Acidification in Tropical Countries
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CHAPTER 11

Acidification in Australia

GREGORY P. AYERS AND ROBERT W. GILLETT

11.1 INTRODUCTION

The purpose of this case study is to provide an overview of what is known or can be deduced about the atmospheric cycles of nitrogen and sulphur over tropical Australia, and about the contribution of sulphur and nitrogen-containing species to atmospheric acidity. Our context is that of a large, sparsely populated tropical region in which current levels of industrial and urban development are minimal by world standards. As such this case study is probably best viewed as providing a useful reference, or baseline perspective, in which the regional atmospheric acidity and chemistry can be seen as only minimally perturbed by human activities. In particular we have attempted to estimate the magnitudes of the annual inputs to the atmosphere of reactive nitrogen and sulphur species from the most likely natural and anthropogenic sources. We then investigate some features of the atmospheric chemistry of tropical Australia. Reference is made to the results of recent field observations at Jabiru (12°40′S, 132°53′E) and Katherine (14°28′S, 132°16′E) in which gas, aerosol, cloud water, and rainwater analyses have helped to provide an understanding of the sources of atmospheric acidity and relevant chemical interconversion pathways. Finally we summarize what we see to be the current state of acidification in tropical Australia and identify unresolved questions and gaps in our knowledge and understanding.

11.2 THE SETTING

11.2.1 Geographical Region

For the purpose of this study tropical Australia will be defined as all land areas north of the Tropic of Capricorn. This area extends from about 23° S to 11° S and about 113° W to 151° W. It comprises 3.33 million square kilometres, which is about 43% of the total land area of Australia (Figure 11.1).

11.2.2 Simple Meteorological Description

The dominant meteorological feature of the Australian tropics is the contrasting wet–dry seasons. The dry, or winter, season extends from about

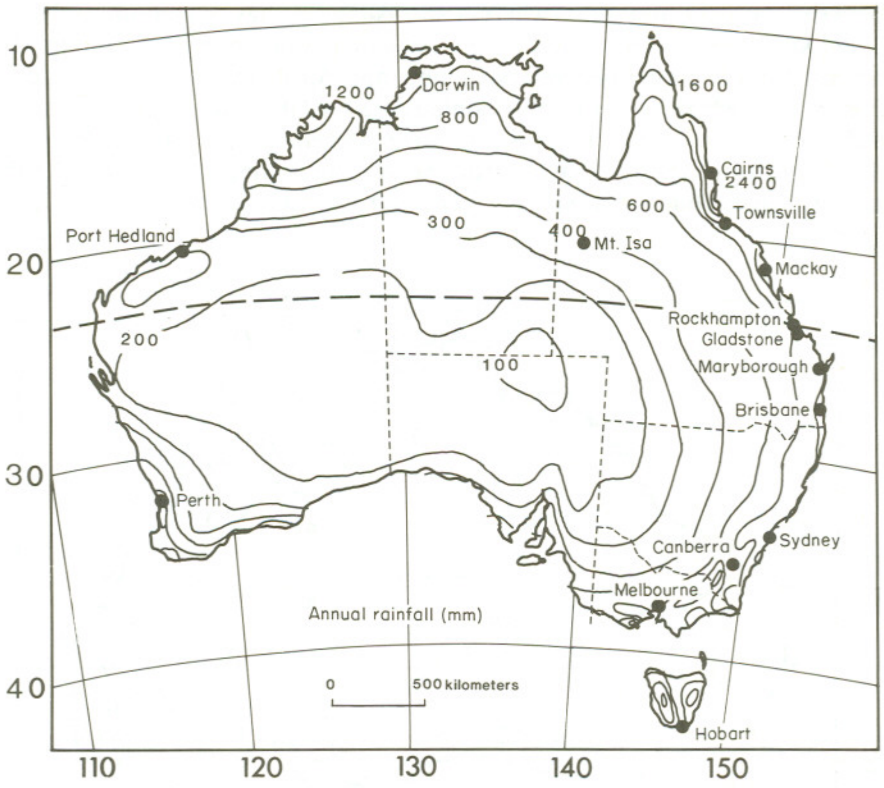

Figure 11.1 Map of Australia indicating state boundaries, location of major cities, and long-term mean annual rainfall isohyets

April until November, and is a consequence of the seasonal, northward shift in the average track of midlatitude anticyclones. During this period typical weather conditions are clear skies, fine, sunny days, and mainly easterly to southeasterly surface winds. The wet season begins about November, as the belt of anticyclones moves further to the south, and lasts until March or April. It results in part from the continental 'heat low', or depression that gradually forms as continental heating increases into summer. When the depression has developed it causes westerly to northwesterly low-level winds in the northern areas and more easterly winds in the southern areas. In comparison with the higher-latitude regions of the continent, temperatures are uniformly high throughout tropical Australia. Figures 11.2 and 11.3 show isotherms for average daily maximum temperatures in January and July. These figures show that the inland tropical areas are invariably hotter and display a more pronounced seasonal temperature cycle than the coastal tropical areas. For example the Darwin maximum (coastal) varies only 3 °C between January and July, whereas the Alice Springs maximum (inland, 1,300 km to the south) varies by 18 °C. As mentioned previously rainfall is confined to the period between November and April. This can be seen from Figure 11.4, where as an example rainfall data for Jabiru are displayed: about 80% of the annual rain total falls between December and March. Rainfall decreases from north to south with Darwin, for example, receiving 1,535 mm per year while Alice Springs receives an average of only 255 mm per year.

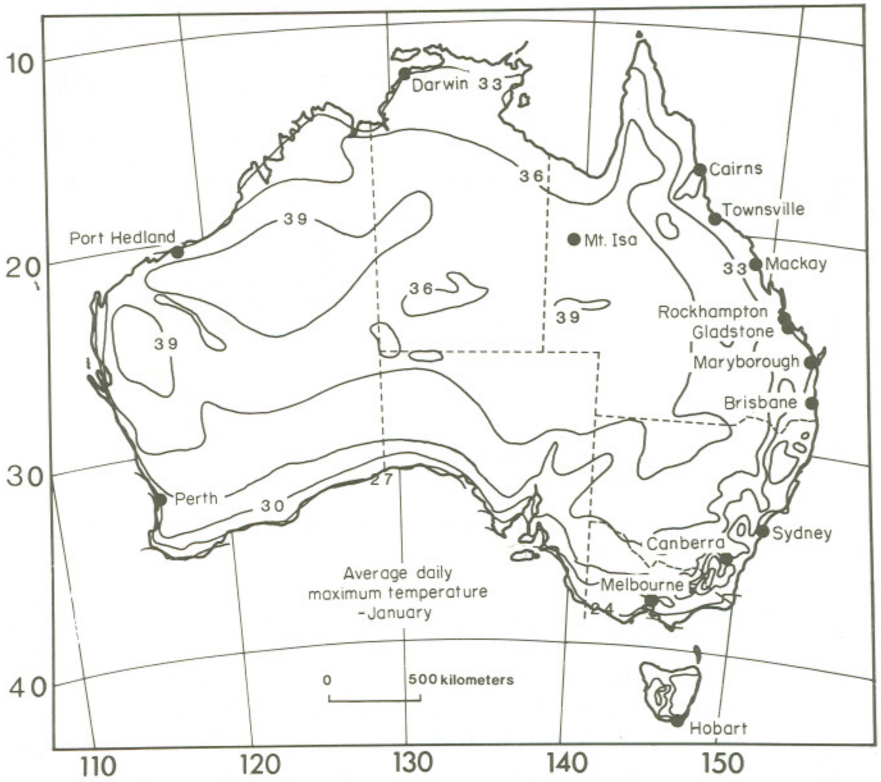

Figure 11.2 Isotherms of average daily maximum temperature over Australia for the month of January (mid-summer)

11.2.3 Soil Properties

At the outset we note that the 1983 publication '*Soils, An Australian Viewpoint*' (see reference list) gives the most contemporary and comprehensive overview of Australian soil properties that is available. Of some impor-

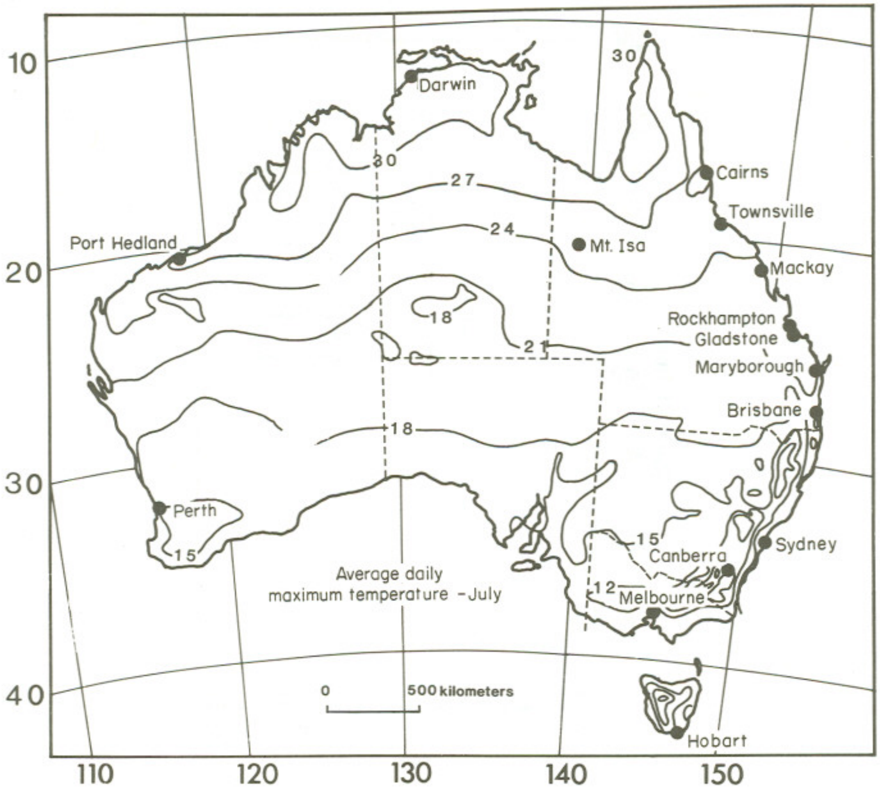

Figure 11.3 Isotherms of average daily maximum temperature over Australia for the month of July (mid-winter)

tance is the chapter (Moore *et al*., 1983) which compares soil classification schemes used in Australia with the two schemes used most commonly in other countries. Approximate correlations between classifications are given in Table 20.3 of Moore *et al*. (1983); these correlations are of considerable utility when data from different countries are compared. An alternative, simpler table of correlations between relevant classification schemes given in Appendix 2 of Sanchez and Isbell (1979), is reproduced here in Table 11.1. References to Australian soils in this brief review are generally in terms of the great soil groups listed in *A Handbook of Australian Soils* (Stace *et al*., 1968).

While the predominant soil features in Australia are not unique to the country, the overall pattern of soil properties and lack of certain features important on other continents give a distinctive character to Australian soils. For example, Australia lacks frozen soils, large areas of Podsols and pod-

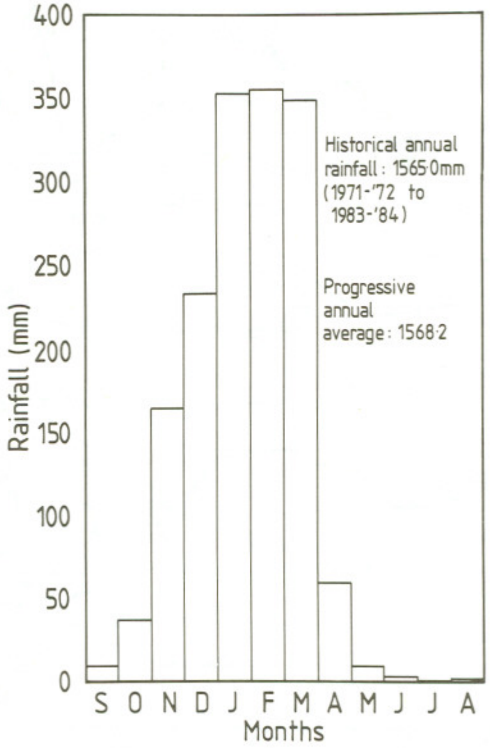

Figure 11.4 Monthly rainfall at Jabiru 1 September 1981–31 March 1985 (courtesy Ranger Uranium Mines)

solic soils, widespread humic soils, or soils derived from recently laid down pyroclastic material (the continent has had no recent volcanism). Less than 200 years of European settlement has also meant that anthropogenic soils are rare. On the other hand sandy soils that may be of minor importance on other continents are prominent in Australia. Hubble *et al*. (1983) give the following summary:

> the continental soil pattern is dominated by little-differentiated sandy soils of varying depth. This and the associated large areas of (i) strongly-leached and highly weathered kaolin-sesquioxide soils, (ii) cracking clay soils, (iii) little-differentiated, mostly shallow loamy soils, (iv) texture-contrast soils with neutral to alkaline red clay subsoils, and (v) soils with a strong texture contrast and sodic, usually heavy clay subsoils, give Australia its distinctive soil character.

According to Hubble *et al*. (1983) the most extensive soils of the arid interior and wet–dry tropical regions are deep siliceous sands and earthy sands, followed by other siliceous sands, sandy Lithosols, with red, yellow, and grey massive earths having prominence in particular regions, for example in certain areas of north Queensland (Isbell and Smith, 1976). A more regionalized description of prominent soil types can be found in papers by Northcote and Wright (1983), Bettany (1983), Isbell (1983), Isbell and Hubble (1983), and Hubble and Isbell (1983).

