunderstorms to the south. Northwest Cloud Bands may also become active over the Territory during winter.

**Spring (September to November)**
Wet-season type weather in the north of the Northern Territory occurs occasionally in September, but generally dry conditions prevail. October is the transitional month linking the wet and dry seasons over northern Australia. Light northerly air flow becomes predominant as the high-pressure ridge moves south. By November, the
wet season has begun and showers and thunderstorm activity occur with increasing frequency. Occasional active monsoon bursts with rain and sustained northwesterly winds occur in the north. Tropical cyclones are rare. In the south, east to southeasterly winds dominate early in spring but northerlies become more frequent as the heat low establishes over northern Western Australia. As spring progresses, southeasterly winds persist but are lighter than in previous months. As the wet season develops in the north, thunderstorms may develop if tropical moisture extends to the south.

**South Australia** (Bureau of Meteorology 1993b) (Figure 2.8c)

*Summer (December to February)*
The weather in South Australia throughout the entire year is strongly controlled by the position of the subtropical high-pressure ridge. During summer the subtropical high-pressure ridge is established to the south of the continent and low-pressure systems cover the interior. The low-pressure systems enable moist tropical air from the north to reach the state, promoting the development of thunderstorms and showers in the north. The southerly position of the high-pressure ridge means that cold fronts that approach South Australia remain to the south of the state, and those that cross are generally weak.

*Autumn (March to May)*
During March the high-pressure ridge remains to the south of the continent and summer conditions persist. By May, the high-pressure ridge begins its northwards movement and oscillates between its summer position in the south and its winter position over the continent. The northern position of the ridge allows the northern movement of temperate cyclones and their associated cold fronts and brings rain to most parts of South Australia.

*Winter (June to August)*
During winter the subtropical high-pressure ridge generally remains in its favoured northern position over the continent at about the latitude of Brisbane. This allows the continued movement of lows and their associated cold fronts onto the south of the state. Northwest Cloud Bands interacting with cold fronts may produce large quantities of rain. The occasional southward movement of the high-pressure ridge to the latitude of Adelaide, may result in the suppression of cold front activity across South Australia by steering lows to the south of the South Australia.
Spring (September to November)
Variable weather is typically experienced across South Australia during spring, because of the mobility of the subtropical high-pressure ridge between the Brisbane and Adelaide latitudes. This is common during September and October when the state experiences mixtures of summer and winter conditions. During November, the high-pressure system becomes established to the south of the state and low-pressure systems form over northern Australia, signaling the return to summer conditions in South Australia.
2.3 WEATHER PATTERNS 1991-1994

Data Description

Meteorological data were purchased from the Bureau of Meteorology. The observation stations (termed Met Stations) were chosen to lie as closely as possible to the sampling localities. Both three-hourly surface wind direction and daily rainfall data were used where available. The Met Stations used, their equivalent sample locality and the data available are listed in Table 2.2. Figure 2.8 shows the location of the Met stations and the sampling sites along the WE array, which extends in a west-east direction from the west coast of Western Australia, and the SN array, which extends in a north-south direction through the Northern Territory and South Australia. Details of these arrays are given in Chapter 3.

In general, except at the formal Met Stations (i.e. Giles), most observation stations are run by local residents who are not professional meteorologists. Thus wind direction data is approximate, and rainfall amounts are measured at 9 am each day, so may have fallen anytime between 9 am on the day of the measurement and 9 am of the previous day. This is taken into account when assigning rainfall to synoptic conditions.

Other data used are the daily surface synoptic charts published in the Monthly Weather Review for each state for each month, and the accompanying synoptic descriptions (Bureau of Meteorology 1992a, Bureau of Meteorology 1993a, Bureau of Meteorology 1993b). The synoptic charts published in the Monthly Weather Review are generalised to apply to the whole of Australia for each month, so that much of the detail described in the synoptic descriptions for each state is not always obvious from the synoptic maps.

Rain-producing Synoptic Classification System

Interpretation of daily surface synoptic charts and their accompanying descriptions has led to the development of a system by which the rainfall at each Met Station during the sampling program can be assigned to a particular synoptic process or a combination of processes. The range of synoptic processes used in the categorising system are described below. It should be noted however, that weather events are complex, and often do not fit into defined categories. In particular, in the development of rainfall, moisture and uplifting may come from a number of sources, and a rain event may be the result of a number of different mechanisms, some working to enhance the rainfall and some working to suppress rainfall. This is recognised in the following categorisation system, which is not designed to be a
TABLE 2.2 Summary of the Met Stations, the closest sample localities, and meteorological data.

<table>
<thead>
<tr>
<th>Met Station</th>
<th>Sample locality1</th>
<th>data type</th>
<th>record period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dongara</td>
<td>Cliff Head (16)</td>
<td>rainfall</td>
<td>March 91 to March 93</td>
</tr>
<tr>
<td>Mt Magnet</td>
<td>Morawa (17)</td>
<td>rainfall, wind</td>
<td>March 91 to March 93</td>
</tr>
<tr>
<td></td>
<td>Badja (18)</td>
<td>rainfall, wind</td>
<td>March 91 to March 93</td>
</tr>
<tr>
<td></td>
<td>Jowna (19)</td>
<td>rainfall, wind</td>
<td>March 91 to March 93</td>
</tr>
<tr>
<td>Meekatharra</td>
<td>Barrambie (20)</td>
<td>rainfall, wind</td>
<td>March 91 to March 93</td>
</tr>
<tr>
<td>Yeelirrie</td>
<td>Yeelirrie (21)</td>
<td>rainfall, wind</td>
<td>March 91 to March 93</td>
</tr>
<tr>
<td>Wiluna</td>
<td>Lake Violet (22)</td>
<td>rainfall, wind</td>
<td>March 91 to March 93</td>
</tr>
<tr>
<td>Carnegie</td>
<td>Carnegie (23)</td>
<td>rainfall, wind</td>
<td>March 91 to March 93</td>
</tr>
<tr>
<td>Giles</td>
<td>Gunbarrel (24)</td>
<td>rainfall, wind</td>
<td>March 91 to March 93</td>
</tr>
<tr>
<td></td>
<td>Everard Junction</td>
<td>rainfall, wind</td>
<td>March 91 to March 93</td>
</tr>
<tr>
<td></td>
<td>(25)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Port Lincoln</td>
<td>Port Lincoln (26)</td>
<td>rainfall</td>
<td>May 92 to June 94</td>
</tr>
<tr>
<td>Kyancutta</td>
<td>Gawler Ranges (27)</td>
<td>rainfall</td>
<td>May 92 to June 94</td>
</tr>
<tr>
<td>Tarcoola</td>
<td>Gawler Ranges (27)</td>
<td>rainfall</td>
<td>May 92 to June 94</td>
</tr>
<tr>
<td>Oodnadatta</td>
<td>Wintinna (28)</td>
<td>rainfall</td>
<td>May 92 to June 94</td>
</tr>
<tr>
<td>Coober Pedy</td>
<td>Wintinna (28)</td>
<td>rainfall</td>
<td>May 92 to June 94</td>
</tr>
<tr>
<td>Alice Springs</td>
<td>Alice Springs (29)</td>
<td>rainfall</td>
<td>May 92 to June 94</td>
</tr>
<tr>
<td>Barrow Creek</td>
<td>Alice Springs (29)</td>
<td>rainfall</td>
<td>May 92 to June 93</td>
</tr>
<tr>
<td></td>
<td>Tennant Creek (30)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tennant Creek</td>
<td>Tennant Creek (30)</td>
<td>rainfall</td>
<td>May 92 to June 94</td>
</tr>
<tr>
<td>Elliott</td>
<td>Dunmarra (31)</td>
<td>rainfall</td>
<td>May 92 to June 94</td>
</tr>
<tr>
<td>Katherine</td>
<td>Katherine (32)</td>
<td>rainfall</td>
<td>May 92 to June 94</td>
</tr>
<tr>
<td>Darwin</td>
<td>Kapalga (33)</td>
<td>rainfall</td>
<td>May 92 to June 94</td>
</tr>
</tbody>
</table>

1 sample locality number in brackets (see Figure 2.8).
definitive work on the synoptic features that produced rainfall across Australia. Instead, this system is a means of assessing the likely sources of moisture and constituents to rainfall during the sampling period in a general sense, as shown in Table 2.3.

**Tropical events**
The northern half of Western Australia is affected by tropical events during summer. Tropical events along the WE array include tropical cyclones, tropical depressions, monsoonal depressions and the heat low, i.e. a synoptic process that involves air masses with moisture sourced from the tropics to the north of Australia. Most of the rainfall that falls in the Northern Territory can be attributed to tropical events. For this reason, the categorisation system for the Northern Territory involves a breakdown of the tropical events group into the components that are applicable (i.e. tropical cyclones and gulf lines). Northern areas of South Australia may also experience tropical events. In particular, incursions of tropical air or the southern limits of monsoonal activity may occur during the wet season.

**Tropical Cyclones**
While several tropical cyclones formed north of Australia during the sampling program, only three were involved in producing rain over northern Australia. These were tropical cyclone Nina sourced in the Gulf of Carpentaria in December 1992, tropical cyclone Naomi sourced off the Western Australian coast in December 1993 (and downgraded to a tropical depression), and tropical cyclone Sadie that formed along the east coast of the Northern Territory in January 1994.

**Gulf Lines and Tropical Flow**
Gulf lines are peculiar to the Northern Territory and only affect the north of the Northern Territory. They are defined as north-south oriented lines of showers or storms that develop over the Cape York Peninsula and move westwards over the Gulf of Carpentaria and the Top End (Bureau of Meteorology 1993a). Tropical flow is the term given to moist northwesterly winds that produce showers and storms mainly in the north of the Northern Territory.

**Troughs**
A trough is an area of low pressure that extends over a wide region, and separates high-pressure ridges. Troughs are commonly oriented in a north-south direction (Tapper and Hurry 1994). Unlike the low, the trough does not have closed isobars. In the northern areas of Australia, lows and troughs act in a similar fashion as areas
of convergence. Thus for the purpose of this classification, lows and troughs are grouped together for northern Australia.

TABLE 2.3 Summary of rain-producing synoptic classification scheme.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Air mass and source of moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tropical Events (TE)</strong></td>
<td>Tm, moisture from north and northwest</td>
</tr>
<tr>
<td>Tropical Cyclones (TC)</td>
<td>Tc, dependent on origin of cyclone</td>
</tr>
<tr>
<td>Gulf Lines (GL)</td>
<td>Tm, moisture from northwest</td>
</tr>
<tr>
<td>Tropical Flow (TF)</td>
<td>Tm, moisture from the northwest</td>
</tr>
<tr>
<td><strong>Troughs</strong></td>
<td></td>
</tr>
<tr>
<td>West Coast Trough (WCT)</td>
<td>Generally Tc</td>
</tr>
<tr>
<td>Inland Trough (T)</td>
<td>IsTm or ITm, moisture from Indian Ocean</td>
</tr>
<tr>
<td>Non-monsoonal Trough (T)</td>
<td>Tm, moisture from the north</td>
</tr>
<tr>
<td>Monsoonal Trough (MT)</td>
<td>Tm, moisture from northwest (Timor and Coral Seas)</td>
</tr>
<tr>
<td><strong>Frontal Activity</strong></td>
<td></td>
</tr>
<tr>
<td>Cold Fronts (CF)</td>
<td>sTm, sPm, moisture from the south</td>
</tr>
<tr>
<td>Cut-off Low (CoL)</td>
<td>various</td>
</tr>
<tr>
<td><strong>Cloudbands</strong></td>
<td></td>
</tr>
<tr>
<td>Middle-level Cloudband (MLCB)</td>
<td>Tm, sTm moisture from the north and northwest</td>
</tr>
<tr>
<td>Middle-level Disturbance (MLD)</td>
<td>various</td>
</tr>
</tbody>
</table>

**West Coast Trough (Figure 2.9)**

The West Coast Trough affects Western Australia in the summer and is especially important along coastal regions. It forms because of the alignment of isobars in an east-west direction over the state which is a consequence of the ridging of subtropical high-pressure cells through the Bight to the south of Western Australia. When the trough lies offshore, winds near the west coast are from an east to northeasterly direction, bringing hot, dry continental air (Tc) from inland areas. This situation usually involves very high temperatures if the offshore winds are strong enough to delay coastal sea breezes. If the West Coast trough deepens or moves inland, cool moist marine air is brought onshore from the west. Occasionally, this moisture may contribute to shower and thunderstorm activity in the unstable airmass to the east of the trough. However, on the majority of occasions, the development of thunderstorm activity near a West Coast Trough is dependent upon
moisture in the low-level continental airmass and in the middle-levels of the atmosphere.

**Inland Troughs**

Inland troughs affect all regions of the study, sourcing differing airmasses.

*Western Australia (Figure 2.10)*

The inland troughs that affect Western Australia are troughs in the easterlies that develop anywhere between the Kimberley and the southern coast in Western Australia. Convective thunderstorms develop usually to the east of the trough line where vertical uplift is enhanced (Tapper and Hurry 1994), and result in large isolated rainfall. Thunderstorms generally involve moisture from lower levels in the atmosphere. The source of moisture is most likely from IsTm. Intense heating of the continent during summer leads to an area of reduced pressure, which helps to draw in moist air from the Indian Ocean.

