Some Observations on the Acidity and Composition of Rainwater in Sydney, Australia, During the Summer of 1980–81

G. P. AYERS and R. W. GILLETT
CSIRO Division of Atmospheric Research, Station Street, Aspendale, Victoria, 3195, Australia

Abstract. During the summer of 1980–81, a rudimentary form of wet-only event sampling was employed to collect a total of 294 rainwater samples at 12 sites spread across the metropolitan region of Sydney, Australia's largest city. From the samples were determined conductivity, pH, ammonium, chloride and nitrate ion concentrations as well as deposited water volume. Supplementary data consisting of city-wide averaged SO_2, NO_2, NO, and O_3 concentrations and 950 mb wind speed and direction were obtained for times coinciding with the period during which each event occurred.

The pH of rainwater upwind of the city and unaffected by urban/industrial emissions was found to be usually $\geqslant 5$, whereas the volume-weighted mean pH of all the metropolitan samples was 4.4, indicating that local emissions significantly increased rainwater acidity in the near field. Time available for conversion of precursors to acids averaged 1–2 h only.

Considerable day-to-day variability in rainwater composition was observed. Factors identified as contributing to this variability included precursor gas concentration, wind speed, wind direction, amount of water deposited per event and possibly time of day. These results show that physical/ meteorological factors cannot be excluded from consideration if variance in rainwater composition data is to be explained.

Key words. Rainwater acidity, rainwater composition.

1. Introduction

Interest by agriculturalists in the amount and composition of precipitation in Australia stretches back well into the last century, being motivated by the continent's relatively low average rainfall and less than fertile soils. However, in recent times interest has become more widespread because of the world-wide realization that wet deposition is a major pathway for the removal from the atmosphere of many anthropogenic effluents. Airborne acids and their precursors have received particular attention.

In Australia, as elsewhere, questions as to the extent of anthropogenic contributions to precipitation acidity and potential long-term consequences are heard in popular, government and scientific circles. It is usually acknowledged that with a population of only 15 million inhabiting a large continent (area $\sim 8 \times 10^6$ km^2) the potential for wide-spread formation of highly acidic rainwater is likely to be small. Furthermore, by world standards Australian coals and oils are low in sulphur, typically containing by mass 0.3–0.5% and 0.1–0.15% S respectively. Sulphur dioxide emissions are therefore correspondingly low.

On the other hand, five out of six state capital cities have populations $\geqslant 10^6$, with the consequence that the concentrations of atmospheric oxidants and acid precursors are elevated to some degree in the region of each urban/industrial area. In addition, large reserves of coal and minerals in Australia make it an attractive site for cheap power generation and activities such as metal smelting, both of which can make significant contributions to regional atmospheric acidity when carried out on a large scale. Thus, although widespread occurrence of acidic rain in Australia seems unlikely on intuitive grounds, it is not so easy to discount the possibility that localised regions having elevated levels of rainwater acidity already exist, or may occur in the future.

An exhaustive survey of both published and unpublised data, mostly agricultural in origin, failed to give any useful picture of either the levels or spatial distribution of rainwater acidity in Australia. In almost all cases either pH was not measured, or the data came from the usual monthly wet-plus-dry deposition that probably tells more about the composition of soil dust than about rainwater acidity. This lack of information prompted us to begin a study of rainwater composition in regions of the country that appear to be most conducive to the formation of acidic rain.

Here we report the results of the first series of observations, carried out in Sydney during the summer of 1980–81. Sydney was chosen for this initial work because it is Australia's most populous (pop. $\sim 3 \times 10^6$) and polluted city (SPCC, 1983). The choice of summertime reflects U.S. experience that rainwater acidity levels are highest in summer. Together these choices should specify worst-case conditions for urban/industrial centres in this country. The aims of this study were (1) to observe whether in Australia, as overseas, the pH of rainwater tends to be lowered by anthropogenic emissions in an urban/industrial region; (2) to discern in broad terms what factors contributed to the observed levels of acidity and their variation. However, a major difference between this and most other studies is that long-range transport plays little part in the atmospheric acidity encountered in Sydney. As a result this study concerns primary acid emissions and 'near-field' conversion of precursors to acids over short timescales — minutes to a few hours only.

2. Experimental

Rainwater was collected between 19 November 1980 and 31 March 1981 at 10 sites distributed across the Sydney metropolitan area, as shown in Figure 1. A further two sites, numbers 2 and 12, were located in the Blue Mountains to the west of Sydney, 65 and 70 km respectively on a bearing of $300°$ from the city centre. Each collector consisted of a 20.3 cm diameter polyethylene funnel draining directly into a polyethylene bottle of 0.6 dm^3 capacity. Initially, and at approximately monthly intervals thereafter, the collectors were cleaned with detergent followed by multiple rinsing with de-ionised water, the pH/conductivity of the rinsewaters serving as a check on cleanliness.

The collectors were located at least 2 m above ground level in such a way as to be free from splashing or any carryover from buildings or trees (cone angle for overhead objects $\leqslant 30°$). Sampling was carried out on an event basis, the collectors being triple-rinsed with
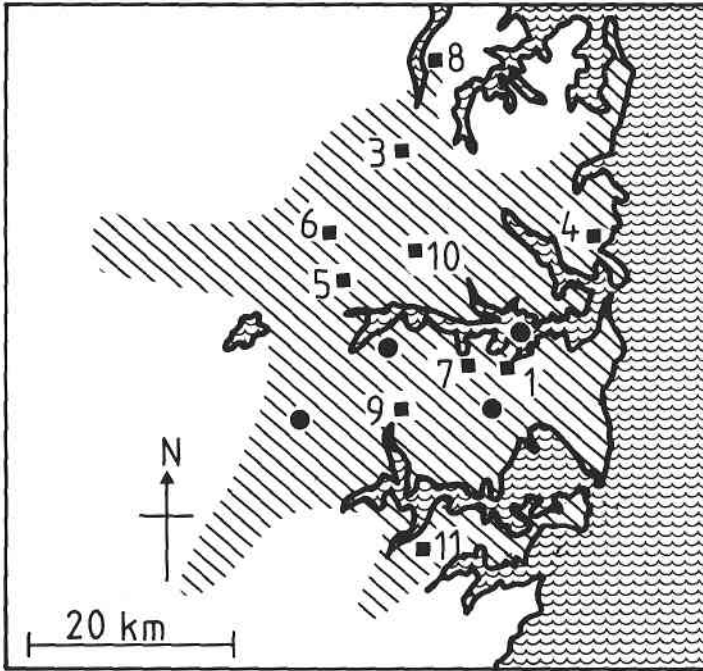
Fig. 1. Rainwater collection sites (numbered squares) and approximate extent of the densely populated urban areas (hatched region). The locations of sites 2 and 12 are given in the text. SPCC monitoring sites are shown as filled circles.