Tropical soils in Australia are almost universally deficient in nitrogen, sulphur and phosphorus, deficiencies that are quite well known in many other tropical regions, particularly high-rainfall areas. However a most distinctive contrast between Australia and a number of other tropical countries is the general absence in Australia of highly acid soils, since surface soils typically have pH values in the range 5.5 to 6.5, or even higher in some areas. Exchangeable cation concentrations also tend to be somewhat higher relative to other tropical areas, with the exception of aluminium, for which soluble levels are mostly well below levels likely to cause aluminium toxicity problems for plants or ground waters. Sanchez and Isbell (1979) have given an excellent comparative overview of soil characteristics in tropical soils of Australia and Latin America. Their work succinctly summarizes soil properties relevant to this study, and is particularly valuable in highlighting the distinctive features of Australian soils mentioned above. Tables 11.2 and 11.3, and Figures 11.5 and 11.6, underline the comparatively low acidity of Australian soils, with the exception of parts of the narrow east-coastal strip north of Brisbane (examples are the McDonnell and Tully soil samples in Table 11.2).

One other feature that may be important stems from the work of Probert (1977, 1980) and Probert and Samosir (1983) which indicates that some northern Australian soils may have a high to moderate capacity to adsorb sulphate. It is likely that a capacity to immobilize sulphate as water percolates through the profile could act as a significant pathway for removal of any sulphuric acid impinging on the surface in rain, at least to the point where the sulphate sorption capacity of the soil was exhausted (Galloway, 1988). If soils in tropical Australia in general have high sulphate sorption capacities (only a few sites have been investigated to date), this feature may make a significant contribution to the potential ability of Australian soils to cope with any future increase in rainwater acidity.

Our conclusion, admittedly based on relatively few soil studies in tropical Australia, is that in general the sensitivity of the dominant soil types to acidification will be less than that found in other tropical regions in which surface soil pH values are low (<5), exchangeable base cation concentrations are low, and Al saturation is high. In broad terms, such as those used in the Swedish Ministry of Agriculture (1982) publication *Acidification Today*

Table 11.1 Approximate correlation between some Australian great soil groups, soil taxonomy orders and great groups, and FAO mapping units (Sanchez and Ishbell, 1979)

Australian Great Groups	Soil taxonomy		FAO World Soil Map
	Order	Great Group	
Siliceous Sands	Entisols:	Quartzipsamment	Eutric Regosol, Cambic Arenosol
Earthy Sands	Entisols:	Quartzipsamment	Cambic Arenosol
Grey, Brown and Red Clays	Vertisols:	Chromustert	Chromic Vertisol
Solodized Solonetz and Solodic soils	Alfisols:	Natrustalf, Paleustalf, Haplustalf	Orthic Solonetz, Albic Luvisol
Soloths	Alfisols:	Paleustalf, Natrustalf Haplustalf	Albic Luvisol, Orthic Solonetz, Solodic Planosol
Red Earths	Alfisols & Ultisols:	Paleustalf, Haplustalf Paleustalt, Paleudult	Eutric Nitosol, Ferric Luvisol, Dystric Nitosol
Yellow Earths	Alfisols & Ultisols:	Haplustalf, Paleustalf Paleustult, Plinthustalf	Ferric, Albic and Plinthic Luvisols, Ferric Acrisol
Grey Earths	Alfisols:	Paleustalf, Tropaqualf	Albic Luvisol, Gleyic Luvisol

Euchrozems	Alfisols & Inceptisols:	Rhodustalf, Paleustalf, Ustochrept, Ustropept	Chromic Luvisol, Eutric Nitrosol, Chromic Cambisol
Xanthosems	Oxisols & Utisols:	Haplorthox, Haplustox, Palehumult, Acrohumox	Xanthic Ferralsol, Humic Ferralsol, Humic Acrisol
Krasnozems	Oxisols & Alfisols:	Acrohumox, Acrothox, Eutrustox, Paleustalf	Humic Ferralsol, Rhodic Ferralsol, Eutric Nitrosol
Red Podsolic soils	Alfisols & Ultisols:	Paleustalf, Paleudult, Haplustult, Tropudult	Albic Luvisol, Ferric and Orthic Acrisols, Dystric Nitosol
Yellow Podsolic soils	Alfisols & Ultisols:	Haplustalf, Haplustult, Paleustalf	Albic Luvisol, Orthic and Ferric Acrisol
Gleyed Podsolic soils	Ultisols:	Paleaquult, Albaquult	Gleyic Acrisol, Dystric Planosol
Podsols	Spodosols:	Tropahumod, Troporthod, Haplohumod	Humic and Orthic Podsols
Humic gleys	Ultisols & Inceptisols:	Palequult, Albaquult, Haplaquept	Gleyic Acrisol, Dystric Gleysol

Table 11.2 Selected topsoil chemical properties of representative soils of the tropical pasture area of Queensland, Australia (Sanchez and Isbell, 1979)

Soil and No.	Location	pH	Org. carbon (%)	Clay (%)	Exchangeable cations (meq/100 g)					Al sat. (%)
					Al	Ca	Mg	K	ECEC	
Alfisols										
Solodic (T30)	Lansdown Sta.	5.3	1.6	9	0.2	1.4	0.7	0.11	2.7	9
Red Earth (T256)	Redlands Sta.	6.3	0.5	16	0.1	1.4	0.6	0.10	2.1	2
Yellow Earth (T255)	Redlands Sta.	6.0	0.4	10	0.1	0.4	0.2	0.04	0.7	14
Euchrozom (T93)	Talavera	6.6	2.5	40	0.0	16.3	7.3	1.75	25.8	0
Vertisols										
Grey Clay (T13)	Hughenden	7.6	0.4	56	0.0	35.0	5.5	1.80	45.3	0
Grey Clay (B297)	Mt. Coolon	8.6	1.6	32	0.0	22.0	5.6	1.50	29.5	0
Entisols										
Siliceous Sand (T76)	Wenlock	5.9	0.4	2	0.0	0.7	0.3	0.02	1.0	0
Ultisols										
Yellow Earth (T137)	McDonnell	4.9	1.3	10	0.9	0.1	0.1	0.02	1.1	77
Red Earth (T241)	Tully	4.6	3.6	22	1.4	0.6	0.5	0.13	3.3	42
Oxisols										
Krasnozem (T62)	Malanda	5.4	8.0	66	0.8	1.3	1.6	0.26	4.0	20
Krasnozem (T84)	Gregory Falls	5.5	6.7	63	0.04	2.5	1.4	0.17	4.1	1
Xanthozem (248)	Lake Tinaroo	5.2	3.6	19	0.5	2.1	1.4	0.18	4.2	11

Table 11.3 Selected topsoil *chemical properties of representative soils of savannas and jungle areas of tropical Latin America (Sanchez and Isbell, 1979)

Soil and No.	Location	pH	Org. carbon (%)	Clay (%)	Exchangeable cations (meq/100 g)					Al sat (%)
					Al	Ca	Mg	K	ECEC	
Oxisols										
Haplustox	Carimague, Colombia	4.5	3.2	35	3.5	0.5	0.3	0.08	4.5	78
Haplustox (LVE)	Brasilia, Brazil	4.9	1.8	45	1.9	0.2	0.2	0.10	2.4	79
Yellow Latosol (28)	Paragominas, Brazil	4.4	1.3	74	1.4	0.7	0.3	0.07	2.4	58
Acrustox (C)	Caicara, Venezuela	4.5	0.4	24	1.0	0.3	0.1	0.10	1.6	63
Haplorthox (T.A.)	La Liberatad, Colombia	4.4	2.7	25	2.2	0.4	0.4	0.06	3.1	71
Eutrustox (1)	Capinopolis, Brazil	5.4	2.8	40	0.6	7.5	2.1	0.53	10.7	25
Ultisols										
Paleustult	Jusepin, Veneuela	4.7	0.9	24	0.5	0.5	0.1	0.01	1.1	43
Paleudult (Y-13)	Yurimaguas, Peru	4.0	1.2	9	2.3	0.2	0.2	0.10	2.9	79
Paleudult (P-2)	Pucallpa, Peru	4.4	1.6	42	3.4	2.5	1.3	0.41	4.2	81
Palehumult (F-3)	Quilichao, Colombia	4.1	4.1	71	2.7	0.7	0.5	0.36	4.2	64
Paleudult (2)	Echapora, Brazil	4.9	0.5	16	0.4	1.0	0.1	0.10	1.6	62
Paleustult (1)	Pres Murtinho, Brazil	4.7	1.0	18	0.8	0.2	0.2	0.06	1.3	63
Alfisols										
Paleustalf (4)	Maracaibo, Venezuela	5.7	0.8	7	0.1	1.7	0.7	0.33	7.9	1
Tropaqualf (Y-7)	Yurimaguas, Peru	5.0	1.2	53	7.4	11.4	6.3	0.67	25.8	29

* When first horizon was <10cm data were weighted with second horizon to depth of no less than 20 cm.

and Tomorrow (for example Figure 63 in that publication) we would somewhat subjectively rate Australian soils as moderate in their susceptibility to acidification, rather than high.

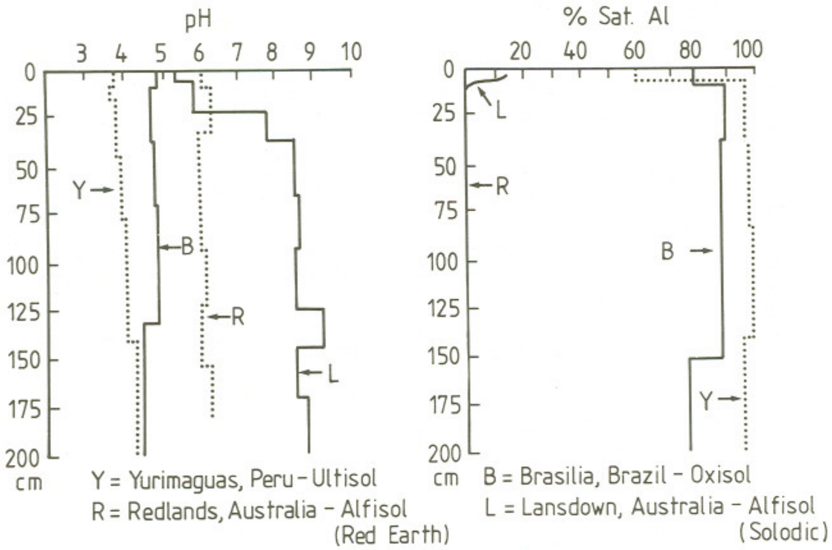

Figure 11.5 pH and Al saturation profiles in selected Australian and South American soils (from Sanchez and Isbell, 1979)

11.2.4 Surface Water Properties

As in other tropical areas where annual evaporation exceeds precipitation and large areas have arid or semiarid climates, there are no natural, large, permanent lakes in tropical Australia and few rivers that flow throughout the dry season. This leads to some difficulty in interpretation of surface water composition data, since most observations in the past have been made during the dry season when access to rivers is not impeded by the flash floods and impassable roads regularly encountered during the wet season. However, we are fortunate that at least the following data are available.

In the case of tropical Western Australia (WA) a network of gauging stations and sampling points has been serviced on a one to several times per year basis for about two decades now. Data on pH and alkalinity from these stations are summarized in Table 11.4. Generally the pH values and mean alkalinities found are sufficiently high as to reveal little evidence of surface water acidification. Indeed, if an alkalinity of 200 μeq/litre is the break point between susceptible and adequately buffered waters the table suggests that susceptible water bodies are rare in WA.

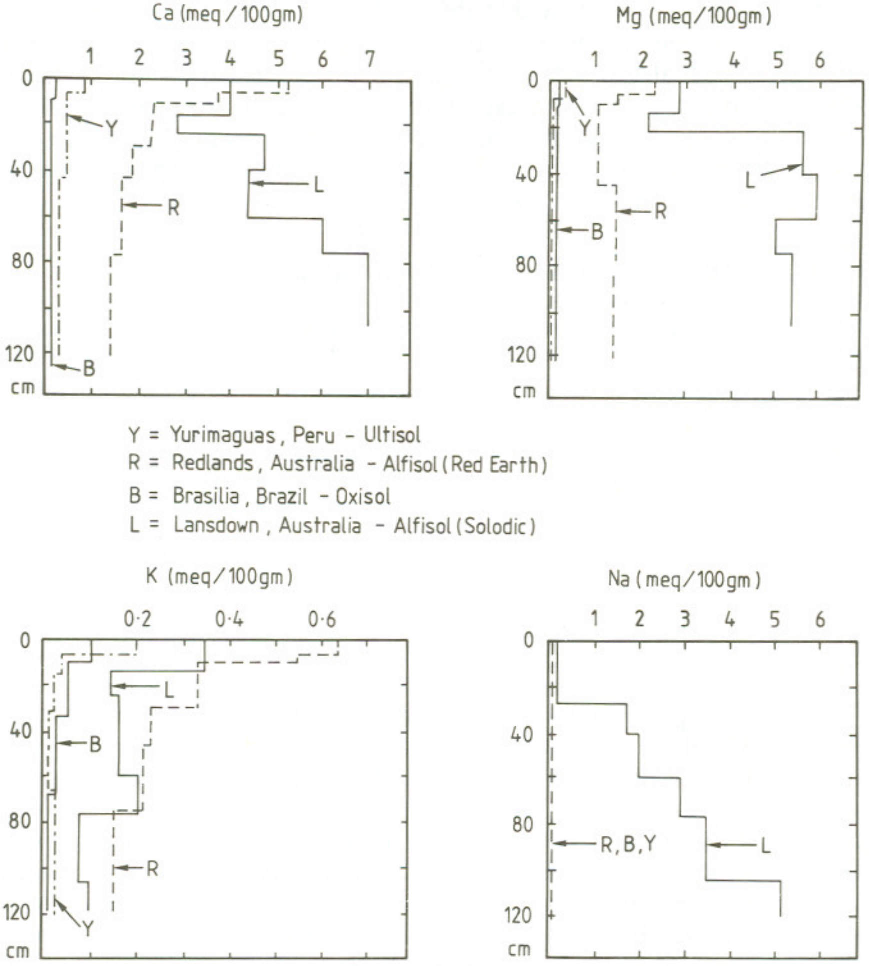

Figure 11.6 Exchangeable cation profiles in selected Australian and South American soils (from Sanchez and Isbell, 1979)

For the Northern Territory (NT) the readily available data base is smaller than in WA, and is summarized in Table 11.5. In this case the data reveal a number of adequately buffered water bodies, although there are also a number of sites at which buffering is poor (alkalinity < 200 μeq/litre), for example in Yirrkala Lagoon, at times in Mary Anne Dam, and at some sites in the Katherine, East Alligator, Finniss, and Daly rivers. In this region it seems likely that at least some of the surface waters would be susceptible to acidification from acidic deposition. We have been unable to obtain comparable data from Queensland (QLD).

