Precipitation composition at Cape Grim, 1977–1985

By G. P. AYERS[1]* and J. P. IVEY[2], [1]*CSIRO, Division of Atmospheric Research, Private Bag 1, Mordialloc, Victoria 3195, Australia,* [2]*Australian Government Analytical Laboratories, P.O. Box 84, Kingston, Tasmania 7150, Australia*

ABSTRACT

Rainwater composition data resulting from monthly, wet-only collections of maritime rain at Cape Grim, Australia, in the period April 1977 to March 1985 have been critically appraised.

High local wind speeds prove to be a major determinant of data quality: extremely high sea-salt loadings (average rainwater sodium and chloride concentrations in the low millimolar range) make estimation of excess sulfate impossible against a background sulfate concentration of about 150 μeq/l derived from sea-salt. The extreme wind speeds also cause considerable erosion of the Cape surface, leading to the ubiquitous presence of local soil components in collected rainwater. Both the rainwater data and data from the analysis of local soil samples show that these soil components significantly elevate rainwater pH (observed mean 6.01) and the concentrations of potassium and calcium. Effects upon other ions appear to be minimal, but cannot be ruled out.

Calculation of pH for rainwater having the long-term mean composition, but with the effects of local contamination excluded, yielded a value of 5.10. Further calculations in which sea-salt content of the rainwater was varied over the range observed at Cape Grim indicated that at this site, sea-salt alkalinity may be a major determinant of rainwater pH, leading to pH variations from <5 to >6.

1. Introduction

The precipitation composition program at Cape Grim commenced late in 1976, as a result of commitments made in Australia to establish at Cape Grim a baseline air-pollution station as part of the Baseline Air Pollution Monitoring Network (BAPMoN) sponsored scientifically by the WMO (World Meteorological Organisation). The early objectives of the BAPMoN program were given by WMO in publication No. 299 (WMO, 1974) and in revised form in WMO No. 491 (WMO, 1978). A further revision of the operations manual is currently under way.

From the beginning of the BAPMoN program, precipitation composition studies were considered to be of high priority, being listed in

WMO No. 299 as one of four elements in the proposed "minimum program" for baseline stations. This was because it was recognized that removal from the atmosphere of virtually all water soluble compounds, gaseous and aerosol-phase, is carried out substantially by incorporation into cloudwater and subsequent deposition in precipitation (the other major removal pathway is dry deposition). Long-term, global perturbations to the atmospheric cycles of many substances, perhaps arising from human activities, could well be expected to be evident in long-term precipitation records from remote regions. Such effects had already been noted on a regional basis in the cases of sulfate, nitrate and hydrogen ion in European precipitation (WMO, 1978).

Neither the scientific rationale behind a long-term observational program nor the observational methods can be expected to remain unmodified as the program progresses and evolves with time. The major change in the Cape Grim precipi-

* Present affiliation: International Meteorological Institute in Stockholm, Arrhenius Laboratory, S-106 91 Stockholm, Sweden.

tation composition program has been to change from monthly sampling to a form of event sampling, in line with recent recommendations. This change was instituted at Cape Grim on the 1st of March, 1985. The purpose of this paper is to present and discuss features of the monthly precipitation composition record obtained prior to then, extending backwards to January 1977. Our aim is two-fold: to point out certain limitations inherent in the data record, while also making some preliminary chemical interpretations. This sort of comment is essential, lest the data be accepted in the public domain at face value, and used in an unedited form to address specific scientific questions without due regard to various biases or errors that can be expected in virtually any raw data of this type. This has happened at least once with the Cape Grim data (Sequiera, 1981). Indeed we believe that all the BAPMoN data, now freely available from the National Climatic Center at Ashville, USA, should be assessed carefully before use.

2. The site

Cape Grim is situated at 40°41′S, 144°41′W, on the northwestern tip of the island of Tasmania, which is itself located 300 km south of the Australian continent. The Cape has almost vertical sides 94 m high, and juts out into the Southern Ocean in a southwesterly direction. This makes the Cape a useful site for sampling the prevailing strong southerly to westerly oceanic winds (the "roaring forties") that impinge frequently upon the Cape. Table 1 gives some meteorological characteristics of the site.