distilled, de-ionised water immediately prior to each event. However at none of the sites was it possible to ensure that every available event was sampled. This reflects the fact that each site was manually operated by Divisional staff, and that staff members were not always available. For the same reason sampling was not strictly 'wet-only' as collectors were sometimes exposed some hours before the onset of rain and sometimes could not be retrieved for some hours after the event. However, at each site at least once during the experiments exposure of the collector for 1–5 h in the absence of rain was employed as a means of assessing dry fallout. After exposure the collector was rinsed with 20 cm³ of de-ionised water having pH ~5.4. In all cases, the pH of the rinsewater was not more than 0.05 pH units from the initial pH, indicating that over short periods dry fallout was unlikely to be a problem.

Samples were brought to the laboratory for analysis with minimum delay after each event, usually within 24 h. Storage was at 2°C in the dark. From each sample were determined volume, pH (Activon model BJ 9210 combination electrode), conductivity ('in-house' cell and 1 kHz bridge) and the concentrations of ammonia (Orion Research model 95-10 ammonia-specific electrode or indophenol blue colourimetric method; Dal Pont *et al.*, 1974), chloride (thiocyanate colourimetric method), and nitrate (*o-p* xylene colourimetric method; Osibanjo and Ajayi, 1980). Measurement uncertainties were estimated

from replicate measurements to be (~95% confidence) ±0.03 pH unit and ±20% in conductivity and ion concentrations.

3. Scope of the Study

Limited manpower and acccess only to simple analytical instrumentation dictated that complete inorganic analyses could not be performed. The choice of pH, conductivity, ammonia, chloride, and nitrate for analysis was made on the basis that these parameters should in some way reflect, respectively, free acidity, total ionic loading, neutralized acids, sea salt and nitric acid. Sulphate concentrations are not reported because attempts to determine sulphate by wet chemical techniques proved to be unsatisfactory.

Since the rainwater data were gathered on an event basis, it was possible to supplement the chemical information with meteorological and air quality data that are gathered on a routine basis in Sydney. Supplementary data used in this study consists of wind information gathered at Sydney airport by the Bureau of Meteorology and hourly mean concentrations of SO_2, NO_2, NO and O_3 recorded by the State Pollution Control Commission (SPCC) at several urban sites. In cases where the gas records showed concentrations to be less than the 1 ppbv detection limit, we assume a value of 0.1 ppbv. This assumption only significantly affects the SO_2 record, which was often near the detection limit, and below it about one quarter of the time. While precision in all these data records is of order 1 ppbv, the absolute calibration could be uncertain by up to 3 ppbv.

One question that affects the selection of appropriate supplementary data concerns the definition of an 'event'. Should each shower be treated as a separate event, or when showers are not too far apart in time and apparently from the same storm system should they be combined and classed as a single event? This type of question has been considered to some extent by Thorp and Scott (1982), and merits further discussion in the literature. However, in the present case pluviographs were not available, so each event could be specified only by the time the collector was exposed and the time it was retrieved. Given that in practice the actual event duration was sometimes significantly less than collector exposure time, and that in any case the gas concentrations generally showed high autocorrelations over lags of a few hours, we made the simplifying assumption that the event had occurred during the middle hour of each collector exposure period: our data thus consists of the mean gas concentration during that hour. Records were available from the SPCC's 2 urban SO_2 monitoring sites and 4 urban NO_x/O_3 monitoring sites (Figure 1). The SO_2 monitoring sites are at Lidcombe and Rozelle; the NO_x and O_3 sites are Lidcombe, Rozelle, Earlwood, and Warwick Farm. For each event the gas concentrations from the various sites were arithmetically averaged to give a single value. This was done because we judge that the overall data quality is such, involving as it does a number of simplifying assumptions, that there is no point in searching for more than a general indication of day-to-day trends in the gas concentrations.

In a similar way, the wind data available from Sydney Airport, located on an extensive plain to the south of the city centre, are tacitly assumed to represent the general pattern of wind velocity and direction over the region. Winds at 950 mb were chosen as being

representative of flow in the polluted, sub-cloud layer. Both the wind data and the air quality data were only selected for occasions when the collector was exposed for ≤24 h and the wind direction could reasonably be interpolated from the available 6-hourly data (four balloons per day). This was taken to be the case if wind direction varied no more than ±45° over the two 6-hourly data points prior to, and the two points after the event.

The complete data set was derived from 294 events spread across 12 sites. Each event yielded data on rainwater amount, pH, and conductivity. Ammonia, chloride, and nitrate determinations were made on 240, 215, and 202 samples, respectively. Wind information and SO_2, NO_2, NO, and O_3 data were obtained for 225 events according to the criteria given above.

4. Results and Discussion

4.1. *Rainwater Acidity*

A summary of the rainwater composition data is given in Table I in terms of volume-weighted means for each site. With the exception of site 11, the mean pH values are similar, the range being −0.19, +0.23 pH units about the mean of 4.44 calculated from all the data.

The distribution of precipitation amount with pH for all the data is shown in Figure 2, from which it is apparent that little of the rainwater had pH > 6 while 90% had pH < 5.4. The lowest pH observed was 3.6. In areas of concern in the Northern Hemisphere, distributions of similar shape have been recorded, but shifted to lower pH values by 0.5 pH units or more, reflecting annual means of ~4.0 and extreme event values of pH < 3. Thus, the acidity we have found in Sydney rainwater is not high by northeastern U.S. standards (see, for example, Miller *et al.*, 1978) but is more akin to levels reported in other areas, such as Florida (Masden, 1981).