At this time it is evident that the available data base is inadequate for an accurate prediction of the capacity of surface waters across the whole of tropical Australia to buffer any acidic atmospheric deposition. Available data are broadly in line with expectations based on known soil properties: lower acidity/higher alkalinity than in many other tropical countries and thus probably overall only a moderate susceptibility to acidification, except in a more or less limited range of particular locations.

Table 11.4 Mean pH and alkalinity of WA surface waters

River basin	Number of stations	Alkalinity median	Arith. av. (μeq/litre)	pH typical	Years of data
802	8	1010	1039	6.8–8.1	1964–82
803	2	1480	1460	6.5–8.4	1967–82
806	7	971	926	6.0–8.1	1968–82
808	1	260	420	6.2–8.0	1970–78
809	14	1780	1941	6.8–8.3	1965–82

Two further points about the inadequacy of the present data base can be made. The first concerns the rather low spatial density of water testing sites, which can lead to erroneous conclusions concerning the buffering capacity of individual rivers. Figure 11.7 contains data from two NT rivers that have been intensively sampled at a number of sites simultaneously: the East Alligator River at 23 sites and the Finniss River at 12 sites. What the data reveal clearly is that alkalinity at any one site cannot be assumed to be representative of alkalinity over tens to hundreds of kilometres of river course. In the case of the East Alligator River, buffering capacity is seen to be extremely low in the inland region where rain falls on the rocky, virtually soil-free Arnhem land escarpment, but rapidly becomes substantial as the river flows over a more alkaline soil type closer to the coast. In the case of the Finniss River there is no such gradation in alkalinity with elevation, but rather the dramatic lowering of alkalinity at about 90 km from the coast coincides with a short stretch in which six tributaries empty into the Finniss, with an apparently dramatic effect upon buffering capacity.

The second point concerns temporal variability of surface water alkalinity. Given the bias toward dry season sampling noted above, we cannot rule out the possibility that the high rainfall rates and high rainfall acidities characteristic of rainfall events at the beginning of the wet season (discussed later)

Table 11.5 pH and alkalinity of NT surface waters

Site	Sampling date	Alkalinity (μeq/litre)	pH
Magela Creek	14–17 Feb. 1984 (*n*=72)		5.22 (s.d. 0.13)
	20 Feb.–5 Mar. 1984 (*n*=337)		5.04 (s.d. 0.20)
Fogg Dam	19 Aug. 1980	560	6.8
Lake Evella	12 Dec. 1985	360	6.3
Lake Woods	10 Sep. 1985		7.5
Manton Dam	Nov. 69–Jan. 1981 (*n*=7)	950 (s.d. 120)	7.3 (s.d. 0.5)
Yirrkala Lagoon	Apr. 76–Aug. 1979 (*n*=3)	147 (s.d. 12)	6.1 (s.d. 0.2)
Mary Anne Dam	Feb. 81–Sep. 1985 (*n*=8)	280 (s.d. 170)	6.8 (s.d. 0.5)
Katherine River	May 1982, 27 sites	120–5800	6.3–8.0
East Alligator	May 1982, 23 sites	40–2800	6.6–7.3
Finnis River	Sep. 1980, 12 sites June 1982, 12 sites	100–640 500–3900	6.5–7.1 6.6–7.8
Daly River	Oct. 1982, 45 sites	100–3700	5.2–8.2

at places such as Katherine and Jabiru may produce short-term acidification of surface waters. This would be akin to the acid pulses characteristic of the first meltwaters from the snowpack in regions such as the northeastern United States. Indeed in our perusal of the data that contributed to Table 11.4 it seemed possible in some cases to discern an inverse relationship between alkalinity and river flow rate, particularly for a few observations near the start of the wet season. However the data, while suggestive, are inadequate for us to reach any positive conclusion.

Clearly we must urge some caution regarding our very preliminary conclusion that a majority of tropical rivers in Australia appear to be adequately buffered against acidic deposition; it is likely that spatial and temporal variability in buffering capacity has not been resolved adequately by the available observational data.

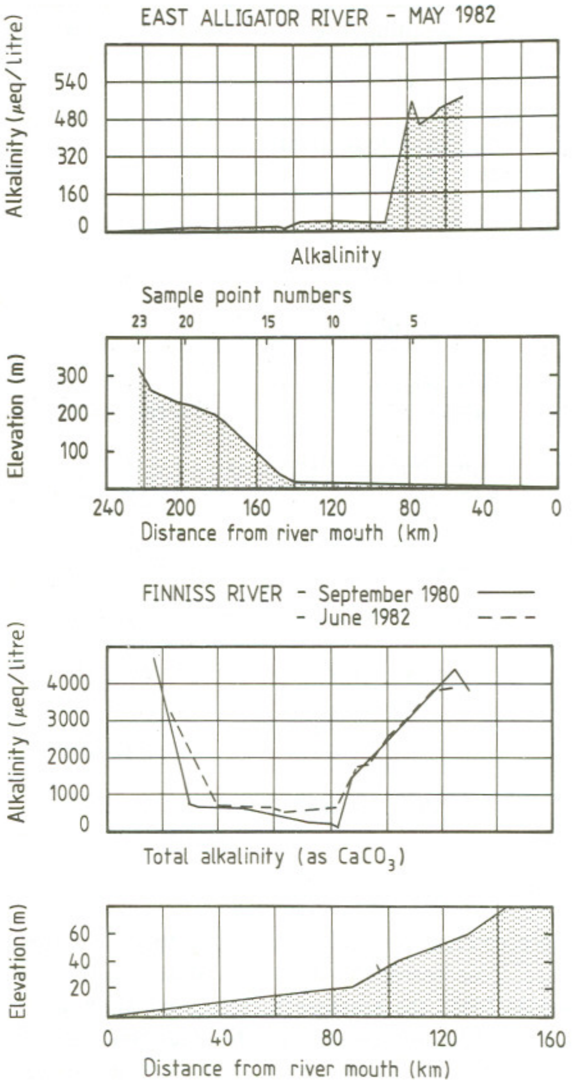

Figure 11.7 Spatial variation in alkalinity along two NT rivers (courtesy NT Water Resources Division)

11.2.5 Population Distribution

Due to the inhospitable climate and remoteness from the southern population centres, tropical Australia is very sparsely populated. The eastern area of Western Australia and the western area of the Northern Territory are virtually uninhabited. The remaining area has a population density of less than 0.03 people per km^2, except for a few isolated towns and a coastal strip of Queensland, which has up to 10 people per km^2. Table 11.6 gives populations of urban areas over 10,000 people and the total population of the tropics.

Table 11.6 Population of tropical Australia, June 1984 (Australian Bureau of Statistics)

Centre	Population	Latitude and Longitude (degrees)	(degrees)
Mount Isa	23,679	20°44	130°44
Rockhampton	50,146	23°22	150°32
Townsville	86,112	19°16	146°49
Maryborough	20,111	25°32	152°42
Mackay	35,361	21°09	149°11
Gladstone	22,083	23°51	151°16
Cairns	48,557	16°55	145°46
Darwin	66,100	12°27	130°50
Port Hedland	12,948	20°18	118°35
Northern Territory (NT)	117,000		
Western Australia (WA)	69,940		
Queensland (QLD)	542,220		
Total in tropics	729,160		

11.2.6 Industrial Development

A number of different industrial activities can be identified in tropical Australia, and so need to be considered in terms of their likely contribution to atmospheric or groundwater/soil acidity. Among these are the following mining operations: copper/lead, coal, iron ore, uranium, and bauxite. As well as mining, other industrial activities such as electricity generation, copper/lead smelting, aluminium smelting, and oil and gas production are carried on in tropical Australia. In this study, attention will only be given to emissions from power stations and copper/lead smelting operations, since the processes involved are considered to be by far the main industrial contributors to tropical atmospheric acidity in Australia. The largest power stations are mostly coal-fired, while the smaller tend to be gas turbine or diesel powered and most are associated with the urban areas listed in Table 11.6. For example, Gladstone (QLD) has a coal-fired power station of 1,650 MW capacity while Mount Isa (QLD) has three power stations in the area, a 126 MW coal, a 23 MW coal, and 10 MW gas turbine.

11.2.7 Flora and Fauna

The only livestock considered for this study were cattle, sheep, and pigs. Other livestock such as poultry were not considered since they represent only a very small proportion of the total. Table 11.7 gives details, and shows that by far the largest crop areas and livestock numbers are found in tropical Queensland, but that the total area under crop in tropical Australia is actually very small compared to the total area.

Tropical Australia has a number of herbivorous animals, the largest of which include water buffalo, wallaby, kangaroo, camel, emu, and donkey. Many other small native and introduced animals are also present, but as these have a lower biomass and probably contribute little to atmospheric chemistry, they will be ignored in this study. Some carnivorous animals such as the dingo, and freshwater and estuarine crocodile, also exist in tropical Australia, but in relatively low numbers.

Little is known of the population of these native and introduced animals. Frith and Calaby (1969) provide a figure of 1 kg/hectare for kangaroos in tropical savannas. Mott *et al.* (1985) suggest that the major introduced species—cattle, sheep, and water buffalo—have a comparatively high biomass. For example cattle biomass ranges from 2 kg/hectare in the north to 6 kg/hectare in the nutritionally richer areas of the subtropical savanna.

Table 11.7 Livestock numbers and crop areas for tropical Australia (Australian Bureau of Statistics)

Livestock	NT	QLD	WA	Totals
Cattle	1,390,000	4,669,680	820,300	6,879,980
Sheep	1,000	3,748,782	349,600	4,099,382
Pigs	3,000	28,516	NIL	31,516
Total livestock	1,394,000	8,446,978	1,169,900	11,010,878
Crop area (km^2)	52	20,722	49	20,823

The diversity and biomass of the native flora in the Australian tropics decrease from north to south in response to the similar variation in rainfall. In the northern coastal areas, mangrove swamps are widespread. Away from the coast the terrain is mostly open woodland consisting primarily of eucalyptus. There are a few rainforests confined to occasional patches on the Queensland coast. Inland, the woodland canopy is very open, allowing enough light to support native grasses which may grow to two metres during the wet season. Termites and their mounds are extremely common in much of this inland region. Further south in the drier regions clumps of spinifex and low shrubs are more common and the tree density per unit area declines.

11.3 SOURCES OF ATMOSPHERIC ACIDITY

11.3.1 Nitric Acid Precursors (Oxides of Nitrogen)

11.3.1.1 Nitric Oxide Production from Lightning

One possible source of atmospheric acidity is via the production of nitric oxide from lightning. Rainfall in the Australian monsoon is accompanied by severe electrical storms and tropical cyclones which produce a high frequency of lightning flashes. These flashes have sufficient energy to fix atmospheric nitrogen into nitric oxide, which is a precursor of nitric acid. To determine the mass of nitric oxide which can be produced, quantitative information on the lightning flash rate, average energy per flash, and the number of molecules of nitric oxide produced per joule, is required.

Since about 1982 the Australian Bureau of Meteorology has maintained a nationwide network of lightning flash counters which provides monthly, annual, and mean annual lightning flash frequencies. These lightning flash counters receive registrations over a radius of about 20 km from the aerial for cloud strikes and 30 km radius for ground strikes. Table 11.8 shows the total number of flashes per year together with mean annual rainfall for sites in tropical Australia. The bureau's tabulated data on rainfall, ground flash density and cloud/ground flash ratio for the five tropical sites listed in Table 11.6 enable us to deduce that the number of flashes/year/km^2 = 0.0134 mm + 0.575. The correlation coefficient = 0.969. Such a direct, linear

Table 11.8 Rainfall and lightning flash rates for tropical Australian (Australian Bureau of Meteorology)

Centre	Rainfall (mm)	Flashes/year
Darwin	1620	29,485
Mount Isa	391	11,662
Port Hedland	326	7,176
Warrumunga	362	6,597
McArthur River	784	20,009

relationship is reasonable, since rainfall and lightning flash rate should both depend on the frequency and intensity of cumulus activity. Thus we have the opportunity to use rainfall, which is reasonably well known over the whole continent, as an estimator for lightning flash rate, which is not.