*Northern Territory (Non-monsoonal Troughs)*

Non-monsoonal troughs in the Northern Territory can form anywhere over the Territory. These troughs involve convergence of air to the trough, usually from the north, and generally move from west to east and or north or south.

*South Australia*

Troughs that produce rainfall in South Australia generally move into the state from the north or west. They involve the convergence of moist tropical air from the north, and are less common than those in the Northern Territory and Western Australia.

*Monsoonal Trough (or active monsoonal bursts)*

The monsoonal season operates in the Northern Territory between November and March, with maximum activity occurring in January and February. Active monsoonal bursts are represented by broad areas of rain with sustained northwesterly winds. During the monsoon season, the monsoonal trough oscillates between onshore and offshore of northern Australia. During an active burst, the trough is usually located at the base of the Top End (Figure 2.8b). The source of moisture during active monsoonal bursts is from the northwest, in the Timor and Coral Seas (i.e. Tm airmass).

**Frontal Activity**

*Cold Fronts and Associated Lows*

A frontal zone represents the interaction of two airmasses of differing properties (usually temperature, relative humidity and density). Cold fronts develop when warm air is displaced by cold air at the surface. The cold fronts that affect the
southern areas of Australia, are associated with lows (or temperate cyclones), which generally remain to the south of the continent. On occasions the associated low may move onshore, bringing large amounts of rain. The temperate cyclones and their fronts move northwards from summer to winter producing maximum rainfall during June and July. For the purpose of this classification lows and cold fronts are grouped together for southern Australia.

**FIGURE 2.9** Sequence of synoptic charts showing the development of a West Coast Trough between the 3rd and 7th of April 1991. A trough developed off the west coast of Western Australia on 3rd of April, deepened on the 4th and 5th of April and began moving eastwards in response to a cold front. On the 6th of April, the trough was stationary over the Goldfields, and eventually disappeared on the 7th. From the Bureau of Meteorology 1991a. *For Figures 2.9 to 2.12 lines are isobars drawn at 4 hPa intervals, thick lines with arrows are cold fronts, dashed lines are troughs.*
Chapter 2 Weather Patterns of Australia

FIGURE 2.10 Sequence of synoptic charts showing the development of an Inland Trough between the 3rd and 5th of December 1991. A trough formed between the Pilbara and lower west coast on the 3rd and moved over the rest of Western Australia producing thunderstorms in the Goldfields and Eucla. From the Bureau of Meteorology 1991b.

Western Australia (Figure 2.11a)

The airmasses that provide the moisture for the cold fronts in Western Australia are most likely the sTm and sPm. Cold fronts affect the coastal regions of Western Australia, generally to the south of Carnarvon, and most frequently during winter. The cold fronts that affect Western Australia are associated with lows that usually pass to the south of the state.
South Australia (Figure 2.11b)
Cold fronts predominantly move from southwest to southeast across South Australia. When the associated temperate cyclone moves onshore, large amounts of rainfall result. The airmasses that produce moisture for cold fronts in South Australia are also sTm and sPm, and the associated lows may occur between the Bight and the eastern margins of the state.

Cut-off Low (Figure 2.12)
A cut-off low develops when a low-pressure system is isolated from the main low-pressure area in the westerlies to the south. A cut-off low only occurred twice during the sampling program in Western Australia, the first time in association with a West Coast trough, and the second time with a cold front. Each time the air involved was sourced from the west of the central west coast (i.e. between Carnarvon and Geraldton). South Australia experienced a cut-off low during Autumn 1994.

FIGURE 2.11 surface synoptic charts showing cold fronts that affected a) Western Australian the 5th of May 1991 (Bureau of Meteorology 1991c) and b) South Australia on 17th of October 1992 (Bureau of Meteorology 1992b).
FIGURE 2.12 Sequence of surface synoptic charts showing a cut-off low affecting Western Australia between the 19th and 21st of July 1991. On the 19th a deep cut-off low had developed west of Carnarvon. This produced a vast cloudband that covered much of the southwest of Western Australia. The low had deepened by the 20th and tracked southeast to enter the Great Australian Bight on the 21st. From the Bureau of Meteorology 1991d.

**Cloudbands**

**Middle-Level Cloud Band**

Incursions of middle-level moist air from tropical regions may bring heavy rainfall to Australia during winter by producing a cloud band under suitable conditions. An example of a cloud band is the Northwest Cloud Band which regularly forms over Australia during May, June and July. The Northwest Cloud Band develops when upper level troughs that are embedded in the westerlies of the middle latitudes extend into the tropics, drawing moist air from over the Timor Sea to the southeast.
The moist tropical air ahead of the trough is cooled as it is forced to rise over the
drier cooler air associated with the approaching trough, and the moisture condenses
to form a cloud band. The amount of precipitation depends on the amount of
moisture in the airstream and the amount of uplift generated (which depends on the
stability of the airmass). For the purpose of this classification, occurrences of the
Northwest Cloud Band are noted as middle-level cloud bands. The important feature
of this category is the provision of moisture by the Tm airmass. In the case of the
Northwest Cloud Band the origin is more specifically west of the Timor Sea.

**Middle-Level Disturbance**

'Middle-level disturbance' is a generic term sometimes used to explain the formation
of weather that cannot be attributed to processes happening near the surface. The
lifting mechanisms are generally associated with the presence of a nearby middle-
level trough or some related development. The term may at times be used in
reference to a middle-level cloudband or cut-off low that does not appear on the
surface (Cram, pers comm. 1995).

**Application of the Rain-producing Synoptic Classification Scheme**

The results of the application of the above classification scheme of rain producing
conditions are shown graphically in Appendix A, and summarised in Tables 2.4 and
2.5. These tables show the single rain-producing condition responsible for the
production of most rainfall at each Met station during each sample collection period
for the WE (Table 2.4) and SN (Table 2.5) arrays.

**WE array**

The winter season sees the predominant influence of cold fronts on the Met Stations
of the western half of the WE array. During winter 91 this influence extends inland
to Giles. Thus winter represents periods of influence by marine air masses from the
south and southwest. West Coast Troughs are most active during autumn and spring
of each year across the array. During summer, inland sites are influenced by tropical
airmasses in the form of tropical events. During winter and autumn, inland sites are
also affected by middle-level cloud bands and tropical flow. The coastal Met Station
is influenced by cold fronts throughout most of the sampling program.

**NS Array**

Rainfall at the Met Stations from the northern half of the NS array are affected by
processes that source tropical air masses north, northwest and north of Australia.
The influence of tropical airmasses extends as far south as Tarcoola in the form of
middle-level cloud bands and tropical flow during spring. The southern half of the NS array is affected by cold fronts that can extend as far inland as Coober Pedy during winter and autumn. The southern-most Met Stations are influenced by cold fronts all year round.

2.4 SUMMARY AND DISCUSSION

A classification scheme of synoptic processes that produced rainfall at Met stations close to sampling sites along the WE and SN arrays attributes moisture to airmasses from the tropical north (Tm, sTm), the south and southwest (IsTm, PsTm and sPm) and the Australian continent (Tc). The extent of the influence of these differing airmasses is dependent on time and location.

**TABLE 2.4** Major rain producing processes at Met Stations along the WE array.

<table>
<thead>
<tr>
<th>Station</th>
<th>A91</th>
<th>W91</th>
<th>Sp91</th>
<th>S91</th>
<th>A92</th>
<th>W92</th>
<th>Sp92</th>
<th>S92</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dongara</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td></td>
<td>WCT</td>
<td>CF</td>
<td>CF</td>
</tr>
<tr>
<td>Mt Magnet</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>WCT</td>
<td>WCT+MLD</td>
<td>CF</td>
<td>WCT</td>
<td>CF</td>
</tr>
<tr>
<td>Meekatharra</td>
<td>T+MLD</td>
<td>CF</td>
<td>CF</td>
<td>WCT</td>
<td>T+MLD</td>
<td>CF</td>
<td>CF</td>
<td>TE</td>
</tr>
<tr>
<td>Yeelirrie</td>
<td>T+MLD</td>
<td>CF</td>
<td>CF</td>
<td>T</td>
<td>WCT</td>
<td>CF</td>
<td>WCT</td>
<td>WCT</td>
</tr>
<tr>
<td>Wiluna</td>
<td>WCT TE</td>
<td>CF+MLCB</td>
<td>WCT</td>
<td>WCT</td>
<td>WCT+MLCB</td>
<td>MLD</td>
<td>WCT</td>
<td>TE</td>
</tr>
<tr>
<td>Carnegie</td>
<td>TE</td>
<td>CF</td>
<td>WCT</td>
<td>T</td>
<td>MLCB</td>
<td>T</td>
<td>WCT</td>
<td>TE</td>
</tr>
<tr>
<td>Giles</td>
<td>WCT+TE</td>
<td>CF</td>
<td>WCT</td>
<td>T+MLD</td>
<td>WCT</td>
<td>T+MLD</td>
<td>WCT</td>
<td>TE+W CT</td>
</tr>
</tbody>
</table>

CF=Cold Fronts; WCT=West Coast Trough; T=Trough; CoL=Cut-Off Low; MLCB=Middle-Level Cloud Band; TF=Tropical Flow; TE=Tropical Event; TD=Tropical Depression, MLD=Middle-level Disturbance

The results of this classification will be of use in the interpretation of the major element chemistry and $^{36}$Cl data. In terms of the major-element chemistry (Chapter 5), the tropical, south and southwest airmasses may contribute a seawater chemical signature to the rainfall chemistry during periods of maximum influence from these airmasses, eg. winter 91 for the WE array, summer for the northern half for the SN array. Rainfall attributed to West Coast Trough activity may provide a continental or marine signature depending on the source of moisture. In terms of the $^{36}$Cl composition of rainfall, these results may be used to explain deviations from the
latitude-dependent predicted fallout of $^{36}\text{Cl}$ to the Earth's surface (Chapter 6). In particular, samples predominantly affected by moisture from the tropical north may be explained in terms of the fallout expected at lower latitudes than the sample location, as samples affected by moisture from the south of Australia may be explained in terms of fallout expected at higher latitudes.

**TABLE 2.5** Major rain producing processes at Met Stations along the SN array.

<table>
<thead>
<tr>
<th>Station</th>
<th>W92</th>
<th>Sp92</th>
<th>S92</th>
<th>A93</th>
<th>W93</th>
<th>Sp93</th>
<th>S93</th>
<th>A94</th>
</tr>
</thead>
<tbody>
<tr>
<td>Darwin</td>
<td>nil</td>
<td>T</td>
<td>MT</td>
<td>GL</td>
<td>T</td>
<td>TF</td>
<td>MT</td>
<td>TF</td>
</tr>
<tr>
<td>Katherine</td>
<td>nil</td>
<td>T</td>
<td>MT</td>
<td>T</td>
<td>nil</td>
<td>TF</td>
<td>MT</td>
<td>T+TD</td>
</tr>
<tr>
<td>Elliott</td>
<td>nil</td>
<td>T</td>
<td>MT</td>
<td>T</td>
<td>MLCB</td>
<td>MLCB</td>
<td>MT</td>
<td>TF</td>
</tr>
<tr>
<td>Tennant Creek</td>
<td>nil</td>
<td>T</td>
<td>MT</td>
<td>MLCB</td>
<td>MLCB</td>
<td>MLCB</td>
<td>T+TD</td>
<td>TF</td>
</tr>
<tr>
<td>Alice Springs</td>
<td>MLCB</td>
<td>T</td>
<td>T(ne)</td>
<td>MLCB</td>
<td>MLCB</td>
<td>T</td>
<td>MLCB</td>
<td>T</td>
</tr>
<tr>
<td>Coober Pedy</td>
<td>?</td>
<td>CF</td>
<td>T+TF</td>
<td>CF</td>
<td>MLCB</td>
<td>T</td>
<td>MLCB</td>
<td>T+TF</td>
</tr>
<tr>
<td>Oodnadatta</td>
<td>T</td>
<td>MLCB</td>
<td>T+TF</td>
<td>MLCB</td>
<td>CF</td>
<td>T</td>
<td>MLCB</td>
<td>T+TF</td>
</tr>
<tr>
<td>Tarcoola</td>
<td>CF</td>
<td>CF</td>
<td>T+TF</td>
<td>CF</td>
<td>CF</td>
<td>CF+T</td>
<td>CF+T</td>
<td>CoL</td>
</tr>
<tr>
<td>Kyancutta</td>
<td>CF</td>
<td>CF</td>
<td>CF+T</td>
<td>CF</td>
<td>CF</td>
<td>CF+T</td>
<td>CF+T</td>
<td>CF</td>
</tr>
<tr>
<td>Port Lincoln</td>
<td>CF</td>
<td>CF</td>
<td>T+TF</td>
<td>CF</td>
<td>CF</td>
<td>CF+T</td>
<td>CF+T</td>
<td>CF</td>
</tr>
</tbody>
</table>

CF=Cold Fronts; WCT=West Coast Trough; T=Trough; CoL=Cut-Off Low; MLCB=Middle-Level Cloud Band; TF=Tropical Flow; TE=Tropical Event; TD=Tropical Depression, MLD=Middle-level Disturbance.
CHAPTER 3 METHODOLOGY

This chapter describes the methods used during sample collection, sample analysis and interpretation of data. The procedures used to ensure the data are of high quality are also detailed.