Table I. Summary of site data, volume-weighted means. Concentrations in $\mu mol/dm^3$

| Site	No. of samples	Conduc-tivity (μ S/cm)	pH	$[H^+]$	$[NH_4^+]$	$[Cl^-]$	$[NO_3^-]$
1	39	30.0	4.36	43.7	14.8	145	8.4
2	27	24.3	4.47	33.9	14.2	73.0	15.2
3	28	25.2	4.44	36.3	16.0	91.5	8.2
4	7	30.9	4.48	33.1	51.6	256	26.8
5	22	22.0	4.52	30.2	32.5	128	23.7
6	30	37.0	4.47	33.9	17.1	111	11.0
7	30	29.9	4.56	27.5	12.7	105	7.8
8	45	28.3	4.67	21.4	21.3	124	14.4
9	11	39.3	4.41	38.9	60.7	175	79.2
10	34	34.4	4.25	56.2	25.9	169	21.8
11	10	28.2	5.08	8.3	9.6	123	11.9
12	11	20.7	4.34	45.7	12.9	57.9	41.1
All sites	294	29.2	4.44	36.3	18.6	119	13.6
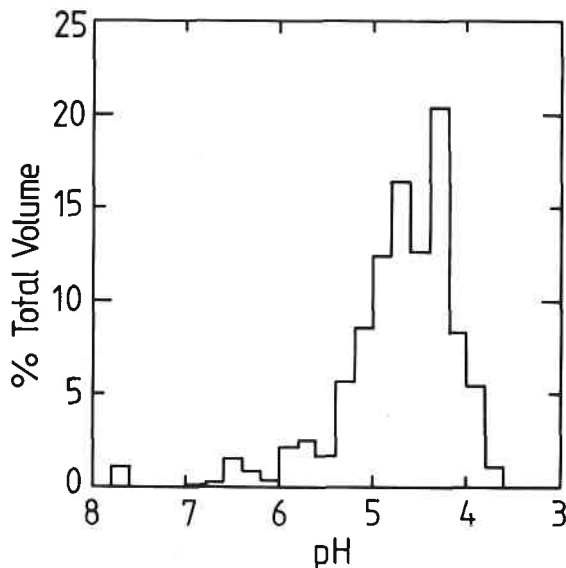
Fig. 2. Percentage of the total rainwater collection having pH in the indicated 0.2 pH unit intervals.

Nevertheless, the levels of acidity found are not insignificant, and do suggest that the Sydney metropolitan region acts as a source of atmospheric acidity. This conclusion results from a number of considerations:

(a) long-range transport seems unlikely to be a major contributor, since sources of NO_x and SO_2 comparable with the Sydney region, in which for this discussion we include the smaller satellite cities of Wollongong 50 km to the south, and New-castle 100 km to the north, are far removed. The nearest urban/industrial areas comparable in size are Brisbane (pop. ~10^6), 750 km to the north, Adelaide (pop. ~10^6), 1200 km to the west and Melbourne (pop. ~2.5×10^6), 750 km to the southwest. Intervening countryside is rural in character with few SO_2 or NO_x sources. In any case, rain-bearing winds in summertime are mostly onshore (south easterly) in Sydney not northerly or westerly.

(b) The coastline affords a sharp distinction between the city, as a potential source of acidity, and the ocean, an area devoid of such sources. The two sites placed close to this boundary, sites 4 and 11, are effectively upwind of the city during onshore wind conditions and downwind during offshore winds. From the 17 events recorded at these two sites the volume weighted mean pH of 11 onshore events (three at site 4, eight at site 11) was 5.12, while for the six offshore cases (four at site 4, two at site 11)·the mean pH was significantly lower at 4.41. (No similar comparison was possible using the two inland sites (2 and 12), since only one of the 38 events sampled happened to occur during offshore winds.)

(c) Scott (1978) reported the pH of cloud water collected from several clouds in the

vicinity of Sydney during August 1976. He found a mean pH of 6.2 for 10 water clouds upwind of Sydney and a mean of 4.9 for three water clouds downwind.

(d) As an adjunct to the present study four events were sampled at the sparsely populated coastal site of Tuross Heads, 270 km south of Sydney during a two-week period in December 1980. Winds were southeasterly, placing the site far upwind of Sydney. The pH values observed ranged from 4.82 to 6.46 and had a volume-weighted mean of 5.19.

These considerations plus the 294 individual rainwater pH measurements provide enough information for our first aim to be met; that of discerning whether the urban area of Sydney affects the pH of rainwater falling over the city. The evidence we have permits the following conclusions concerning the acidity of rainfall in the Sydney region, at least during the summer of 1980–81:

(1) the pH of rainfall uninfluenced by urban/industrial activities was probably mostly $\geqslant 5$;

(2) in contrast the pH of rainfall influenced by Sydney was most often <5; and

(3) the overall mean pH of 4.4 and extreme low value of 3.6 indicate that pH values were still ~0.5 pH units on average higher than those observed routinely in some areas of Europe and the U.S.

4.2. *Factors Affecting Rainwater Composition*

4.2.1. *Spatial Variability.* During the period of data collection it became apparent that even on days of widespread rain there was large variability in rainwater composition from site to site. To investigate this observation pairwise site-site correlation coefficients were calculated for same-day events for each of the ion concentrations, conductivity, and rainfall amount. Results for rainfall amount and $[H^+]$ are shown in Table II, where values of correlation coefficient are shown only when seven or more pairs of observations were available for computation.

The results shown are typical of all cases, there being both positive and negative correlations, and few coefficients greater than ±0.6. The lack of consistently positive correlations and the generally low correlation coefficients compared with results for some other studies (for example, MAP3S/RAINE, 1982) probably originate in the physical nature of the rainbearing systems encountered (and perhaps to some extent in the fact that shorter time and space scales were under study in Sydney). Summertime clouds in Sydney tend to be vigorously convective in nature, producing rainfall patterns variable in space, time and intensity over scales comparable with site-site separations. Individual cells may also cause some patchiness in precursor gas concentrations by perturbing local wind fields and local mixing depth. Under these conditions, it may be that no high correlations can be expected on less than seasonal time scales.

4.2.2. *Wind Direction and Time of Day.* As shown in Figure 1, Sydney is a coastal city extending westwards from the continental coastline, which in the vicinity of the city

Table II. Site-site correlation coefficients. Minimum number of data pairs contributing to each coefficient is seven; the average number is 11.5

Rainfall amount

Site 1	2	3	4	5	6	7	8	9	10	11	12
1											
2											
3	−0.25										
4											
5											
6	−0.47	−0.60									
7		0.33			0.11						
8		0.32			−0.03	−0.06					
9	−0.41	0.51									
10	−0.39	0.25			0.05	0.51	0.54				
11				−0.12	−0.30	−0.20	−0.45		−0.12		
12					−0.14	−0.10	0.06		−0.49		

[H⁺]

Site 1	1	2	3	4	5	6	7	8	9	10	11	12
1												
2												
3	−0.38											
4												
5												
6	0.72	0.17										
7		−0.39				−0.02						
8		−0.22				0.12	0.24					
9		0.26	0.18									
10		0.04	0.08			−0.50	0.26	0.02				
11					0.35	0.48	0.74	−0.29		0.23		
12						0.56	−0.47	0.36		0.55		

approximates a straight line along a 30–210° bearing. Since oceans and continents have well-documented differences in source strengths for a number of gas and aerosol species, it seems reasonable to hypothesise that rainwater composition in Sydney may depend somewhat upon wind direction.