Lightning flash rate was employed to calculate the mass of nitric oxide fixed from atmospheric nitrogen using the estimates of average lightning energy per flash and nitric oxide conversion efficiency made by Borucki and Chameides (1984). Nitric oxide production was then calculated using the flashes/area/rainfall relationship deduced above for the areas receiving specified mean annual rainfall, as shown in Table 11.9. Table 11.9 also shows that the estimated total mass of nitrogen fixed by lightning is about 23,000 tonnes/year.

Furthermore, if it is assumed that all the nitric oxide is oxidized to nitric acid within a day at the most (Borucki and Chameides, 1984), that during this time none is advected off the continent, and that in an ensuing day all the nitric acid is scavenged and deposited in rain, an average figure for the nitrate concentration in rain can be calculated. The calculation simply involves dissolving all the nitrate produced in each rainfall area (Table 11.9) in the total annual rainfall for that area. Of course as a consequence of the linear relationship between nitrogen fixation rate and rainfall deduced above, the estimated upper bound to nitrate concentration in rain is actually constant, at about 0.85 micromoles/litre. This also means that the mass of fixed nitric oxide varies linearly with the isohyets shown in Figure 11.1.

11.3.1.2 Nitric Oxide Production from Bushfires

Tropical Australia is an area that is prone to bushfires. The large land mass is covered mostly by woodland and grassland and experiences extreme heat, very low population densities, and high frequency of lightning, which create an ideal mix for fires to begin. Due to the low population density, the manpower available to fight fires is minimal, so in practice many fires are simply left to burn themselves out.

Fires in tropical Australia are normally of two main types: wildfires and controlled burns. Wildfires generally begin either from accidental (anthropogenic) causes or from natural causes. Accidental causes may be escapes from controlled burns and general carelessness of people, while natural causes include such things as spontaneous combustion and lightning. Controlled burns are deliberately started by pastoralists or government agencies with the purpose of clearing large areas of native pasture. Controlled burning commences toward the end of the dry season as the natural vegetation becomes dry and virtually useless for cattle consumption. Soon after the burn the first rains arrive and cause regrowth of grasses which rapidly become a source of palatable and nutritious cattle fodder.

Table 11.9 Estimated nitrogen fixation by lightning over tropical Australia

Rainfall (mm)	Land area (km^2)	N/year (tonnes)
>2500	1,940	55
1,500–2,500	58,204	1,336
1,000–1,500	294,900	4,282
700–1,000	495,380	4,968
500–700	686,483	4,957
300–500	735,310	3,658
200–300	1,061,575	3,492
		Total 22,748

Because of their prevalence, bushfires in the Australian tropical areas apparently could be a major contributor to total acid precursor emissions, thus it is of interest to try and estimate nitrogen oxide emissions from fires. The total area burned in tropical Australia is difficult to assess since the only records kept by state forestry commissions are those for controlled burns, and these represent a small proportion of the total land area burned each year. Anecdotal evidence, conveyed by many people in government agencies having interests in fire control, prevention or use, suggest that about 30% of tropical Australia is burnt each year by all types of fire. Although these data are unsupported, the lack of any other data necessitates their use in this study. Data on fuel are conveniently supplied by Matthews (1984) in the form of carbon loadings of standing biomass and litter biomass in 1° by 1° grids. These data, along with carbon/nitrogen ratios in the tropical biomass, provided by Galbally (1985), were used to provide a total of litter and standing biomass available for fuel and nitrogen available for conversion. Ratios of nitrogen/carbon in fuel in Australia have been estimated to be between 1.8% for grass fires, 1.3% for prescribed forest burn, and 0.3% for felled forest burn (Galbally, 1985). For the present calculation a nitrogen/carbon ratio of 1.3% has been adopted for the estimation of nitrogen content of biomass. The efficiency of conversion of nitrogen in biomass into nitrogen oxides has been estimated by Galbally (1985) from the ratio of nitrogen oxides in bushfire smoke to nitrogen content of biomass. These ratios for northern Australia vary from 5% to 19% so in this study we have used a figure of 10% for fuel nitrogen conversion efficiency.

From the above ratios of nitrogen/carbon, nitrogen conversion efficiency and area burnt, a flux factor of 3.9×10^{-4}/year was determined.

Table 11.10 gives estimated litter biomass for 1° latitude bands in tropical Australia, the respective nitrogen flux and the total nitrogen flux. This flux is only for litter biomass, but some standing biomass is also burnt during bushfires. We have no way of estimating the flux of nitrogen from standing biomass burnt, so for this study it will be assumed that the mass burnt is equivalent to that for litter biomass. The nitrogen flux from litter biomass is equivalent to about 194,000 tonnes of fixed nitrogen per annum, so total emissions from bushfires would be about 388,000 tonnes of fixed nitrogen. Since the fixed nitrogen flux from bush fires is about 17 times that from lightning, fires could potentially contribute about 14 micromoles/litre nitrate to the rain. However this would be an upper limit as bushfires in the main occur before the onset of the monsoon proper, so that a significant proportion of the nitrogen oxides produced may be dry deposited or transported out of the system.

Table 11.10 Litter mass and estimated nitrogen oxides flux from bushfires for 1° by 1° latitude bands over tropical Australia

Latitude band (degrees)	Litter mass (megatonnes carbon)	NO_x Flux (tonnes N)
11–12	14.5	5,660
12–13	19.3	7,530
13–14	28.9	11,300
14–15	35.8	14,000
15–15	40.5	15,800
16–17	46.2	18,000
17–18	57.8	22,500
18–19	50.4	19,600
19–20	46.6	18,200
20–21	49.8	19,400
21–22	48.3	18,800
22–23	59.4	23,200
Totals	497.5	194,000

11.3.1.3 Nitrogen Oxide Emissions from Soil

Another possible source of acid precursors is microbial processes in soils. Providing suitable conditions are present, processes of nitrification and denitrification can oxidize ammonium ions to nitrate, then anaerobically convert nitrate to either nitrous oxide or nitric oxide or ultimately to nitrogen (Galbally, 1985). The rate of denitrification depends on soil parameters such as temperature, pH, moisture, and presence or absence of inhibitors. Similarly the ratio of nitrous oxide to nitric oxide produced depends on such things as physical transfer processes in the soil.

In a recent survey of nitrogen oxide emissions from soils (Galbally, 1985), data were presented for various ecosystems. This survey showed that there are virtually no measurements of nitrogen oxide emissions from tropical soils. The lack of such data makes the estimation of nitrogen oxides from soil in tropical Australia very difficult. Nitric oxide fluxes of 0.02–0.08 g N/m^2/year (Galbally and Roy, 1978) have been measured for temperate woodlands in Australia. Due to the lack of any other data, a nitric oxide emission rate of 0.02 g N/m^2/year has been used in this study to make some attempt at determining the importance of soil emissions of nitrogen oxides. The result is an estimated soil emission of about 66,000 tonnes/year. However to take account of the large area of aridic soils in the Australian top end, we arbitrarily halved this figure to 33,000 tonnes per annum.

11.3.1.4 Nitrogen Oxide Emissions from Power Stations

In tropical Australia there are five coal-fired power stations, all located in Queensland, and a single oil-fired station, located in Darwin in the NT. By world standards the only significant station is that at Gladstone (QLD), rated at 1,650 MW. The remaining four coal-fired and one oil-fired stations are all rated at less than 200 MW, and have a combined installed capacity of less than 600 MW. Annual emissions of nitrogen dioxide from these power stations were estimated using 1983/84 (June to June) figures on coal and oil use from the respective state electricity generation authorities, plus a figure of 10 kg NO_2/tonne of fuel taken as a best guess from Table 2 of Logan (1983).

A further 15 small (a few to a few tens of MW capacity) diesel-powered electricity generation stations are scattered across northern Australia serving isolated communities. Nitrogen dioxide emissions from these plants were estimated from published figures on distillate usage for 1983/84 and a figure of 50 kg NO_2/kilolitre of distillate used, deduced again from Table 2 in Logan (1983). Results of these calculations in the form of emissions by state are given in Table 11.11.

11.3.1.5 Nitrogen Oxide Emissions from Motor Vehicles

After power stations, the next most significant urban/industrial source of nitrogen oxides in Australian towns and cities is motor vehicle emissions (Farrington and Boyd, 1981). Other stationary sources are third in significance, and in the sparsely populated top end of Australia need not be considered, as industrialization other than mining is slight.

Vehicle emissions for the top end are estimated by using population as an estimator for motor vehicle emissions. This calculation follows from the uniformity of lifestyle found for Australia on inspection of census statistics. Ayers *et al*. (1982) have shown that the ratio of private motor vehicles to people was essentially uniform across 11 Australian towns and cities that varied in population from 2×10^3 to $>3 \times 10^6$. Here we extend this idea by considering figures available on population, and inventory estimates of automotive nitrogen oxide emissions for the six state capital cities (Table 11.12). As can be seen from the figures, the ratio of automotive nitrogen oxide emissions to people is rather constant, averaging about 5.5 kg/person/year. Using this figure and the population totals for the tropical regions of WA, NT and QLD leads to the estimated motor vehicle emissions shown in Table 11.13.

Table 11.11 Estimated sulphur and nitrogen emissions from power stations in tropical Australia

State	Sulphur emitted (tonnes/year)	Nitrogen emitted (tonnes/year)
Queensland	28,600	17,400
Northern Territory	6,760	680
Western Australia	95	724
Totals	35,500	18,800

Table 11.12 Nitrogen oxide emissions and population in Australian cities

City	Population	Nitrogen emitted (tonnes N/year)	Nitrogen/person (kg/person/year)
Adelaide	857,000	4,425	5.2
Brisbane	893,000	4,562	5.1
Hobart	132,000	627	4.8
Melbourne	2,480,000	13,020	5.3
Perth	731,000	5,673	7.8
Sydney	2,770,000	13,7000	5.0
Mean			5.5

Table 11.13 Automotive emission of fixed nitrogen over tropical Australia (sulphur emissions are negligable)

State	Population (tropical)	Nitrogen emitted (tonnes/year)
Queensland	542,220	2,326
Northern Territory	117,000	645
Western Australia	69,940	39
		Total 3,010

11.3.2 Sulphuric Acid Precursors

11.3.2.1 Sulphur Gas Emissions from Soils and Vegetation

This section is entirely speculative as there are no relevant data available. We simply adopt the United States emission figure of 0.021 g/m^2 of sulphur discussed by Andreae (1985) and use the area of tropical Australia of 3.3×10^6 km^2 to calculate a figure of 70,000 tonnes sulphur per annum. However, since a considerable fraction of tropical Australia is arid or semiarid this figure may be overestimated, so we have arbitrarily halved it to produce a final guess of 35,000 tonnes S per year. Clearly this figure is open to criticism.

11.3.2.2 Sulphur Gas Emissions from Bushfires

Emissions of sulphur are estimated by assuming an average nitrogen/sulphur ratio of 10 for litter and vegetation in the Australian top end (Wetselaar and Hutton, 1963; Probert, 1977; Probert and Jones, 1982) then applying this factor to the estimated nitrogen emissions from bushfires given in Table 11.10. The result is an estimated sulphur emission rate of 39,000 tonnes/year. This figure is also very uncertain.

11.3.2.3 Sulphur Dioxide Emissions from Power Stations

As in the case of nitrogen dioxide emissions, fuel usage figures for 1983/84 are available for the power stations located in tropical Australia. Sulphur content of Australian black coals averages 0.5% by mass (Davey, 1980), while imported fuel oil used in the Darwin power station averages 3.75% sulphur. Distillate used in the smaller diesel-powered installations has about 0.25% sulphur. Combining these figures yields the totals by state for annual sulphur emissions given in Table 11.11. Note that the contribution from distillate use is actually negligible, being only 0.45% of the overall total sulphur emission.

11.3.2.4 Industrial Emissions

There is only one industrial source of note to consider, the large copper and lead smelting complex at Mt. Isa, in western QLD. Annual emissions of sulphur are typically 250,000 tonnes; about 25% comes from the lead smelter's 275 m stack, and about 75% comes from the copper smelter's 170 m stack.

11.3.3 Summary of Estimated Nitrogen and Sulphur Emissions

Our estimates of nitrogen and sulphur emissions from the various sources discussed, and the total emissions from all sources, are tabulated in Table 11.14. Anthropogenic emissions of nitrogen account for only 5% of the total nitrogen emissions (excluding ammonia); however total sulphur emissions

Table 11.14 Summary of estimated sulphur and nitrogen inputs to and outputs from the atmosphere over tropical Australia (tonnes/year)

	Nitrate-N	Sulfate-S	Ammonia-N
Bushfires	388,000	39,000	?
Soils	33,000	35,000	?
Lightning	23,000		
Animal wastes			12,800
Total (natural)	444,000	74,000	12,8000
Power stations	19,000	36,000	4,700
Automobiles	3,000		
Mt. Isa smelters		250,000	
Fertilizers			3,500
Animal wastes			51,000
Total (anthropogenic)	22,000	286,000	59,200
Total emissions	466,000	360,000	72,000+
Sink			
Wet deposition	181,000	132,000	181,000
Dry deposition			
gas (Mount Isa)		45,000	
gas	81,000	63,000	?
aerosol	36,000	11,000	?
Total deposition	298,000	251,000	181,000+

are dominated by anthropogenic emissions (80% of the total). This is a consequence of the extraordinarily strong sulphur source provided by the Mt. Isa smelters, which alone account for the vast majority (70%) of the total estimated emissions. Anthropogenic sources account for only 32% of the total sulphur estimate if emissions from Mt. Isa are excluded.