The observatory building sits atop the Cape some 10–20 m inland from the seaward edge, with the rainwater collector situated 2 m above ground and 20 m to the northwest. The immediate area is grass covered, while the cliff faces are composed of rather porous and friable rock and in places are subject to considerable wind erosion. More details can be found in the various Annual Reports (for example see DOS, 1986).

3. Collection methods

The data discussed here represent monthly, wet-only collections as recommended by the early WMO manuals, although it should be noted that during the initial phase more frequent sampling was carried out. An ERNI collector was used, with the spinning disk sensor set to open the collector at a perceived rainfall rate of 3 drops/min. From November 1977 the collector has been inhibited from operating if the station 10 m wind is not from the maritime, or "base-

Table 1. *Meteorological data from Cape Grim for calendar year 1983, except for rainfall for which the 8 year average, 1977–1983, was available. Annual average rainfall over the 8 year period was 794.3 mm*

Frequency distributions (annual)

wind speed		wind direction		Monthly averages			
(m s^{-1})	(%)	(degrees)	(%)	month	temp. (°C)	r.h. (%)	rain (mm)
0.3–2.9	1.2	1–45	7.4	Jan.	13.9	75.1	36.4
3.0–5.7	10.4	46–90	10.6	Feb.	16.4	77.9	27.2
5.8–8.4	21.2	91–135	13.3	Mar.	15.4	80.3	68.5
8.5–11.2	22.5	136–180	5.3	Apr.	12.6	81.6	58.1
11.3–13.9	21.2	181–225	15.6	May	12.3	82.3	77.5
14.0–16.8	14.1	226–270	27.2	Jun.	10.2	80.1	99.5
16.9–19.4	6.0	271–315	13.5	Jul.	9.4	78.4	91.9
>19.4	3.4	316–360	7.1	Aug.	11.0	78.9	107.7
				Sep.	10.6	76.8	75.2
				Oct.	11.2	81.9	63.0
				Nov.	12.9	80.2	53.6
				Dec.	14.1	76.8	35.8

line" sector, 190°–280°. Two years later, the criterion that the Aitken nucleus concentration be less than 600 cm^{-3} was added, followed in a further two years by the requirement that wind speed be greater than 5.6 ms^{-1}. Ayers and Gras (1983) have shown that these sampling restrictions should ensure that air masses having recent contact with land are infrequently sampled, so that rainwater collected should be as close to representative of Southern Oceanic rain as is possible to get at this coastal site.

It is impossible to quantify the accuracy with which rainwater volume is determined at Cape Grim, either by the ERNI or the standard raingauge. The problem is that strong winds (up to 40 ms^{-1}) are common during rainy, maritime airstreams. Often raindrops can be observed to have trajectories closer to horizontal than vertical, conditions under which it is notoriously difficult to accurately determine precipitation amount.

Prior to November 1978, the samples were collected at the end of each month and shipped in steam-cleaned polyethylene bottles to AGAL, (Australian Government Analytical Laboratory, Kingston, Tasmania) where pH and labile ion (nitrate and ammonium) concentrations were determined immediately, after which the samples were stored at 4°C in the dark. Remaining analyses took place over a few days.

In November 1978, the sampling procedure was modified by the installation of a 47-mm diameter filter between the funnel and collection bottle in the ERNI in an effort to exclude from the sample large particles eroded from the cliff face by wind. The pre-weighed, 8 μm pore-size cellulose acetate filters were changed monthly along with the collection bottle.

A further modification to the procedure was made in January 1981, after which rainwater was collected from the ERNI on a daily basis, was filtered through a 0.45 μm pore-size filter, added to any previous rain that month, and stored on-site at 4°C in the dark. At the end of each month the accumulated sample was sent to AGAL for analysis in the usual way. Determination of insoluble particulate mass was discontinued with this change in sampling protocol. As neither of these filtering protocols had any discernible effect upon average concentrations of hydrogen ion, excess calcium or excess potassium, the ions most

affected by soil contamination (see Subsection 6.3) the data below are discussed as a single set.