In Figure 3 volume-weighted chloride and ammonium ion concentrations are shown plotted as a function of 30° wind direction sectors. As a general classification wind directions between 30 and 210° may be considered to be 'onshore' winds, while 210 to 30° can be considered to be the 'offshore' wind sector. It is evident from Figure 3 that the expected onshore maximum in chloride, originating from sea salt aerosol, is observed. On the other hand, ammonium ion is highest in concentration during offshore winds, an observation consistent with ammonia gas measurements that show the continent to be a much stronger source of ammonia gas then the ocean (Ayers and Gras, 1979).

A similar stratification of the data on number of events and rainfall amount per event is represented graphically in Figure 4. Not only did the vast majority of events occur during onshore winds, but rainwater volume deposited per event was also very much higher for onshore winds while most of that (72% of the total rain) occurred during winds from the 90–180° quadrant. These observations accord very well with historical records from the Bureau of Meteorology showing south-easterly winds to be the dominant rain-bearing winds for Sydney in summer. They also suggest that if scavenging efficiencies are
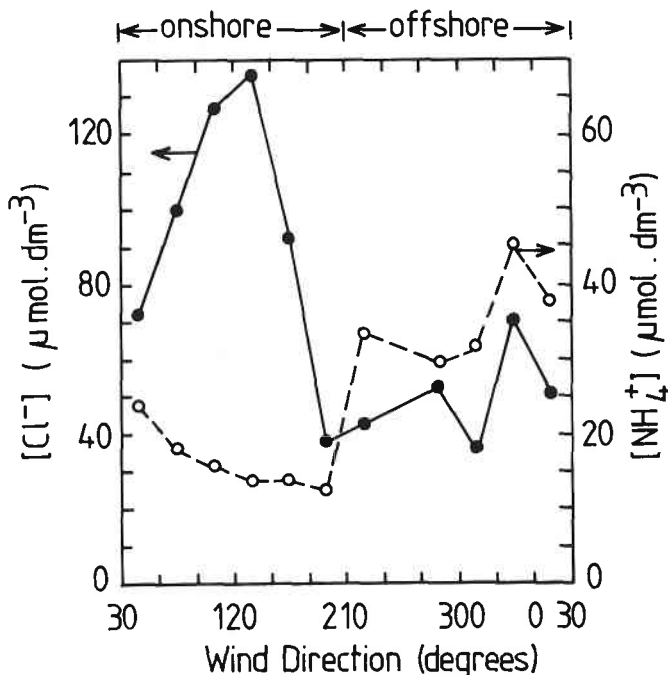

Fig. 3. Variation of rainwater chloride and ammonium ion concentrations with variation in 950 mb wind direction. 225 events, all sites included, 30° wind sectors.
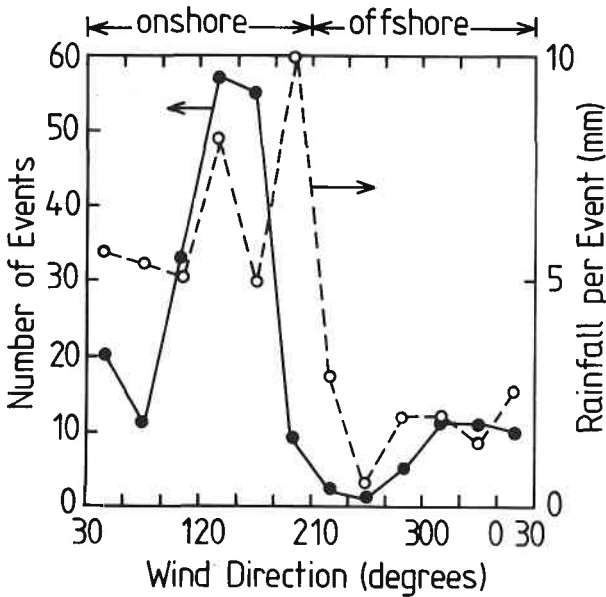
Fig. 4. Number of events and mean rainfall per event as a function of 950 mb wind direction. 225 events, all sites included, 30° wind sectors.

in any way related to rainfall amount per event, as has often been suggested (for example, Junge, 1963; Dawson, 1978), then this factor may be one source of any significant differences between the composition of rain in offshore and onshore winds.

As well as a dependence on wind direction, it seems reasonable to hypothesise that rainwater composition may be dependent upon time of day. There are well-known diurnal variations in such relevant factors as temperature, UV radiation (photochemistry), atmospheric mixing, and source strengths (for example, the morning NO maximum associated with peak hour traffic).

We have attempted to gain some insight into the effects of both wind direction and diurnally varying processes by stratifying all the data into four broad categories: daytime-onshore winds, daytime-offshore winds, nighttime-onshore winds, and nighttime-offshore winds. The onshore/offshore categories follow the wind-direction criteria given earlier. Daytime and nighttime reflect approximate local conditions: 0600–2000 and 2000–0600 local time. The results of this stratification for the various rainwater composition parameters are given in Table III where the calculated mean concentration is presented for each category. The standard error associated with each estimate is given parenthetically. In the case of the volume-weighted means, the associated standard error is estimated from the average variance of the data (Bevington, 1969). The average number of data points contributing to each mean was about 70, 100, 10, and 30, respectively, for the day-onshore, night-onshore, day-offshore, night-offshore categories. Both volume-weighted and geometric means are given since both receive common usage in the literature.