11.3.4 Organic Acids

It is clear from the published work of Galloway *et al*. (1982) and our own unpublished studies that the major contributors to observed levels of rainwater acidity in the NT, at least, are weak organic acids, principally methanoic and ethanoic acids. At present there is no firm, theoretical understanding available concerning the source or precursors of these acids, relevant reaction schemes, or pathways involving these acids. Indeed their distribution between gas, aerosol, cloud, and rainwater phases is virtually unknown. However two possible sources have been suggested: bushfires and vegetation. In each case it is supposed that the source emits hydrocarbons that are converted to the appropriate organic acid by either gas or solution phase processes, probably photochemically driven.

In the case of bushfires we have no way of estimating the organic acid flux direct from the combustion process or the flux of gaseous pyrolysis products that might convert photochemically to organic acids. However, the source of carbon from bushfires is large; our estimate is that on the order of 5×10^8 tonnes of litter carbon is available for combustion each year, and that approximately one third is burnt annually (Table 11.10). Thus if an equal quantity of standing biomass carbon is burnt, a total on the order of 3×10^8 tonnes of carbon may be burnt annually, some fraction of which must ultimately pass through the form of atmospheric organic acids.

Emissions of reactive organics such as terpenes, and isoprene (2-methyl-1,3-butadiene), have long been identified as potential contributors to atmospheric photochemical processes and aerosol formation (Duce *et al*., 1983). Isoprene in particular has received some attention as a very reactive gas that is emitted in large quantities by most tropical forest species (Brewer *et al*., 1984). For our purposes, isoprene serves as a useful indicator of the type of reactive emission that could act as a source for atmospheric organic acids, or their aldehyde precursors, in tropical Australia. While we do not have sufficient information at this stage to estimate isoprene fluxes or calculate production rates for organic acids, isoprene concentrations in surface air and aloft were determined during airborne field work in November 1985, in the vicinity of Jabiru. As would be expected for a reactive gas having a surface source, concentrations in midafternoon decreased with altitude from concentrations of 1 to several ppbv at 300 m, to concentrations of 1 ppbv or less at 2 km.

Clearly there are many open questions regarding the sources of organic acids in rainwater at places such as Katherine and Jabiru. At this stage both bushfires and vegetation emissions appear to be potentially significant sources of the observed acids or their precursors.

11.3.5 Ammonia

Ammonia is an important nitrogen species to consider since it is the only atmospheric trace gas with the capacity to neutralize atmospheric acids. Gaseous ammonia is assumed to have a ground level source and for the case of tropical Australia the overall flux is considered to result from five possible subsources. An attempt is made here to quantify the strengths of three of the subsources and to estimate an overall flux for ammonia from tropical Australia.

Volatilization of ammonia from animal urine has been suggested as the main source of atmospheric ammonia in remote areas (Galbally *et al*., 1980). The data required to estimate the strength of this subsource are animal numbers, urea excretion rates, and the rate of release of ammonia from urea. Table 11.7 gives total numbers of cattle, sheep, and pigs in tropical Australia, these being the only agricultural animals which would have any effect on the ammonia flux. Native animals must also be included here as they provide a significant contribution to the ammonia flux. Reliable estimates of native animal numbers are difficult to obtain in tropical Australia so here we use the data quoted previously from Frith and Calaby (1969) and Mott *et al*. (1985). Mott *et al*. give a figure of 1 kg/hectare for kangaroo biomass in tropical Australia. In this study a figure of 4 kg/hectare was adopted for cattle biomass to which 30% was added to account for native animals (25% kangaroos, 5% other non-agricultural animals). These data, combined with rates of urea excretion provided by Healy *et al*. (1970) and the rate of ammonia volatilization from urea provided by Galbally *et al*. (1980), can be used to estimate the ammonia emissions from animal urine.

The second subsource of ammonia gas emissions is that from power stations. This ammonia source can readily be quantified from the figure of 1 gram of ammonia per kilogram of coal burnt, supplied by Galbally *et al*. (1980). The annual ammonia emissions from power stations were calculated using 1983/1984 (June to June) coal usage rates obtained from the electricity commissions of the Northern Territory, Western Australia, and Queensland.

The ammonia emission from fertilizer use in tropical Australia was estimated next. The total area of crops in Australia and the total nitrogenous fertilizer used in Australia were obtained from Australian Bureau of Statistics publications. The total crop area of tropical Australia given in Table 11.7 was then used to calculate the total mass of nitrogenous fertilizer used in tropical Australia, assuming uniform fertilizer application rates countrywide. This calculation resulted in a total mass of 43,000 tonnes/year which results in 4,300 tonnes of ammonia released, using an ammonia release rate of 10% (Galbally *et al*., 1980).

Bushfires are a potentially very large source of ammonia release to the atmosphere. This source is impossible to quantify due to a complete lack of data. Although the biomass litter and the nitrogen content is known, the chemical forms of nitrogen-containing species within the biomass vary considerably, and consequently the release rates of ammonia from biomass burning are hard to predict. Although release rates from coal burning are known, these cannot simply be applied to biomass burning since many fires in tropical Australia are low temperature grass fires and ammonia release rates may be quite dependent upon combustion temperature. We conclude that biomass burning potentially may contribute a substantial proportion to the total ammonia flux, but for the reasons given above no attempt is made here to quantify the ammonia released from this source.

The final subsource to be considered is that of ammonia emission (or possibly uptake) by plants through the stomata. Considering the large area of tropical Australia this could be a significant source or sink of ammonia gas. Farquhar *et al*. (1979, 1980) have developed this concept and have identified a finite ammonia gas pressure, or compensation point, at which no net ammonia gas is exchanged between the atmosphere and the plant. In four plant species studied, this compensation point has a range of values of 2 to 6 ppbv; when the atmospheric ammonia pressure is greater than this, the plant takes up ammonia, while when it is lower, ammonia is emitted to the atmosphere. No attempt can be made here to estimate this source (or sink) of ammonia since the ammonia concentration of intercellular fluid found in plants in tropical Australia is not known.

The estimates presented in Table 11.14 show that ammonia volatilization from animal urine accounts for about 88% of the total quantifiable ammonia flux. This result is consistent with two previous studies. Galbally *et al*. (1980) concluded that probably greater than 70% of the ammonia flux over Australia was from animal urine, although biomass burning was not considered in the study. Bottger *et al*. (1978) show that in the Northern and Southern Hemispheres about 86% and 91% of the ammonia flux originates from animal urine. Bottger *et al*. (1978) concluded that cattle contribute about 54% of the ammonia flux in the Southern Hemisphere, while Table 11.14 in this study indicates that our estimate for tropical Australia was a comparable figure of 59%.

The total ammonia flux from Australia was tentatively estimated by Galbally *et al*. (1980) to be 600,000–700,000 tonnes as N/year. This is about 10 times the ammonia flux for tropical Australia, as shown in Table 11.14, and is consistent with the fact that most grazing, pastoral activities, and electricity generation are carried out in the nontropical areas of Australia.

11.4 SINKS OF ATMOSPHERIC ACIDITY

11.4.1 Wet Deposition

Annual deposition of sulphate, nitrate, and ammonia in rain can be estimated from the tropical land areas receiving a given annual average rainfall (Table 11.9), and from average rainwater concentrations of the species of interest. Table 11.15 summarizes available data on tropical Australian rainwater composition: we assume that over all of tropical Australia nitrate averages 5 micromoles/litre, excess sulphate averages 3 micromoles/litre, and ammonium averages 5 micromoles/litre. The calculated annual depositions are then 181,000 tonnes N as nitrate, 132,000 tonnes S as sulphate, and 181,000 tonnes N as ammonium.

11.4.2 Dry Deposition

It is important to acknowledge that dry deposition processes may make a significant contribution to the overall transfer of atmospheric acidity to the earth's surface, perhaps particularly so in a wet–dry region such as tropical Australia which is devoid of wet deposition for half of the year. However we have only very meagre information upon which to base our estimates of dry deposition over Australia, so the calculated values must be treated with caution.

Consider first sulphur dioxide. We take the observed sulphur dioxide concentration at Jabiru (Table 11.18; discussed more fully later), assume that this is representative of the whole of tropical Australia, combine it with the tropical area of 3.33×10^{12} m^2 and a dry deposition velocity of 0.005 metres/second, to calculate a total deposition of 126,000 tonnes S/annum. However, we have arbitrarily halved this estimate to account for reduced turbulent transport near the surface during nighttime (12 of each 24 hours) and are left with an estimate of 63,000 tonnes S/year. Note that the deposition velocity chosen is somewhat lower than that often used over less arid midlatitude surfaces, but is somewhat higher than the unusually low values reported by Milne *et al*. (1979) for the arid area around Mt. Isa.

Deposition of gaseous nitric acid is similarly estimated, again using the measured value from Table 11.18 as the assumed continent-wide surface gas concentration. However a dry deposition velocity of 0.015 metres/second is used in this case, since it seems likely that nitric acid deposits more readily than sulphur dioxide (Huebert and Robert, 1985). Calculated deposition in this case (also arbitrarily halved) is 81,000 tonnes/year.

The only anthropogenic source that we need to consider is the Mt. Isa smelting complex which is by far the dominant source of sulphur dioxide in the tropical region. To estimate dry deposition from the Mt. Isa plume we note that in the absence of cumulus convection the plume in daytime takes the form of a well-mixed, divergent slab, moving downwind from the source and spreading crosswind with a rather constant half angle of about 10°, confined vertically by the surface and a capping inversion averaging about 2 km (Ayers *et al*., 1979; Bigg *et al*., 1978; Roberts and Williams, 1979). At distances larger than about 20 km downwind, this type of simple picture, in which we consider the plume to be well-mixed both horizontally and vertically (constant concentration in the plume) was found by Manton and Ayers (1982) to adequately capture the major plume features with regard to the effects of meteorology, source inhomogeneity, dispersion and coagulation, when applied to modelling aerosol fluxes downwind of a number of Australian towns, including Mt. Isa.

In the present case, let

$$P = CA \tag{3}$$

where C is the plume sulphur concentration, and A is the cross sectional area of a thin, crosswind slice of plume. Thus

$$A = HW \tag{4}$$

where H is the inversion height and W is the crosswind plume width. Assuming that dry deposition is the dominant sulphur dioxide removal process (Roberts and Williams (1979) state that loss of sulphur dioxide due to oxidation by OH radical is about 5% per day, while the calculations performed below suggest a dry deposition figure of about 9% per day), the sulphur conservation equation is

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{U\mathrm{d}P}{\mathrm{d}x} + VCW = 0 \tag{5}$$

where U is mean wind speed, V is sulphur dioxide deposition velocity and x is downwind distance of the plume slice from the source. Thus

$$\frac{U\mathrm{d}P}{\mathrm{d}x} = -VCW \tag{6}$$

which becomes, using (3)

$$\frac{U\mathrm{d}P}{\mathrm{d}x} = \frac{-VPW}{A} \tag{7}$$

and, using (4)

$$\frac{\mathrm{d}P}{\mathrm{d}x} = \frac{-VP}{UH} \tag{8}$$

Table 11.15 Volume-weighted mean concentration data for rainwater in tropical Australia. With the exception of pH all values in micromoles/litre

Site	Date	*n*	Comment	References	pH	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	$HCOO^-$	CH_3COO^-	CH_3CH_2C
Alice Springs	1957–62	22	event samples	Hutton, 1962		28	9	11.5	16							
Katherine	1958–59	30	event samples	Hutton, 1962						5.4	4.9	6.2				
	1959–60			Wetselaar and Hutton, 1963		5.2	0.8	0.9			5.5	3.9				
Queensland	1968	?	bulk samples? 5 sites	Douglas, 1968		44.6	11.8	6.8	13.8		80.0					
Townsville	1971–74	23	monthly, bulk	Probert, 1977		74.5	5.0	10.9	20.4	7.8	112.0	2.8	14.4			
Lansdowne		14	samples, 2 sites			37.5	3.2	5.9	12.6	15.0	55.7	4.8	8.3			

West Australia	1973–74	200	monthly, bulk samples, 15 sites	Hingston and Gailitis, 1976, 1977	5.00	13.6	5.0	4.0	9.7		20.0		5.4			
Queensland	1974–77	?	weekly and monthly bulk samples	Brasell and Gilmour, 1980; Brasell and Knowlton, 1979		80.0 80.0 36.0 31.0	2.4 2.4 4.6 10.8	9.3 9.3 4.7 6.2	5.0 5.0 2.7 5.7							
Groote Eylandt	1979–80	40	event samples	Langkamp *et al*., 1982; Langkamp and Dalling, 1983	4.28	65.7	20.2	4.5	13.7	5.0			1.1			
Katherine	1980–81	40	event samples	Galloway *et al*., 1982	4.78	7.0	0.9	1.0	1.3	2.0	11.8	4.3	3.2			
Jabiru	1982–83	18	event samples	Ayers, Noller and Gilbert, unpublished	4.27	10.4	1.5	1.5	1.1	5.3	13.8	6.0	4.0			
	1983–84	17			4.63					3.5	16.9	6.3	5.2	10.4		
	1984–85	17			4.29					3.2	19.9	6.3	3.5	31.3	14.1	4.3

