Chemistry of Precipitation From a Remote, Terrestrial Site in Australia

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Wet-only rain samples were collected and chemically analyzed during 1980–1984 at Katherine, Australia, as part of the Global Precipitation Chemistry Project. Rainfall averaged 104 cm/yr and ranged from 74.6 cm in 1982–1983 to 135.7 cm in 1983–1984. Total cation concentration was about 29 μeq/L. The volume-weighted mean H^+ concentration expressed as pH was 4.73, 64% of the free acidity was due to organic acids (formic and acetic). The pH due to strong mineral acids only was 5.08. Air mass trajectories during the wet season were predominantly from the northeast (51%), and this trajectory was most important in terms of deposition. Although there is a high frequency of lightning during the wet season, no evidence was found that it contributed significantly to the nitrate concentration in rain. Because concentrations decreased markedly with amount of precipitation, the total deposition of dissolved substances was not correlated directly with the amount of rain. Comparisons were made between the chemistry of rain at Katherine and with other remote areas and with the eastern United States.

INTRODUCTION

There are relatively few data on the chemistry of precipitation in remote, continental sites, particularly in the southern hemisphere [e.g., *Hutton and Leslie*, 1958; *Visser*, 1961; *Wetselaar and Hutton*, 1963; *Probert*, 1976; *Westman*, 1978; *Lewis*, 1981; *Galloway et al.*, 1982, 1985; *Kellman et al.* 1982; *Hutton* 1983; *Keene et al.*, 1983; *Keene and Galloway*, 1984b; *Hendry et al.*, 1984; *Noller et al.*, 1984, 1985a, b; *Ayers and Gillett*, 1987]. However, such data offer large potential for clarifying the effects of urban, industrial, and agricultural emissions on the chemistry of precipitation, as well as for understanding the processes that control the chemical composition of the atmosphere in remote regions. There currently is much interest in such questions because of the political and economic ramifications of air pollution in the northern hemisphere [e.g., *Galloway et al.*, 1984].

As part of the Global Precipitation Chemistry Project (GPCP), data have been collected and analyzed since 1979 at various sites to determine what biogeochemical factors regulate the chemical composition of precipitation in continental and marine areas remote from industrial and agricultural influences [*Galloway et al.*, 1982]. The study is designed to evaluate the background or natural composition of rain and snow and to infer what precipitation chemistry may have been like in the North Temperate Zone prior to major influences from fossil-fuel combustion. Currently, precipitation is being collected as a part of the GPCP at Amsterdam Island in the South Indian Ocean; Torres del Paine, Chile; Cape Point and Kruger Park, South Africa; Katherine, Australia; Mauna Loa, Hawaii; and on ships of opportunity in the Atlantic and Pacific Oceans. Previously, samples were collected under the GPCP at Poker Flat Research Range, Alaska; St. George's Biological Station, Bermuda; and San Carlos de Rio Negro, Venezuela.

Because of the length of record and other characteristics, the marine site on Amsterdam Island [*Galloway and Gaudry*,

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1984] and the continental site at Katherine, Australia, have become particularly informative locations within the GPCP. This paper will report on data from the Katherine site during 1980 through 1984, will relate these data to air mass trajectories, and will compare them to data from other remote areas.

STUDY SITE AND COLLECTION PROCEDURES

The Katherine site is located in northern Australia, about 275 km southeast of Darwin, at a research station operated by the Commonwealth Scientific and Industrial Organisation (CSIRO) Division of Tropical Crops and Pastures. The site is at 14°28'S, 132°18'E, is at an elevation of 108 m, and is surrounded by tropical savannah, including scattered eucalyptus trees and numerous ant and termite mounds.

Annual precipitation at Katherine averaged about 104 cm during the period of our study, with a distinct wet (November through April) and dry (May through October) season. The dry season of this monsoonal climate is characterized by southeasterly trade winds, whereas in the wet season, particularly during January and February, north-northwesterly equatorial winds predominate [*Gentilli*, 1971].

There is extensive burning of the savannah vegetation in the Katherine area each year during the dry season. Fires are started naturally (e.g., by lightning), by aborigines (see, for example, *Haynes*[1985]), and for agricultural purposes. The Australian monsoon is accompanied by a high frequency of lightning flashes, and fires started in this way are usually allowed to burn themselves out [*Ayers and Gillett*, 1987]. However, little burning occurs during the wet season (see also, *Wetselaar and Hutton* [1963]). According to the Brush and Fire Council in Katherine, approximately 70% of the area is burned each year.

The general protocol for sample collection and analysis is given by *Galloway et al.* [1982]. Procedures for collection and analysis of organic acids are given by *Keene et al.* [1983]. Volume-weighted mean (VWM) values for inorganic constituents are calculated according to *Galloway et al.* [1984] and those for organic constituents are calculated according to *Keene and Galloway* [1984a]. Volume-weighted mean pH or arithmetic mean pH refer to volume-weighted or arithmetic mean H^+ concentration expressed as pH. Samples of precipitation were collected on an event basis with an Aerochem Metrics, automatic wet-only collector, using clean, acidwashed polyethylene containers. When a sample was collected, the pH was measured immediately by the technician at the

site. If sufficient volume remained, the sample was divided into two 250-ml aliquots. Chloroform was added to one aliquot to prevent biological activity and the other aliquot was untreated. Both aliquots were shipped to our laboratory at the University of Virginia in Charlottesville for detailed chemical analysis.

RESULTS

Amount of Precipitation

The amount of precipitation at the Katherine site is measured by personnel of the CSIRO Katherine Research Station using a standard Australian National Rain Gauge and a standard Weather Measure Rain Gauge. An average of 104.4 ± 12.8 cm of rain fell during the wet season of each year for the period 1980–1984. However, there were large differences between the years: 97.1 cm in 1980–1981; 110.4 cm in 1981–1982; 74.6 cm in 1982–1983, the driest year; and 135.7 cm in 1983–1984, the wettest year (Table 1). There also were major differences in average monthly precipitation during the wet seasons (Figure 1). No rain was recorded during September and October of 1982 and only 53.2 mm was measured in January 1983. These extremely low amounts were due to the worldwide influence of a very strong El Niño phenomenon which occurred during this period [*Rasmusson and Wallace*, 1983]. September, October, and April had markedly less rainfall than during the remainder of the wet season (Figure 1). There was no statistically significant difference in amount of average monthly rainfall between December, January, February, and March, although the mean value for January was the highest during the year. Some 470 mm of rain were measured during January 1984 of the wet year of 1983–1984; 133 mm of rain fell on January 1, 1984. The amount of rainfall in November was intermediate between the onset months of the wet season (September and October) and the wetter months.

Data Base

The total number of precipitation samples collected at Katherine and chemically analyzed is given in Table 2. Two hundred and twenty-seven samples had sufficient volume for measurement of pH at the field site. Because aliquots of samples not treated with a biocide were chemically unstable, subsequent evaluations concentrate primarily on data generated from the treated aliquots. Of the 181 treated aliquots analyzed chemically at the University of Virginia, precipitation gauge readings were recorded for 178. Of these, 158 aliquots had

TABLE 1. Precipitation at the Katherine Station During the Wet Seasons of 1980–1981 Through 1983–1984

	1980–1981	1981–1982	1982–1983	1983–1984	$\bar{x} \pm s_{\bar{x}}$
Sept.	0	43.2	0	9.4	13.1 ± 10.3
Oct.	1.6	36.0	0	49.0	21.6 ± 12.3
Nov.	111.6	151.0	47.8	119.8	107.6 ± 21.6
Dec.	183.0	139.6	277.0	134.6	183.5 ± 33.0
Jan.	380.1	208.0	53.2	470.0	277.8 ± 92.5
Feb.	269.8	288.5	145.1	157.6	215.2 ± 37.2
March	24.8	237.4	147.8	416.4	206.6 ± 82.4
April	0	0.2	75.4	0	18.9 ± 18.8
Total	970.9	1103.9	746.3	1356.8	1044 ± 127.6

All precipitation is stated in millimeters; precipitation measured 132.6 mm on January 1, 1984; 12.0 mm in May 1980; no rain after March 13, 1981; 2.6 mm in May 1981 and 12.8 mm in June 1981; 0.2 mm on April 18, 1982; 90 mm on November 18, 1980. There were two events in October 1980.
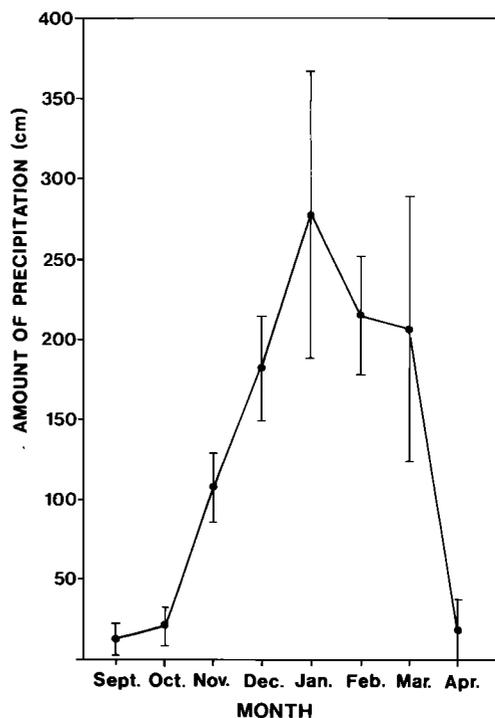

Fig. 1. Average monthly amounts (in centimeters and standard error bars for precipitation at Katherine, Australia, during 1980–1984.

sufficient volume for analysis of all major inorganic chemical constituents while organic anions were measured in a subset of 107 aliquots. Relationships between the loss of free acidity in untreated aliquots ($\Delta H^+ = H_{field}^+ - H_{lab}^+$) and the corresponding measured concentrations of dissociated organic anions ($\Sigma RCOO^-$) in treated aliquots allowed us to estimate the concentrations of dissociated organic anions for the 51 samples in which these compounds were not measured directly [*Keene et al.*, 1983]. Specifically, $\Sigma RCOO^-$ was plotted against ΔH^+ for all samples with sufficient data (Figure 2). Because it provides the best representation of the linear relationship between two independent random variables that are subject to measurement error, the technique of reduced major axis was used to calculate the slope and intercept parameters [*Miller and Kahn*, 1962; *Sokal and Rohlf*, 1981; *Hirsch and Gilroy*, 1984]. Dissociated organic anions ($\Sigma RCOO^- = HCOO^- + CH_3COO^-$) were estimated from the resulting regression,

$$\Sigma RCOO^- = (1.04 \times \Delta H^+) + 2.82 \tag{1}$$

and were included in the ion-balance calculations for subsequent quality control determinations. The standard error of the slope was ±0.02 and that of the intercept was ±0.34.