3.1 FIELD SAMPLING PROGRAM

Procedures

Bulk deposition precipitation samples were collected from two arrays of rain collectors: one in a west-east transect from the coast of Western Australia inland to Everard Junction in the Gibson Desert, (labelled WE), and the other a south-north transect from Port Lincoln in South Australia to Kakadu in the Northern Territory (labelled SN). The specific sites that make up the transects are shown in Figure 3.1. The collection periods are defined in Table 3.1. Reference to samples in the following text will follow the form site~collection period. For example, 23-Sp91 refers to site 23 (Carnegie) and collection during Spring 91 (September to November 1991).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Autumn</td>
<td>March to May</td>
<td>A91</td>
<td>A92</td>
<td>A93</td>
<td>A94</td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td>June to August</td>
<td>W91</td>
<td>W92</td>
<td>W92</td>
<td>W93</td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>September to November</td>
<td>Sp91</td>
<td>Sp92</td>
<td>Sp92</td>
<td>Sp93</td>
<td></td>
</tr>
<tr>
<td>Summer</td>
<td>December to February</td>
<td>S91</td>
<td>S92</td>
<td>S92</td>
<td>S93</td>
<td></td>
</tr>
</tbody>
</table>

Collection sites along the WE transect were chosen to lie along a narrow band of latitude (between 25°S and 29°S), and to be placed equidistant from both the north and south coasts of Western Australia. It was also important that they were removed from sources of contamination such as localised salt lakes, and anthropogenic pollution in areas of concentrated populations eg. Kalgoorlie and Perth. Collection sites along the SN array adhered to a narrow band of longitude (132°E to 135°E) and encompassed a variety of climates including coastal, semi arid and subtropical. Accessibility to sites was also an important criteria when deciding the location of
Chapter 3 Methodology

collectors. The WE array consisted of ten collectors, spaced approximately 100 km apart. The SN array was made up of eight collectors separated by distances of 200 to 500 km. Descriptions of the collection sites, including details of land use, soil type, local climatic conditions etc, are listed in Appendix B. Both collection arrays operated over a two-year period, the WE array between March 1991 and February 1993, and the SN array between May 1992 and May 1994. Samples were retrieved from the field every three months at times that roughly coincided with the change of seasons. Seasons are defined in Table 3.1.

**FIGURE 3.1** Location of samples sites on the WE and SN arrays

<table>
<thead>
<tr>
<th>WE Array</th>
<th>SN Array</th>
</tr>
</thead>
<tbody>
<tr>
<td>site 16 Cliff Head</td>
<td>site 26 Port Lincoln</td>
</tr>
<tr>
<td>site 17 Morawa</td>
<td>site 27 Gawler Ranges</td>
</tr>
<tr>
<td>site 18 Badja</td>
<td>site 28 Wintinna</td>
</tr>
<tr>
<td>site 19 Iowna</td>
<td>site 29 Alice Springs</td>
</tr>
<tr>
<td>site 20 Barrambie</td>
<td>site 30 Tennant Creek</td>
</tr>
<tr>
<td>site 21 Yeelirrie</td>
<td>site 31 Dunmarra</td>
</tr>
<tr>
<td>site 22 Lake Violet</td>
<td>site 32 Katherine</td>
</tr>
<tr>
<td>site 23 Carnegie</td>
<td>site 33 Kapalga</td>
</tr>
<tr>
<td>site 24 Gunbarrel Highway</td>
<td></td>
</tr>
<tr>
<td>site 25 Everard Junction</td>
<td></td>
</tr>
</tbody>
</table>
Precipitation was collected using bulk deposition collectors designed for the project to withstand three months of exposure to extreme wind, rain and heat conditions. The collection vessels consist of two types. The apparatus is shown in Figure 3.2.

**FIGURE 3.2** Photograph of the rain collecting apparatus

The first type consisted of a stainless steel square bin (dimensions 10 x 10 x 60 cm, 30 x 30 x 60 cm or 40 x 40 x 60 cm) and a funnel placed approximately 1.5 m above the ground. Stainless steel mesh (grade 250-300 μm) in the funnel opening prevented large particles such as insects and sand grains from entering the collection vessels. Vertical stainless steel spikes encircled the funnel to prevent birds fouling the samples. Housed in the steel bin was a five-litre borosilicate glass bottle in
which the sample was collected. This will be referred to as the "glass collector" in the following discussion.

The second type consisted of an arrangement of high density polyethylene plastic jerry cans (either five- or ten-litre) and high density polyethylene plastic funnels (average diameter 14.7 cm) placed approximately one metre above the ground. Again, stainless steel mesh was used to reduce contamination. Two jerry cans were deployed during the first half of the WE collection program, and four jerry cans were deployed during the second half of the WE and entire SN collection programs. Throughout the entire program, one of these jerry cans was designated the "paraffin collector" and contained approximately 100 ml of paraffin to prevent water loss by evaporation. At later stages in the sampling program, a third or fourth plastic jerry can was deployed, containing approximately 200 mg of thymol for every litre of sample expected to be collected. Thymol is recommended (Gillett and Ayers, 1991) as a suitable biocide allowing reliable analysis of pH and organic acids, without substantially influencing the major-element chemistry of the samples. However, it was of limited success in this program because of a previously unreported reaction that occurs between thymol and plastic when exposed to sunlight for prolonged periods of time. Finally, one or two plastic jerry cans per site, with no additives, were used to collect precipitation for boron isotope analysis for an independent study, and will be referred to as "boron collectors".

The entire arrangement of collectors was enclosed in a fence to prevent interference from animals, particularly livestock. For the most part this fence arrangement appeared satisfactory. However, at one site on the SN array, a herd of cattle did manage to break through the fence and disturb the collector on one occasion. Table 3.2 summarises the purpose of each collection vessel.

**TABLE 3.2** Purposes of different sampling vessels used in the raincollecting arrays.

<table>
<thead>
<tr>
<th>Collection Vessel</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>glass bottle</td>
<td>general analysis, $^{36}$Cl</td>
</tr>
<tr>
<td>plastic jerry can with paraffin</td>
<td>measure of volume</td>
</tr>
<tr>
<td>plastic jerry can</td>
<td>boron isotopes</td>
</tr>
</tbody>
</table>

**Pre-Field Collection Procedures**

All field sampling apparatus was cleaned thoroughly before use in the field. The stainless steel bins were scrubbed with laboratory grade detergent, rinsed at least 3
times with deionized water, soaked for 24 hours in deionised water, rinsed at least 3 times, allowed to dry overnight and wrapped in plastic and bubble plastic for safe transport. The glass bottles and stoppers were scrubbed using a special bottle brush, rinsed at least 10 times with Milli-Q® water of 18 MΩm resistance and soaked for at least 24 hours with Milli-Q® water. This procedure was carried out at least 3 times. The glass bottles were then dried in an oven overnight and weighed before being sealed in plastic. The cleaning and drying of the glass bottles was carried out in a specially designed Cl-free laboratory at the Research School of Earth Sciences, Australian National University. The plastic jerry cans were rinsed with deionised water at least 3 times, soaked in deionised water for 24 hours, dried in a clean oven, weighed and sealed in plastic. Early in the sampling program, an approximate volume of 100-300 ml of paraffin was added to one of the plastic jerry cans before transport into the field. At later stages, a precise weight of paraffin was added. Jerry cans were only recycled twice, as it was found that the plastic of the jerry can weakened after more than 6 months exposure to sunlight. All cleaning was carried out with disposable gloves, so that hands never came into contact with the sampling vessels.

Field Collection Procedures
All equipment in the field was handled using disposable plastic gloves. Equipment was sealed in plastic for transportation to and from the field.

Post-Field Collection Procedures
Once samples were collected from the field, they were stored at 4°C. All samples were weighed, and from this and the weight of collection vessels before deployment, sample volumes calculated. During the early stages of collection from the WE array, volumes were measured using a graduated measuring cylinder. A 250 ml aliquot was taken from the glass collection vessels for major element, pH and in the early stages of the program, bicarbonate measurement. If the glass bottle was dry (i.e. no precipitation was collected), the bottle was soaked in a precisely known volume of Milli-Q® water (~250 ml) for at least 7 days, and an aliquot of this taken for general analysis. Samples collected in the paraffin collector were separated from paraffin using separator funnels.

Quality Assurance
The aim of the sampling procedure is to collect precipitation samples that are representative of the material being deposited from the atmosphere to the Australian
continent. It is recognised that this is a very difficult task to undertake, even fundamental questions such as what sort of collection surface most closely approximates that of the earth are hard to answer. The procedures used in this project try within the means available to carry out this aim. There are several aspects of the field collection procedure that must be scrutinised with regard to their effect on the chemical composition of the sample collected. In particular, the effect of the collection vessel materials, dry deposition and the assumption of the sample collected under paraffin representing the amount of rainfall collected must be examined. The following discussion looks at each of these issues.

**Collection Vessels**
The effect of the collection vessel material (i.e. borosilicate glass or plastic) on the chemistry of rainfall sample was investigated by measuring the concentration of various species in Milli-Q® grade water that had been stored in clean collection vessels and exposed to sunlight in the laboratory for approximately 3 months. For both types of collection vessels (glass and plastic) all species concentrations were below the level of detection. Thus it is concluded that the collection vessel type does not contribute to the chemistry of rainfall collected.

**Dry Deposition**
The nature of the collection vessels (i.e. bulk depositional collectors) means that they collect both wet and dry deposition. Thus the chemistry of the rainfall sample is a measure of material that is deposited both during and between rainfall events. For many investigations the collection of dry deposition is commonly not recommended, and consequently, bulk depositional collection techniques are often disapproved of in rainfall investigations. For example, in a review of deposition monitoring techniques, Erismann et al (1994) cite bulk depositional collectors as a serious source of error for wet depositional measurements. In another review of wet depositional collection techniques, Vet (1991) attributes the reduction in use of bulk depositional collectors in many North American monitoring networks to high measurement uncertainty caused by the unknown and highly variable input of dry deposition. On the other hand, bulk depositional collectors have been used successfully in some wet depositional programs, when located at sites away from direct sources of dry contamination such as seawater, anthropogenic emissions or when sampled over short time periods, eg. 24 hours (Vet 1991).

It is recognised that dry deposition does contribute to the chemistry of rainfall collected in the present investigation. However, this is not seen as a disadvantage
here, as one of the main aspects of this project is an investigation of the accession of material to the Australian continent, whether it be by wet or dry deposition. It would however, be useful to characterise the extent of the effect of dry deposition on rainfall samples collected. A very rough estimate may be made by comparing the deposition of ions in dry samples (i.e. samples for which zero volume of rainfall was collected in both the glass and paraffin collectors) with the average deposition at a site in which rainfall volumes were greater than zero. Unfortunately, only the four sites in the Top End of the SN array experienced zero rainfall. An investigation of the proportion of species contributed by the dry samples (Figure 3.3) shows that there is variation in the amount of dry deposition both between sites and at the same site over different times. This makes it very difficult to generalise about the extent of dry deposition across each array over time.

![Figure 3.3: Dry deposition at northern sites on the SN array (sites 30 to 33). % dry represents the proportion of ions deposited in the dry sample (i.e. nil rainfall) relative to the mean flux of ions deposited at each site. W92 = winter 92, A94 = autumn 94 etc. Calculated from depositional units (μeq/m²/s).]

In summary, bulk depositional collectors were chosen to be the most practicable form of collection vessel for this project, as they are the most suitable method of collection for long periods in remote areas. Both wet and dry deposition is collected in these sampling vessels, and while the extent of dry deposition cannot be quantitatively constrained, it is recognised as a feature of the samples, and will be taken into account during data interpretation.
Evaporation

The paraffin collector is used to measure the volume of rain that has fallen during the collection period (assuming that no evaporation can occur through the 1 cm paraffin layer). An evaporation correction is applied to all data based on the volume of sample measured in the paraffin collector. The effectiveness of the paraffin collector as a measure of unevaporated rainfall has been tested by placing four paraffin collectors with known volumes of Milli-Q® grade water at the most continental site (Everard Junction) or the WE transect, for periods of 3, 6, 9 and 12 months. The results of this experiment are displayed in Figure 3.4, which compares the volumes of Milli-Q® grade water before and after the evaporation experiment over time. If evaporation was occurring, we would expect to see a gradual decrease in volume over time. The absence of a trend of increasing loss of Milli-Q® grade water with increasing time and the agreement within 1 σ error between volumes (except for the first three months, when sample was lost during separation of paraffin, and agreement does occur at 2 σ) indicates that our assumption of no evaporation occurring beneath the paraffin layer is valid.

![Graph showing evaporation test at Everard Junction](Figure 3.4)

**FIGURE 3.4** Evaporation test at Everard Junction (site 25) on the WE array. Four paraffin collectors with known volumes of Milli-Q® grade water were placed at site 25 for periods of 3, 6, 9 and 12 months. The graph shows the volume of water deployed (initial) and the volume of water collected (final). There is no trend of decreasing final volume over time. All final and initial volumes are within 1σ error, except at 3 months when sample was lost during final volume measurement. Error bars represent 1σ error.
The question of how closely evaporation in the plastic jerry can arrangement approximates evaporation in the glass bottle housed inside the stainless steel bin arrangement, is addressed by comparing volumes recovered in each collector. In most situations, when corrected for funnel sizes, the volume collected in the glass bottle is less than that of the paraffin collector (Figure 3.5). However, it is noted that volumes in the glass collectors are not always equal to those found in the jerry cans without paraffin, as would be expected if evaporation conditions were the same in both arrangements. Differences of up to ± 10% are noted, most likely representing the natural level of variability of rainfall deposition in the environment and sampling errors.