Therefore

$$\int_{P_0}^{P} \frac{dP}{P} = \int_{x_0}^{x} \frac{-V dx}{UH} \tag{9}$$

which yields

$$\ln\left(\frac{P}{P_0}\right) = \frac{-V}{UH}(x - x_0) \tag{10}$$

or

$$P = P_0 \exp\left\{\frac{-V}{UH}(x - x_0)\right\} \tag{11}$$

giving

$$C = \frac{C_0 A_0}{A} \exp\left\{\frac{-V}{UH}(x - x_0)\right\} \tag{12}$$

with θ the half angle of plume spread in the downwind direction, and subscript zero referring to the conditions at which the plume is first mixed down to the ground from the stack height (170–275 m), we achieve finally (putting $W = W_o + 2(x - x_0)\tan\theta$),

$$C = \frac{C_0 W_0 \exp\{-V/UH(x - x_0)\}}{W_0 + 2(x - x_0)\tan\theta} \tag{13}$$

The result is an expression for sulphur concentration in a slice of plume as a function of mean wind speed, angle of plume spread, inversion height, deposition velocity and initial concentration (determined by emission rate). Total deposition rate over any length of plume can be readily obtained from

$$\text{deposition (kg/sec)} = \int_{x_0}^{x_1} VCW dx \tag{14}$$

Given the predominance of southeasterly surface winds at Mt. Isa in the dry season we assume an average plume track to the northwest, giving a total distance to the coast, x_1, of 1,300 km. A mean wind speed of 7.25 metres/second averaged over the boundary layer comes from the observations of Ayers *et al*. (1979). From the same work a daytime mixed layer depth of 2,000 m is obtained. A deposition velocity of 0.005 metres/second is assumed, being a compromise between the often used figure of 0.01 metres/second and the unexpectedly low figure of 0.0012 metres/second reported for tropical Australia by Milne *et al*. (1979). A value of 10° for θ was taken from Bigg *et al*. (1978).

C_0, W_0 and x_0 were estimated from the mean wind speed of 7.25 metres/second and an estimated vertical velocity for convective elements of about 0.75 metres/second (Manton and Ayers, 1982). For a stack height of 170 m, an average vertical velocity of 0.75 metres/second implies about 230 seconds for the plume to be mixed to ground, during which time it would have travelled about 1.5 km downwind. We thus have x_0 as 1,500 m, and with plume width as $2x \tan \theta$, obtain W_0 as 530 m. Since the initial flux of sulphur from Mt. Isa, F_0, averages 8 kg/second (250,000 tonnes/year) and $F_0 = UCC_0$, C_0 can readily be calculated as 1.0×10^{-6} kg/m^3. An alternative estimation would be to consider the time taken to mix the plume up to the 2000 inversion height. In this case the values found are: x_0 of 20 km, W_0 of 7050, and C_0 of 7.8×10^{-8} kg/m^3.

In fact, calculation of the total sulphur deposition over the 1300 km length of plume is insensitive to the difference between these two sets of initial conditions, as it changes by less than 2%. Averaging the two results gives a total sulphur deposition of 90,000 tonnes/year. However it is necessary to halve this figure to allow for the fact that the nighttime radiation inversion effectively decouples the plume, emitted at 170 to 275 metres, from the surface for about half of each day. Thus our final estimate is 45,000 tonnes sulphur/year.

Finally we consider the dry deposition of aerosol, about which virtually nothing is known in tropical Australia. The only relevant work of which we are aware arises from the two-year record of high-volume filter collections carried out by Savoie (1984). In that work considerable attention was given to estimation of appropriate dry deposition velocities. Here we simply quote the results (Table 38 in Savoie, 1984) for Broome, WA, which are dry deposition fluxes of 130 and 26 μg/m^2/day for aerosol nitrate and aerosol excess sulphate respectively. Extrapolation of these figures to the whole area of tropical Australia yields annual depositions of 36,000 tonnes N and 11,000 tonnes S.

11.4.3 Atmospheric Sulphur and Nitrogen Budgets

Given the prevalence of uncertainties in our emissions calculations and lack of any data in certain parts of the budgets, such as off-continent advection, it is too optimistic to expect to be able to construct closed cycles for the atmospheric inputs and outputs of sulphur and nitrogen over tropical Australia. However a summary of our estimates to date is given in Table 11.14.

11.5 ATMOSPHERIC DATA

11.5.1 Recent Observations near Jabiru, NT

Rainwater collections began at Jabiru in the 1982/83 wet season and continued for the following three wet seasons. Collections, carried out by B. Noller of the Alligator Rivers Region Research Institute, have been on an event basis, the collectors being exposed just before the onset of rain and collected as soon as possible after cessation. This sampling protocol was selected so that collections were wet-only, as far as possible, thus minimizing collection of soil dust and particulate matter. Table 11.15 shows the species which have been quantified from each event, and the volume-weighted means from the available data.

The last four lines in Table 11.15 contain volume-weighted mean pH values derived from the only recent wet-only studies so far carried out in tropical Australia. Three of these were obtained from rain samples taken at Jabiru. These pH values are very low considering that the collection sites are in a remote area, far from population centres and urban or industrial sources of acid precursors. As a comparison, pH values of rain collected in the two remote Australasian areas of Cape Grim, Tasmania (Baseline, 1978) and New Plymouth, New Zealand (Ayers *et al.*, 1986) are considerably higher than those at Jabiru. At Cape Grim the pH of event-sampled rain averages about 5.5 (unpublished data from 12 months of event samples), this being a maritime site where samples are only collected during onshore winds. New Plymouth is also a maritime site and the volume-weighted mean pH was also about 5.5 (Ayers *et al.*, 1986). There is a clear difference in acidity between the remote, maritime, and midlatitude sites and the equally remote tropical sites.

Jabiru is situated in the Northern Territory about 60 km from the coast and thus cannot really be considered a maritime site, particularly in the early, transition part of the wet season when prevailing surface winds tend to be southeasterly, from the continental interior. This is reflected by the rather low concentrations of sodium and chloride seen in Table 11.15. Nevertheless, some oceanic influence on the rain composition might be expected since the surface wind direction changes to the north (onshore) during the later, monsoonal part of the wet season. Accordingly, we have used data on the composition of seawater from Millero (1974) to calculate the oceanic contribution of sulphate, magnesium, calcium, and potassium to rainwater at Jabiru. This was done by assuming that all chloride found in the rain had an oceanic origin, that ionic ratios in seawater are constant, and that little or no enrichment of chloride occurs due to aerosol formation at the ocean surface (Duce and Hoffman, 1976). The calculated levels of excess sulphate, magnesium, calcium, and potassium are given in Table 11.16.

One of the characteristics of rain at Jabiru is the large fractional excess of sulphate, calcium, and potassium and the small excess of magnesium. Table 11.16 shows that around 70 to 80% of sulphate, calcium, and potassium are of non-seasalt origin. The main continental influence on rain at Jabiru is the incorporation of soil material into the rain. The main cationic compo-

Table 11.16 Ionic excesses (additional to seasalt) in rain from Jabiru (μeq/litre)

		SO_4^{2-}		Ca^{2+}	Mg^{2+}	K^+	Na^+
Wet season	1982–83	1983–84	1984–85	1982–83	1982–83	1982–83	1982–83
Total	8.0	10.4	7.0	2.20	3.00	1.50	10.4
Excess	6.6	8.6	5.0	1.68	0.30	1.24	−1.4
Seasalt	1.4	1.8	2.0	0.52	2.70	0.52	
Percentage excess	82.5	82.7	71.4	76.4	10.0	82.7	

nents of soil, like seawater, are sodium, potassium, calcium, and magnesium (Hutton, 1968). The difference between soil and seawater is that calcium and potassium are apparently enriched in soil, compared with sodium and magnesium (Hutton, 1968; Langkamp and Dalling, 1983). Therefore these large excesses of calcium and potassium can be interpreted as being largely soil-derived. Sulfate is unlikely to be soil derived, since sulphate levels in most Australian soils are rather low, and mole ratios of sulphate to excess calcium plus excess potassium are greater than unity, suggesting that excess sulphate is incorporated into rain via another pathway, such as sulphur dioxide oxidation.

The absolute concentrations of sodium, potassium, calcium, magnesium, sulphate, and chloride are very low compared with remote maritime sites such as Cape Grim (Baseline, 1978) and New Plymouth (Ayers *et al*., 1986) where concentrations of sodium and chloride can range up to 3,000 micromoles/litre. This is a further indication that the marine influence on the rainwater at Jabiru is small.

Nitrate probably originates from oxidation of nitrogen precursors emitted from bushfires, lightning, power stations, and soil processes. The concentration of nitrate in rain at Jabiru is somewhat higher than for the above mentioned midlatitude sites, probably due to higher levels of precursor emissions in the continental tropics, in comparison with midlatitude, maritime regions.

When the three organic acids measured at Jabiru in 1984/85 are combined they obviously account for most of the hydrogen ions calculated from the

Table 11.17 Anion and cation sums for Jabiru East rainwater event samples

	1982/83	1983/84	1984/85
H^+	53.7	23.4	51.3
NH_4^+	5.3	3.5	3.2
Total cations	59.0	26.9	54.5
NO_3^-	6.0	6.3	6.3
Excess SO_4^{2-}	6.6	8.6	5.0
Methanoate		9.2	24.2
Ethanoate			3.6
Propanoate			0.9
Total anions	12.6	24.1	40.0

pH. Table 11.17 shows that in 1984/85 the sum of methanoic, ethanoic, and propionic acids accounted for about 72% of the total measured free acidity. Moreover, of the organic acids measured, methanoic acid is by far the most concentrated. Since ammonia is the predominant atmospheric acid-neutralizing species, the sum of hydrogen ion plus ammonium ion concentrations is taken to be a reasonable estimator for neutralized plus free acidity. In rain, therefore, there should be a balance between the total acidity and the sum of acidic anions.

Table 11.17 also shows that for the years with most complete data (1983/84 and 1984/85), the sum of hydrogen ions plus ammonium ions is somewhat greater than the sum of acidic anions. We attribute the cation excess to the presence of other unidentified organic acid anions in the samples. The high performance liquid chromatographic (HPLC) method used for the chemical analyses (Gillett and Ayers, 1985) revealed many peaks other than those of the three acids identified. Although no quantitative work was done to identify other acids, qualitative studies suggested that several additional mono- and di-acids were present in most samples. Previous studies at Katherine, by Galloway *et al*. (1982), have indeed revealed that acids such as citric, glycolic, and lactic were present in rainwater samples in small quantities. Another study on the photochemical oxidation of isoprene reveals that many acids may result (Brewer *et al*., 1984). If an average pK_a of 4.46 (average of values for five C_2–C_5 mono-acids) is assumed for other organic acids, then at the observed pH of 4.29 there would need to be an extra 35.8 micromoles/litre

Table 11.18 Composition of aerosol, gas and cloud water near Jabiru, NT

Species measured	Aerosol* (nanomoles/m^3)	Gas† (nanomoles/m^3)	Cloud water (micromoles/litre)
pH			3.81
Hydrogen ion			154.9
Methanoate	0.15	39	78.8
Ethanoate	0.46	5.2	39.6
Propanoate	<0.3	<0.3	12.8‡
Nitrate	1.6	6.6	66.9
Nitrite	0.006	0.44	0.21
Chloride	7.4	7.4	ND
Sulfate	5.1	7.0 (SO_2)	ND

Notes:
* Surface measurements made in 1984/85; ND—not determined.
† Measurements made in November 1985.
‡ May include contribution to HPLC peak from other unidentified acids.

of organic acids to achieve charge balance in the 1984/85 mean composition (Table 11.17). If di-acids were involved their lower pK_{a1} values and double ionization would mean only a few micromoles/litre would be required to produce charge balance.

During November 1985, a field expedition was mounted to collect cloud-water and vertical profiles of hydrocarbons, carbon monoxide, carbon dioxide and ammonia. Some results, along with results of aerosol and acid gas measurements made in 1984/85, are presented in Table 11.18 and Figures 11.8–11.10. Ammonia gas was collected using denuder tubes (Possanzini *et al.*, 1983) coated with oxalic acid and then analysed by the indophenol blue technique (Dal Pont *et al.*, 1974); hydrocarbons were collected in whole air samples at about 200 kPa (0.5 litre glass flasks) and were later analysed by standard gas chromatographic methods using a flame ionization detector (Evans *et al.*, 1985). Aerosols were sampled (24 hours) on the ground at Jabiru using 1 micron pore-sized teflon (Fluoropore) filters at a flow rate of 14.5 litres/minute. After extraction with deionized water they were analysed using HPLC techniques (Gillett and Ayers, 1985). Acid gas concentrations were determined by first collecting the gas on potassium hydroxide-coated denuder tubes (three tubes in series), followed by extraction into deionized water and chemical analysis by HPLC (Gillett and Ayers, 1985).