The data base was then evaluated to exclude samples with probable analytical errors. Initially, of the 158 treated samples, 29 samples had ion imbalances exceeding ±5 µeq/L or ±25%. Because unmeasured acids appear to be important sources of acidity in precipitation at Katherine [*Keene et al.*, 1983], additional tests were required to further evaluate those questionable samples. Following the procedures of *Keene et al.* [1983], total acidities were titrated in 10 of the 29 samples. To identify unmeasured anions, measured total acidities (TA_m) were compared with total acidities (TA_c) calculated from all other measured chemical constituents in the treated aliquots. The equilibrium concentrations of NH_3 and NH_4^+ at the end of the

Description of Sample	Number
Collections and field analyses	
A1. Total number of collections	232
A2. Samples with sufficient volume for field pH	227
A3. Number of A2 with gauge readings	224
Untreated aliquots received at University of Virginia	
B1. Total number of aliquots received (for small-volume events corresponding to samples K1 through K171, only untreated aliquots were sent to the University of Virginia)	194
B2. Number of B1 with gauge readings	192
B3. Number of B2 with complete inorganic analyses (as of sample K182, complete analysis of untreated aliquots was discontinued)	142
Treated aliquots received at University of Virginia	
C1. Total number of aliquots received (for small-volume events corresponding to samples K172 through K227, only treated aliquots were sent to the University of Virginia)	181
C2. Number of C1 with gauge readings	178
C3. Number of C2 with complete inorganic analyses	158
C4. Number of C2 with complete organic and inorganic analyses (K76 through K227)	107
C5. Number of C2 with dissociated organic anions estimated from ΔH^+ (K1 through K75)	51
C6. Number of C2 with total acidities titrated (K76 through K119)	37
Quality Assurance Evaluation	
D1. Number of C3 with ion imbalances greater than $\pm 5\ \mu eq/L$ or $\pm 25\%$ (includes C5 estimates)	29
D2. Number of D1 with differences between the anion deficit and a ΔTA (measured total acidity – calculated total acidity) less than 5 $\mu eq/L$ (this indicates unmeasured anions)	10
D3. Number of D1 with differences between anion deficits in treated and untreated aliquots less than 5 $\mu eq/L$ (total acidities were not measured in these samples but the presence of a residual, nonbiologically active anion deficit in both aliquots suggest unmeasured anions)	8
D4. Removed from data base C3	11
Summary Data Set	
E1. Total number of field pH measurements with gauge readings	224
E2. Total number of treated aliquots with gauge readings (excluding D4)	167
E3. Total number of E2 with complete inorganic analyses	147
E4. Total number of E2 with complete organic and inorganic analyses (K76 through K227)	101
E5. Total number of E2 with dissociated organic anions estimated from ΔH^+ (K1 through K75)	46

titrations were calculated from the initial concentrations of NH_4^+ measured in the samples, the equilibrium pK_a of 9.25 [*Butler*, 1964], and the end point pH of 9.00, using the relationship of *Keene and Galloway* [1984a].

$$TA_c = (\Sigma E_{org} + \Sigma A_{inorg} + NH_3) - (\Sigma C_{base} + NH_4^+) \quad (2)$$

where

$$\Sigma A_{org} = HCOO_{total} + CH_3COO_{total}$$

$$\Sigma A_{inorg} = SO_4^= + NO_3^- + Cl^-$$

$$\Sigma C_{base} = Ca^{++} + Mg^{++} + Na^+ + K^+$$

and NH_3 and NH_4^+ are equal to the total dissociated and

total undissociated amounts at end of titration (pH 9.00), respectively.

$$\Delta TA = TA_m - TA_c \quad (3)$$

If all major chemical constituents had been accurately measured, ΔTA would equal 0, whereas positive ΔTA would indicate the presence of unmeasured anions. The value of ΔTA was then compared with the anion deficits (Σcations – Σ anions) in treated and untreated aliquots for these 10 samples (Table 3). In all 10 cases, ΔTA was positive and within $\pm 3\ \mu eq/L$ of anion deficits in treated aliquots. These data suggest that ion imbalances for the 10 samples resulted from unmeasured anions rather than random analytical errors, and therefore these samples were retained in the data base. Systematic bias also could have accounted for these relationships, although quality control evaluations indicated that such errors were unimportant [*Galloway et al.*, 1982].

Total acidities were not titrated in the remaining 19 questionable samples. However, a comparison between treated and untreated aliquots in Table 3 revealed that for eight out of the 10 samples, differences between corresponding anion deficits were within $\pm 5\ \mu eq/L$. These relationships support the speculation that the unmeasured acids were resistant to biological transformation, and also provide an indirect, but admittedly somewhat imprecise, method for differentiating random analytical errors from actual unmeasured anions in the remaining 19 aliquots. For eight of these 19 samples, anion deficits in treated and untreated aliquots were within $\pm 5\ \mu eq/L$ and, based on the previous discussion, we believe that these relationships indicate the presence of unmeasured anions. These eight samples were therefore retained in the data base, while the remaining 11 samples were removed. The numbers of samples comprising the final data base evaluated in this paper are summarized in Table 2.

We realize that some of the decisions regarding data quality may seem somewhat arbitrary. These data, however, do suggest that unmeasured anions are important chemical constituents of some samples, and as such, ion balances cannot be considered as absolute quality control criteria. In our opinion this protocol represents a reasonable compromise between the retention of samples with accurate, though incompletely characterized, compositions and the removal of those which exhibit probable analytical errors.

Copies of the raw data are available upon request from the authors.

Precipitation Chemistry

The 147 samples with complete inorganic chemical analyses represent 71% of the total rainfall during the period (74% during 1980–1981; 75% during 1981–1982; 81% during 1982–1983 and 61% during 1983–1984). Yearly averages are computed from July through June to include the complete wet season. The chemical composition of precipitation at Katherine is given in Table 4a, for all chloroform-treated aliquots ($N = 167$); Table 4b, for treated aliquots with complete inorganic analyses ($N = 147$); and Table 4c for all samples with complete analyses for both organic and inorganic constituents ($N = 101$).

Electrical conductivity of rain at Katherine ranged from 2.4 to 32 $\mu S/cm$. Hydrogen ion was the dominant cation and formate was the dominant anion in precipitation. Chloride was the dominant inorganic anion. Annual VWM concentrations varied from year to year for the various ions
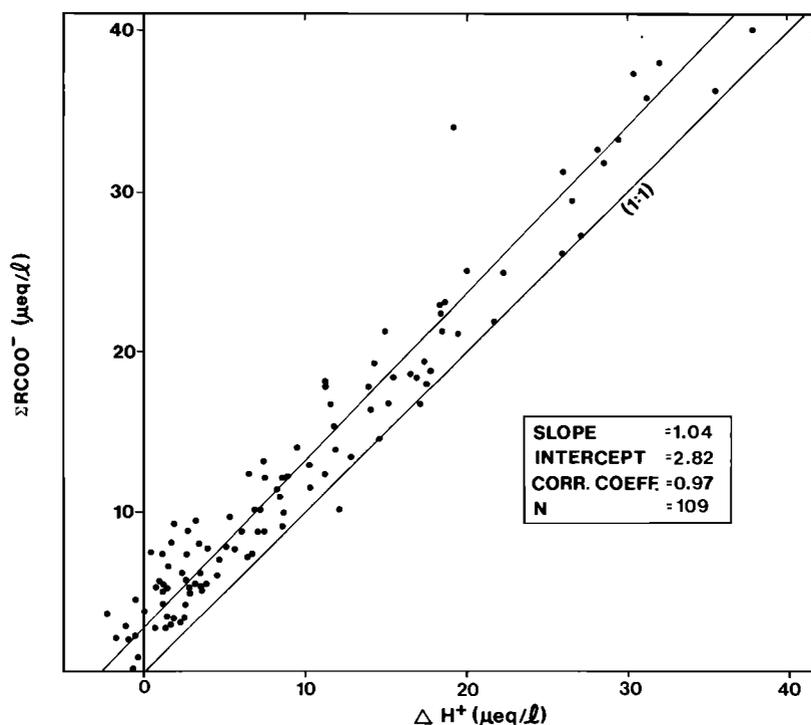
Fig. 2. The relationship between the $\Sigma RCOO^-$ ($HCOO^- + CH_3COO^-$) and $\Delta H^+(H_{field}{}^+ - H_{lab}{}^+)$ in all samples with sufficient data.

(Figure 3), but in general they were lower during the wet year (1983–1984) and higher during the dry year (1982–1983). When plotted as a function of the amount of annual precipitation, VWM concentrations for all constituents exhibited a decreasing trend (Figure 4), suggesting that dilution might be an important factor controlling the ionic strength of precipitation at Katherine. Variability in these trends indicates, however, that other factors such as variations in source areas and source strengths also must be important. For example, the number of air mass trajectories from the NW sector for a given period increased directly with the amount of rainfall; there were three NW cases in 1982–1983 when the rainfall amount was the lowest, and 15 cases in 1983–1984 when the rainfall amount was the highest (see Table 1).