4. Analytical methods

Sodium, potassium, magnesium and calcium were determined by atomic absorption spectroscopy, ammonia by colorimetry (indophenol-blue method), pH and conductivity by standard electrode methods. Chloride, nitrate and sulfate were originally determined by potentiometric titration, colorimetry (Cd reduction) and nephelometry, respectively. From February 1983 suppressed ion chromatography (Dionex columns) has been used for these three anions. Technical details can be found in the series of Baseline annual reports, as can further details regarding the various aspects of sample collection (for example see DOS, 1986).

Replicate analyses of rainwater samples and of US NBS synthetic rainwaters suggest precision to be better than 10% for all ions, except ammonia, over the concentration ranges encountered. For ammonia uncertainty is within 20%. AGAL has participated in 8 rounds of international comparisons in which particular synthetic rainwaters were analysed by all participating laboratories. Results were quite satisfactory and consistent with the in-house estimates of precision noted above. Indeed the second BAPMoN Newsletter (WMO, 1987) summarises the performances of the 52 laboratories that have so far participated in the intercomparisons and ranks AGAL (Lab-code No. 4) second overall.

Cape Grim rainwater samples were analysed for pH, conductivity and ammonia within 2–3 days of receipt at AGAL, and were stored at 4°C for subsequent analysis of remaining ions within the following 1–2 weeks.

5. The data record

The data record consists of ion concentration data from a total of 99 monthly samples (DOS, 1986, pages 55–57). Scrutiny of the data record and removal of suspect data elements is necessary before any interpretation can begin. Sources of unrepresentative data include sample contamination at the point of collection, later contami-

nation, chemical reaction or biological activity during sample transport and handling, and analytical errors. In common with most others working with this type of data we acknowledge a degree of subjectivity in the data editing process adopted. Our aim was to produce a data record representative of "background", maritime air masses over the Southern Ocean. Thus our first step was to adopt the stringent sampling restrictions mentioned earlier, in an effort to exclude from the record data exhibiting any recent influence of the Australian continent.

Next, the statistical filtering technique of Rodhe and Granat (1984) was used to identify and eliminate data from samples that may have been heavily contaminated. The procedure simply involves exclusion of data points lying outside the range $(m - 3\sigma, m + 3\sigma)$, where m is the arithmetic mean and σ the standard deviation. After a few iterations this procedure converges to yield constant values of m and σ. A total of 41 data elements (see Table 2) were eliminated from the data record in this way, all by the $m + 3\sigma$ edge of the procedure, in keeping with our experience that positive outliers are the usual result of contamination.

Finally we made use of the fact that in clean, maritime rain the relative concentrations of the ions sodium, magnesium, chloride, potassium, calcium and sulfate vary little from those found in ocean surface water, this being particularly the case for the first three (Keene et al., 1986). For each rainwater sample from Cape Grim ratios of each ion to sodium, magnesium and chloride

were calculated, and in any case where a ratio was less than 70% of that found in seawater (Millero, 1974), data for the two ions concerned was further ratioed against potassium, calcium and sulfate. In the 13 such instances found the resultant pattern of ratios unequivocally identified one ion as having a suspect concentration value, which was then deleted from the data file. The number of values for each ion deleted in this way is given in Table 2.

The final data record obtained at the end of the editing procedures consisted of 66 samples for which all ion concentration data were available, and 33 samples for which one or more of the data elements was absent. Mass of insoluble particulates was available for 47 samples collected prior to January 1981. For the 66 complete sets of ion data linear regressions of cation sum on anion sum and calculated conductivity on measured conductivity, yielded results which indicate that the quality of the edited data is good (Table 3). Here and elsewhere in this paper the regression technique used is the reduced major axis technique advocated by Keene et al. (1986).