3.2 LABORATORY PROCEDURES

Major Elements

Procedures

The analytical techniques used to measure major elements in this project are listed in Table 3.3. Also shown are detection limits and estimated errors for each technique. Standards were prepared gravimetrically using Spec Pure or Analytical Reagent grade primary salts.

Quality Assurance

External examinations of the accuracy of the analytical techniques were performed throughout the program using seawater (Jervis Bay seawater, collected by the Environmental Geochemistry group in February 1986, and diluted by approximately 1000 times to approximate rainwater concentrations), and in the later stages, using a standard reference simulated rainfall material (SRM 2694A-1 and SRM 2694A-11 from the National Bureau of Standards, USA). The reference concentrations of ions in seawater is taken from Millero (1974).

More than one method was available to measure cations, dependent on the stage of the sampling program. Before November 1992 (collections WE A91 to Sp91), all cations were measured by atomic absorption spectrophotometry (AAS)\(^1\). However the accuracy (relative to seawater) of the AAS techniques was poor for each species, so inductively coupled plasma atomic emission spectrometry (ICPEAS ) was adopted for Ca and Mg, and high pressure liquid chromatography (HPLC) for Na and K. At later stages of the program, the HPLC measurement of Ca and Mg also

\(^1\)Collections WE A91, W91 and Sp91 were analysed by E Kiss.
FIGURE 3.5 Comparison of volumes collected by the different collector types (glass, paraffin and boron) at a) site 16 (Cliff Head) and b) site 25 (Everard Junction). Error bars represent 1σ measurement errors. The difference in volumes collected by each collector type is less than 10% (within 1σ error bounds). A91 = autumn 91, W91 = winter 91, Sp91 = spring 91, S91 = summer 91 etc.
### TABLE 3.3 Analytical methods, detection limits and accuracy.

<table>
<thead>
<tr>
<th>Species</th>
<th>Methodi</th>
<th>Instrument</th>
<th>detection limit µg/ml</th>
<th>accuracy SRMii</th>
<th>accuracy sw ii</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>electrode</td>
<td>Solomat 2000</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>HPLC</td>
<td>Dionex 4500;iiii</td>
<td>0.01</td>
<td>1.5%</td>
<td>0.31%</td>
</tr>
<tr>
<td>SO₄</td>
<td>HPLC</td>
<td>Dionex 4500;iiii</td>
<td>0.01</td>
<td>1.4%</td>
<td>0.9%</td>
</tr>
<tr>
<td>NO₃</td>
<td>HPLC</td>
<td>Dionex 4500;iiii</td>
<td>0.01</td>
<td>5.6%</td>
<td>5.6%</td>
</tr>
<tr>
<td>HPO₄</td>
<td>HPLC</td>
<td>Dionex 4500;iiii</td>
<td>0.01</td>
<td>5.6%</td>
<td>5.6%</td>
</tr>
<tr>
<td>Br</td>
<td>HPLC</td>
<td>Dionex 4500;iiii</td>
<td>0.01</td>
<td>9.6%</td>
<td>9.6%</td>
</tr>
<tr>
<td>Na</td>
<td>AA</td>
<td>Perkin Elmer 303;iv</td>
<td>0.02</td>
<td>14.25%</td>
<td>14.25%</td>
</tr>
<tr>
<td>K</td>
<td>AA</td>
<td>Perkin Elmer 303;v</td>
<td>0.1</td>
<td>36%</td>
<td>36%</td>
</tr>
<tr>
<td>NH₄</td>
<td>HPLC</td>
<td>Dionex series 4500;iv</td>
<td>0.08</td>
<td>5.7%</td>
<td>4.5%</td>
</tr>
<tr>
<td>Ca</td>
<td>AA</td>
<td>Perkin Elmer 303;vii</td>
<td>0.05</td>
<td>32%</td>
<td>32%</td>
</tr>
<tr>
<td>ICPAES</td>
<td>RSES high-resolution</td>
<td>0.013</td>
<td>3.2%</td>
<td>3.2%</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>AA</td>
<td>Perkin Elmer 303;ix</td>
<td>0.014</td>
<td>11%</td>
<td>11%</td>
</tr>
<tr>
<td>ICPAES</td>
<td>RSES high-resolution</td>
<td>0.002</td>
<td>4.7%</td>
<td>4.7%</td>
<td></td>
</tr>
<tr>
<td>HPLC</td>
<td>Dionex 4500;viii</td>
<td>2.8%</td>
<td>6.2%</td>
<td>6.2%</td>
<td></td>
</tr>
</tbody>
</table>

i HPLC = Ion Chromatography, AA = Atomic Absorption Spectrophotometry, ICPAES = Inductively Coupled Plasma Atomic Emission Spectrometry; ii calculated by comparing the measured value of a calibration standard to the 'known' concentration: seawater, Millero 1974; SRM, National Institute of Standards and Technology 1991; iii ASA4 column; eluant 1.7mmole NaHCO3 and 1.8mmol Na2CO3; regenerant 25mmol H2SO4; iv wavelength 589nm; flame air:acetylene; v wavelength 755.5nm; flame air: vi acetylenewavelength 422.7nm; flame acetylene:N2O: viii CS10 column; eluant 10mmol HCl and 1mmol DAP.HCl; regenerant 100mmol tetrabutylammoniumhydroxide; vi wavelength 755.5nm; flame air: vii acetylenewavelength 422.7nm; flame acetylene:N2O: viii CS10 column; eluant 60mmol HCl and 6mmol DAP.HCl; regenerant 100mmol tetrabutylammoniumhydroxide: ix wavelength 285.2nm; flame acetylene:N2O.

The accuracy for both the ICPAES and HPLC determinations of Ca and Mg are comparable.

The reproducibility between analytical runs is shown in Figure 3.6, which shows the results of repeated analysis of Jervis Bay seawater over the sampling program, compared with published seawater concentrations (Millero 1974). It can be seen that

Throughout the text Na = Na⁺, K= K⁺, NH₄=NH₄⁺, Ca=Ca²⁺, Mg=Mg²⁺, H=H⁺, Cl=Cl⁻, SO₄=SO₄²⁻, NO₃ =NO₃⁻, HPO₄=HPO₄²⁻ and Br=Br⁻
for the major ions of seawater, the analytical techniques have a reproducibility of better than 6.2% between sample runs.

**Chlorine-36**

*Procedures*

All sample handling and precipitation of Cl was carried out in a specially designed Cl-free laboratory at the Research School of Earth Sciences, Australian National University. Disposable gloves were used at all stages during sample handling.

**Preconcentration**

Up to 5 litres of rainwater was filtered through Whatman 54 filter paper, the volume accurately measured and concentrated to approximately 150 ml using a condenser with a 1 litre round-bottomed flask. The pre-concentration stage took approximately two days. The waste from the preconcentration procedure contained no measurable Cl. The concentrate was stored in a 250 ml borosilicate glass bottle until precipitation.

All glassware and equipment used during the preconcentration procedure was cleaned by rinsing with Milli-Q® water (18 μohm) at least 12 times, soaking for 24 hours with very dilute HNO₃, rinsing at least 12 times with Milli-Q® water, soaking for 24 hours in Milli-Q® water, rinsing a least 12 times and drying in an oven. Glassware was then covered with parafilm and stored until use. Scrubbing was commonly required to remove carbon accumulations in the round-bottomed flask. Occasionally, concentrated HNO₃ or laboratory grade detergent was required to remove the residue. A test of the effect of detergent on Cl concentrations was carried out by measuring the Cl concentration of Milli-Q® water that had been soaked in a round-bottomed flask for 7 days which had been washed with the detergent. No measurable amounts of Cl were noted. If the residue could not be removed the round-bottomed flask was discarded. Clean, new boiling chips were used with each sample.

**Precipitation**

All precipitations were carried out in subdued light or darkness to prevent photodegradation of AgCl. The amount of expected Cl in the concentrate was calculated from the total volume of sample filtered and the concentration of Cl measured by HPLC. If less than 1 mg of Cl was expected, up to 1 mg of carrier was added to the sample. The carrier used was Weeks Island Halite which has a
FIGURE 3.6 Concentration of a) major anions and b) major cations measured in Jervis Bay seawater over time. Jervis Bay seawater was used as a standard to measure reproducibility between analytical runs. Measurements were performed by high pressure liquid chromatography (HPLC), except Ca and Mg values marked with an asterix, which were measured by inductively coupled plasma emission spectroscopy (ICP-AES). The straight lines are published concentrations of the particular element in seawater. Published concentrations taken from Millero 1974. Error bars represent 1 σ error.
negligible $^{36}$Cl/Cl ratio. The carrier solution was also used to prepare blanks for each batch of precipitations. All carrier additions were precisely measured.

All reagents used during the precipitation procedure were of Spec Pure (AgNO$_3$, BaNO$_3$) or Analytical Reagent Grade (NH$_4$, HNO$_3$). Samples were precipitated in batches of 8 to 12. Approximately 100 to 150 ml of concentrated samples were heated in a glass beaker at a low hot plate setting for 1 to 2 hr, by which time the sample was slowly convecting. Some samples, particularly from the Northern Territory turned black upon heating. Five ml of 10% AgNO$_3$ were added to each sample and left to heat further for 30 minutes. After this time a precipitate had formed on the bottom of the beaker. The samples were then allowed to cool, covered with parafilm and left to stand overnight. These were then centrifuged at 2900 rpm for 10 minutes in a 50 ml centrifuge tube. Depending on how much supernatant was present, this process was repeated several times. A bead of AgCl formed in the bottom of the centrifuge tube and this was rinsed twice.

The bead of AgCl was dissolved using 1 ml of concentrated NH$_4$ solution. In some instances when AgCl remained caked to the beaker (this was particularly common for the blank), NH$_4$ was used to dissolve the AgCl in the beaker, and this added to the material in the centrifuge tube. The dissolved AgCl was diluted to 40 ml with Milli-Q® water, heated in a water bath for 10 minutes and 5 ml of saturated BaNO$_3$ added. After a further 10 minutes of heating in the water bath, the centrifuge tubes were removed and allowed to stand overnight, by which time a precipitate of primarily BaSO$_4$ (and most likely BaCO$_3$) had formed. The supernatant material was carefully extracted using a disposable cleaned plastic pipette, and transferred to a clean 50 ml centrifuge tube. The precipitate was discarded.

In a 100 ml glass beaker, 15 ml of 2N HNO$_3$, 10 ml of Milli-Q® water and 5 ml of 10% AgNO$_3$ were heated at a low setting on the hot-plate for 30 minutes. The beaker was removed from the hot-plate and the extracted supernatant material was added. A clean white precipitate of AgCl formed instantly and began to settle. In most cases it was possible to manipulate the formation of this precipitate into a cohesive lump, by tapping the base of the beaker occasionally. After heating for a further hour, samples were removed from the hot-plate, allowed to cool, covered with parafilm and allowed to stand overnight. The clear supernatant material was then carefully poured off and the precipitate centrifuged at 3000 rpm for 5 minutes. This was rinsed, and centrifuged twice. The centrifuge tube and precipitate which had formed a bead in the base of the tube, was dried in an oven overnight. In some
cases, the precipitate did not form a cohesive lump, but a fine powder. This entailed allowing the powder to settle into the base of the centrifuge tube overnight. However, this did result in lower yields.

The dried AgCl bead was then weighed and yields calculated. The AgCl was wrapped in weighing paper and aluminium foil and stored until pressed. Figure 3.7 shows the distribution of yields. The median yield was 77%. Low yields may be attributed to the loss of sample during the final clean-up procedure when AgCl formed a fine powder instead of a cohesive lump. High yields may be attributed to the presence of BaNO₃ in the final precipitate.

**FIGURE 3.7** Yields of AgCl retrieved from the precipitation of AgCl for ^{36}Cl/Cl measurements by accelerator mass spectrometry (AMS). Median yield is 77%. Low yields (less than 60%) can be attributed to the formation of a fine powder rather than a cohesive lump during the final stage of precipitation. Yields greater than 100% can be attributed to the presence of BaNO₃.

All glassware that had been in contact with AgCl was rinsed with concentrated NH₄ solution, rinsed at least 3 times with Milli-Q® water, wiped with ethanol, rinsed at least 3 times with Milli-Q® water, soaked in very dilute HNO₃ for 24 hours, rinsed 12 times with Milli-Q® water, soaked for 24 hours in Milli-Q® water, rinsed 12 times with Milli-Q® water, dried in the oven, covered with parafilm and stored until use.
Chapter 3 Methodology

Sample Pressing
AgCl was pressed into a AgBr substrate coating the surface of a copper holder. Approximately 10 mg of sample was generally pressed, although one mg was adequate for analysis.