From Table III it is apparent that the mean values of hydrogen ion concentration and

Table III. Mean values according to wind direction and time of day, all site data pooled. Standard error for each mean is given in parentheses. Concentrations in $\mu mol/dm^3$, conductivity in $\mu S/cm$, SUM = $[H^+]$ + $[NH_4^+]$. On average the number of points contributing to each mean was ~ 70, 100, 10, and 30 for day-onshore, night-onshore, day-offshore and night-offshore categories respectively

Variable	Mean			
	Volume-weighted		Geometric	
	Onshore	Offshore	Onshore	Offshore
$[H^+]$				
(day)	43.1 (5.1)	35 (11)	14.3 (3.1)	15.9 (9.7)
(night)	33.2 (3.4)	34.5 (6.3)	14.0 (2.1)	10.2 (3.6)
$[Cl^-]$				
(day)	85 (15)	85 (22)	88 (15)	91 (19)
(night)	122 (17)	41 (13)	97 (16)	46 (11)
SUM				
(day)	58.2 (6.2)	87 (19)	47.8 (4.9)	66 (15)
(night)	51.1 (4.7)	78 (13)	46.7 (4.8)	66 (11)
$[NH_4^+]$				
(day)	13.1 (2.4)	43.6 (9.1)	17.1 (2.2)	36.0 (9.5)
(night)	16.2 (2.9)	36 (10)	19.0 (2.4)	36.6 (8.3)
$[NO_3^-]$				
(day)	11.6 (3.7)	62 (19)	8.8 (1.7)	43 (11)
(night)	9.1 (3.4)	44 (16)	6.7 (1.1)	22.9 (7.3)
conductivity				
(day)	27.6 (1.9)	43 (12)	30.3 (2.2)	34.8 (7.3)
(night)	29.0 (2.7)	28.2 (2.8)	30.3 (2.2)	31.6 (2.3)

conductivity show no significant variation with respect to the day/night, onshore/offshore categories. For ammonium ion also there are no significant diurnal differences, however the onshore/offshore differences mentioned earlier in conjunction with Figure 3 are indeed found to be significant for both the daytime and nighttime categories (for the geometric means significance is at ~97% and >99% confidence respectively).

The overall maximum in chloride concentration during onshore winds is shown in Table III to be produced entirely by the two-thirds of total data that fall in the nighttime categories (difference in geometric means significant at >99% confidence). The lack of onshore/offshore difference for the daytime categories could be a statistical artifact, since two of the only eight points in this category were unusually high, contributing a 21 $\mu mol/dm^3$ upwards bias in the mean. On the other hand, a real physical process may be indicated; for instance, there is some evidence (SPCC, unpublished data) that stationary source HCl emissions in Sydney are substantial, of order 10^9 g/yr, although it is not known how the emissions are distributed diurnally. Clearly a larger data set and further information on HCl source characteristics are needed for this apparent anomaly to be resolved.

For nitrate ion the means in Table III are much larger in concentration in offshore winds than in onshore winds (the differences in both pairs of geometric means are signifi-

cant at >99% confidence). At least in part, this is probably a reflection of the fact that urban and industrial activities that occur on the continent are strong sources of NO_x whereas the ocean is believed to be a rather minor source. In addition, the data give a weak indication of a day/night difference in mean concentration, with a daytime maximum (in the onshore case the geometric means are different at 70% confidence, in the offshore case the difference is significant at 87%). A daytime maximum, especially during offshore winds, could be reasonable on two counts. The first is that NO_x emissions are higher in the daytime, leading to higher NO_x concentrations (discussed later). The second is that the conversion of NO_x to nitrate may be modulated by photochemical processes, which peak in daytime (OH radical maximum in daytime, minimum at night. For example, see Davis et al., 1979).

The final concentration parameter considered, SUM, was included on the basis that U.S. experience shows the sum of hydrogen ion plus ammonium ion concentrations to be a fair estimator of the total nonsea salt sulphate plus nitrate concentrations in areas of elevated rainwater acidity (Bowersox and DePena, 1980). Thus, in the absence of data on sulphate, it provides our only means of estimating the total contribution of nitric plus sulphuric acids to the observed rainwater composition. The values in Table III give some indication (90% confidence) that the total of free, plus ammonia-neutralised acids is higher in the offshore wind case, but there is no obvious diurnal variation in mean concentration.

Table IV. Format as for Table III except arithmetic means replace volume-weighted means. Wind speed in m/s, rainwater amount in mm, gas concentrations in ppbv

Variable	Mean			
	Arithmetic		Geometric	
	Onshore	Offshore	Onshore	Offshore
windspeed				
(day)	4.7 (0.3)	3.7 (0.6)	4.2 (0.2)	3.2 (0.6)
(night)	4.5 (0.2)	4.6 (0.3)	4.0 (0.2)	4.2 (0.4)
SO_2				
(day)	1.9 (0.2)	1.8 (0.2)	0.94 (0.20)	1.6 (0.3)
(night)	1.5 (0.1)	1.7 (0.2)	0.84 (0.14)	1.2 (0.2)
O_3				
(day)	13.2 (0.9)	19.6 (3.6)	10.0 (1.2)	14.8 (4.8)
(night)	8.6 (0.5)	7.9 (1.3)	6.3 (0.7)	4.0 (1.2)
rain amount				
(day)	6.4 (0.7)	1.6 (0.4)	3.0 (0.6)	1.2 (0.3)
	6.2 (1.2)	2.1 (0.3)	3.1 (0.8)	1.2 (0.3)
NO_2				
(day)	11.5 (0.7)	13.1 (0.8)	10.1 (0:6)	12.0 (2.0)
(night)	9.6 (0.6)	13.7 (1.0)	8.0 (0.5)	12.3 (1.1)
NO				
(day)	6.8 (0.5)	8.6 (0.4)	4.9 (0.7)	7.4 (1.6)
(night)	5.1 (0.6)	7.8 (1.8)	3.0 (0.3)	4.3 (0.9)

The remaining variables in the data set were subjected to the same stratification as the ion data, with the results shown in Table IV. Note that arithmetic means replace the volume-weighted means of Table III. It seems unlikely that difference in wind speed would have contributed greatly to any of the differences in mean ion concentration discussed earlier, since the mean wind speeds vary relatively little. However, the data on rain deposition per event confirms that this factor does differ significantly ($>$99% confidence) between the onshore and offshore wind cases, as had been deduced previously from Figure 4. However, the added stratification into day/night categories reveals no additional difference.

For SO_2, NO_2, and NO, particularly in the case of the geometric means, there seems to be a weak, but general indication that the gas concentrations are slightly larger in offshore than in onshore winds. (the significance of the differences for the day/night categories is 95% and 87% for SO_2, 64% and $>$99% for NO_2, and 85% and 85% confidence for NO). Once again such observations seem reasonable since continental sources of these gases are generally thought to be stronger than oceanic sources. It also implies that the same behaviour with wind direction is shown by these gaseous acid precursors and the acid-related rainwater components NO_3^- and SUM. In the cases of NO and NO_2 there is also some identication of a difference in the means between the day/night categories. (Significance at $>$99% confidence for the NO and NO_2 onshore categories, and 91% for the NO offshore category.) Thus, the NO_x means appear to mirror the behaviour of the rainwater NO_3^- means in that weak diurnal as well as wind-direction differences can be discerned. It seems likely that if they are real, higher gas concentrations in daytime would simply reflect greater daytime emissions, particularly by automobiles, which are the major NO source in Sydney (SPCC, 1983).