6. Results

For the major ions determined in this work the maritime atmosphere can be expected to contain at least two major classes of material which can be incorporated into rainwater, sea-salt aerosol, and the submicrometer particles and reactive trace gases that are ubiquitous in the troposphere.

Table 2. *Summary of data elements excluded by 3σ filter, and ion ratio consistency arguments, the latter in parentheses. Numbers tabulated for each ion identify the sample number as given in the data summary provided in Baseline 83–84 (DOS, 1986)*

	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	NH$_4^+$	Cl$^-$	NO$_3^-$	SO$_4^{2-}$
3σ filter	64	22	94	104	10	54	6	94
(consistency)	94	54	104		11	64	22	104
	104	64	(26)		22	77	29	(64)
	(96)	77	(31)		34	78	31	(75)
		104	(32)		35	94	34	(85)
		(51)	(40)		67	104	36	
			(64)		68	(35)	56	
			(85)		83	(82)	74	
					85		76	
					91		77	
					94		85	

Table 3. *Linear regression coefficients, standard errors, and correlation coefficients for ion sums ($\mu eq/l$) and conductivity ($\mu S/cm$); 66 data points*

Y	X	Slope (s.e.)	Intercept (s.e.)	r
cation sum	anion sum	1.002 (0.015)	−11.3 (28.6)	0.993
calc. cond.	obs. cond.	1.048 (0.035)	7.5 (6.9)	0.966

This expectation is born out by the long-term mean values for the ion data, shown in Table 4.

6.1. Sea-salt components

Included in Table 4 are potassium, magnesium, calcium, chloride and sulfate concentrations calculated assuming all sodium is from sea-salt, and that the seawater ionic ratios are as given by Millero (1974). This shows, as expected, that most of the observed concentrations of these ions can be attributed to sea-salt, with the mean rainwater composition having the character of seawater diluted by a factor of about 420, with the addition of some other minor components.

The absolute concentration of sea-salt components at Cape Grim is higher than that reported in most other studies of maritime rainwater composition. For example other southern hemispheric studies have reported mean rainwater sodium concentrations of 95 $\mu eq/l$ for 31 samples from Samoa (Pzenny et al., 1982), 225 $\mu eq/l$ for 79 samples from Amsterdam Island

Table 4. *Volume-weighted means ($\mu eq/l$), standard errors and standard error expressed as a percentage of the mean for the 66 Cape Grim rainwater samples having complete ion data; also included for comparison are ion concentrations for seawater diluted to produce a sodium concentration of 1167 $\mu eq/l$*

Ion	Mean	s.e.	s.e./mean	Dil. seawater
hydrogen	0.98	0.12	12	—
sodium	1167	77	6.6	(1167)
potassium	30.2	2.3	7.6	25.4
magnesium	247	16	6.7	265
calcium	78.0	5.7	7.3	51.2
ammonium	1.55	0.22	14	
chloride	1372	89	6.5	1360
nitrate	2.68	0.28	10	
sulfate	152	9.9	6.5	141

(Keene et al., 1986) and 483 $\mu eq/l$ for 33 samples from New Plymouth, New Zealand (Ayers et al., 1986a). The much higher sea-salt content of Cape Grim rainwater, evidenced by the mean sodium concentration of 1167 $\mu eq/l$, can be attributed to the rather high wind speeds commonly encountered at the Cape (Table 1), since it is well known that production of sea-salt aerosol increases with wind speed (Erickson et al., 1986).

Linear relationships between each of potassium, magnesium, calcium, chloride and sulfate calculated by the reduced major axis technique are given in Table 5. In the absence of any significant contribution to rainwater composition additional to sea-salt the intercepts would be zero and the slopes would equal the relevant seawater ratios of each ion concentration to that of sodium. In agreement with this picture all of the calculated intercepts differs from zero by less than two standard errors, and for magnesium, chloride and sulfate the slopes differ from the expected seawater concentration ratios by less than two standard errors. Thus at a confidence level of approximately 95% we can conclude that these parameters are explicable solely in terms of dissolved sea-salt. However in the cases of potassium and calcium the calculated slopes exceed the seawater ratios by 4.1 and 6.9 standard errors respectively, indicating the presence of at least one other component in the rainwater in addition to sea-salt. It will be suggested below that this additional component is local soil material eroded from the cliff face at Cape Grim.