Measurement
Measurement of $^{36}$Cl/$^{35}$Cl ratios was made on the 14UD Tandem Accelerator Mass Spectrometer in the Research School of Physical Sciences and Engineering at the Australian National University (Fifield et al 1987). The measurement of $^{36}$Cl/$^{35}$Cl ratios involves the production of 3-5 μA by caesium sputtering. This beam then undergoes pre-acceleration to 128 keV and is mass analysed by a double focussing injection magnet before being focussed into the 14UD accelerator. An electrostatic beam chopper is used to attenuate the stable Cl beam, but is switched off during $^{36}$Cl measurement. The negative Cl ions are stripped in the terminal of the accelerator by carbon foils. The resulting positive ions are accelerated a second time to ground at the base of the accelerator and steered around a 90° analysing magnet and onto a detection system comprised of a retractable Faraday cup (where the stable Cl is measured) followed by an ionisation chamber filled with propane in which the $^{36}$Cl is detected. A typical measurement sequence consisted of 30 second measurement of $^{35}$Cl and $^{37}$Cl beam currents followed by a 10 minute counting period of $^{36}$Cl, repeated two or three times. The system is set up for final analysis of 154 MeV Cl$^{10+}$ ions in the detector, these high energies allowing clean separation of $^{36}$Cl from the isobar $^{36}$S and isotope $^{37}$Cl, the main sources of interference and background.

Quality Assurance

Blank Measurements
A blank of approximately 10 to 20 mg of Cl, prepared from Weeks Island Halite, was precipitated with each batch to check for contamination during the precipitation process. Table 3.4 shows the $^{36}$Cl/$^{35}$Cl ratio for each blank measurement. All were at or below $1 \times 10^{-15}$ $^{36}$Cl/$^{35}$Cl.

Procedural Blank
The entire procedure (i.e. collection, preconcentration and precipitation) was tested for contamination by measuring the $^{36}$Cl/$^{35}$Cl ratio of Weeks Island halite (50 mg) dissolved in 5 litres of Milli-Q® water and stored in a glass collection bottle in the laboratory for 3 months. The ratio measured was $0.5\pm1.0 \times 10^{-15}$ $^{36}$Cl/$^{35}$Cl,
confirming that no $^{36}$Cl was being introduced by the preparation procedure or the collection vessel.

**TABLE 3.4** $^{36}$Cl/Cl ratios of Weeks Island Halite precipitated with each batch of samples. The $^{36}$Cl counting time for the blank and samples was the same within each batch of measurements (i.e. 20 or 30 minutes). The ratios listed are limits based upon n+1 counts.

<table>
<thead>
<tr>
<th>Sample batch</th>
<th>$^{36}$Cl/Cl x 10$^{-15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 93</td>
<td>0.3±0.3</td>
</tr>
<tr>
<td>November 93</td>
<td>0.2±1.1</td>
</tr>
<tr>
<td>November 93</td>
<td>0.6±1.1</td>
</tr>
<tr>
<td>December 93</td>
<td>0.8±1.2</td>
</tr>
<tr>
<td>December 93</td>
<td>0.2±1.0</td>
</tr>
<tr>
<td>March 94</td>
<td>0.4±1.0</td>
</tr>
<tr>
<td>March 94</td>
<td>0.1±1.0</td>
</tr>
<tr>
<td>May 94</td>
<td>0.1±1</td>
</tr>
<tr>
<td>November 94</td>
<td>1.0±1.2</td>
</tr>
<tr>
<td>November 94</td>
<td>0.4±1.1</td>
</tr>
</tbody>
</table>

**Field Sampling**

The reproducibility of the sampling procedure was tested by deploying two collectors side by side at site 27 (Gawler Ranges) on the SN array. The ratios measured were 52±5 and 49±5 x10$^{-15}$ $^{36}$Cl/Cl. These values are within the error bounds of each measurements, suggesting that the sampling procedure is collecting a representative sample of $^{36}$Cl deposition.

**Accuracy**

A GEC standard was measured with every batch of 11 samples (1 wheel) run on the accelerator. The GEC standard has been used as a standard for $^{36}$Cl/Cl measurements at the ANU since 1988 and acts to monitor the precision and accuracy of the AMS measurements. During the course of measurements for this project, the GEC standard displayed no significant deviations from its weighted mean value of 436±2 x10$^{-15}$ $^{36}$Cl/Cl (Table 3.5).
TABLE 3.5 The $^{36}\text{Cl}/\text{Cl}$ ratios of the GEC standard measured with each batch of 11 samples. The error is the statistical error.

<table>
<thead>
<tr>
<th></th>
<th>GEC1</th>
<th>GEC2</th>
<th>GEC3</th>
<th>GEC4</th>
<th>GEC5</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 93</td>
<td>441±3</td>
<td>441±3</td>
<td>397±11</td>
<td>439±12</td>
<td></td>
</tr>
<tr>
<td>November 93</td>
<td>432±12</td>
<td>436±11</td>
<td>418±12</td>
<td>396±11</td>
<td></td>
</tr>
<tr>
<td>December 93</td>
<td>447±5</td>
<td>417±6</td>
<td>428±13</td>
<td>449±10</td>
<td>438±11</td>
</tr>
<tr>
<td>March 94</td>
<td>457±19</td>
<td>447±18</td>
<td>493±20</td>
<td>421±18</td>
<td>460±22</td>
</tr>
<tr>
<td>May 94</td>
<td>484±48</td>
<td>445±17</td>
<td>434±21</td>
<td></td>
<td>437±22</td>
</tr>
</tbody>
</table>

3.3 DATA ANALYSIS PROCEDURES

Data Quality
There are many sources of errors in measurements of precipitation chemistry. These include analytical measurement errors and contamination during sampling (e.g. bird droppings, insect infestation, human intervention). The following section contains methods used to identify data that are obviously contaminated or questionable. These data were subsequently excluded from further interpretation.

Ion balance
An initial test of data quality is an ionic balance. This is based upon the assumption that there is an equal number of positive and negative charges in a solution that is in equilibrium. Percentage imbalance is defined as

\[
\% \text{ imbalance} = \frac{100 \times (\text{sum of cations} - \text{sum of anions})}{0.5 \times (\text{sum of cations} + \text{sum of anions})} \quad (3.1)
\]

Samples with imbalances of greater than 100% were generally removed from the data set if they also failed the outlier analysis criteria discussed below.

Regression
Regression of cation and anion concentrations provides another means of investigating data quality. Many regression procedures involve fitting a line to a collection of observations, so that the squared deviation of one of the lines is
minimised. In the present investigation, deciding which variable (total anions or total cations) is to be minimised is purely arbitrary. Hence, the reduced major axis technique (Hirsch and Gilroy, 1984) is used here and is recommended by various authors (Keene et al 1986, Ayers and Manton 1991, Gillett et al 1990). This method involves fitting a line that minimises the deviation of observations from both variables. The fitted line is the line for which the sum of the areas of right angles formed by the horizontal and vertical lines from the point to the line is minimised. Hence an equivalence between variables is established. The line is defined by

\[ b = y + \frac{\text{sgn}(r)sy(m-x)}{sx} \]  

(3.2)

where \( b \) is intercept, \( m \) is slope, \( y \) is the mean of the \( y \) variables, \( sy \) the standard deviation of the \( y \) variables, \( x \) and \( sx \) as for \( y \) and \( sy \), and \( sgn(r) = 1 \) if \( r > 0 \); 0 if \( r = 0 \); -1 if \( r < 0 \). This regression procedure is used in the present investigation as a supplementary test to the ion imbalance to check the relationship between the total number of cations and the total number of anions in each sample. In an ideal situation the two variables would be equal, so the ideal line would have a slope (\( m \)) of 1 and an intercept (\( b \)) of 0. Thus, these parameters will quantify the quality of the data sets.

**Outlier analysis**

The method of outlier analyses adopted here follows that of Saylor (1992), in which data points that lie outside \( 2\sigma \) from the geometric mean of each chemical species measured were investigated. If justification for the removal of the suspected outlier was found, the data point was removed from the data set. Justification includes visible contamination of the sample by foreign matter.

**Multivariate Statistics**

With the advent of the relatively simple production of large data sets in atmospheric chemistry investigations, the use of multivariate statistics has increased due to the impracticality of simultaneous assessment of variations between individual components with multiple variables. Many different multivariate techniques have been applied in atmospheric chemistry investigations. The techniques used in this project are factor analysis (FA) and principal component analysis (PCA). The following discussion briefly describes the theory of these techniques and reviews some examples of their application in previous investigations. Finally, the way in which these methods are applied to the data sets in Chapter 5 is discussed.
Theory of Factor Analysis and Principal Component Analysis

A detailed account of the theoretical background to FA and PCA is beyond the scope of this work, and can be found in Davis (1986).

Both FA and PCA are forms of eigenvector analysis, i.e. a correlation matrix (a matrix that is standardised to have a mean of 0 and a variance of 1) is produced which indicates the relationship between pairs of variables. Eigenvector analysis is used to convert the correlation data into multivariate information so that the interrelationships between several variables may be assessed. The first difference between FA and PCA lies in how the eigenvectors are calculated. In FA, eigenvectors are calculated in normalised form and are transformed so that they define vectors whose lengths are proportional to the amount of variation they represent. In PCA, this normalisation does not take place, so that the magnitude of the vector does not represent the amount of variation the component is depicting. Thus factors derived by eigenvalue extraction in FA, and components derived by eigenvector extraction in PCA, will have the same direction, but different loadings. Hence while the proportion of variance accounted for by each factor and component will be the same for FA and PCA, the apparent importance of each variable in the factor or component will differ. The normalisation process carried out during FA has more statistical relevance if data sets with large numbers of cases are used, while PCA is more appropriately used on data sets with low numbers of cases, e.g. data sets for individual sites where the maximum number of cases is 8. However, for the entire WE data set for example, (i.e. all ten sites for eight collection periods) the case number is up to 80, and FA can be used.

The extraction of the appropriate number of factors or components to be used is an important step in both FA and PCA. There are various methods employed to do this. The most common is to choose factors with eigenvectors greater than one. The argument for this is based upon the normalization of the variables so that each variable carries a variance of one. Therefore eigenvectors of less than one represent single variables. Many argue that this is not the most appropriate method, and it has been suggested that while eigenvectors of greater than one set a lower limit on the number of factors retained they do not automatically set an upper limit (SPSS 1990). Instead, an investigation of residual correlations (i.e. the difference between correlation coefficient estimated by the FA or PCA and the observed correlation coefficient), and the variance attributable to each factor allows for a more rigorous determination of the number of factors to be used in FA and PCA.
Chapter 3 Methodology

The normalisation of the eigenvectors in FA makes the loadings of variables simpler to interpret. Interpretation is further aided by the rotation step in FA, which represents the second difference between FA and PCA. PCA does not involve a rotation step. Rotation of the factor axes in FA is performed in order to create a simpler structure. Interpretation of factors may be clouded by the position of orthogonal axis in space being constrained by unnecessary axes. Rotation provides a means of removing these unnecessary axes. The rotation method commonly used is varimax rotation, which moves each axis so that projections from each variable onto the factor axis are either near the extremities or origin of the axis. Thus the factor loadings are adjusted so that they are either near ±1 or 0. Variables with loadings close to 1 have a high proportion of their variance explained by that factor, while those that are close to 0 have very little variance explained by that factor.

Previous Uses Of Multivariate Statistics In Atmospheric Chemistry Investigations

Factor analysis is a tool that has been used extensively in recent investigations of rainwater chemistry (eg. Crawley and Sievering 1986, Ayers and Manton 1991, Kessler et al 1992). The purpose of using FA in these investigations was to assess the sources of various components in rainwater. Ayers and Manton (1991) describe the presence of two major sources of rainwater ions from Coffs Harbour and Wagga Wagga: seasalt, dominated by Na, Mg, Cl and SO4; and a continental source with ions such as K and Ca (characteristic of soil-dust), SO4 (an oxidation product of anthropogenic emissions), NO3 (from anthropogenic and soil emission) and NH4 (from soil and plant emissions of NH3). Crawley and Sievering (1986), as part of the MAP3S/RAINE precipitation study, determined three sources of ions (seasalt, ammonia/dust soil and an acid factor) in rainwater in the northeastern United States. As a final example, Kessler et al (1992) interpreted four factors to be contributing to rainwater chemistry based on seven years of rainfall data from Texas. These included a Gulf factor (marine origin), a soil factor, an acid factor and an aged aerosol factor.

Zeng and Hopke (1989) used FA to indicate three sources of components to rainfall in Canada; an acid precursor source (SO2 and NOx), a Ca and Mg source and a Na and Cl source (marine aerosol). They extended the use of FA further to investigate in more detail the acid precursor source, by incorporating into the FA back-trajectory information. The results of this showed the relationship between the chemical nature of the sources and the geographic regions over which the air parcels passed, pinpointing areas along the east coast of Canada as being the major source of acid precipitation to Ontario.
There are numerous examples of the application of PCA to atmospheric chemistry investigations, in which as for FA, the primary use of PCA has been to determine the source of constituents to precipitation. Smeyers-Verbeke et al (1984) investigated the variations in organic air pollutants in the Netherlands from 1979 to 1981, and interpreted the relationships between pollution and meteorological parameters. They stressed the use of PCA as a simple way to graphically display the total variation of a data set in a few dimensions. Also in the Netherlands, Janssen et al (1989) used eigenvector analysis to investigate the relationships between SO$_4$, NO$_3$, Cl and NH$_4$ concentrations in aerosols; the gaseous components SO$_2$, NO, NO$_2$ and O$_3$, and meteorological parameters. Shaw (1991a) investigated the chemical composition of aerosols from Alaska over a four-year period, and using PCA, found high levels of metallic elements were associated with Arctic airmasses. These airmasses sourced material from Eurasia. Investigation of non-anthropogenic sources in the Alaskan data set, revealed an Al-rich dust, a marine seasalt, and a Br component (Shaw 1991b).