The various ions can be grouped roughly into four different

TABLE 3. Comparisons Among Anion Deficits in Treated Aliquots, Anion Deficits in Untreated Aliquots, and Differences Between Measured and Calculated Total Acidities in Treated Aliquots of Precipitation Collected at Katherine, Australia

| | Anion Deficits | | Δ Total Acidity |
Sample	Untreated	Treated	(Measured − Calculated)
K85-C	15.2	17.6	20.3
K86-C	5.0	5.6	5.0
K99-C	10.7	5.2	5.4
K101-C	6.8	11.8	14.1
K106-C	9.8	6.4	4.8
K107-C	9.8	5.4	3.4
K112-C	8.2	8.8	8.7
K113-C	5.6	9.8	9.3
K114-C	13.4	5.0	7.0
K119-C	5.5	8.4	9.3

All values are given in microequivalents per liter.

patterns (see Figure 4, although groupings there are done according to different scales of VWM concentration for clarity of presentation).

1. The VWM concentration of nitrate showed a strikingly linear, inverse relationship with amount of precipitation.

2. VWM concentrations of H^+ and $NH_4{}^+$ showed a more variable, inverse relationship with amount of precipitation.

3. Formate, acetate, and K^+ had generally decreasing VWM concentration with increased amount of precipitation.

4. The base cations Ca^{++}, Mg^{++} and Na^+, and the anions $SO_4{}^=$ and Cl^- had the highest VWM concentrations during 1980–1981 (not the driest year).

Soil particles are likely sources for portions of these constituents; during 1980–1981 the air mass trajectories coming from the SE were 39 (1982–1983) to 130% (1981–1982 and 1983–1984) more common than in the other three years. This increase in flow from the interior of the continent may have increased the crustal component in the atmosphere, leading to higher concentrations of associated ions in precipitation during 1980–1981. This speculation is consistent with the lower VWM concentrations of hydrogen ion measured during 1980–1981 (Figure 4). Carbonate from increased soil dust could have neutralized a portion of the acidity resulting in the observed inverse trend.

Organic ions dominated the anions in all years, although chloride was approximately the same concentration as organic ions in 1980–1981. The nitrate VWM exceeded the sulfate VWM in 2 of the 4 years (Figure 3).

The average pH of rain at Katherine during 1980–1984 was 4.73 (lab value). A maximum of 64% of this free acidity was contributed by organic acids (Table 4b). The volume-weighted field pH for the entire data set ($N = 224$) during 1980–1984 was 4.76. The frequency of all field pH values collected at Katherine during 1980–1984 is shown in Figure 5. The pH values were normally distributed, with 62% of the samples

TABLE 4a. Volume-Weighted Means, Minimums, and Maximums for all Chloroform-Treated Aliquots of Precipitation from Katherine, Australia, During 1980–1984

	H^+ (Field)	H^+ (Lab)	Ca^{++}	Mg^{++}	Na^+	K^+	NH_4^+	NO_3^-	$SO_4^=$	Cl^-	$HCOO_T$ [$HCOOH_{aq} + HCOO^-$]	CH_3COO_T [$CH_3COOH_{aq} + CH_3COO^-$]
VWM	16.9	18.4	1.9	1.4	4.5	1.1	2.9	4.1	4.0	8.0	10.5	4.2
Minimum	2.5	3.8	<2	<0.3	<0.4	<0.5	0.2	<0.3	<0.4	0.6	0.2	0.2
Maximum	60.3	72.4	54.1	47.9	64.9	220	31.8	25.1	24.6	180	50.2	15.8
n	167	166	155	155	155	155	157	156	159	152	114	114

All values are given in microequivalents per liter.

between pH 4.25 and 5.25. Some 25% of the samples had a pH between 4.50 and 4.75. One sample, collected on November 18–19, 1982, had a field pH of 3.88 and a laboratory pH for an untreated aliquot of 4.01. There was only 1.3 mm of precipitation in this sample, and no other chemical analyses were done. G. Ayers (unpublished data, 1986) measured a pH of 3.74 on November 13–14, 1985, in Katherine for a 3.1 mm rain event. In general, the low pH values measured at Katherine were correlated with very small amounts of rain (few tenths of a cm, Figure 6).

Organic acids (mostly formic and acetic) were the major source of free acidity in most samples. On an annual basis they constituted 68% of the free acidity in 1980–1981, 57% in 1981–1982, 74% in 1982–1983, and 60% in 1983–1984. Concentrations of organic acids were generally greater during the early part (September through November) of the wet season and were markedly lower during the latter part (January through March) of the wet season (Figure 7) when amounts of precipitation were greater (Figure 1). Organic acids contributed some 93% of the measured acidity in one sample collected in April 1983.

In an airborne study done in November 1985, G. Ayers (unpublished data, 1986) and colleagues collected more than 30 samples of cloud water near Katherine with an arithmetic mean pH of 3.81. Concentrations of formate and acetate in these samples "... were commensurately high."

Our analysis identified two classes of unmeasured chemical constituents which influence the acidity of precipitation at Katherine. Anion deficits for the 101 samples in this study, which were analyzed for all major identified organic and inorganic chemical constituents (Table 4c), indicate that unmeasured acids contributed a maximum of 16% (2.7 μeq/L) of the free acidity measured in treated aliquots in our laboratory in Charlottesville. These more recent results are consistent with previous observations by Keene et al. [1983] and support the hypothesis that as yet unidentified acids may be important sources of acidity in precipitation at Katherine. Possible unmeasured proton donors include pyruvic acid [Andreae et al., 1987], propionic acid [Chapman et al., 1986], oxalic acid [Norton et al., 1983], and methane-sulfonic acid [Andreae and Andreae, 1987].

A second class of unmeasured species was deduced from observed changes in chemical composition during shipment to the analytical laboratory in Virginia. The free acidities of treated aliquots consistently increased between measurement at the field site and at the analytical laboratory. On a volume-weighted basis, laboratory H^+ was 1.4 μeq/L greater than field measurements for the 147 treated aliquots (Table 4b). Field blanks and laboratory blanks stored in sample bottles showed no corresponding changes in free acidity, indicating that contamination of samples during shipping and storage did not result in biased measurements at the analytical laboratory. Field measurements were verified with blind audit solutions of dilute acid that were periodically sent to the site operator. Results showed no significant measurement bias. When normalized for the loss of free acidity associated with microbial transformation of organic acids in untreated aliquots, increases in free acidity also were evident in these aliquots (Figure 2). If the disappearance of organic acids were the only process changing H^+ concentrations, the regression of $\Sigma RCOO^-$ versus ΔH^+ would have a slope of 1.0 and an intercept of 0.0. At 95% confidence the slope of 1.04 is not significantly different from 1.0, but the intercept 2.82 is significantly different from 0.0. Because this effect is evident in both treated and untreated aliquots, we speculate that the reaction is not associated with biological activity. One possible mechanism which could explain this observation is the oxidation of bisulfite to sulfate (e.g., see Dana [1980]; Jacob [1986]) as follows:

$$HSO_3^- + H_2O_2 + H^+ \rightarrow SO_4^= + 2H^+ + H_2O \qquad (4)$$

We have no experimental evidence with which to test this speculation, and other reactions are therefore possible. This effect is another as yet unexplained aspect concerning the chemistry of precipitation at the Katherine site.

Deposition

The deposition of dissolved substances in rainfall is the product of the concentration times the amount of rainfall. On a mass basis, deposition of chloride and sodium exceeded all other dissolved substances in rainfall (Table 5). In addition,

TABLE 4b. Volume-Weighted Means, Minimums, and Maximums for 147 Chloroform-Treated Samples of Precipitation With Complete Inorganic Analyses From Katherine, Australia, During 1980–1984

	H^+ (Field)	H^+ (Lab)	Ca^{++}	Mg^{++}	Na^+	K^+	NH_4^+	NO_3^-	$SO_4^=$	Cl^-	Dissociated Organic Anions (101 Measured + 46 Estimated)
VWM	16.9	18.3	1.7	1.3	4.3	0.9	2.9	4.0	3.9	7.7	11.8
Minimum	2.5	3.8	<2	<0.3	<0.4	<0.5	0.2	<0.3	<0.4	0.6	0.2
Maximum	60.3	72.4	50.3	15.4	64.9	60.3	28.5	25.1	24.6	84.9	47.7

All values are in microequivalents per liter. Total precipitation represented: 297.8 cm; sum of cations = 29.4 μeq/L; sum of anions = 27.4 μeq/L.

TABLE 4c. Volume-Weighted Means, Minimums, and Maximums for 101 Samples of Precipitation With Complete Inorganic and Complete Organic Analyses From Katherine, Australia, During 1980–1984

	H^+ (Field)	H^+ (Lab)	Ca^{++}	Mg^{++}	Na^+	K^+	NH_4^+	NO_3^-	$SO_4^=$	Cl^-	$HCOO^-$	$HCOO_{total}$	CH_3COO^-	CH_3COO_{total}
VWM	15.5	17.1	1.5	1.0	3.3	0.8	2.8	3.6	3.0	6.1	9.6	10.5	2.1	4.2
Minimum	2.5	3.8	<2	<0.3	<0.4	<0.5	0.2	<0.3	0.4	0.6	0.2	0.2	0.1	0.2
Maximum	53.7	61.7	21.3	15.4	51.0	60.3	28.5	25.1	12.0	78.4	37.2	50.2	4.3	15.8

All values are in microequivalents per liter. Total precipitation represented: 207.2 cm; sum of cations = 26.5 μeq/L; sum of anions = 24.4 μeq/L.

approximately 100 mg N/m^2 per year and 60 mg S/m^2 per year were input to the landscape of Katherine from rainfall during 1980–1984. About 40% of this inorganic nitrogen was provided by $NH_4 - N$ and 60% by $NO_3 - N$. Because organic N was not measured, total deposition of nitrogen is underestimated by some unknown amount in our data.

Maximum rates of deposition for most species occurred during December and January (Figure 8), although maxima in precipitation amounts were observed during January through March (Table 1). These observations suggest that source strengths for chemical constituents in precipitation at Katherine may decrease during the latter months of the wet season. This decrease may reflect different source regions for air masses generating precipitation at the site, associated with a shift from easterly trades to a westerly monsoon (see following section).

Classification of Air Mass Trajectories

The air trajectory model developed at the Air Resources Laboratory of the National Oceanic and Atmospheric Administration (NOAA) was used to calculate back trajectories from Katherine during our study [Harris, 1982]. The model, which is intended for use in evaluating transport on a regional, continental, or global basis, can produce forward or backward trajectories in time from any point of origin in the world. Input data used in this version of the model are the National Meteorological Center's (NMC) gridded winds which, in the

data-sparse southern hemisphere, are derived from the NMC model.