The situation with the mean O_3 concentrations can be interpreted as follows. Photochemical production of O_3 during the day contributes to the daytime maximum, nighttime minimum observed in both offshore and onshore wind categories, and also to the larger mean concentration in offshore winds during the day. At nighttime, however, the offshore category exhibits the lowest mean concentration because diminished turbulent mixing in the boundary layer and destruction of O_3 at the Earth's surface combine to reduce the O_3 concentration. Ozone is also destroyed by reaction with any nighttime NO emissions. The O_3 reduction is less pronounced for onshore winds at night because turbulent mixing diminishes less in the marine boundary layer and destruction of O_3 at the water surface is far slower than at the land surface (Galbally and Roy, 1980).

One further comment worth making is that the gas observations probably cannot be interpreted completely on the basis of the usual diurnal patterns found in smoggy regions. The reason for this is that in the present work, the gas observations correspond exclusively to periods during which rainfall occurred, whereas smog processes generally are discussed for cloud-free/rain-free occasions. Atmospheric mixing processes and stability are quite different in these two cases, so the chemical conversion processes are probably also not equivalent.

4.2.3. *Regression Analysis*

(a) Precursor Gases. As applied to the analysis of rainwater composition data here, and elsewhere (for example MAP3S/RAINE, 1982), multiple regression is applied in an empirical fashion. As such the results should be considered to be qualitative only, since misleading correlaions can sometimes occur, particularly if a complete set of dependent variables cannot be specified (Mosteller and Tukey, 1977). Furthermore, it should always be kept in mind that in any group of variables correlated with each other at, say, 90% confidence, on average one in ten of the correlations will be fortuitous.

Prior to analysis of the full data set the gas concentration and wind speed data was fitted to a simple linear equation of the form

$$\log_{10} Y = A + B \cdot \log_{10} X \tag{1}$$

where Y is gas concentration and X is windspeed (observed range $0.5-11$ m/s). Resultant regression coefficients are given in Table V for the onshore wind category. The low correlation coefficients are to be expected, since factors other than wind speed certainly affect the gas concentrations. Nevertheless, the correlation coefficients are significant and the slopes are different from zero at a high significance level ($>99\%$ confidence). However, no results are shown for the offshore wind category since for this smaller data set none of the regressions was significant even at 85% confidence.

Table V. Regression coefficients, Equation (1). Onshore winds only. Gas concentrations in ppbv, rain amount in mm

Y	A	Standard error	B	Standard error	Correlation coefficient	Number of points
SO_2	0.40	0.05	-0.35	0.09	-0.29	162
NO_x	1.32	0.05	-0.34	0.08	-0.33	160
NO	0.88	0.08	-0.45	0.13	-0.25	182
O_3	0.65	0.07	0.43	0.12	0.27	180
rain amount	0.21	0.12	0.46	0.20	0.17	185

The fact that in Table V the slopes for both SO_2 and NO_x are negative and identical, within experimental error, is consistent with our knowledge that the gases have the same ground level source (the metropolitan area). Thus, it seems that diurnal variations in source and sink strengths are not large enough to mask the expected physical relationship that concentration and wind speed should be inversely related for ground-level sources. However, unlike SO_2 and NO_x which appear to have acted somewhat as conservative tracers in the near field over the city, O_3 can be rapidly created or destroyed in the urban atmosphere and also has a natural source aloft. The major destruction processes are reaction with freshly emitted NO and heterogeneous destruction at the Earth's surface. During rainy periods production of O_3 by photochemical smog processes should be minimal. Increase in wind speed under these conditions should have two effects on O_3 concentration. First, any decrease in NO concentrations with increase in wind speed (Table V) should reduce the magnitude of the homogeneous O_3 sink; second, turbulent

Table VI. Regression coefficients, Equation (2). Calculated standard errors are given in parentheses

Y		A	B_i for specified X_i									Multiple correlation coefficient	Number of points
			$x_i = u$ (m/s)	h (mm)	SO_2 (ppbv)	NO_x (ppbv)	O_3 (ppbv)	$[H^+]$ (μmol/dm³)	$[NH_4^+]$ (μmol/dm³)	$[Cl^-]$ (μmol/dm³)	$[NO_3^-]$ (μmol/dm³)		
Conductivity	(onshore)	0.63 (0.09)								0.36 (0.09)	0.12 (0.03)	0.74	124
μS/cm	(offshore)	0.98 (0.34)								0.20 (0.12)		0.51	20
$[Cl^-]$	(onshore)	-0.15 (0.59)		-0.47 (0.08)		-0.63 (0.21)	-0.25 (0.15)	0.20 (0.07)				0.52	134
	(offshore)	-0.22 (0.27)		-0.57 (0.11)				-0.14 (0.09)				0.75	27
$[NO_3^-]$	(onshore)	-1.55 (1.11)	-0.83 (0.26)	-0.19 (0.13)		0.41 (0.23)	0.49 (0.18)	0.17 (0.08)	0.59 (0.12)			0.68	104
	(offshore)	-0.10 (0.36)							1.20 (0.26)			0.79	15
$[NH_4^+]$	(onshore)	-0.15 (0.35)	0.25 (0.17)	-0.27 (0.08)							0.30 (0.06)	0.64	90
	(offshore)	0.58 (0.17)									0.51 (0.11)	0.79	15
$[H^+]$	(onshore)	-0.86 (0.75)	-0.80 (0.29)	0.20 (0.12)	0.29 (0.20)					0.25 (0.10)	0.15 (0.10)	0.47	106
	(offshore)	-0.60 (0.69)	-0.73 (0.50)	0.35 (0.23)								0.33	39
SUM	(onshore)	-0.53 (0.62)	-0.23 (0.16)	0.20 (0.09)	0.27 (0.12)		-0.14 (0.06)			0.18 (0.06)	0.30 (0.06)	0.68	85
	(offshore)	-1.28 (1.10)	-0.18 (0.11)	0.32 (0.22)	0.36 (0.15)		0.48 (0.08)			-0.25 (0.13)	0.31 (0.10)	0.97	15

mixing down of O_3 from aloft should increase in efficiency with increasing wind speed. Both effects would lead to a trend for O_3 concentration to increase with wind speed, as observed, in contrast to the decrease expected and observed in SO_2 and NO_x concentrations.