6.2. Sulfate, nitrate and ammonia

Contributions to dissolved ionic material from the ubiquitous "background" reactive trace gases and submicrometer aerosol can be anticipated in any maritime rainwater. While modern studies will acknowledge the presence of a wide variety of individual species such as organic acids (Galloway and Gaudry, 1984), methane sulfonate

Table 5. *Coefficients from reduced major axis regression analysis of Cape Grim rainwater ion data, 66 samples with complete ion data used; also included are correlation coefficients and expected values if slopes were determined by seawater ionic ratios*

Y	X	Slope (s.e.)	Intercept (s.e.)	r	s.w. ratio
potassium	sodium	0.0299 (0.0020)	−4.6 (3.1)	0.840	0.0218
magnesium	sodium	0.220 (0.006)	−6.4 (8.4)	0.978	0.227
calcium	sodium	0.0755 (0.0046)	−7.8 (7.1)	0.870	0.0439
chloride	sodium	1.176 (0.017)	9.8 (25.6)	0.993	1.166
sulfate	sodium	0.132 (0.007)	0.8 (11.1)	0.896	0.121

(Ayers et al., 1986b), and amino acids (Mopper and Zika, 1987), the original aims of the monthly collections advocated for the WMO format were designed to evaluate perturbations to the sulfur and nitrogen cycles as revealed by the components most likely to be directly influenced by anthropogenic activities—sulfate, nitrate and ammonia. Thus consideration here is restricted only to these three species, which are, nevertheless, important components in the wet-deposition part of the atmospheric sulfur and nitrogen cycles over the ocean (see Galloway (1985), and references therein).

In the case of sulfate we are considering here the contribution to dissolved sulfate from the scavenging of species such as the submicrometre aerosol, and scavenging of gaseous sulfur dioxide which may then be oxidised to sulfate by rapid aqueous-phase reactions. This is the "excess" sulfate, additional to that derived from sea-salt. At a maritime site such as Cape Grim, in air masses not recently in contact with continents and anthropogenic emissions, the level of rain-water excess sulfate should be low. Galloway (1985) tabulates much of the small amount of relevant data available for the southern hemisphere: he gives figures for excess sulfate from four separate studies. Mean concentrations ranged from 2.0 to 6.3 μeq/l with an average of 4.1 μeq/l. The corresponding four figures for sea-salt sulfate ranged from 9.7 to 24.3 μeq/l with a mean of 17.5 μeq/l.

Equivalent figures cannot be deduced from the Cape Grim data. The problem is that the extremely high sea-salt loadings make it impossible to resolve the small excess sulfate signal from the very high sea-salt sulfate component. The figures in Table 4 show a volume-weighted mean total

sulfate concentration of 152 μeq/l, almost an order of magnitude higher than the figures quoted by Galloway (1985). If excess sulfate were typically 5 μeq/l, as suggested by the figures quoted above, then in the Cape Grim samples excess sulfate would comprise only 3.3% of total sulfate. For an individual sample this level of excess is not quantifiable when the sulfate and sodium (or magnesium, or chloride) concentrations used for calculation of the excess have analytical uncertainties on the order of 5%. If a particular sample actually had the composition given by the mean values in Table 4, and we take analytical uncertainties to be 5%, then using sodium as a tracer for sea-salt input excess sulfate would be calculated as

$$\text{sulfate excess} = (152 \pm 8) - (141 \pm 7)$$

$$= 11 \pm 15 \ \mu\text{eq/l.}$$

Clearly, excesses of order 5 μeq/l may well exist at Cape Grim but cannot be quantified in individual rainwater samples given the present levels of analytical uncertainty and the high sea-salt input.