**Application**

Factor analysis was carried out using the factor analysis program contained in the Statistical Package for Social Sciences (SPSS). The generalised procedure involves determining a correlation matrix followed by extraction of factors using principal component analysis. Finally rotation of the factors allows simpler interpretation of results (SPSS 1990). Principal component analysis was performed using Genstat 5 (Genstat 5 Committee 1989).

Multivariate analysis was carried out on the major-element and $^{36}$Cl data sets. Both FA and PCA performed on the same data sets (and subsets) produced the same number of factors or components, explaining the same amount of variance. This is not unexpected when it is considered that FA is really just an extension of PCA. The factor loadings produced by FA were much clearer to interpret than the component loadings produced by PCA. However both techniques are adopted here because of the inability of the SPSS factor procedure to deal with data sets that have smaller case numbers than variables (eg. individual site data subsets).

The use of multivariate techniques in many environmental investigations has been heavily criticised. A major problem lies in trying to determine quantitative input rates of each source and trying to extract more information from the data than there really is. Henry (1987) shows that the lack of physical constraints placed on factor models suggest that the results of many models mean very little as they are based
upon incorrect assumptions. In this study, FA and PCA are used only as a qualitative tool to group variables that have common variances. In conjunction with other arguments it enables an indication of the major sources of components to precipitation across the WE and SN transects and the relationships between $^{36}$Cl and major elements.

**Graphical Procedures**

Graphical techniques are used to investigate the seasonal variations demonstrated by the $^{36}$Cl data set. The multivariate techniques discussed above will indicate some general characteristics of the major element data set, such as the source types of chemical constituents to the arrays. Further assessment of these general characteristics will require techniques that pinpoint finer scale details, such as how these sources affect each site, and the change in the influence of these sources over time.

Seawater and soil/dust are two probable sources of constituents to rainfall in unpolluted areas for which we have some idea of chemical composition. The chemistry of seawater is well constrained (eg. Millero 1974). The influence of seawater on the ionic concentration of rainfall can be assessed by comparing the ratios of "characteristic" seasalt ions measured in rainfall with the ratios found in seawater. The concentrations of the characteristic seasalt ions used here are shown in Table 3.6. In many rainfall investigations Na is often assigned as a quantitative tracer of seasalt (eg. Ayers and Manton 1991). By assuming that all Na measured in the rainfall sample is of seasalt origin, we can investigate the influence of seasalt on other ions measured in the rainwater samples and assess the influence of seasalt on non-coastal sampling localities. Using characteristic seasalt ratios the extent of a non-seasalt contribution of the ions for $SO_4$, $K$, Ca and Mg can be investigated by looking at the "non-seasalt" (nss) fraction of these ions in rainfall. Non-seasalt fractions are calculated from the following equation

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Chapter 3 Methodology

\[
\%C_{\text{nss}} = \left( \frac{\frac{C_x(\text{rw})}{Na(\text{rw})} - \frac{C_x(\text{sw})}{Na(\text{sw})}}{\frac{C_x(\text{rw})}{Na(\text{rw})}} \right) \times 100 \tag{3.3}
\]

where C is \(\mu\text{eq/L}\) of species x (SO\(_4\), Ca, Mg or K) in rainwater (rw) or seawater (sw).

**TABLE 3.6** Composition of seawater. From Millero 1974.

<table>
<thead>
<tr>
<th>species</th>
<th>concentration g/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>10.76</td>
</tr>
<tr>
<td>Mg</td>
<td>1.29</td>
</tr>
<tr>
<td>Ca</td>
<td>0.41</td>
</tr>
<tr>
<td>K</td>
<td>0.39</td>
</tr>
<tr>
<td>Cl</td>
<td>19.34</td>
</tr>
<tr>
<td>SO(_4)</td>
<td>2.71</td>
</tr>
<tr>
<td>Br</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Figure 3.8 illustrates the use of seasalt versus non-seasalt contributors as will be used in later discussions. In Figure 3.8a, the ratios of Cl/Na and SO\(_4\)/Na are shown as a function of distance from the coast for the WE array during winter 1992. The Cl/Na ratio approximates that of seawater across the WE array, while the SO\(_4\)/Na ratio increases with increased distance from the coast, reflecting the decreased influence of seasalt on SO\(_4\) at inland sites. This is also displayed in the non-seasalt plot (Figure 3.8b), where nss SO\(_4\) and Ca contribute approximately 40-50% of the SO\(_4\) and Ca at inland sites. Non-seasalt Mg is a minor contributor to the Mg content of precipitation across the array, while nss K is a significant contributor to total K.

Unlike seawater, the chemical composition of soils is not well constrained and can differ markedly from place to place. To overcome this problem, samples of surface soil and dust material were collected from each site, at distances of approximately 10 m to the north, south east and west of each collector. These samples are assumed to represent the locally derived material that enters the rain collector due to local wind movement. Characteristic soil/dust concentrations for each site were measured after leaching the soil/dust material from each site in Milli-Q\® water for 2 months. The proportion of soil/dust to Milli-Q\® was calculated from the average amounts of undissolved material measured in the rain collectors at each site. The soil/dust composition at each site is given in Appendix C. The rainwater compositions can
then be compared with soil/dust compositions in a similar fashion as the seawater comparisons.

FIGURE 3.8 Examples of a graphical techniques used to interpret spatial and temporal variations displayed by the major-element data sets. a) Ratios of elements to Na (considered to be a conservative seawater tracer) are compared with the ratio of the particular element with Na in seawater. This figure shows the ratios of Cl and SO₄ with Na for the WE array during winter 92. A trend of increasing ratio (i.e. moving away from the seawater ratio) is observed for SO₄ with increasing distance from the coast. Ratios are calculated from depositional units (i.e. μeq/m²/s). b) The non-seasalt (nss) fraction represents the proportion of the particular element measured in precipitation of non-seawater origin and is calculated as described in the text. This figure shows the nss fractions of SO₄, K, Ca and Mg in precipitation along the WE array during winter 92. There is a general increase in nss concentration with increasing distance from the coast.
CHAPTER 4 INTRODUCTION TO PRECIPITATION CHEMISTRY

A summary of the current understanding of the formation of precipitation, the incorporation of chemical species into precipitation, and the sources of the species describes the framework from within which results of the present investigation can be interpreted. A summary of previous precipitation investigations in Australia will help place interpretations from the present investigation into context.

4.1 INCORPORATION OF CHEMICAL SPECIES INTO RAINFALL

Rainfall is an important part of the hydrological cycle as it involves the exchange of water and chemical constituents between the atmosphere, oceans and landmasses. Details of the processes involved in the formation of precipitation and the incorporation of chemical constituents in precipitation were given by Pruppacher and Klett (1980) and Warneck (1988), and can be summarised below.

Cloud Formation
Condensation resulting from adiabatic cooling in rising air is responsible for the formation of clouds and precipitation. Uplift of the air parcel occurs by convection, frontal activity or orographic interference (Linacre and Hobbs 1982). Figure 4.1 is a schematic representation of ascending air undergoing adiabatic expansion and cloud formation.

Aerosols are important in cloud formation as they may act as condensation nuclei and provide inorganic salts that make up the ionic chemistry of rainfall. Generally, aerosol particles greater than 0.1 μm will act as cloud condensation nuclei, with the largest particles being used first (Figure 4.2). As an air parcel rises and supersaturation increases, smaller particles become activated. Ice particles will be generated only in clouds at temperatures below -20°C (or 6 km into the troposphere), since special ice-forming nuclei are required to form ice in clouds. Thus in the middle troposphere supercooled liquid water in clouds is common. However all clouds that reach temperatures below 250K host a certain population of ice (Barry and Chorley 1976).
FIGURE 4.1 A schematic diagram showing the ascent of air in the atmosphere and cloud formation. From A to B, air is unsaturated and cools adiabatically (i.e. does not gain or lose heat), the temperature decrease (or adiabatic lapse rate $\beta_d$) is $9.8 \text{K/km}$. If the air from A to B contains water vapour, it will cool as it rises and if it rises far enough will become saturated. Further rising causes supersaturation, or if nuclei are present, condensation. When condensation takes place, the pressure change is no longer adiabatic since latent heat is released. The latent heat released by condensation offsets cooling due to adiabatic expansion, so that the lapse rate in the cloud $\beta_s$ (from B to C) is less than the lapse rate for the process in the absence of condensation (from A to B).

Rainfall Formation

Not all clouds produce precipitation. In order to produce rain a cloud must form drops with an initial radius of greater than $500 \mu \text{m}$ (Figure 4.2), otherwise evaporation of the drop will occur at the base of the cloud before the drop is able to reach the ground. The formation of rain occurs in two ways: by cold-rain formation and warm-rain formation (Warneck 1988). Cold-rain formation occurs over continental regions where high reaching clouds promote the growth of ice particles in the upper reaches of the cloud. Falling ice particles melt as they descend through warmer layers of the atmosphere. Warm-rain is produced over tropical landmasses and oceans where cloud tops cannot reach 273 K, and involves only the liquid phase, with growth first by coalescence and then condensation.
The chemical composition of rainfall is governed by the incorporation of aerosols and gases from the atmosphere into cloud and rain drops. This scavenging occurs both within the cloud (within-cloud) and below the cloud (below-cloud), processes that have been termed "rainout" and "washout" (eg. Junge 1963), respectively. The following section describes the processes of aerosol and gas scavenging as they occur within and below the cloud.

Aerosol Scavenging

Within-cloud scavenging of aerosols involves nucleation of aerosol particles with radii greater than 0.2 μm. These make up 60 to 80% of the total air mass (Warneck 1988). Aerosols not used for nucleation once the cloud has formed may join other aerosols and cloud droplets, although this adds very little mass to the cloud. The

FIGURE 4.2 Schematic diagram showing the size ranges of particles involved in the formation of clouds and rain. After Iribarne and Cho 1980.
aqueous concentration of ionic species resulting from within-cloud scavenging ($c_W$) is dependent upon the concentration of species in the aerosol ($c_a$), the liquid water content of the cloud (L) and the scavenging efficiency ($E_a$) according to:

$$c_W = c_a E_a / L$$ \hspace{1cm} (4.1)

$E_a$ combines the effects of nucleation, Brownian motion and collision capture, but is dominated by nucleation (Junge 1963). Warneck (1988) showed that within-cloud scavenging and precipitation is the dominant process for the removal of particulate matter from the troposphere. Congruency was found in the residence time of particulate matter in the atmosphere removed by within-cloud scavenging and precipitation, and the residence time of bulk aerosols in the atmosphere, as calculated from radioisotope tracers.

Below-cloud scavenging of aerosols involves the incorporation of aerosols by collision capture. The airflow around a spherical drop results in the modification of capture cross section of the falling droplet, since particles follow hydrodynamic streamlines of a droplet (Pruppacher and Klett 1980). The scavenging efficiency becomes a function of the radii of both the water droplet and particle, and may be increased by drop oscillation and electric charge. The efficiency is also increased when a standing eddy develops in the lee of the falling water droplet (common for water droplet radii of 200-600 μm), so that particles escaping frontal collisions are trapped in the rear of the eddy and undergo rear capture. A schematic representation of a falling spherical raindrop is shown in Figure 4.3. Falling ice particles behave in a similar way to water droplets with regards to scavenging efficiencies.

Below-cloud scavenging affects particles in the 2-15 μm range, while within-cloud scavenging incorporates aerosol particles greater than 0.2 μm. Thus below-cloud scavenging enhances elements in precipitation associated with the mineral fraction of the aerosol (eg. Cl, Na, Ca, Mg, K).

Gas Scavenging

The extent to which gases absorb into cloud and rain drops depends on the solubility of the gas in water. Gases and water vapour are incorporated into cloud and water drops at the same rate because of their similar coefficients of molecular diffusion. Within clouds, gases equilibrate quickly with the liquid phase. However, below clouds, gas concentrations are different from those within the clouds so that
Chapter 4 Introduction to Precipitation Chemistry

FIGURE 4.3 Schematic representation of the air flow around a falling sphere. As the water drop falls, particles are incorporated into the drop by collision (or impaction) capture. A drop with radius $r$ falling at velocity $v$ will sweep out all particles in a cylinder $\pi r^2$ if there was no air flow around the spherical drop. The figure shows that the hydrodynamic streamlines around a falling drop modify the capture cross-section of the drop. This modification is accounted for by an efficiency factor which is a function of the radii of both the falling drop and the collected particle. Electric charges and drop oscillation can increase the collection efficiency. Particles escaping frontal collision may be trapped in the rear eddy of the falling drop and undergo capture. After Warneck 1988.