The picture revealed by this simple analysis is that the gas concentration and wind speed data contain at least some qualitative information consistent with known atmospheric processes. It was important to establish this point, since a number of assumptions were made in the selection of this data, which it was hoped would make a useful addition to the ion concentration data in a multiple regression analysis.

The final entry in Table V shows the existence of a positive correlation (significant at 95% confidence) between rainfall amount per event and wind speed. This result, together with the others in Table VI, illustrates the complexity of factors that may be involved in determining rainwater composition. In this particular case only wind speed serves as a dependent variable, yet variations in this single variable are correlated with variations in concentration of two acid precursor gases (SO_2 and NO_2), one oxidising species (O_3) and one variable probably related to overall sub-cloud scavenging efficiency (rainwater amount per event). Clearly there is an interplay of many factors, physical, chemical and dynamical, leading to a given rainwater composition.

(b) Complete Data Set. To investigate the factors contributing to the observed variance in rainwater composition the four available gas concentrations and two simple meteorological parameters, wind direction and wind speed, were included in a multiple regression analysis. The data were fitted to an equation of the form

$$\log_{10} Y = A + \sum_i B_i \log_{10} X_i \tag{2}$$

where Y was ion concentration or conductivity and the X_i were other variables in the data set. The procedure adopted was to start with all possible X_i, then in successive calculations to delete the least significant X_i and repeat the fit until there remained only those X_i for which the associated estimates of B_i were different from zero by more than $\sim 1.5\ \sigma_i$, where σ_i is the calculated standard error associated with the estimate of B_i. For a fit using more than ~ 20 sets of normally-distributed data the arbitrary choice of $\sim 1.5\ \sigma$ represents $\sim 85\%$ confidence.

Wind direction was included in the analysis not explicitly as an additional X_i, but by stratification of the data into onshore and offshore wind categories prior to analysis. Although the onshore category always contained about 100 sets of data, the offshore category usually contained only 15–25 sets. Consequently, calculated uncertainties were larger in the latter case and few associations between variables were apparent according to the $\sim 1.5\ \sigma$ criterion. Calculated regression coefficients and associated standard errors are given in Table VI. (The hydrogen ion offshore regression was significant at 90%, conductivity/offshore at 98%, and all others at $>99\%$ confidence.)

Consider first the gaseous species SO_2, NO_x and O_3. At the $1.5\ \sigma$ level these gases contribute to the explanation of variance in ion concentration in only three cases, those of chloride, nitrate and SUM (hydrogen ion plus ammonium ion). The inverse relationship of NO_x and O_3 with chloride has no direct chemical significance of which we are aware,

nor are we aware of any physical or meteorological explanation for why days conducive to high NO_x and O_3 concentrations would be unfavourable to high rainwater chloride concentration.

For nitrate the positive correlation with NO_x, although not strong, adds weight to the conclusion that rainwater nitrate levels in Sydney are directly related to the locally emitted precursor gas concentrations. The additional strong positive correlation with O_3 is suggestive of this gas playing an important part in the NO_x to nitrate oxidation step. Given that the majority of the rain events occurred at night (137 events compared to 88 in daytime) a mechanism of the type suggested by Richards (1983) may be reflected in this result (see also the modelling results of Stockwell and Calvert, 1983).

The only regressions to which SO_2 contributed were those for which the dependent variable was H^+ or SUM, our estimator for total free-plus-neutralised acidity. This observation is consistent with the idea that rainwater acidity results in part from the atmospheric oxidation of SO_2 to H_2SO_4. The strong positive correlation between O_3 and SUM in offshore winds is at first sight suggestive of O_3 having an important role as an oxidant, however the negative correlation in onshore winds creates some doubt for this interpretation. At present this difference cannot be explained.

Rainwater amount per event, h, was a significant variable at the 1.5 σ level in five cases (Table VI), showing a positive correlation with hydrogen ion and with SUM, and inverse relationships with chloride, nitrate and ammonium ions. The latter behaviour is typical of virtually all other observations of this type reported in the literature and can be taken to be a general characteristic of in-cloud/sub-cloud scavenging processes. (Junge, 1963; Dawson, 1978; Lindberg, 1982; Kins, 1982). However, the increase in hydrogen ion concentration and SUM with increase in h is unusual. We are aware of only two other studies in which hydrogen ion concentration increased with rainfall amount (Dawson, 1978; Seymour and Stout, 1983). The explanation offered in these cases was, in effect, as follows. If the concentration of hydrogen ion in rainwater were determined principally by the balance between a strong acid and a strong base and were greater than about 10 $\mu mol/dm^3$ then we could write

$$[H^+] = [acid] - [base]. \tag{3}$$

If the acid and base incorporated in the rainwater were scavenged independently, then differentiating (3) with respect to h gives

$$\frac{d[H^+]}{dh} = \frac{d[acid]}{dh} - \frac{d[base]}{dh}. \tag{4}$$

Given the general observation that almost all species show a decrease in concentration with increase in h, we assume that the rate of decrease is constant, so

$$\frac{d[acid]}{dh} = -A,$$

and that the difference in the rate of scavenging between the acid and base can be accounted for by the factor B, such that

$$\frac{d[base]}{dh} = -B \cdot A \tag{5}$$

Substitution in (4) gives

$$\frac{d[H^+]}{dh} = A(B-1) \tag{6}$$

From which it can be seen that $d[H^+]/dh$ is positive if $B > 1$, that is if the base is scavenged more rapidly with increasing h than the acid.

This much-simplified picture does suggest that under some conditions hydrogen ion concentration may increase with increasing water deposition per event, the conditions being that $[H^+]$ results from a balance between acids and bases that have differing rates of scavenging, that for the bases being larger. In the study by Dawson (1978) in Arizona, the efficiently-scavenged alkaline substance was calcium carbonate aerosol. Since SUM also had a positive h-dependence in our case something other than ammonia, like $CaCO_3$, is also implicated in Sydney.