The Katherine back trajectories summarized in this paper cover four wet seasons (October to April) from 1980 to 1984. Trajectories were calculated 10 days back in time at the 850-hPa level. The calculations were made twice a day at 0000 and 1200 UT. An example of a back trajectory from Katherine is shown in Figure 9, along with the procedure for classifying the Katherine trajectories. Since the main flow patterns tend to be either easterly (trade winds) or westerly (monsoons), a division was made north and south relative to Katherine. To distinguish also between possible continental and maritime sources, four main categories were decided upon (NW, NE, SW, and SE), and the lines dividing these sectors were drawn to maximize the continental and marine differences, as shown in Figure 9. Because of transitions between sectors, a fifth category was established for those cases in which the trajectories were in more than one of the above categories; this category was designated by "T." Owing to data gaps, some trajectories could not be calculated. All trajectories ($N = 1698$) for the period of interest were classified using the above scheme. The percentages were as follows: NW, 13%; SW, 4%, SE, 14%; NE, 51%; T, 7%; and missing, 11%. The conclusion from this analysis was that easterly trades were important at the beginning and at the end of the wet season, while the westerly monsoon dominated in January, February, and March during 1980–1984. It also should be noted that during trades flow, precipitation comes from local convective storms, whereas the monsoons bring more widespread and organized precipitation events. The flow was somewhat atypical, especially during 1982–1983, because of the disruption of the general circulation by the El Niño phenomenon during the period [Rasmusson and Wallace, 1983].

From the above set of trajectories, a subset was formed of those that could be associated with the precipitation events sampled at the site. The percentages of this subset by category are as follows: NW, 29%; SW, 3%; SE, 7%; NE, 37%; T, 15%; and missing, 9%.

Relation of Precipitation Chemistry to Air Mass Trajectories

Volume-weighted mean concentrations were calculated for all rainfall events during 1980–1984 that occurred in each trajectory class (Table 6). Eastern storms (Class 3 and 4) generally had higher levels of Ca^{++}, K^+, $SO_4^=$, H^+, NH_4^+, NO_3^-, and Cl^-, and statistically significant higher concentrations of organic anions than did western storms (Class 1 and 2). Storms in the northwest sector generally had the lower acidities and lowest concentration of organic anions. Relatively little difference in chemistry was observed between northern trajectories (Class 1 and 4) and southern trajectories (Class 2 and 3), except that Ca^{++}, Mg^{++}, K^+, and NH_4^+
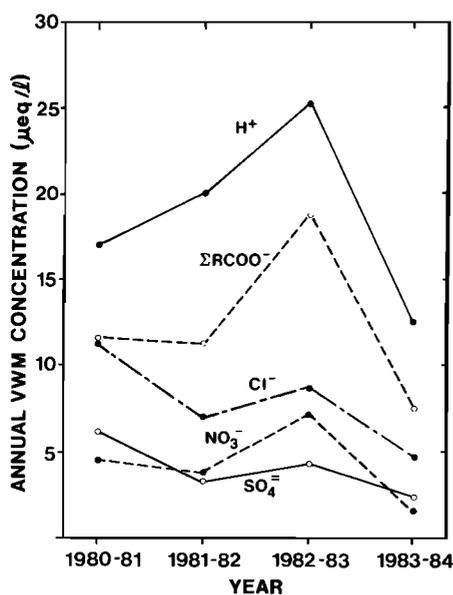

Fig. 3. Volume-weighted annual concentrations of various ions in precipitation at Katherine, Australia ($N = 147$). Estimated concentrations for dissociated organic anions are included (see text).
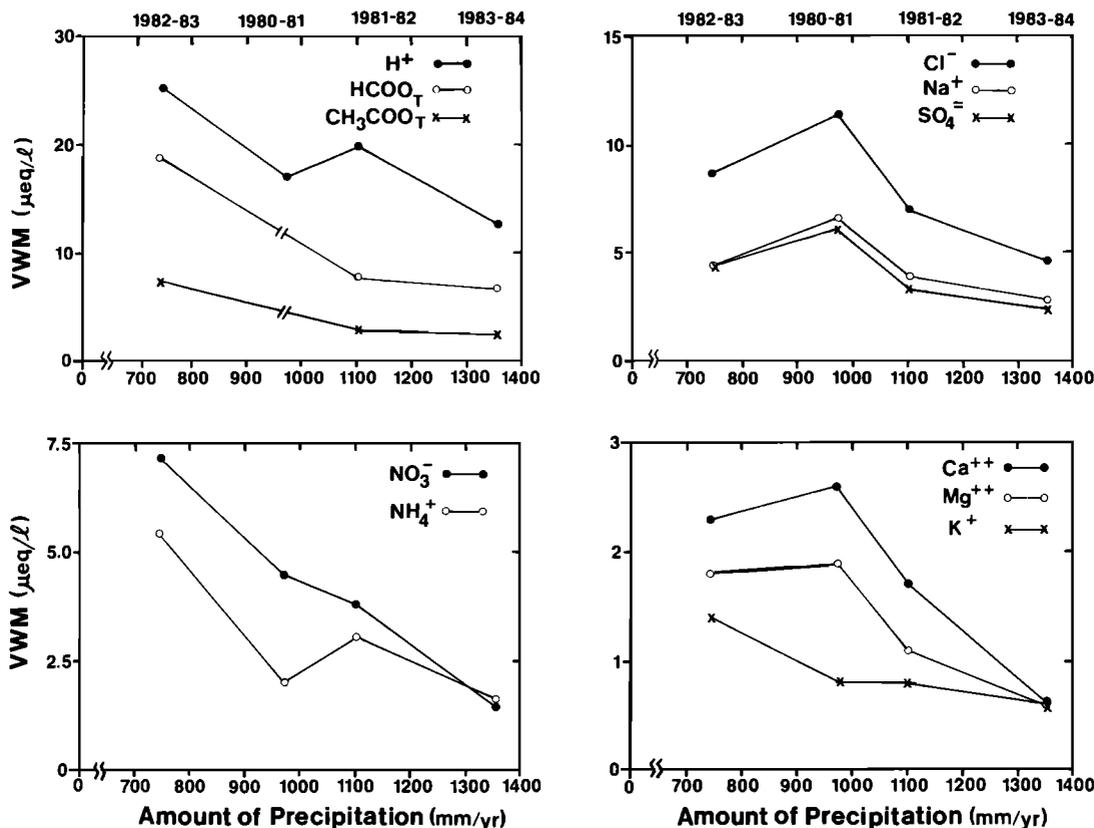
Fig. 4. Relationships between annual volume-weighted means (VWM) and precipitation amount in samples of precipitation collected at Katherine, Australia. For clarity the chemicals are grouped and plotted according to different scales of VWM concentration rather than by pattern (see text). (N for inorganic ions = 147; N for organic anions = 101).

were somewhat higher in the southern, more terrestrial trajectories, and Na^+, and to a lesser extent, Cl^- were higher in the northern, more marine trajectories (Table 6). Storms from the northeast trajectory had concentrations appreciably higher than those from the northwest, especially for organic anions and nitrate. In general, however, there were not large (order of

magnitude) differences in the concentrations of inorganic ions between any of the trajectory classes. No trajectory classes contained high concentrations of sea-salt constituents.

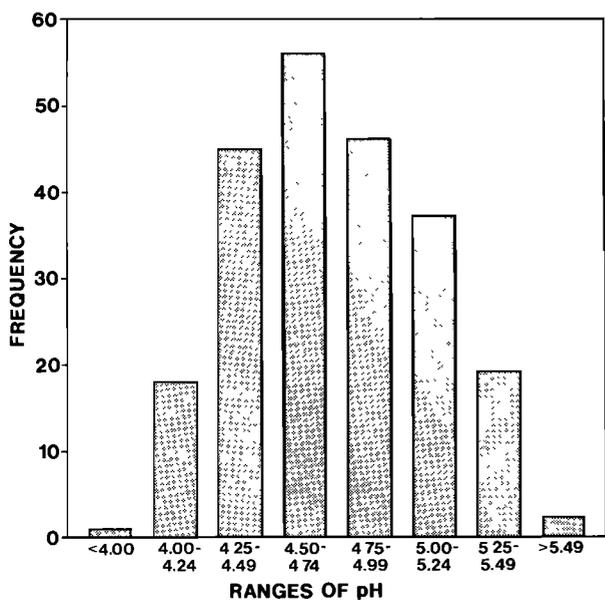The average deposition of chemicals in meq/m^2 (Table 7)

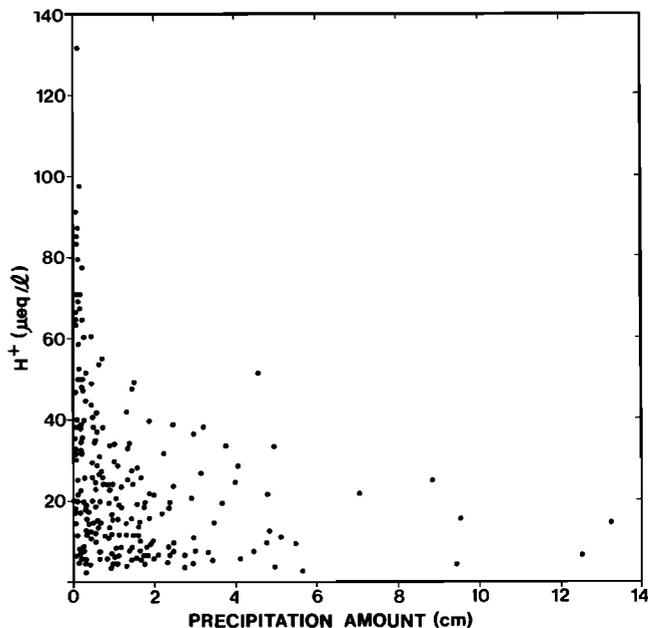Fig. 5. Frequency of field pH values for all samples analyzed (N = 224) during 1980–1984 at Katherine, Australia.