Recourse to mean values averaged over the whole data set (Table 4) is suggestive of an excess of about 11 μeq/l, as noted in the example calculation above, however the inherent variability in the data results in the estimated standard errors for the means in Table 4 being too large for this average excess to have significance. The alternative of looking for an average excess in the regression coefficients given in Table 5, likewise is unsuccessful in the face of "noise" in the data: the intercept of the sulfate–sodium regression is not statistically different from zero, and the slope is not statistically (at twice the standard error of

the coefficient, or $\sim 95\%$ confidence) different from the seawater sulfate to sodium ratio of 0.1206.

The nitrate concentrations in the Cape Grim data are far less problematic. The volume-weighted mean concentration of 2.7 μeq/l (Table 4) sits comfortably with the other southern hemispheric, mid-latitude values of 3.1 μeq/l from New Plymouth, New Zealand (Ayers et al., 1986a) and 1.4 μeq/l from Amsterdam Island (Keene et al., 1986). Values of this order are consistent with total gas-phase plus aerosol-phase concentrations of at most a few nmol/m^3 of nitrate in the southern mid-latitude marine boundary layer (Heubert and Lazrus, 1980a), since 1 nmol/m^3 just below cloud base would translate to 1 μeq/l in cloudwater for complete scavenging into a cloud liquid water content of 1 g/m^3.

The situation with ammonia is almost identical to that for nitrate. Total gas plus aerosol ammonia concentrations at southern mid-latitudes are at most a few nmol/m^3 (Huebert and Lazrus, 1980b; Ayers and Gras, 1983), indicating likely cloudwater/precipitation concentrations of at most a few μeq/l in wet, precipitating clouds. The mean value of 1.6 μeq/l in Table 4 accords well with this expectation, as well as with the New Plymouth and Amsterdam Island values of 1.5 and 2.0 μeq/l (Ayers et al., 1986a; Keene et al., 1986).

6.3. Local contamination

A major deficiency of Cape Grim as a site for observation of maritime rain is the seemingly unavoidable collection, along with rainwater, of dust eroded from the cliff face: insoluble particulates identical in appearance to cliff-face debris are found in most rainwater samples. This occurs despite the use of a wet-only collector, and is apparently another consequence of the rather high wind speeds common at Cape Grim, especially during storms.

The data exhibit prima facie evidence of chemical modification as a result of the local soil/dust contamination. For example the absolute values of the ionic ratios (slopes) in Table 5 are clearly elevated from the expected sea-salt values for both potassium and calcium. Furthermore, the variances exhibited by the potassium and calcium data are higher than that of the other

major sea-salt ions. In Table 4, the standard errors expressed as a percentage of the mean are 6.6, 6.7, 6.5 and 6.5% for sodium, magnesium, chloride and sulfate, whereas for potassium and calcium the figures are 7.6 and 7.3%, respectively. This extra variance is also evident in the lower correlation coefficients for regressions involving potassium and calcium in Table 5.

A probable effect upon pH can also be discerned. The volume-weighted mean pH for the Cape Grim data is 6.01, which seems unusually high for southern maritime rain, given values of 5.54 for dust-affected rain at New Plymouth (Ayers et al., 1986a) and 5.05 for Amsterdam Island (Keene et al., 1986). For 47 of the Cape Grim monthly samples the mass of insoluble particulates was quantified by filtering the sample through pre-weighed filters which were subsequently re-weighed after drying. Arithmetic mean particulate masses were calculated for two categories, samples with pH greater than 6 and samples with pH less than or equal to 6.

Means, with 95% confidence intervals, were 95 ± 28 mg for the higher pH category and 45 ± 25 mg for the lower pH category. The indication is that higher dust loadings are associated with higher pH.