The partitioning of gases between the aqueous and gaseous phases of a cloud is determined by Henry's law and the associated partition coefficients (Warneck 1988). The scavenging efficiencies of most gases are very small, except for water vapour. The residence time of water-soluble gases due to within-cloud removal is dependent on the column density of the gas in the troposphere and the mass flux of the gas from the troposphere. The mass flux of the gas is dependent on average rainfall amount. Slightly soluble gases have long residence times, while permanent gases are not
Chapter 4 Introduction to Precipitation Chemistry

retained by the ground surface and are soon released back to the atmosphere. Residence times of less than one year require scavenging efficiencies of 2% (e.g. H$_2$O$_2$).

Within a cloud, acid and base precursors such as SO$_2$, CO$_2$, NH$_3$, HCl and HNO$_3$ react with water to form ions by dissolution. Dissolution involves two steps, hydration and formation of ions from the hydrate. A third step exists for diprotic acids. For weak acids (SO$_2$ and CO$_2$) Henry's Law can be adapted to account for dissolution, and an adapted Henry's Law coefficient determines the degree of gas liquid partition of a substance within the cloud. Weak acid-forming gases are poorly absorbed by cloud water that is of low pH, while weak base-forming gases are poorly absorbed by cloud water that is of high pH. For strong acids (HCl and HNO$_3$) it is difficult to separate the ion equilibrium constant for H (KH) and the dissociation constant, so Henry's Law is modified to account for the product of the two constants. For pH of 4.5 (the typical value of cloudwater) all HNO$_3$, HCl and NH$_4$ is directly scavenged from the gas phase. In order to return HCl and HNO$_3$ to the vapour phase from solution, liquid water contents would have to be decreased.

A falling droplet below the cloud experiences different conditions from those existing within the cloud. Mass flux occurs in the process of equilibrating to these new conditions. The rate of mass flux is dependent on a number of parameters that include mass molecular diffusion inside and outside of the droplet and transport resistance at the gas-liquid interface. These parameters, combined with the heterogeneous distribution of trace gases, mean that a raindrop falling in a below-cloud region will experience rising gas phase concentrations. Thus the raindrop cannot attain equilibrium and will scavenge only a fraction of the material that it is potentially capable of absorbing. However periods of prolonged rainfall will deplete gas-phase concentrations below a cloud.

Models of the Incorporation of Species into Rainfall

Many models have tried to incorporate some of the complex processes of cloud microphysics and dynamics associated with removal of constituents from the troposphere. For example, Brimblecombe and Dawson (1984) suggested a model in which a species concentration in a cloud is determined by species solubility and liquid water content of the cloud, as based upon thermodynamic partitioning. Qin and Chameides (1986) used a one-dimensional, time-dependent model of a warm precipitating stratiform cloud to determine that the rate of removal of highly soluble species is controlled by transport process rather than thermodynamic processes. The
Chapta

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model of Qin and Chameides was extended to include below-cloud scavenging (or washout) by Lin Xing and Chameides (1990) to compare the relative roles of rainout and washout. The model showed that below-cloud removal dominates within-cloud removal for very soluble gases. This arises because the gas-phase mixing ratio within the cloud is lower than below the cloud, so that the falling droplet leaving the cloud is undersaturated with respect to trace gases below the cloud. Thus more of the soluble gas is able to dissolve into the falling raindrop. The model also showed that during periods of extended rainfall, the rate of wet removal becomes independent of microphysical parameters such as rainfall rate and liquid water content, but is determined by the rate at which new material is transported into the precipitating column.

Cautenet and Lefevre (1994) developed a model that contrasted the behaviour of gas and aerosol species scavenging (SO₂ gas and SO₄ aerosol) during convective rain over an African equatorial forest. A reduction in aerosol scavenging with increasing rain intensity was found. A difference in scavenging efficiencies according to the origin of the element (i.e. gas or aerosol) was noted, with the dilution effect of increased rain being more important for aerosols than gases. Finally a decrease in atmospheric concentrations of the sulphur species during rainfall was noted.

Likens et al (1984) showed an inverse relationship between rainfall amount and rainfall ionic concentrations at Hubbard Brook, New Hampshire. Rainfall concentrations are also dependent on rainfall type, i.e. convective or frontal (Lacaux et al 1992). Convective showers show the development of rainfall intensity maximum corresponding with a concentration minimum through the course of the rainfall event (Gatz and Dingle 1971). Frontal precipitation events, however, have initially high concentrations which diminish to a constant value that is independent of rainfall amount. Frontal rainfall concentrations are explained in terms of evaporation of raindrops during the initial stages of precipitation and by the removal of scavengable material by below-cloud processes (Warneck 1988).

Summary

The most significant points to arise from the above discussion concerning the incorporation of chemical species into precipitation can be summarised. The bulk of aerosols in the atmosphere are removed by within-cloud scavenging, while below-cloud scavenging enhances the mineral fraction of aerosols in precipitation. Henry's Law controls the absorption of gases by clouds and raindrops. Strong acids are directly scavenged from the gas phase within clouds, and the scavenging of gases in
the below-cloud region is inefficient, except during periods of extensive rain. Modelling studies however, reveal that below-cloud scavenging dominates over within-cloud scavenging for highly soluble gases (Lin Xing and Chameides 1990). Comparison of aerosol and gas scavenging shows a negative relationship between aerosol scavenging and rainfall amount, with the dilution effect of rainfall being more significant for aerosols than gases (Cautenet and Lefeivre 1994).

4.2 SOURCES OF THE CHEMICAL CONSTITUENTS OF PRECIPITATION

The major constituents of precipitation in remote areas are Cl, SO₄, NO₃, Na, K, Mg, Ca, H and NH₄ (eg. Brimblecombe 1986). The concentration of these different constituents is dependent upon both location and time. For example, coastal localities have higher Na and Cl concentrations than non-coastal localities as displayed by Hingston and Gailitis (1976) for Western Australian rainfall. European rainfall shows maximum concentrations of all species during spring, probably due to increased photochemical activity (Brimblecombe 1986). Sources can be described under three headings: seawater, continental dust and acid-base precursors. In addition, phosphate is briefly discussed because of the presence of phosphate measurements in the analytical program.

Seawater

Seawater is an important source of Na, Cl, SO₄, Mg, Ca, K and Br to the atmosphere. Seasalt aerosols are injected into the atmosphere by bubble bursting at the sea surface. (Blanchard and Woodcock 1957). Most of this aerosol is directly returned to the ocean, but approximately 10% can be carried over continents (Andreae 1984). Partial evaporation of water in the seasalt droplet leads to the formation of a brine droplet or solid seasalt particle, which is transported until dissolved. Indeed, salts (eg. NaCl) are important to the production of rainfall since clean air, even under conditions of supersaturation, will not condense water vapour (Barry and Chorely 1976). The equilibrium vapour pressure over small droplets is greater than over plane surfaces; the presence of salts acts to lower the water vapour pressure sufficiently that salt particles act as condensation nuclei.

Continental Dust

Aeolian weathering in arid regions has been shown to inject large amounts of dust into the atmosphere (Ryaboshapko 1983). Soil or dust introduces similar cations as seawater to the atmosphere. However, precipitation strongly influenced by soils will be enriched in Ca and K compared with Na and Mg (Hutton 1968). The composition
of soils is geographically very variable as shown by Moore et al (1983), and is reflected in the wide range of compositions measured in the soil/dust samples from the WE and SN arrays (Appendix C). Extensive amounts of carbonate, sulphate and chloride salts are found in arid to sub-humid soils of Australia (Isbell et al 1983), with salt accumulation occurring when annual precipitation is insufficient to leach soils below 0.7 to 1m depth. Salts also accumulate at the surface when the local water table is at a depth shallow enough to maintain an upward flow of soil solution to the surface where evaporation occurs. Gypsum (CaSO₄) is common in a wide range of soils in arid and semi-arid regions. It may be pedogenic or inherited from parent material rich in gypsum such as salt-lake sediments. The common occurrence of salt lakes in Australia, in particular in proximity to the WE array, suggests that salt lakes may be an important source of continental material to the chemical load of precipitation in the present study. Salts such as halite and gypsum form as the latest stable phases during evaporite formation, and therefore are most likely to be available for deflation from the surface.

Acid-Base Precursors
Rainwater is commonly moderately acidic, i.e. the pH is less than 7, and H ions are derived from the dissociation of acids. Acids in the atmosphere include strong acids (HNO₃, HCl, H₂SO₄) and weak acids such as CO₂(aq) and organic acids. Bases in the atmosphere include NH₄. The following discussion describes the sources of each of these acid and base precursors, and these species will subsequently be grouped together as the 'acid-base' balance.

Sulphur
The presence of SO₄ in the atmosphere is due to the injection of seasalt and aeolian weathering salts as described above, as well as the oxidation of SO₂ in the atmosphere. Atmospheric SO₂ is primarily derived from anthropogenic emissions, in particular the burning of fossil fuels. The levels of SO₄ introduced by oxidation of SO₂ therefore depend on the level of industrialisation and the sulphur content of fuel used. The transformation of SO₂ to SO₄ proceeds on time-scales of several hours to days, so that urban concentrations of SO₄ (i.e. near the source of emission) do not differ substantially from regional average concentrations (Ryaboshapko 1983). While the sampling localities in the present study were chosen to lie away from direct sources of anthropogenic emissions, the presence of possible sources of emission need to be borne in mind during interpretation of the precipitation chemistry. It should be noted that Ayers and Gillett (1988a) in a review of
acidification of tropical Australia, estimate that the Mt Isa smelter in Queensland accounts for 70% of total sulphur emissions in tropical Australia.

Another source of sulphur to the atmosphere arises from biological emissions. Sulphur is an element that is essential for the life processes of many biological organisms, and biological emissions occur from both continents (plants, soils, wetlands and biomass burning), and from oceans (eg. dimethylsulphide). For the present study biological emissions may be of particular significance for the northern section of the SN array. Ayers and Gillett (1988a) estimate biological emissions in the north of Australia to be the major natural source of sulphur to the atmosphere.

Volcanic emissions are also an important source of SO$_4$ to the atmosphere, both during eruptive and non-eruptive stages, emitting both gaseous sulphur and particulate SO$_4$ (Andreae 1984). For example, SO$_2$ emissions from the crater lake of Mt Ruapehu in New Zealand during a period of relative inactivity in 1993 were measured at 171 metric tonnes/day (Smithsonian Institute 1993). Australia is flanked to the north and east by a rim of volcanoes. Prevailing wind directions suggest eruptions in areas north of Australia are most likely to affect Australia. The largest volcanic eruption during the sampling program occurred from Pinatubo (Philippines) in June of 1991, where ash was ejected a maximum of 40 km into the atmosphere, with an average ejection height of 10 km over several days (Bulletin of Volcanic Eruptions 1991). Activity from Pinatubo continued on a smaller scale (eg. erupting a column of ash 15 km high in August of 1993), periodically throughout the sampling program. Continued, smaller-scale activity was observed in Papua New Guinea (Manman, Langila and Ullawun), and from Indonesia (Krakatau, Rinjani and Gamalama to name a few).

Chloride
Volatile inorganic Cl (available for the formation of HCl among other Cl compounds) is introduced to the atmosphere by heterogeneous reactions involving seasalt aerosols (Keene et al 1990). Approximately 3 to 20% of Cl is released as vapour from aerosols introduced by bubble bursting at the ocean surface (Cicerone 1981), and this particle-gas conversion process is the major source of gaseous Cl to the global troposphere. The mechanism involved in the particle-gas transformation over continental regions involves the direct volatilization from the seasalt particle at a pH of less than 3 by the incorporation of H$_2$SO$_4$ and HNO$_3$ (Ericksson 1959, Duce (1969), Martens et al 1973) according to the following reactions
Chapter 4 Introduction to Precipitation Chemistry

\[
\begin{align*}
\text{HNO}_3(g) + \text{NaCl}(p) &= \text{HCl}(g) + \text{NaNO}_3(p) \\
\text{H}_2\text{SO}_4(g) + \text{NaCl}(p) &= 2\text{HCl}(g) + \text{Na}_2\text{SO}_4(p)
\end{align*}
\]

(4.2)
(4.3)

The importance of the above acid-base desorption reactions in the marine troposphere is debated, and alternative mechanisms involving reactions of various N gases have been suggested. For example, the reaction of NO\(_2\) with seasalt has been demonstrated as a source of volatile Cl (Finlayson-Pitts 1983) according to the following reaction

\[
2\text{NO}_2(g) + \text{NaCl}(p) = \text{NOCl}(g) + \text{NaNO}_3(p)
\]

(4.4)

where NOCl undergoes photolysis to generate Cl atoms which initiate oxidation of hydrocarbons to produce HCl or hydrolysis to generate OH radicals and HCl. Finlayson-Pitts et al (1989) reported reactions of ClNO\(_3\) and N\(_2\)O\(_5\) with NaCl to generate Cl vapour. Keene et al (1990) showed that acid-base desorption reactions could account for only 38% of HCl production in the marine atmosphere, and suggested that reaction of O\(_3\) at seasalt aerosol surfaces generates Cl\(_2\), which is rapidly converted to HCl via the photochemical transformation of Cl\(_2\) to Cl radicals. The authors also suggested that HCl was eventually recaptured by the aerosol.