Fig. 6. The relationship between the H^+ concentration of rain and amount of rain in samples collected at Katherine, Australia, during 1980–1984 (N = 224).
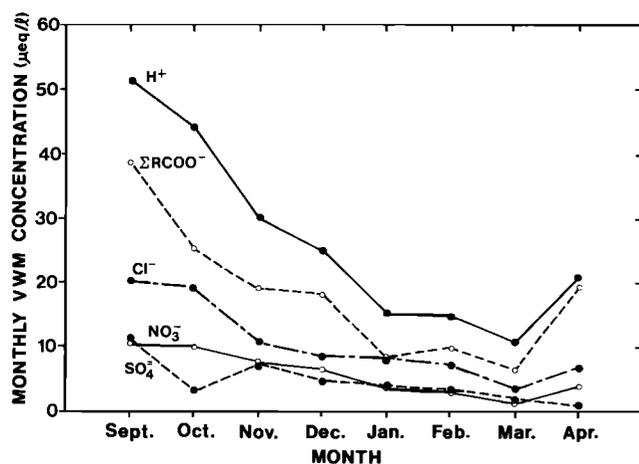
Fig. 7. Volume-weighted monthly concentrations of various ions in precipitation in Katherine, Australia ($N = 147$). Only one sample was available for September and April and only two for October. Estimated concentrations for dissociated organic anions are included (see text).

associated with the various trajectory classes was calculated by multiplying the VWM concentrations (Table 6) times the appropriate amount of precipitation. In every respect the northeast trajectory (Class 4) was the most important in terms of average deposition to the landscape around Katherine. In sharp contrast, the southwestern trajectory (Class 2) provided at least an order of magnitude less deposition of water and dissolved substances than the northeast trajectory, except for Ca^{++} and K^+ (Table 7). Comparing the two most important classes (NE = Class 4 and NW = Class 1), the NE provided about twofold more Ca^{++}, Mg^{++}, Na^+, K^+, $SO_4^{=}$, and Cl^-, and about threefold to fourfold more NH_4^+, NO_3^-, H^+, and organic anions than did the NW trajectory. A portion of these differences in deposition can be explained by the fact that 1.24 times more water fell in storms from the NE, as compared to those from the NW.

Evaluating the effect of spatial scale on transport from marine and terrestrial source areas is complicated, in part, because eastern trajectories tended to be associated with more localized convective storms, whereas widespread, monsoonal rains were more common in northern sectors. Overall, the marine influence on chemistry in northern sectors appears to

TABLE 5.　Deposition of Dissolved Substances in Precipitation at Katherine, Australia, During 1980–1984

Substance	1980–1981	1981–1982	1982–1983	1983–1984	VWM 1980–1984*
H^+	16.6	22.6	19.0	17.5	19.4
Ca^{++}	56.4	37.6	37.4	16.3	39.8
Mg^{++}	22.4	16.1	18.1	9.9	17.8
Na^+	152	104	73.8	87.3	108
K^+	30.4	34.5	73.0	31.8	44.9
$NH_4 - N$	27.2	48.0	57.6	32.4	42.5
$NO_3 - N$	61.2	60.3	75.2	28.5	59.9
$SO_4 - S$	96.5	58.4	52.6	52.2	69.9
Cl^-	389	282	254	231	296
Organic C†	⋯	146	234	155	184

Values are in milligrams per square meter per year and are based on Table 4a.

*VWM concentration times average precipitation (104.4 cm) during the period.
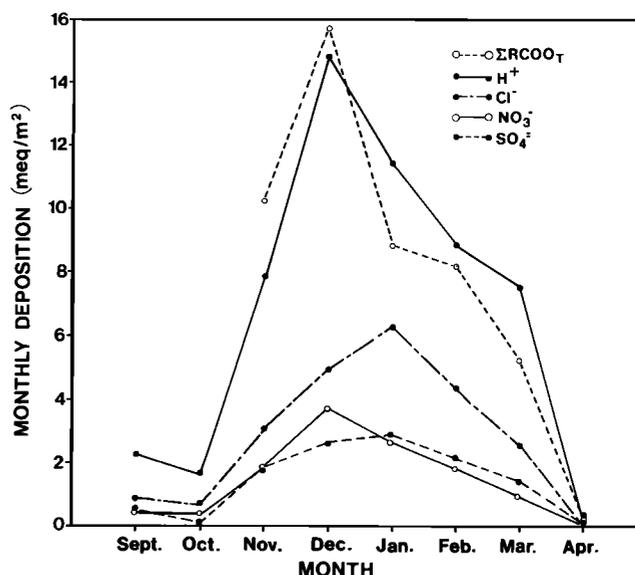
†$HCOO_{total} + CH_3COO_{total}$.

Fig. 8. Monthly deposition of various chemical constituents in precipitation at Katherine, Australia ($N = 147$). Organic species ($\Sigma RCOO_T = HCOO_T + CH_3COO_T$) were measured in only 101 of the samples. For comparative purposes, it was assumed that monthly volume-weighted concentrations of $\Sigma RCOO_T$ for the entire data set ($N = 147$) equaled those for the subset of 101 samples in which these species were analyzed. Organic species were not measured in the three samples collected during September and October. Units of deposition for $\Sigma RCOO_T$ are $mmol/m^2$.

be small, whereas continental influences appear to predominate in all four sectors. In addition, it appears that even a relatively short passage of air masses over densely vegetated, terrestrial ecosystems in the NE sector near Katherine, even though this sector is predominately marine, is of greater importance to the input of chemicals than long trajectories across deserts in the SW sector (see Tables 6 and 7). Some caution is warranted, however, because only five storms originating from the SW sector were analyzed chemically. Apparently, long-distance transport is relatively unimportant for the major, chemical constituents in rainfall at Katherine.

DISCUSSION

Studies of precipitation chemistry are important for several reasons. They reflect the air chemistry for a region and provide some measure of atmospheric pollution. Moreover, wet and dry deposition provide important inputs to natural ecosystems [e.g., Gorham, 1961; Likens et al., 1977]. These inputs may supply critical limiting nutrients such as nitrogen and phosphorus or potentially toxic constituents such as hydrogen ion, lead, or pesticides. The biological effects of these atmospheric inputs provide the major raison d'être for such studies.

Although we collected rainfall at Katherine during only four wet seasons, we were fortunate to observe almost a twofold difference in amount of precipitation (Table 1). Major differences in amount of monthly rainfall also occurred during individual wet seasons as well (e.g., Figure 1). Only a few samples were collected during the months of September and October, but these data would suggest that the early part of the wet season has higher average concentrations of the major chemical constituents (Figure 7). In contrast, the average concentrations in January, February, and March (particularly January and February) were lower and much less variable.

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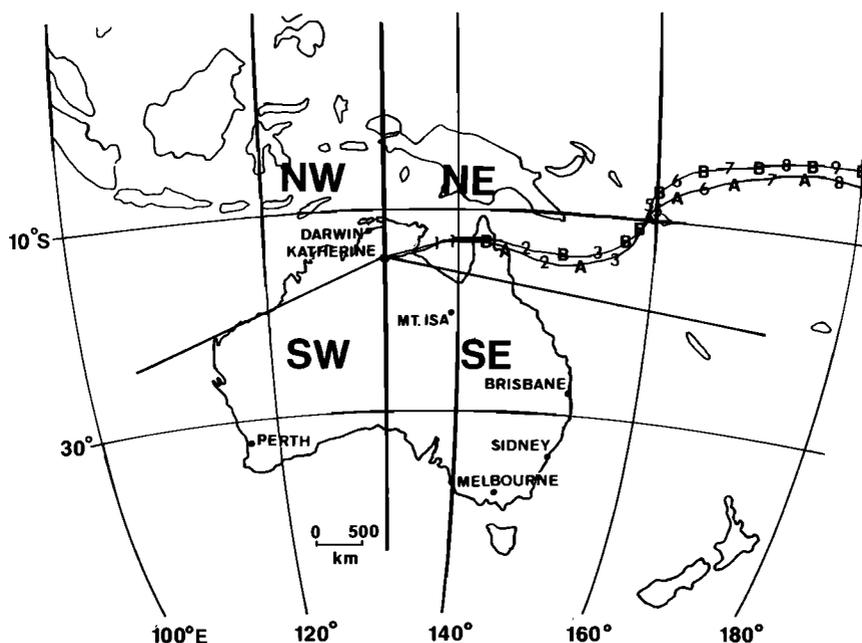**A: 0Z 850 hPa**
B:12Z 850 hPa

Fig. 9. Back trajectories of winds for Katherine, Australia, calculated at the 850-hPa level (see text).

The monsoonal rains were heaviest during this latter period (Figure 1), suggesting a dilution of ions in the atmosphere with increased rainfall.

The wet season of 1983–1984 had more than 1.8 times greater rainfall than the wet season of 1982–1983 (Table 1). A major difference between these 2 years is shown by the amount of rainfall in January: January 1983 had 53.2 mm and January 1984 had 470 mm (8.8 times greater) of rainfall. Accordingly, concentrations of H^+ were 2.2 times greater; Ca^{++}, 9.3 times greater; Mg^{++}, 4.7 times greater; K^+, 3.5 times greater; Na^+, 4.1 times greater, NH_4^+, 5.3 times greater; NO_3^-, 5.1 times greater; $SO_4^=$, 2.0 times greater; Cl^-, 3.8 times greater; and dissociated organic anions, 3.0 times greater in January 1983 than in January 1984.

The patterns of concentration and deposition for inorganic

and organic ions relative to air mass trajectories (Tables 6 and 7) suggest the following:

1. Large amounts of sea salt are not transported long distances. Other studies have reached the same conclusion [*Junge and Werby*, 1958; *Eriksson*, 1959, 1960; *Stallard and Edmond*, 1981].

2. The average deposition of water for storms from the NW sector (2.0 cm) was similar to that for storms from the NE sector (1.9 cm), indicating that dilution effects may have accounted for only about 5% of the differences in concentration of dissolved species between storms from these two sectors. This observation supports the hypothesis that relative to the NW, the NE region contains stronger sources for all species measured.