In May 1985, in order to further characterise likely effects of local contamination on rainwater composition, surface mineral soil/dust samples were collected from six separate locations spread randomly across the Cape surface/cliff tops in the vicinity of the observatory building. 0.2 g of each sample was extracted for 10 minutes in an ultrasonic bath in 100 ml of deionised water, or in 100 ml of local seawater diluted by a factor of 5000 with deionised water. After filtration through a 0.45 μm pore-sized filter the two aqueous extracts for each sample were then analysed chemically in the same way as the rainwater samples. Results averaged over each set of 6 extracts, together with results for the diluted seawater extraction solution, are given in Table 6. Also included in the table are the results obtained in April 1984 from the analysis of a single aqueous extraction (0.1 g/100 ml) of surface soil organic matter.

The data in Table 6 indicate that the local soil/dust at the Cape contains significant quantities of all the major ions found in rainwater at the site, giving local dust the potential to significantly

Table 6. *Mean composition (standard error) of Cape Grim soil samples, $\mu eq/l$; mineral refers to mineral soil fraction, organic to the soil surface organic layer; H_2O signifies extraction in deionised water, s.w. to extraction in a solution of seawater diluted by a factor of 5000 with deionised water; the mineral fractions were extracted at a level of 0.2 g/100 ml, while the organic sample was extracted at 0.1 g/100 ml*

Sample	pH	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}
mineral, in	7.12	229	7.7	36.4	69.0	3.3	111	0.87	13.6
H_2O, $N = 6$	(0.29)	(95)	(1.4)	(12.8)	(101)	(0.9)	(60)	(0.60)	(6.0)
mineral, in	7.38	333	6.4	39.8	68.2	2.7	227	0.54	24.4
s.w., $N = 6$	(0.25)	(108)	(2.2)	(26.4)	(85.0)	(1.9)	(77)	(0.24)	(6.6)
s.w., $N = 1$	6.00	96.1	2.1	21.8	4.2	—	112	—	11.6
organic, in H_2O, $N = 1$	8.04	909	187	460	120	140	700	5.3	84.8

alter observed composition from that of pristine maritime rain. However it should be noted that insoluble particulates in rainwater averaged only about 0.007 g/100 ml, 30 times less than the 0.2 g/100 ml used in the mineral soil extractions.

The most important features of the data from the mineral soil extracts are that relative to the expected ionic ratios from diluted seawater, the soil extracts exhibited excess calcium, elevated pH and a deficit of chloride. The chloride deficit is apparently due to the high soil alkalinity, which leads to bicarbonate assuming a major role as a counter ion for the soil cations. Clearly the major effect of the mineral soil material on rainwater would be to increase rainwater alkalinity and produce excess calcium, exactly what is found in the rainwater data.

The composition of the single extract from soil organic matter suggests that the excess potassium found in the rainwater data may be derived from this source, since relative to seawater ionic ratios, the soil organic extract shows particularly excessive potassium levels, as well as very high pH and high ammonia.

Overall these soil analyses indicate that the major unexpected features of the rainwater data can be attributed to pollution of the collected rainwater by local soil materials eroded from the Cape itself. Clearly caution must be exercised in any attempt to interpret the data set as an example of unpolluted maritime rain.

7. Discussion

The most characteristic feature of the Cape Grim rainwater composition data is the unusually high sea-salt loading, no doubt caused by the strong prevailing winds, as mentioned above. A consequence of this finding is that literature estimates of quantities related to atmospheric sea-salt loading may tend towards underestimation at this site. For example Varhelyi and Gravenhorst (1983) calculated the wet deposition of total sulfate to be in the range 0.4–0.6 gS m^{-2} yr^{-1} for both the South Indian and South Pacific Oceans. However using the long-term volume-weighted mean sulfate concentration of 152 μeq/l (Table 4) and an annual rainfall of 0.8 m (Table 1) the wet deposition of total sulfate at Cape Grim is calculated to be 1.9 gS m^{-2} yr^{-1}. This is not only considerably higher than the figures of Varhelyi and Gravenhorst (1983) for the southern oceans, but is higher than all the figures tabulated by Galloway (1985).