Wind speed made a significant contribution to the explanation of variance in four cases, but was not important for chloride or conductivity (Table II). The inverse relationship with wind speed apparent for nitrate, hydrogen ion and SUM is not surprising if the concentrations of these species are related to those of the precursors SO_2 and NO_x, since these gases showed an inverse wind speed dependence. The positive correlation of ammonium with wind speed is a puzzle. However, it does suggest that ammonia and the precursor gases SO_2 and NO_x have different sources. In the case of chloride ion, the lack of any wind speed dependence similarly may be related in some way to the particular source of this ion. It has long been known that in maritime air masses the mass loading of sea salt in the aerosol increases with wind speed (Woodcock, 1953), so it is not surprising that, in onshore winds, the rainwater chloride ion concentration behaves differently with wind speed than ions having precursors that decrease in concentration with wind speed. The lack of any wind speed dependence for conductivity follows the lack for chloride, since this ion serves as a major estimator for conductivity in the fitted regression (Table VI).

The most noticeable of the relationships between ionic species revealed by Table VI is that of nitrate with ammonium ion, hydrogen ion and SUM. It provides very clear confirmation that nitric acid makes an important contribution to rainwater acidity in Sydney.

Finally, as mentioned at the outset a confidence level of $\sim85\%$ could lead to a few apparent correlations that are fortuitous. Indeed there are some inconsistencies in Table VI. In addition to the unexplained positive wind-speed dependence on ammonium ion and the inverse relationships of NO_x and O_3 with chloride, the relationships of O_3 and chloride with SUM are hard to explain, insofar as the sign of each coefficient changes in going from the onshore to offshore wind category. One might postulate that the positive correlation of chloride with SUM for the bulk of the samples (the onshore case) may reflect primary HCl emissions in Sydney, as is apparently the case, for example, in the

U.K. (Martin, 1979). Unfortunately, however, little is known about HCl emissions in Sydney.

An alternative explanation for a correlation between acidity and chloride ion concentration in onshore winds could be that the sea salt aerosol acts in some way as a reaction medium in which hydrogen ions are produced. Certainly for SO_2 the deliquesced sea salt aerosol would provide an ideal aqueous medium in which oxidation to sulphuric acid could proceed via a number of pathways (Graedel and Weschler, 1981; Hitchcock *et al.*, 1980). Analogous pathways may operate for NO_2, or reaction with sea salt aerosol could proceed directly according to the mechanism discussed by Junge (1956) and Robbins *et al.* (1959). In fact, nitrate has been detected in individual particles thought to be modified sea salt particles, in Sydney, by Ayers (1978). However, the inverse relationship of O_3 with SUM and the change in sign of coefficients for both chloride and O_3 upon going to the offshore category remain as difficulties.

4.2.4. *Contribution of Nitric Acid to pH*. Acids likely to contribute significantly to observed pH include sulphuric, nitric and hydrochloric acids, and possibly formic and acetic acids (Galloway *et al.*, 1982; Keene *et al.*, 1983). In this study lack of complete data on composition restricts our consideration to nitric acid only.

The ratio of nitrate to hydrogen ion concentration gives an upper bound to the contribution of nitric acid to observed rainwater acidity. From Table I the volume-weighted means for the pooled data yield a value of 0.37 for this ratio, indicating that the maximum possible contribution of nitric acid to observed hydrogen ion concentration was only 37%.

An alternative approach is to use values for the nitrate to hydrogen ion ratio calculated for each individual event. For example, consider the pH range from 4.0 to 4.2: a total of 23 events had pH values within this small range. For these 23 events the geometric mean nitrate to hydrogen ion ratio was 0.23. Thus, for these relatively acid samples the upper bound for the contribution of nitric acid to hydrogen ion concentration was calculated to average 23%. The overall impression is that nitric acid was a significant acid in the Sydney samples, but perhaps not the major acid.

However, the geometric mean just discussed came from 23 values distributed over a rather wide 2 σ range extending from 0.01 to 6.3. This variability is an important feature of all the data. It shows that actually the nitrate to hydrogen ion ratio on any given day could be quite different from the calculated mean value. Clearly there were some occasions when nitric acid alone could have more than accounted for the observed pH, and other occasions when it made essentially no contribution to observed acidity. The implication is that a proper understanding of the role played by nitric acid, or any other acid, should be sought in terms of the processes underlying the day-to-day variability in and covariability between the concentrations of all rainwater acids, in addition to assessment of the long-term mean contributions of each acid.

5. Summary and Conclusions

During the summer of 1980–81 in Sydney the pH of rain unaffected by urban/industrial emissions was generally above 5. In contrast rainwater falling at 10 metropolitan sites and two sites 70 km downwind (west) of the city mostly had pH <5, the overall volume-weighted mean for 294 samples being 4.44. The lowest pH observed was 3.6. For geographical reasons, long-range transport of acids or precursors from other regions can be ruled out, so the lowering of rainwater pH over the metropolitan region must be attributed directly to local emissions of NO_x, SO_2, and any other unidentified acids.

A mean wind speed of ~4 m/s and a metropolitan area ~40 km across imply a maximum time for conversion of precursors to acids averaging less than 3 h. In fact since the city sites were randomly distributed across the metropolitan area, averaging a distance of 20 km rather than 40 km from the upwind boundary of the city, this time would typically be more like 1–2 h. Thus the lowering of rainwater pH from ~5.1, on average, at the upwind boundary of the city to ~4.4 over the urban area during conversion times averaging only 1–2 h might be thought of as a 'near-field' process. This is certainly so in the context of extended reaction times of 1–3 days typical of the long-range transport of acids and precursors observed in Europe and the U.S. Thus the present work shows that extended conversion times are not essential for the production of acidity: local sources can be a major source of local rainwater acidity.

Two important relationships between variables deduced from the data were (1) a positive dependence of rainwater nitrate concentration on the concentrations of gaseous NO_x and O_3; and (2) strong positive correlations between nitrate concentration and each of ammonium concentration, hydrogen ion concentration, and the sum of these two ions. The first relationship points to local NO_x emissions as the source of nitric acid and implicates O_3 in the conversion process. The second confirms the importance of nitric acid as a major contributor to rainwater acidity in Sydney and the importance of ammonia as a neutralizing agent. However, it was also found from the nitrate to hydrogen ion ratio for individual events with pH ~4 that highly acidic events still occurred on some occasions in the absence of a significant nitric acid input.

Finally, it is also quite clear from this relatively simple study that rainwater composition, at least in Sydney, cannot be understood purely in chemical terms. Variance in observed composition originates in the complex interplay of meteorological and physical as well as chemical factors: wind speed, wind direction, time of day and rainwater deposition per event are a few examples that could be deduced from the present study. It seems likely that no consistent picture or quantitative understanding of rainwater chemistry on a global scale will be forthcoming if the physical and meteorological aspects are not accounted for.

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