3. The consistently higher concentrations of organic

TABLE 6. Average Chemistry of Precipitation as Related to Air Mass Trajectory in Katherine, Australia, During 1980–1984

Trajectory Class*	Total Number of Samples	Samples for Organic Anions	H^+ (Field)	H^+ (Lab)	Ca^{++}	Mg^{++}	K^+	Na^+	NH_4^+	NO_3^-	Cl^-	$SO_4^=$	$HCOO_T$†	CH_3COO_T†
1 (NW)	42	32	9.4	11.3	1.4	1.0	0.6	3.9	1.6	2.0	6.8	2.8	4.9 (4.6)	2.3 (1.4)
2 (SW)	5	4	15.4	15.9	0.9	2.2	0.4	2.5	2.2	4.9	5.7	2.2	10.3 (9.5)	3.8 (2.0)
3 (SE)	10	6	19.9	22.0	3.4	1.6	2.2	2.8	3.9	5.1	7.6	4.3	16.1 (14.3)	7.3 (3.2)
4 (NE)	55	36	23.8	24.5	2.4	1.5	0.9	4.8	3.6	6.0	8.8	4.9	17.7 (15.6)	6.6 (2.8)
5 (transitory)	22	17	11.4	12.6	0.9	0.9	0.7	4.7	2.2	2.5	6.5	3.4	9.0 (8.5)	3.1 (1.9)
6 (missing)	13	6	18.6	21.1	0.7	1.4	0.9	5.2	3.7	4.1	8.7	4.4	6.8 (6.2)	3.2 (1.5)
1 + 4	97	68	17.4	18.6	1.9	1.3	0.8	4.4	2.7	4.2	7.9	4.0	10.7 (9.7)	4.2 (2.1)
2 + 3	15	10	18.7	20.4	2.8	1.7	1.7	2.7	3.5	5.0	7.1	3.8	14.3 (12.9)	6.2 (3.0)
1 + 5	64	49	10.1	11.8	1.2	1.0	0.7	4.1	1.8	2.2	6.7	3.0	6.0 (5.7)	2.5 (1.6)

Volume-weighted concentrations are in microequivalents per liter.
*See Figure 9.
†Numbers in parentheses represent the dissociated portion.

TABLE 7.　Average Deposition as Related to Air Mass Trajectory in Katherine, Australia, During 1980–1984

Trajectory Class*	Total Number of Samples	Samples of Organic Anions	Precipi- tation, cm	H^+ (Field)	H^+ (Lab)	Ca^{++}	Mg^{++}	K^+	Na^+	NH_4^+	NO_3^-	Cl^-	$SO_4^=$	$HCOO_T$†	CH_3COO_T†
1 (NW)	42	32	83.9	7.89	9.48	1.17	0.84	0.50	3.27	1.34	1.68	5.71	2.35	4.11 (3.86)	1.93 (1.17)
2 (SW)	5	4	8.2	1.26	1.30	0.07	0.18	0.03	0.21	0.18	0.40	0.47	0.18	0.84 (0.78)	0.31 (0.16)
3 (SE)	10	6	23.0	4.58	5.06	0.78	0.37	0.51	0.64	0.90	1.17	1.75	0.99	3.70 (3.29)	1.68 (0.64)
4 (NE)	55	36	104.2	24.8	25.5	2.50	1.56	0.94	5.00	3.75	6.25	9.17	5.11	18.4 (16.3)	6.88 (2.92)
5 (transitory)	22	17	40.4	4.61	5.09	0.36	0.36	0.28	1.90	0.89	1.01	2.63	1.37	3.64 (3.43)	1.25 (0.77)
6 (missing)	13	6	38.2	7.11	8.06	0.27	0.53	0.34	1.99	1.41	1.57	3.32	1.68	2.60 (2.37)	1.22 (0.57)
1 + 4	97	68	188.0	32.7	35.0	3.57	2.44	1.50	8.27	5.08	7.90	14.8	7.52	20.1 (18.2)	7.90 (3.95)
2 + 3	15	10	31.2	5.83	6.36	0.87	0.53	0.53	0.84	1.09	1.56	2.22	1.19	4.46 (4.00)	1.93 (0.94)
1 + 5	64	49	124.3	12.5	14.7	1.49	1.24	0.87	5.10	2.24	2.73	8.33	3.7:	7.46 (7.09)	3.11 (1.99)

Chemical deposition values are in microequivalents per square meter.
*See Figure 9.
†Numbers in parentheses represent the dissociated portion.

anions in rainfall from the eastern sectors relative to the pattern for inorganic ions suggest a disproportionately greater source strength for dissolved organic substances in these sectors.

4. The predominance of the deposition of inorganic nitrogen species in the northeast sector suggests a larger source strength in that region.

5. Greater concentrations of sulfate associated with eastern sectors may reflect in part anthropogenic emissions, such as those from the Mt. Isa smelters to the southeast of Katherine (Figure 9). The greater concentration of sulfate in the eastern sectors is similar to the pattern for base cations, suggesting the possibility of a common crustal source as well. Wetselaar and Hutton [1963], Hutton[1983], and Probert [1976] all have suggested that plant residues and surface soils may influence rain chemistry in northern, tropical Australia.

Potential Sources for Nitrogen and Sulfur

Ayers and Gillett [1987] considered various sources of atmospheric nitrogen and sulfur that could contribute to rain chemistry in tropical Australia. For nitrogen they considered lightning flashes and emissions from bush fires, soil, motor vehicles, and power plants as sources of NO_x in the atmosphere. Emissions from soils, vegetation, bush fires, power plants, and industry were evaluated for sulfur.

Over an entire year, bush fires may be the major source of nitrogen and a smaller source of sulfur emissions to the atmosphere [Ayers and Gillett, 1987]. It seems unlikely, however, that fires contribute significantly to rain chemistry during the wet season.

Severe electrical storms with a high frequency of lightning flashes do occur during the wet monsoonal period at Katherine. Lightning flashes can oxidize atmospheric nitrogen to NO_x [e.g., Drapcho et al., 1983], which then may contribute to the nitrate content of rain. Ayers and Gillett [1987] found a direct relationship between rainfall amount and lightning flash rate in tropical Australia ($r^2 = 0.97$). Using this relation in combination with an estimate of the amount of nitric oxide formed from the average energy of each lightning flash [Borucki and Chameides, 1984], they calculated the total mass of atmospheric nitrogen fixed by lightning per year. On the basis of amount of rainfall at Katherine, using these estimations and assuming that all of the nitric oxide formed from lightning would be precipitated with rain, which seems highly unlikely,

some 10 to 15 mg N/m^2 per year could originate from lightning at Katherine. Ayers and Gillett [1987] suggested that the constant, upper limit of nitrate formed from lightning in rain would be about 0.85 $\mu mol/L$. This amount would represent about 21% of the VWM concentration at Katherine (Table 4a). Overall, Ayers and Gillett [1987] concluded that anthropogenic emissions of nitrogen accounted for only 15% of the total emissions of N to the atmosphere in tropical Australia, with the remainder from natural sources such as brush fires and the decay of animal wastes.

Sulfur emissions in the region around Katherine, however, may be dominated by anthropogenic emissions. One large source, the Mt. Isa smelters, located about 1000 km to the SE of Katherine, contributes about 69% of the total emissions of sulfur (250,000 tonnes S/yr) to the atmosphere over tropical Australia [Ayers and Gillett, 1987]. Sulfur emissions from the Mt. Isa smelters or from the much smaller Ranger Uranium Mine and Mill, some 200 km northeast of Katherine, could reach the Katherine area [Williams, 1984; M. G. Ridpath, personal communication 1986], although B. N. Noller (unpublished data, 1987) has determined that SO_2 emissions from the Ranger operation have an insignificant effect on the sulfate content of rain at nearby Jabiru East. In any event, sulfate concentrations in rain at Katherine are quite low (Tables 4a–4c).

Sea salt was only a minor source of $SO_4^=$ in precipitation at the site. On a volume-weighted basis, storms from the NW sector contained the highest concentrations of Na^+ relative to $SO_4^=$. If we assume that all of this Na^+ were derived from seawater, only 0.5 $\mu eq/L$ or 17% of the total $SO_4^=$ in the storms from the NW sector would have originated with sea salt (see Keene et al. [1986] for sea-salt ratios). Considering the concentrations of Na^+ in storms from other sectors, it is likely that a portion of the Na^+ in the NW sector was of continental origin, and if so, the sea-salt contribution to total $SO_4^=$ given earlier overestimates the actual marine fraction by an unknown but probably substantial amount.

Potential Sources for Organic Acids

Obviously, formate and acetate are important chemical components in precipitation at Katherine (Tables 4a–4c). Noller et al. [1986] also have measured high concentrations of formate and acetate in the vapor phase (39.0 and 5.2 $nmol/m^3$, respectively) and in cloud water (78.8 and 39.7 $\mu mol/L$, respectively) at Jabiru East, approximately 200 km northwest of
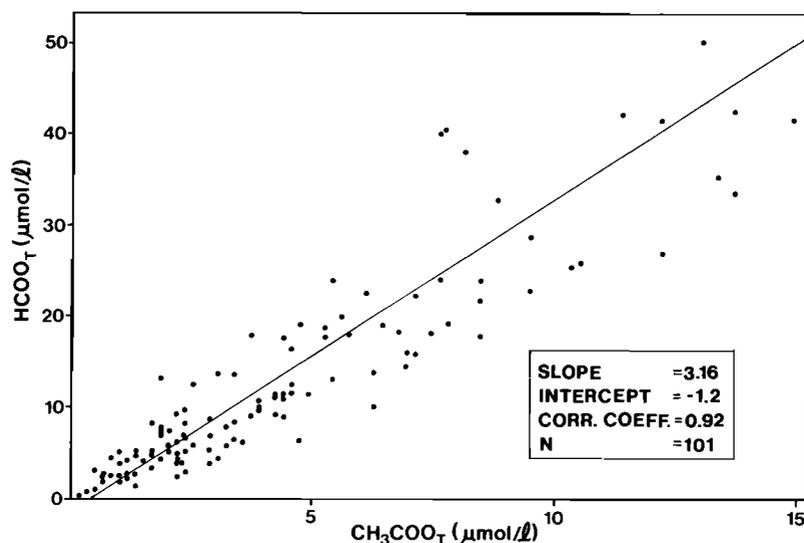
Fig. 10.   Reduced major axis regression of $HCOO_T$ versus CH_3COO_T in samples of precipitation collected at Katherine, Australia.