**Nitrogen**

There are six major processes that supply nitrogen compounds to the atmosphere. These are emissions from soil microbial processes, lightning, combustion of biomass, anthropogenic fuel combustion, fertiliser application and volitilization of ammonia (Galbally 1984).

Soil microbial processes include nitrification (biological oxidation of fixed nitrogen) and denitrification (anaerobic reduction of NO\(_3^2^-\) or NO\(_2\)). These processes result in the exchange of NO, NO\(_2\) and NO\(_3^2^-\) at the Earth's surface. The emissions of nitrogen compounds from soils of different ecosystems have been summarised by Galbally (1984). While recognising the need for a larger data base, Galbally has attributed most of nitrogen emissions on a global scale to soil, with a significant proportion involving agricultural land use. Ayers and Gillett (1988a) recognised the complete lack of data on nitrogen oxide emissions from tropical soils, but were able to attribute 7% of emissions of nitrogen compounds to soil in tropical Australia, based on NO fluxes from temperate woodlands in Australia and the area of tropical soil cover.
Lightning produces NO in the atmosphere through the high-temperature combustion of N₂ and O₂ (Chameides et al 1977). NO is then oxidised to NO₃ within a short period of time (i.e. 1 day), scavenged and deposited in rainfall. The global emission of NOₓ-N by lightning has been estimated by Galbally (1984) to represent only a small fraction (less than 10%) of the total emissions of nitrogen compounds.

Burning of biomass generates NO, NO₂, NH₃ etc. On a global scale, emission of nitrogen compounds by biomass burning is a small fraction of total nitrogen emissions (Galbally 1984). However in tropical Australia, where anecdotal evidence quoted in Ayers and Gillet (1988) suggests that approximately 30% of tropical Australia is burnt each year, biomass burning provides a substantial proportion of nitrogen emissions (80%).

Anthropogenic sources of nitrogen emissions arise from combustion of fuel, such as in the use of motor vehicles and operation of power stations. Ayers and Gillet (1988a) show that anthropogenic sources of nitrogen emissions account for less than 5% of all emissions in the tropical north of Australia. During coal burning, for example, 1g of NH₃ is emitted for every kg of coal consumed (Robinson and Robbins 1972). The application of fertiliser is also an important anthropogenic source of NH₃ to the atmosphere. Galbally et al (1980) estimate an average of 10% of NH₃ applied as fertiliser in Australia is lost to the atmosphere.

NH₃ is an important species in precipitation because it can neutralise atmospheric acids. The primary sources of NH₃ to the atmosphere are volatilization of NH₃ from animal urine, soils and microbial decomposition (Galbally et al 1980). Volatilization of NH₃ results from the difference in the partial pressure of NH₃ in equilibrium with the liquid phase (in a moist soil or a solution) and that of ambient atmosphere above the soil or solution. Volatilization is controlled by pH, NH₄ concentration, binding of NH₄ to clays, soil buffer capacity, presence of CaCO₃, soil moisture, evaporation, turbulence and presence of vegetation. The large area of Australia given over to grazing means that agricultural emissions of NH₃ are significant, sourced from both volatilization of animal urine, soil emissions and fertiliser application (Galbally et al 1980). Soils in ungrazed pasture also emit significant amounts of NH₃, but most of this is absorbed by the growing plants above the soil surface (Denmead et al 1976).
Galbally et al (1980) summarise the emission of NH$_3$ to the atmosphere for Australia, as mostly being due to rural sources, with 70% due to volatilization of animal urine. Ayers and Gillett (1988a) attribute the lower amount of emissions in tropical northern Australia (10% of Australian-wide emissions) to the lower proportion of agricultural activity that occurs in these regions.

**Organic Acids**

Organic acids contribute up to 40% of the free acidity of rainfall from Katherine (Galloway et al 1982). Possible sources of organic acids to the atmosphere include volatilization of plant material, photochemical oxidation of hydrocarbons and aqueous phase oxidation of formaldehyde to formic acid (Herlihy 1987).

**Phosphate**

Information relating to the source of HPO$_4^{2-}$ to the atmosphere is scarce. However the most likely source to rainfall would seem to be from fertilisers or bird excreta.

### 4.3 PREVIOUS RAINFALL STUDIES IN AUSTRALIA

Previous rainfall investigations in Australia have been designed to address several issues. These include: acidic precipitation both in populated areas such as Sydney (Ayers and Gillett 1982, Ayers et al 1987), the Hunter Region (Bridgeman et al 1988a, Bridgeman et al 1988b) and Newcastle (Avery 1984), and remote areas such as Northern Australia (Noller et al 1990, Gillett et al 1990); baseline level monitoring, as part of Global Precipitation Chemistry Network (GPC; Galloway et al 1982, Likens et al 1987) and Baseline Air Pollution Monitoring Network (BAPMoN; Ayers and Ivey 1988, Ayers and Manton 1991); and the accession of salts to the Australian landmass and the subsequent effects of salinity (Teakle 1937, Hutton and Leslie 1958, Hingston and Gailitis 1976, Blackburn and McLeod 1983, Farrington and Bartle 1988, Farrington et al 1993).

The present investigation is concerned with unpolluted background precipitation. Thus the following review of previous rainfall investigations in Australia will focus on those studies from remote areas, in particular areas that coincide with sample localities used in the present investigation. A review of acid precipitation investigations from urban areas of Australia is given by Bridgeman (1990). All sites discussed in this section are shown in Figure 4.4, and results of previous relevant investigations are listed in Table 4.1.
### FIGURE 4.4 Location of previous precipitation investigations discussed in the text. The small crosses in Western Australia mark sample localities from Hingston and Gailitis 1976. The shaded box in Western Australia marks the Gnangara Mound area from Farrington and Bartle 1988. Squares in Western Australia mark sample localities from Farrington et al 1993.
Baseline Monitoring
Investigations into background levels of constituents in rainfall include research in both maritime and continental areas. An important maritime location included in the BAPMoN project is at Cape Grim in Tasmania. Ayers and Ivey (1988) noted high seasalt loadings and extreme wind speeds were found to cause soil components to concentrate in the rainwater samples, affecting pH, K and Ca concentrations. Acidity values were also thought to be affected by seasalt alkalinity. Also as part of the BAPMoN project, Ayers and Manton (1991) compared a coastal site (Coffs Harbour) with a continental site (Wagga Wagga). Both sites were influenced predominantly by seawater, the extent of which was dependent on wind direction. A continental source was also recognised at both sites, and at Wagga Wagga, NH₄ was interpreted to have a biological source, attributable to the extent of agriculture in the vicinity of Wagga Wagga.

Acidity Investigations in Northern Australia
As part of the GPC Network, precipitation at Katherine in the Northern Territory has been extensively investigated. Precipitation at Katherine has been found to be acidic (eg. Galloway et al 1982) measured a mean pH of 4.78), with 64% of acidity attributed to organic acids (Likens et al 1987) sourced from the extensive burning that occurs at the beginning of the wet season. Thus as the wet season progresses, the amount of burning decreased and hence there were less organic acids emitted to the atmosphere, ultimately decreasing the free acidity of rainfall as the wet season continued (Galloway et al 1982). Airmass trajectories were used to determine that airmasses from the northeast were the most important trajectory in terms of deposition. The contribution of ions from anthropogenic sources was found to be small, with non-seasalt SO₄ concentrations at Katherine an order of magnitude lower than sites in eastern North America. No evidence was found to suggest that lightning contributed to the nitrate concentration in rainfall at Katherine (Likens et al 1987).

Acidity in precipitation from the Alligator Rivers Region in the Northern Territory for the wet season of 1982/1983 (Noller et al 1990) has also been attributed to the presence of organic acids. Strong correlations between H and NO₃ were found and excess concentrations of SO₄ could not be attributed to anthropogenic emissions, in particular from the Ranger Uranium Mine. Rainfall events were separated into monsoonal and non-monsoonal, based on the presence of the monsoonal trough over Northern Australia. It was found that monsoonal rain showed relative concentrations
of Ca, Mg, Na and K that approximate those of seawater. In further work at Alligator Rivers (Gillett et al. 1990), non-monsoonal rainfall was found to be more acidic than monsoonal rainfall. Anthropogenic emissions from the Mt Isa smelter in Queensland, while not being completely ruled out as a source of non-seasalt SO4 to rainfall at Jabiru, were found to have only a very minor influence. The source of organic acids was speculated to be from bushfires or photochemical OH oxidation of reactive biochemical emissions such as isoprene. Continued investigations during the 1984/1985 wet season (Gillett et al. 1990) revealed the organic acids, formic, acetic and propionic acids to be responsible for 74% of free acidity in the rainfall. It was also suggested that HCl may be a contributor to acidity.

Cloudwater and rainwater samples were taken from the Alligator Rivers Region and Katherine during the wet season of 1985/1986 (Noller et al. 1986, Ayers and Gillett 1988b). Cloudwater was found to be highly acidic (pH less than 4) and the solute concentrations of cloudwater and rainwater were consistent if the expected variations in cloud liquid water between precipitating and non-precipitating clouds were taken into account. Systematic variations in the rainwater/cloudwater ratios of formic and acetic acid suggested that these solutes exist below the cloud in the gaseous phase. However, cloud acidity was high only 100m above the base of the cloud, suggesting that most acids are incorporated directly from boundary layer air during cloud nucleation.

Accession Investigations

The initial investigations of rainfall chemistry in Western Australia to address the issue of the source of salts in soils and groundwaters suggested a cyclic source rather than a geological source of salts (Willsmore and Wood 1929, Teakle 1937). Hingston and Gailitis (1976) used bulk-depositional collectors to investigate the accession of salts to 59 sites across Western Australia between 1973 and 1974. Concentrations of solutes in coastal rainfall were found to be an order of magnitude greater than at inland sites. Regional differences in volume weighted non-seasalt ionic compositions have been explained in terms of the proximity of the sampling site to other sources, for example the amount of dissolved salts in rainfall collected from Wiluna was about twenty times that of nearby locations, and was attributed to a large salt lake (Lake Way) located 10 km south of Wiluna (Hutton 1983). The greater accession of oceanic salts to sites in the southwest relative to those in the north of the state was thought to have been an important factor in the development of salinity in the southwest of the Western Australia. It is now recognised however,
that land management practices are also a big determining factor in the development of salinity (Peck et al 1983). Therefore, the more extensive agriculture in the southwest of the state is probably an important factor in the increased development of salinity in that region.

Farrington and Bartle (1988) looked at chloride concentrations in bulk deposition north of Perth between 1982 and 1986 in order to use the accession of chloride to the Gnangara groundwater mound to assess recharge rates for groundwater supplying the mound. Chloride composition was shown to decrease with increasing distance from the coast, and annual accession over the period of measurement was considerably lower than recorded during 1973 and 1974 by Hingston and Gailitis (1976). The difference was attributed to the lower incidences of winter and spring storms during the 1982 to 1986 sampling season. It was suggested that Cl accession increases when strong westerly onshore winds are able to transport oceanic spray further inland.

A regional bulk-depositional collection program in the southwest of Western Australia was established by Farrington et al (1993) between 1989 and 1992, to improve the available information on the regional balance of dissolved salts by looking at spatial and temporal variation in the accession of major ions in rainfall. This information could then be used to develop strategies to reduce salinity. The results confirmed that the atmospheric deposition of major ions from rain was principally controlled by distance from the coast. At inland sites important sources of material to rainfall were also soil, smoke, plant debris and industry. The lakes and drainage systems associated with the sampling localities are saline and therefore may have been a source of terrestrial salt. Excessive non-seasalt Ca concentrations at coastal sites were attributable to aeolian dust originating from calcareous dunes, and at inland sites, from gypsum in salt lakes. The annual variation in Cl accession was attributed to differences in weather patterns and to rainfall amount.

In an investigation of nutrient accession to Katherine during the wet season, Wetselaar and Hutton (1962) reported low concentrations of soluble material, despite high rainfall amount. It was concluded that the material found in rainwater at Katherine represented input from the terrestrial cycle rather than true accession. Noller et al (1985) showed that half of all nutrients were deposited in the Alligator Rivers region of the Northern Territory during the early transition period between the wet and the dry season (November to February in this particular wet season). The input of nutrients was found to be lower or similar to those of drier tropical locations,
and NH₄ and NO₃ were found to be of terrestrial origin. A recycled terrestrial origin was also attributed to components of bulk-depositional precipitation 100 km north of Alice Springs, collected between 1957 and 1962 (Hutton 1983). The high Ca/Cl ratios (twenty times that of seawater) and similar ratios of Ca, Na, Mg and K to Todd River water, led to the suggestion that rainfall at this site was heavily influenced by the Todd River. Thus rainfall at Alice Springs did not represent true accession, but represented a small return of a larger net loss of material suspended in the atmosphere as dust.

Summary
The above review of previous rainfall chemistry investigations in Australia highlights the lack of comprehensive information about the spatial and temporal properties of precipitation chemistry that affects the remote areas of the Australian continent. This investigation addresses these deficiencies by sampling from far-reaching arrays over two years. The arrays span a variety of climates, and the seasonality of sampling allows insight into the affects of different meteorological and climatic processes in producing precipitation. Several of the localities in the present investigation overlap with those of previous studies. Thus the results from this study will add to the Australian precipitation chemistry data base, as well providing the first data on precipitation chemistry from some areas of Australia.