During the November 1985 field work, 35 cloud-water samples were collected in the vicinity of Katherine and Jabiru using CSIRO's Fokker F27 research aircraft. Sampling was carried out at 100–300 metres above cloud base in non-raining clouds. Table 11.18 gives the arithmetic mean results for ions determined in the 19 samples analysed to date. These cloud-water samples displayed very low pH levels and high concentrations of methanoate, ethanoate, and nitrate, the ionic concentrations being rather larger than those typically found in rainwater (for example, see Table 11.15). This concentration enhancement is probably explicable in terms of the difference in cloud liquid water content, L, between clouds producing rain, in which L is typically 1 to 2 g/m^3, and the dryer, non-raining cloud samples which typically have L of 0.1 to 0.5 g/m^3. Thus concentration enhancement of up to an order of magnitude could be explained simply in terms of the differences in L between the clouds sampled and those that produced rain (the reason why raining clouds were not sampled for cloud water is quite practical: clouds that were actively raining often contained lightning, and always yielded radar returns indicative of severe, aircraft-threatening turbulence). After allowance for this sampling bias it can be concluded from Tables 11.15 and 11.18 that for the acids considered, rainwater composition appears to be readily explained in terms of cloud-water composition: the mix of acids at cloud level is similar to that found in rain at the surface.

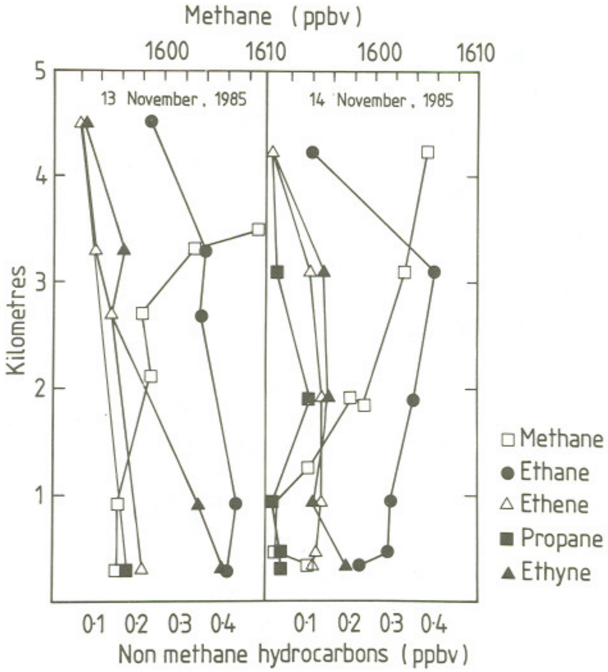

Figure 11.8 Vertical profiles of gaseous hydrocarbons derived from aircraft flask samples collected near Jabiru in November 1985

Aerosol and gas measurements, also made at the surface at Jabiru during the 1984/85 wet season, yielded the results shown in Table 11.18. The gas tubes used were a slight modification of those used by Possanzini *et al.* (1983), and in our case employed a coating solution of potassium hydroxide instead of tetrachloromercurate. It has been clearly demonstrated that in these tubes particles proceed unaffected while reactive gases diffuse to the tube wall (Possanzini *et al.*, 1983) and there react with the tube coating. Use of a carbonate or hydroxide coating ensures that gaseous acids are collected (Ferm and Sjodin, 1985), as well as sulphur dioxide, which is determined as sulphate. All acids were determined by our usual HPLC methods as the appropriate acid anion (nitrate, chloride, methanoate, etc.) in a 5 ml aqueous sample obtained by washing out the tubes with deioniZed water. Sulfuric acid vapour in equilibrium with sulphate aerosols does not contribute to the collected sulphur dioxide burden, since the equilibrium sulphuric acid vapour pressure above a typical aqueous aerosol of 10% sulphate by mass is a negligible 1.4×10^{-6} pptv at 40 °C (Ayers *et al.*, 1980). The sulphur dioxide (sulphate in Table 11.18) concentration of 7.0 nanomoles/m^3 corre-

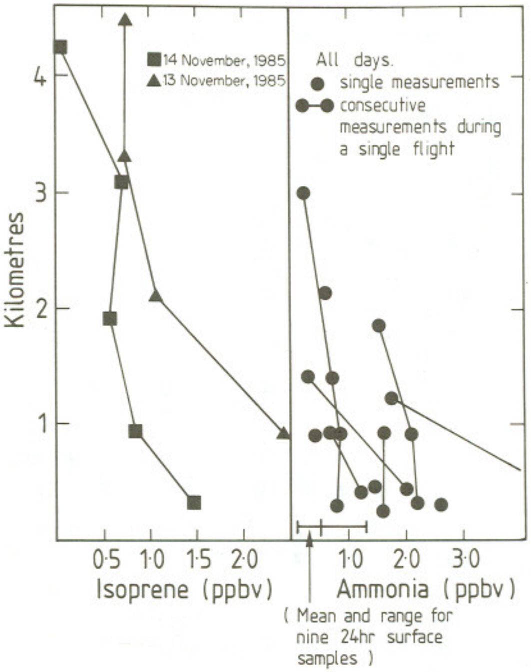

Figure 11.9 (a) Vertical profiles of isoprene; (b) vertical profiles of gaseous ammonia, both obtained during airborne sampling carried out near Jabiru in November 1985

sponds to a concentration of 179 pptv, which is comparable with previous measurements of 112 pptv for continental areas (Maroulis *et al.*, 1980).

One noticeable feature of the data in Table 11.18 is that with the exception of sulphate and chloride, the gas concentrations substantially exceed the corresponding aerosol concentrations. We note that the data presented are preliminary, and while presented so as to stimulate discussion, must be acknowledged as still requiring some verification. However the nitrate concentration in Table 11.18 corresponds to a gaseous nitric acid concentration of 168 pptv, which is consistent with the values found by Huebert and Lazrus (1980) at about the same latitude in the mixed layer over the south Pacific Ocean.

Chloride ions were also easily detected in the aqueous extracts from both the denuder tubes and aerosol filters. The data show that equal concentrations of gaseous hydrochloric acid and chloride aerosol were measured. The source of chloride is probably to a large extent seasalt, which must also contribute some fraction of the sulphate aerosol.

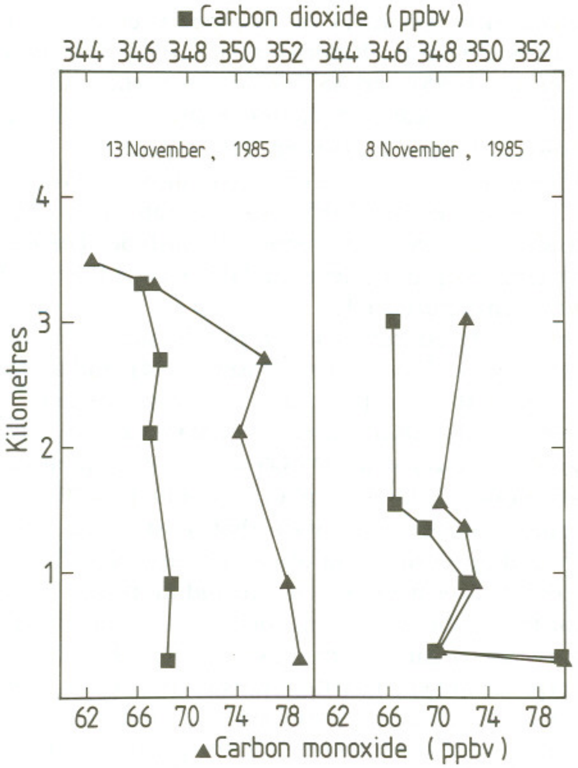

Figure 11.10 Profiles of carbon monoxide and carbon dioxide derived from aircraft flask samples collected near Jabiru in November 1985

Two sets of vertical profiles resulting form hydrocarbon determinations carried out on whole-air samples collected by aircraft in November 1985 are shown in Figure 11.8. In these profiles methane increases and ethane, ethene, ethyne, and propane decrease with altitude. This is consistent with the non-methane hydrocarbons (nmhc) having a ground level source and undergoing destruction at higher altitudes. Methane may be taken up at the surface, or has a source aloft, possibly through inter-hemispheric transport. The concentrations of nmhc closest to the surface in the two profiles are 0.41 and 0.32 ppbv for ethane, 0.21 and 0.11 ppbv for ethene, 0.40 and 0.20 ppbv for ethyne, and 0.17 and 0.03 ppbv, for propane. With the exception of ethyne these concentrations compare favourably with previous measurements in the remote troposphere (Penkett, 1982): ethane 0.24 ppbv, ethene 0.1 ppbv and ethyne 0.02 ppbv (Southern Hemisphere) and propane 0.085 ppbv (Northern Hemisphere).

Isoprene was also determined from the same glass flask samples collected during November 1985. The two vertical profiles corresponding to those in

Figure 11.8 are shown in Figure 11.9a. Isoprene is emitted almost entirely from living plants and forests (Isidorov *et al*., 1985; Brewer *et al*., 1984; Chee-Iiang Gu *et al*., 1985) and so has only a surface source. It is very reactive with hydroxyl radical and therefore the decline in concentration with altitude shown in Figure 11.9a is entirely expected.

Figure 11.10 shows concentrations of carbon dioxide and carbon monoxide measured during November 1985. Both carbon monoxide and carbon dioxide concentrations appear to decrease with altitude. The carbon dioxide concentration at close to ground level at Jabiru varied from about 347 to 349 ppmv as shown in Figure 11.10.

The carbon monoxide concentration near the surface is somewhat enhanced over that found at Cape Grim (Fraser, 1984), and at Samoa (Khalil and Rasmussen, 1983). It seems likely that this enhancement is at least partially a consequence of the photochemical oxidation of isoprene, which the model calculations of Brewer *et al*. (1984) suggest may increase the column burden of carbon monoxide in the tropics by as much as 30%. More important for our purposes is their conclusion that most of the isoprene carbon does not initially end up in the form of carbon monoxide, but rather in the form of oxygenated hydrocarbon species, including peroxy acids.

In tropical Australia, the main contributors to acidity in rainwater and cloud water clearly are organic acids. It seems plausible that isoprene and possibly other terpenes are the initial precursors of organic acids in tropical Australia, although the chemical pathways and mechanisms, like that of Brewer *et al*. (1984) mentioned above, are not proven. Our results suggest that during November 1985, isoprene concentrations were at least as high as the total nmhc concentration. These data are supported by Brewer *et al*. (1984) and Hanst *et al*. (1980) who estimate that 90% of the 1×10^9 tonnes of nmhc emitted annually is of natural origin and furthermore that 35% of this is isoprene. The absolute concentration of isoprene may be higher in tropical Australia than at higher latitudes since temperatures in the tropics are uniformly higher than in southern Australian areas and isoprene emissions are probably correlated with temperature. It seems likely, then, that isoprene emissions in tropical Australia provide a carbon source that can lead to relatively high atmospheric concentrations of organic acids, and ultimately carbon monoxide.

Apart from its high concentration, isoprene can be identified as a plausible acid precursor because it is more reactive with hydroxyl radical than are most other nmhc. For example, at 40 °C, an isoprene concentration of 2.6 ppbv and an hydroxyl radical concentration of 2×10^6 molecules/cm^3 (Crutzen, 1982), isoprene is oxidised at a rate of 1.8×10^{-14} moles/litre/second. Using the same conditions and an appropriate ethane or ethene concentration (Figure 11.8), ethane is oxidized at a rate of 6.0×10^{-18} and ethene at 6.1×10^{-17} moles/litre/second. It should be pointed out that the hydroxyl radical concentration used here is the average for all daylight hours and as such the midday oxidation rates would be higher. This would lead to an isoprene lifetime of something less than one hour in tropical Australian conditions. Only a few hydrocarbons of atmospheric significance react with hydroxyl radical faster than isoprene. One example is limonene, which has a rate constant about double that for isoprene, and although it has been proposed as being of potential importance in one Australian study (Quigley, 1984), nothing is known about emission rates.

11.6 FURTHER DISCUSSION

11.6.1 Groundwater Acidity and Fish Kills

The Magela Creek floodplain near Jabiru is one case in which some effects of the acidification of groundwaters can be observed in the Australian top end. Fish and mussel kills are recorded periodically during the first flush period at the start of the wet season, when the first rains fill pools and channels between the permanent billabongs and the water in these pools and channels first reaches the billabongs. As the wet season progresses the whole area becomes inundated. It reverts back to small, separate billabongs along the dry creek bed only after the wet season ends and the dry season progresses.

A conceptual model proposed by Noller and Cusbert (1985) describes the increase in surface water acidity and mobilization of aluminium associated with fish kills as arising from the presence of an acid-sulphate soil layer at 0.5–1.5 metres below the floodplain soil surface. Table 11.19, taken from Noller and Cusbert (1985), gives details of interstitial water composition through the floodplain soil profile. They suggest that high levels of acidity and labile aluminium (and sulphate, manganese, and other elements) are leached out of the subsoil into the pools and channels that fill at the first rains, and that ensuing rains displace this highly acidic (pH 3.0–4.0) water and slowly flush it downstream into the billabongs. It is at this point that episodic lowering of pH and increase in the concentration of surface water aluminium (and manganese, copper, sulphate etc.) leads to fish mortalities. As more rain falls and the flush proceeds, the surface waters are rapidly diluted and the fish kills cease. Table 11.20, taken from Noller *et al*. (1985), shows an example of the downstream progress of the first flush waters in the Leichardt Billabong during the 1982/83 wet season. Table 11.21, from Brown *et al*. (1983), gives as an example the change in water quality in Ja Ja Billabong during the fish kill of January 1980, in which more than 2300 fish of 10 different species were counted as dead. Other examples and additional information may be found in Bishop (1980), Noller (1983), Morley *et al*. (1983, 1984).