Katherine. Particulate phase concentrations were approximately 1 or 2 orders of magnitude less than those in the vapor phase. The source of these organic anions in the atmosphere is unknown, but precipitation over continental areas during growing seasons has higher concentrations generally than that over marine areas [*Keene and Galloway*, 1986]. Thus it is reasonable to speculate that organic anions in continental rain originate as volatile substances from biological activity in terrestrial ecosystems. Emissions of reactive organic substances, such as isoprene and monoterpenes from terrestrial vegetation, have been known for some time [e.g., *Zimmerman et al.*, 1978; *Graedel*, 1979; *Duce et al.*, 1983]. Isoprene especially seems to be emitted in larger quantities in the tropics, probably because emissions are correlated with temperature [*Ayers and Gillett*, 1987]. Isoprene has been hypothesized as a source for carboxylic acids in the atmosphere [*Duce et al.*, 1983; *Brewer et al.*, 1984; *Gu et al.*, 1985; *Jacob and Wofsy*, 1987]. Emissions of HCOOH from Formicine ants have also been suggested as a potentially important continental source [*Graedel*, 1987].

The aqueous phase reaction of aldehydes with OH radicles is also thought to be a potential source for formic and acetic acids in the atmosphere [*Chameides and Davis*, 1984; *Graedel and Goldberg*, 1983; *Adewuyi et al.*, 1984; *Chameides*, 1984; *Graedel et al.*, 1985; *Jacob*, 1986]. Based on aldehyde concentrations modeled by *Jacob* [1986], aqueous phase concentrations of formate predicted by this mechanism are low ($\sim$ 2–4 μmol $HCOO^-/L$ at pH 4.7) relative to concentrations measured in precipitation at Katherine, and it is therefore likely that in situ chemical production by this reaction pathway is not an important source for organic acids in the region.

The concentrations of formic and acetic acids in precipitation at the site were highly correlated (Figure 10), suggesting that they may originate with a common source or be controlled by a common reactant. Similar correlations were observed for precipitation collected at a wide variety of continental and marine locations around the world and, considering all available evidence, we agree with the speculations of *Keene and Galloway* [1986] that the organic acids measured in our samples originated primarily from a common terrestrial, vegetative source in the region.

We were concerned that the high concentrations of organic acids measured in precipitation at Katherine might have resulted from contamination associated with local sources such as insect (ant and termite) activity in the vicinity of the collector and/or windblown vegetative debris. During January 1985 a semiquantitative experiment was performed to assess the potential for such contamination. Field blanks consisting of 250 mL of deionized water were poured into and swirled around buckets which had been mounted on the automatic collector during dry periods of 48 hours. Uninjured individuals and pairs of ants which had been captured in the vicinity of the collector were incubated in a second set of 250-mL aliquots of deionized water at room temperature for 8 hours. Increasing amounts of vegetative debris, which had been collected in the vicinity of the sampling site, were added to a third set of three 250-mL aliquots of deionized water and incubated at room temperature for 8 hours. The amount of material added corresponded to the site operator's semiquantitative estimates of the range of particulate contamination observed in samples (i.e., a few particles, a large number of particles, gross contamination). All solutions were subsequently decanted, treated with $CHCl_3$ and sent to the University of Virginia for analysis of all major chemical constituents. No significant contamination was detected in the field blanks or in the aliquots to which ants were added. With the exception of Na^+ for which measurable contamination was not detected, however, the concentration of all other inorganic ions and H^+ increased significantly with increasing amounts of plant debris. Measurable concentrations of $HCOO^-$ and CH_3COO^- were detected only in the aliquot containing the greatest amount of vegetative material. The results of these tests indicate that organic acidity appears to be a natural component of precipitation at Katherine, rather than an artifact of collection procedures or local contamination. Windblown vegetative material could, however, contribute measurable concentrations of dissolved inorganic ions and, in extreme cases, of organic compounds to precipitation at the site. Because the collector was open only during precipitation events, particulate matter was observed infrequently (20%) in the samples and, when observed, was generally at low concentrations (a few particles per

sample). Therefore we do not believe that vegetative debris contributed significantly to the chemistry of wet-only precipitation at the site.

Deposition

The annual deposition of most ions was inversely related (NO_3^-, organic acids, K^+, Mg^{++}, Ca^{++}, and NH_4^+, in decreasing order of correlation) to the amount of rainfall (Tables 1 and 5). Correlations with the amount of rain, however, were not strong ($r^2 = 0.33$ to 0.59; with the exception of NO_3, $r^2 = 0.91$ and organic carbon, $r^2 = 0.75$), indicating that other factors, which also affected the VWM concentrations, were important in regulating deposition. No significant trends were observed for annual deposition of H^+, Na^+, Cl^-, and $SO_4^=$ relative to amount of rainfall. The annual deposition of Cl^- and $SO_4^=$ was essentially the same in 1981–1982, 1982–1983, and 1983–1984, even though the amount of precipitation ranged from 746 mm/yr to 1,357 mm/yr during these years (Tables 1 and 5). In contrast, the annual deposition of K^+ was more than twofold greater during the driest year (1982–1983) than during the other 3 years, which had similar depositions (Table 5), reflecting the pattern of VWM concentrations during these years with different amounts of rainfall (Figure 4). The patterns of annual deposition relative to amount of rainfall were similar for Na^+ and Cl^- and for Ca^{++} and Mg^{++}.

If there were an infinite pool of ions in the atmosphere or a rapid rate of replenishment of this pool, then deposition should be directly related to amount of rainfall, on the average. In contrast, if the pool were very small or rapidly depleted with increasing amounts of rain, then the annual deposition of dissolved substances should be inversely related to amount of rainfall. These considerations assume that other sources of annual variability (e.g., different mix of source regions) are small relative to the dilution effect. The fact that the annual deposition of most ions at Katherine is inversely related to amount of rainfall suggests therefore that during rainfall events the source of ions in the atmosphere may be very small or rapidly depleted, or both. For example, the inverse relationship for deposition of Ca^{++} and Mg^{++} and amount of rainfall suggests a strong washout of these largely terrestrially derived ions. The one possible exception is hydrogen ion (where there was no statistically significant trend, but there was a suggestion of a direct relationship between deposition and amount of rainfall). This relation for hydrogen ion probably is explained by a combination of factors. Although the pH of rain is highly variable, the VWM pH is lower than 5.0 because of the presence of organic acids primarily, and to a lesser extent, of nitric, hydrochloric, and sulfuric acids. The deposition of these latter anions is inversely related to amount of rainfall in the order given above, and the deposition of hydrogen ion then represents this mixture accordingly.

The negative linear relation between annual deposition of NO_3^- and amount of rainfall was the only one that was statistically significant at $p < 0.05$ ($p > F$ ratio = 0.04; $r^2 = 0.91$):

$$Y = -0.074X + 133 \qquad (5)$$

where Y is equal to the annual deposition of $NO_3 - N$ in mg/m², and X is equal to the annual rainfall in millimeters.

This relationship is particularly interesting because, as discussed earlier, Ayers and Gillett [1987] showed a direct relation between lightning flash rate and rainfall amount. Thus if

lightning flashes were an important source for nitrate in rain at Katherine, a direct relation between amount of rainfall and deposition of nitrate would have been predicted. In fact, the opposite occurred, which argues against lightning flashes as an important source of nitrate in rain at Katherine. Earlier, Wetselaar and Hutton [1963] also found "... no obvious correlation between nitrate ion in rain and lightning" at Katherine.

In the relatively polluted atmosphere of the northeastern United States, where the annual amount of precipitation varied by twofold during 1963 to 1985 (long-term data from the Hubbard Brook Experimental Forest, New Hampshire), deposition of NO_3^-, $SO_4^=$, and H^+ generally increased with increasing amount of precipitation [Likens et al., 1980, 1984, 1985]. This pattern is in sharp contrast to the situation at Katherine.

Other Data From Northern Australia

Some other data on precipitation chemistry are available from northern Australia (Table 8). Unfortunately, different collection and analytical procedures were used in these earlier studies, and the results may reflect these differences. For example, the studies at Alice Springs, Lansdown, and Jabiru East relied on collections of bulk precipitation, which are more likely to include dry deposition of local soil or vegetation particles. In addition, the average annual data from Lansdown included monthly bulk samples collected during the dry season. Contributions from sea salts at Lansdown and Jabiru East, and sulfur from the nearby Mt. Isa smelter at Jabiru East, are seen relative to data from Katherine. In spite of the different procedures, the wet-only data collected in Katherine some 20–25 years ago by Wetselaar and Hutton [1963] are remarkably similar to those collected in 1980–1984 (see Table 8). Lower concentrations of K^+ and NH_4^+ in current samples from Katherine may indicate contamination in the earlier samples or reflect the differences in methodology. Wetselaar and Hutton [1963] cautioned, in fact, that their method for NH_4^+ "... was not very precise." Overall, these data suggest that relatively little change has occurred in precipitation chemistry at Katherine during the past 2 or 3 decades.

Comparison With Other Areas

In comparison with the Hubbard Brook Experimental Forest in West Thornton, New Hampshire, a relatively remote, North Temperate Zone location with similar rainfall amounts (although distributed over 12 months instead of 6 or 8 months), the volume-weighted concentrations and wet deposition at Katherine are quite low. In particular, the long-term average chemical composition of $SO_4^=$, NO_3^-, and Ca^{++} in precipitation at Hubbard Brook is enriched by more than 5.5 times relative to Katherine (Table 9). The enrichment of sulfur, nitrogen, and hydrogen ions reflects the heavy combustion of fossil fuels in North America. Galloway et al. [1984] reported that sulfate and nitrate were enriched by approximately an order of magnitude in precipitation in eastern North America, as compared to remote areas of the southern hemisphere.