Table 11.19 The composition of interstitial water and leaching of white alluvium by rainwater. (Samples from mid-Magela Creek Floodplain, between Ja Ja and Leichhardt Billabongs; Noller and Cusbert, 1985)

Description	Depth	pH	Aluminium (μg/litre) Total	Aluminium (μg/litre) ($<0.1\mu$m)
1. *Nature of Interstitial Water*				
White alluvium layer (below surface humus layer)	30–40 cm	4.2	64,500	14,400
Base of Jarosite-containing layer	1.0 m	3.5	210,000	210,000
"Old Marine" Layer	2.5 m	7.8	1,100	65
2. *Leaching by Rainwater*				
White alluvium leached with rainwater (on standing for 1 week)	30–40 cm	–	19,500	18,000
Rainwater (mid floodplain)		4.2	3.2	<5

The reason for citing this interesting natural phenomenon is not necessarily to imply a connection between fish deaths and current levels of atmospheric acidity. Rather, it is illustrative; in at least one region of Australia, episodic reduction of groundwater pH to 4.0 or less is clearly associated with increased levels of dissolved aluminium, manganese, and other toxic substances, and the result is mortality of aquatic life. Thus the fish and mussels found in inland waters in tropical Australia show no special

Table 11.20 pH of surface waters at Leichardt Billabong during entry of first flush and main flush (all samples at 0.5 m depth; Noller *et al.*, 1985). Sites 1–4 are respectively 0.11, 0.29, 0.36 and 0.88 km downstream from the point of entry of the flush waters

Date	Site pH 1	2	3	4
6 Feb., 1983	4.3	6.5	6.6	6.6
7 Feb., 1983	4.2	4.8	5.6	6.3
8 Feb., 1983	4.2	4.3	4.3	5.7
23 Feb., 1983	4.0	4.2	4.3	4.3
4 March, 1983	5.6	4.5	4.6	4.5
16 March, 1983	–	–	5.5	5.7

Table 11.21 Water quality data for Ja Ja and Ja Ja extension billabongs during a fish kill, January 1980 (Brown *et al.*, 1983)

Parameter	Units	Ja Ja Billabong				Ja Ja Extension Billabong			
		26 Dec. 1979	3 Jan. 1980	7 Jan. 1980	9 Jan. 1980	26 Dec. 1979	3 Jan. 1980	7 Jan. 1980	9 Jan. 1980
pH		4.4	3.5	3.3	5.4	4.5	3.6	3.6	5.0
Conductivity	μsec/cm	187	324	469	44	164	227	296	49
Turbidity	NTU	180	7.2	2.7	19	175	14	1	19
Sodium	mg/litre	13.4	15.1	15.6	1.5	15.3	15.1	15.6	1.6
Potassium	mg/litre	7.3	8.5	7.2	1.0	8.8	7.1	6.4	0.9
Calcium	mg/litre	2.3	5.8	7.0	0.6	2.7	5.3	5.0	0.8
Magnesium	mg/litre	1.9	6.6	10.1	11.0	2.5	5.4	6.8	1.4
Iron (filtered)	mg/litre	0.10	0.64	0.95	0.10	0.15	0.94	0.52	0.11
(unfiltered)	mg/litre	6.80	0.75	1.30	0.30	6.20	1.06	0.53	0.28
Manganese	mg/litre	0.116	0.610	0.840	0.040	0.150	0.500	0.550	0.110
Copper	μg/litre	0.8	ND	1.1	<0.1	1.2	ND	0.9	<0.1
Zinc	μg/litre	11.5	ND	27.6	2.1	9.9	ND	19.0	1.4
Cadmium	μg/litre	<0.1	ND	0.1	<0.1	<0.1	ND	0.2	<0.1
Lead	μg/litre	<0.2	ND	0.2	<0.2	0.3	ND	0.2	<0.2
Nickel	μg/litre	3.1	ND	24.5	<0.2	2.9	ND	12.2	<0.2
Chromium	μg/litre	4.0	ND	1.7	<0.2	2.0	ND	0.8	<0.2
Aluminium	μg/litre	30	ND	500	17*	24	68	98	ND
Sulphate	mg/litre	18.5	85	122	7	18.9	60	55	8.2
Chloride	mg/litre	22.3	23.6	23.3	4.5	25.6	23.5	22.7	3.7
Bicarbonate	mg/litre	0	0	0	1.59	0	0	0	0
Nitrate	mg/litre	0.60	ND	0.28	0.15	0.10	ND	0.55	0.12
Phosphate	mg/litre	0.006	ND	0.005	0.007	0.005	ND	0.008	0.007

ND = not determined *12 January 1981 value.

adaptation to acidic conditions, and we may hypothesize that ecological consequences of the types found in some groundwaters in Europe and the northeastern United States would arise in the Australian top end if acidic deposition were to increase significantly.

11.6.2 Buffering of Cloud Water and Rainwater by Organic Acids

The fact that the acidity of cloud water and rainwater in the NT has been found to be high and contributed mostly by weak organic acids raises the possibility that these aqueous phases might be somewhat buffered against a decrease in pH if increased tropical emissions of sulphur dioxide and nitrogen oxides lead to increased atmospheric levels of sulphuric and nitric acids. We have calculated buffer intensities (Stumm and Morgan, 1970) with respect to the organic acids from the mean cloud-water data in Table 11.18 and the 1984/85 rainwater data for Jabiru in Table 11.15. Results are 412 micromoles/litre/pH unit for the cloud water and 138 micromoles/litre/pH unit for the rainwater. These figures suggest that the additional strong acidity required to result in a decrease of 0.05 pH would be 20.6 micromoles/litre for the cloud-water example and 6.9 micromoles/litre for the rainwater example. These figures compare with values of 18.9 and 6.2 micromoles/litre if the cloud water and rainwater were unbuffered. The differences between the buffered and unbuffered cases are sufficiently small for us to conclude that they would only have a minor mitigating effect on decrease in pH if nitric and sulphuric acid concentrations are increased to levels found in Europe or the northeastern United States, for example.

11.6.3 Effects of Temperature and pH

Other differences between the chemical properties of tropical Australian clouds compared with their more commonly studied midlatitude equivalents can be hypothesized to result from systematic differences in atmospheric temperature and aqueous phase acidity between the tropics and midlatitudes. For example, the mean cloud water pH of 3.81 found recently near Katherine and Jabiru (Table 11.18) is at least 1 pH unit lower than typical values reported in a study at midlatitudes by Scott (1978). A number of consequences follow: one is that the solubility of sulphur(IV) (sulphur dioxide plus bisulphate ion) species is considerably lower at the tropical pH. Calculations employing the formulation of Hales and Sutter (1973) with a gaseous sulphur dioxide concentration of 7.0 nanomoles/litre (Table 11.18), and cloud-water pH values of 3.81 (Table 11.16) and 4.81 (representing a midlatitude cloud) yield total dissolved sulphur(IV) concentrations of 84 nanomoles/litre for the tropical case and 736 nanomoles/litre for the higher pH at 0 °C. This order of magnitude difference in solubility could significantly alter the sulphur dioxide scavenging rate from that found at midlatitudes (a similar order of magnitude difference results if the calculation is performed for a Jabiru rainwater pH of 4.29 and a hypothetical midlatitude value 1 pH unit higher).

Another example is provided by the oxidation of aqueous-phase sulphur dioxide by ozone which may be an important sulphate production pathway under some conditions at midlatitudes. However it may be insignificant at the lower tropical cloud-water pH, since the rate expression goes as the inverse root of hydrogen ion concentration (Penkett *et al*., 1979). In addition the rate is proportional to bisulfite ion concentration, which decreases with an increase in hydrogen ion concentration.

The temperature difference between warm tropical and colder midlatitude clouds may also have significant effects. During recent airborne work near Jabiru, cloud base temperatures were as high as 18 °C when surface temperatures ranged up to 44 °C. From available solubility data (Hales and Sutter, 1973; Martin and Damschen, 1981; Battino *et al*., 1983) it is clear that on going from a cold cloud at 0 °C to a tropical cloud at 18 °C, the solubilities of sulphur dioxide, hydrogen peroxide, and ozone would decrease by factors of 3, 5, and 3 respectively.

These examples are certainly not exhaustive, but they do serve to illustrate the point that the processes of acid production (probably also of transport and deposition) in the tropical atmosphere need to be viewed firmly within the context of tropical conditions. An uncritical application of knowledge learned from mid- and high-latitude studies without modification for tropical conditions may lead to significant errors in interpretion and prediction. Clearly it will be very important in studying tropical atmospheric chemistry to support theoretical studies with carefully planned observational programmes in which the tropical conditions encountered are accurately documented.

11.6.4 Future Industrialization

Tropical Australia is not a region currently experiencing rapid growth in industrial, urban, or agricultural activities. Inspection of power generation statistics for each of the WA, NT, and QLD electricity generation authorities underlines this fact: power consumption has been growing at a few per cent per year for the past five years, and this is the typically predicted growth rate in the near future. With this sort of growth rate also likely for urban activities (motor vehicle emissions, etc.), the figures in Tables 11.11 and 11.13 lead to the conclusion that widespread acidification as a result of urban/industrial activities is unlikely in tropical Australia in the near future. No other large industrial projects likely to affect atmospheric acidity are known to us, with the possible exception of the northwest shelf gas project. However most of the gas produced is expected to be exported from the area, so at this stage this project is probably not of concern. The other dominant source of acid precursor, Mt. Isa, has held a relatively constant output over the past decade and is unlikely to significantly increase output with time.

11.6.5 Unanswered Questions/Gaps in Understanding

1. A comprehensive, observational data base is required for tropical Australia. We need data on the spatial and temporal distribution of rainwater composition, cloud-water composition, and acid precursor concentrations. The distribution of acids between the aqueous, gas, and aerosol phases, and the existence of as yet unidentified organic mono- and diacids need to be determined. The vertical profiles of hydrocarbons and acid gases and their precursors are also important. More complete data on soil and water properties relevant to acidification are required. Meteorological data relevant to vertical and horizontal transport are needed. The role played by convective cloud transport needs to be assessed.
2. Important chemical pathways need to be identified, particularly those relevant to acid production. For example, what is the relative importance of ozone and hydrogen peroxide for aqueous-phase oxidation of sulphur dioxide and other precursors? How important are homogeneous gas-phase processes? What are the pathways that lead to the observed high levels of organic acidity (are there direct emissions of organic acids; are aldehyde emissions important; is isoprene a major precursor and what are the important conversion processes)?
3. Better estimates of the source strengths of the major atmospheric sulphur and nitrogen sources are needed. In particular the emissions of sulphur and nitrogen from soils, vegetation and animal wastes are virtually unquantifiable at present. Bushfires may potentially be a large source of ammonia but this cannot be quantified due to a complete lack of appropriate data.
4. Better estimates of the rates of wet and dry deposition, currently based on rather small data sets and large numbers of assumptions, are needed.
5. The largest gap in current budget calculations is the complete lack of information on advective inputs to and outputs from the atmosphere over tropical Australia.

11.7 CONCLUSION

Rainwater at several sites in tropical Australia is unusually acidic, with individual rainfall events having pH values down to 3.5. However this acidity is contributed mostly by organic acids, probably of natural origin. The low levels of nitrate and sulphate in rainwater point to only minor anthropogenic contributions to rainwater acidity. This conclusion is supported by estimates of emission rates from the major natural and anthropogenic sources of atmospheric sulphur and nitrogen over northern Australia.

Soils and surface waters appear as if in general they would be only moderately susceptible to acidification by any future atmospheric acidic deposition. In fact some areas could be characterized as well buffered against acidification, although there are also some areas in which the soils and surface waters are extremely poorly buffered, for example on the Arnhem Land escarpment near Jabiru. There is some evidence from these areas to suggest that aquatic life forms in tropical Australia are not especially adapted to cope with the consequences of groundwater acidification.

In the foreseeable future, industrial growth is unlikely to significantly alter the picture sketched so far; thus acidic deposition as a result of anthropogenic activities need not be seen as a current threat to the environment of tropical Australia. However we must emphasize that this conclusion is preliminary, and tentative to the extent that certain gaps in our knowledge exist, and open questions of considerable relevance could not be answered within the limitations of the currently available data. Most importantly we have no detailed knowledge of the toxicology of Australian flora and fauna with respect to acidification, nor a good knowledge of the distribution and total area of poorly buffered soils.

The qualifications attached to our conclusions are only to be expected, since prior to this workshop, acidification in tropical regions has not been a subject receiving systematic attention from the scientific community. Indeed there is a dearth of "tropical" information in many scientific disciplines, so there is special value in the compilation of the initial case studies on acidification in tropical countries. Our own Australian study highlights the importance of this exercise, since (a) large sources of atmospheric acidity were identified; (b) current instances of acidification (not necessarily of anthropogenic origin) also were identified, along with some poorly-buffered sensitive areas; and (c) the inadequacy of available information for the purposes of this work was made clear, as was the lack of scientific understanding about important physical/chemical/biological processes.

This and the other case studies thus provide a much-needed compendium of hitherto unavailable or widely scattered data, and a framework within which to begin filling in the many gaps identified in both data and scientific understanding. There can be no doubt that these gaps merit attention, since we do have enough evidence to conclude that tropical regions have no special immunity from the increases in atmospheric acidity that continued industrialization brings. The important thing now is to continue to develop scientific understanding before the industrial development of tropical regions progresses too far in the absence of adequate knowledge concerning potential effects upon the tropical environment.

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