The maximum amount of volume-weighted $SO_4^=$ attributed to sea salt (0.6 μeq/L) represents only a small fraction (13%) of the total sulfate in rain at Katherine. Even so, the so-called excess $SO_4^=$ concentrations are extremely low compared to concentrations in the northeastern United States [Galloway et al., 1984].

TABLE 8. Volume-Weighted Mean Concentrations of Dissolved Inorganic Substances in
Precipitation in Northern Australia

Dissolved Substance	Katherine* (1980–1984)	Katherine† (1958–1960)	Alice Springs‡ (1957–1962)	Jabiru East§ (1982–1983)	Lansdown‖ (1971–1974)
$SO_4^=$	3.9	ND	<30	7.7	16
NO_3^-	4.0	4.9	···	5.6	5.3
H^+	18.3	ND	<10	54**	ND
NH_4^+	2.9	5.4¶	···	5.0	15
Ca^{++}	1.7	ND	32	2.0	25
Mg^{++}	1.3	1.8††	23	2.9	12
Cl^-	7.7	5.2	25	16	56
K^+	0.9	1.6	9	1.5	3.2
Na^+	4.3	5.2††	28	10	37
Number of Samples	147	73‡‡	22	20	?

Values are in microequivalents per liter. ND indicates no data.
*Table 4b.
†Wetselaar and Hutton [1963], manual wet-only.
‡Hutton [1983], bulk precipitation, 100 km north of Alice Springs.
§Noller et al. [1985a], bulk precipitation weekly.
‖Probert [1976], bulk precipitation, mostly monthly including dry season, average for 2 years.
‡‡All chemical analysis not done on each sample.
¶For 1958–1959 only.
††For 1959–1960 only.
**Noller et al. [1985b]; number of samples equals 18.

Based on comparisons between the chemistry of precipitation in polluted and remote regions, Keene and Galloway [1986] hypothesized that organic acidity in precipitation from predominantly rural areas of eastern North America originated primarily from natural rather than anthropogenic sources. The volume-weighted concentrations of $HCOO_T$ and CH_3COO_T in precipitation at Katherine are similar to those in precipitation from central Virginia. If inorganic acidity in precipitation at Katherine were representative of remote continental precipitation in general, then the present-day, volume-weighted pH of precipitation at Katherine (4.76) would be similar to that for precipitation in eastern North America prior to the advent of fossil fuel combustion. However, because of inadequate protocols for sample preservation and the associated loss of organic acidity prior to laboratory analysis [see Keene and Galloway, 1984a], most reported pH values for precipitation in eastern North America are not directly comparable to values for treated aliquots from Katherine. Untreated aliquots of precipitation from Katherine that were analyzed in Charlottesville (N = 192) had a volume-weighted pH of 5.08. Measurements of organic anions in a paired subset of treated and untreated aliquots revealed that virtually all (>95%) of the formic and acetic acids were consumed between collection and analysis. The pH of 5.08 is therefore an estimate of only the strong mineral acidity in precipitation at Katherine [Keene et al., 1983] and is the most appropriate value for comparison with reported pHs for untreated aliquots of precipitation from eastern North America. Such a comparison suggests an approximate order of magnitude higher concentration of strong mineral acidity in precipitation in eastern North America relative to Katherine, and these higher acidities correspond to the enrichments of sulfate and nitrate estimated by Galloway et al. [1984]. It is interesting to note that if all of the NO_3^- and $SO_4^=$ measured in samples of precipitation at Katherine (Table 4b) originated as acids, the corresponding pH would be 5.10. This calculation assumes that the contribution of HCl would be negligible.

In contrast to Katherine or eastern North America, the data from Amsterdam Island (Table 9) indicate strong sea-salt contributions (particularly Na^+, Cl^-, Mg^{++}, and $SO_4^=$) to the precipitation, smaller amounts of NH_4^+ and NO_3^-, and a higher pH. The volume-weighted mean pH at Amsterdam Island, based on 66 samples, was 5.06, with H_2SO_4 contributing 30%; organic acids, 25%; and HNO_3, 15% [Galloway and Gaudry, 1984]. The contribution of HCl also may be significant [Keene et al., 1986]. The relatively small contribution of organic acids in precipitation on Amsterdam Island is consistent with the hypothesis that source strength for these constituents in remote marine regions is substantially lower than it is in terrestrial regions during growing seasons [Keene and Galloway, 1986].

Precipitation at Torres del Paine, Chile, contains very low concentrations of free acidity, NO_3^-, NH_4^+, Ca^{++} (Table 9), and organic anions [Keene and Galloway, 1986], and similar amounts of $SO_4^=$ relative to Katherine. We speculate that lack of significant amounts of organic acidity and NH_4^+ in most of our samples from southern Chile results from the climatological factors associated with high latitude (e.g., lower temperatures), the short (~ 100 km) fetch over land, and the associated low source strength for vegetative emissions in the mountainous area between the ocean and the site. Small amounts of marine sea salt are reflected in the enriched concentrations of Na^+, Cl^-, and Mg^{++} (and $SO_4^=$) at Torres del Paine relative to Katherine. Volume-weighted acidity of precipitation at this remote South American site is contributed in order of importance, by sulfuric, carbonic, formic, nitric, and acetic acids.

SUMMARY AND CONCLUSIONS

1. Two-hundred and thirty-two samples of wet-only precipitation were collected for chemical analysis during four wet seasons (1980–1984) at Katherine in northern Australia.

2. Rainfall averaged 104.4 ± 12.8 cm/yr and ranged from 74.6 cm in 1982–1983 to 135.7 cm in 1983–1984.

TABLE 9. Volume-Weighted Mean Concentration of Dissolved Inorganic Substances in Precipitation at Katherine, Australia, Amsterdam Island in the South Indian Ocean, Torres del Paine, Chile, and the Hubbard Brook Experimental Forest, United States

	Katherine* (K)	Amsterdam Island[†] (A)	Torres del Paine Chile[‡] (T)	Hubbard Brook[§] (HB)	A/K	T/K	HB/K
$SO_4^=$	3.9	31.9	4.4	54	8.2	1.1	14
NO_3^-	4.0	1.4	0.5	24	0.35	0.12	6.0
H^+	18.3	9.0	4.9	70	0.49	0.27	3.8
NH_4^+	2.9	2.0	0.7	11	0.69	0.24	3.8
Ca^{++}	1.7	9.8	1.2	6.5	5.8	0.71	5.8
Mg^{++}	1.3	50.2	4.3	3.3	39	3.3	2.5
Cl^-	7.7	262	21.9	11	34	2.8	1.4
K^+	0.9	4.9	1.4	1.5	5.4	1.6	1.7
Na^+	4.3	225	18.7	4.8	52	4.3	1.1
Number of samples	147	79	23	>750	···	···	···

Values are in microequivalents per liter. Inorganic substances include sea salt.
*For 1980–1984, Table 4b; VWM pH = 4.74; average annual precipitation = 104 cm.
[†]For 1980–1983; VWM pH = 5.05; average annual precipitation = 112 cm [Keene et al., 1986].
[‡]For 1984–1985; VWM pH = 5.31.
[§]For 1963–1980; VWM pH = 4.15; average annual precipitation = 131 cm [Likens et al., 1985].

3. Free acidity in remote, terrestrial regions may be quite high (pH < 5), but it is caused primarily by organic acids (formic and acetic), presumably of natural origin. Some 64% of the volume-weighted, free acidity at Katherine was due to organic acids. In contrast, volume-weighted free acidity attributable to nitric and sulfuric acids was quite low (a maximum of ~21% and ~18%, respectively). The VWM pH at Katherine was 4.73, but that due to strong mineral acids only was 5.08.

4. Formic and acetic acids were highly correlated in rain at Katherine, but on a volume-weighted basis, formic acid was about 2.5 times higher in concentration than acetic acid. Because of its lower pK_a, the volume-weighted contribution of formic acid to free acidity is approximately 4.5 times that of acetic acid. Organic acids in rainfall at Katherine probably originated from terrestrial vegetation in the region.

5. Contributions of ions from anthropogenic sources to rain at Katherine are small. Average concentrations of sulfate and nitrate in rain at Katherine are about an order of magnitude lower than those in eastern North America.

6. In general, inorganic cations and anions are low in concentration in precipitation at remote, continental locations relative to sites in eastern North America. On average, hydrogen ion was the dominant cation (62% of total cationic equivalents), followed by Na^+ (16%) and NH_4^+ (10%); organic anions predominated (43%), followed by Cl^- (28%), NO_3^- (15%), and $SO_4^=$ (14%) in rain at Katherine.

7. Most ions had highest concentrations during the early part of the wet season (September through December).

8. Generally, concentrations of organic acids were greater during the early part of the wet season, when continental air mass trajectories predominated, and lower during the latter part, when amounts of precipitation were greater.

9. Air masses came to Katherine during the wet season primarily from the NE (51%), followed by the SE (14%), NW(13%), and SW (4%). Some 18% were missing or transitory between sectors. The trajectories associated with rainfall, however, had a different pattern: NE, 37%; NW, 29%; SE, 7%; and SW, 3%.

10. Precipitation at Katherine that was associated with air

masses from the northeast had the highest concentrations for most constituents and the largest wet depositions for all constituents measured in this study. These results are consistent with the hypothesis of higher source strengths for all constituents in the sector to the northeast of Katherine. Eastern trajectories tended to be associated with more localized convective storms, rather than with widespread monsoonal rains.

11. Approximately 60% of the inorganic nitrogen deposition (~100 mg/m² per yr) was due to $NO_3 - N$.

12. Although Katherine is characterized by a high frequency of lightning flashes, there was no support in the data for the hypothesis that lightning contributes significantly to nitrate in rainfall.

13. Inorganic ions attributable to sea salts were quite small at Katherine. For example, a maximum of 13% of the total sulfate was due to sea salt. Although chloride was the dominant inorganic anion, there was only a small increase in its concentration in precipitation from the more marine, air mass trajectories.

14. Individual rain events of low volume typically had higher concentrations of inorganic and organic dissolved ions.

15. Annual deposition of dissolved substances in rain at Katherine was either inversely related or not related to amount of rainfall.

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