The lack of precision in excess sulfate estimation discussed above ensures that little can be deduced about the non-sea-salt sulfur cycle. If the excess sulfate of 5.5 μmol/l that can be deduced from the sodium and total sulfate concentrations in Table 4 is taken at face value then an annual deposition of 0.14 gS m^{-2} yr^{-1} is calculated for 0.8 m rainfall. This figure is within the range tabulated by Galloway (1985) for remote maritime regions, however it should be re-emphasised that this figure for Cape Grim rainfall lacks statistical significance.

For the nitrogen species nitrate and ammonia annual deposition figures of 0.030 and 0.017 gN m^{-2} yr^{-1} can be calculated respectively from the means in Table 4. The nitrate figure falls in the middle of the range tabulated for remote maritime regions by Galloway (1985), while the

ammonia figure falls at the lower end of the tabulated range. Thus these two figures also seem quite acceptable, although once again it must be admitted that some caution is needed—in this case because it cannot be guaranteed that these biologically labile species would be unaffected during the average two week period that the rainwater samples spent sitting in the collector, during accumulation of the monthly samples. There is also the possibility that nitrate and ammonia concentrations are affected by the local soil contaminant, although this is not obvious from the data. Arithmetic mean ion concentrations for samples with insoluble particulate contents less than the mean value of 0.07 g, compared with samples having >0.07 g, were indistinguishable, being 1.9 ± 0.8 and 1.6 ± 0.8 μeq/l for ammonia, and 3.7 ± 1.2 compared with 2.6 ± 0.8 for nitrate (95% confidence limits). Additionally, it should be mentioned that no systematic change occurred in the nitrate or ammonium concentrations when daily retrieval, filtering, compounding and refrigeration of samples was introduced into the monthly sampling protocol.

Finally, the pH of the rainwater at Cape Grim is unusually high, with individual samples having pH as high as 7.4. As noted above these high levels seem to be correlated with high levels of local soil contamination, and analysis of local soil showed the soil to be a significant source of alkalinity. Thus the volume weighted mean pH of 6.01 deduced from Table 4 is probably higher than that of truly maritime rain in the vicinity of Cape Grim. To get an indication of the pH that would be expected in the absence of local soil debris in the rainwater we repeated the calculation performed by Pzenny et al. (1982), in which pH is calculated for a diluted seawater system on the assumption that total seawater alkalinity is a conservative property. Like Pzenny et al. (1982) we included nitrate and excess sulfate in the calculation as strong acid anions, but we also made the minor addition of including ammonia in the calculation in analogy to the way in which the borate equilibrium is included. For the ammonia/ammonium equilibrium a pK_a of 9.633 was used. In addition, except for the ammonia equilibrium, we used specifications for the equilibrium constants that took into account variations with temperature and salinity. Finally,

we specified a carbon dioxide concentration of 340 ppmv rather than the 330 ppmv used by Pzenny et al. (1982).

The effects of these minor modifications to the calculation are small. For pure water in equilibrium with carbon dioxide at 20°C we calculated a pH of 5.67 compared with 5.65 obtained by Pzenny et al. (1982). When we repeated their calculation for the mean composition of Samoan rain at 20°C we obtained a pH of 5.50, identical with their value of 5.50.

For the case of rainwater at Cape Grim, a temperature of 12°C was assumed, along with total ammonia and nitrate concentrations taken from Table 4 of 1.6 and 2.7 μeq/l. In the face of no good figures for excess sulfate we have simply assumed the average excess sulfate concentration to be 5.0 μeq/l. Calculations were then performed for salinities corresponding to the sodium concentrations reported for Amsterdam Island (225 μeq/l; Keene et al., 1986), New Plymouth (483 μeq/l; Ayers et al., 1986a), the mean sodium concentration at 1167 μeq/l from Table 4, and for a concentration of 5000 μeq/l, which represents the upper limit of sodium concentration found in the Cape Grim data record. Calculated pH values were, respectively, 4.92, 4.96, 5.10 and 6.28.

Clearly, the calculated pH of 5.10 for the mean composition given in Table 4 is incompatible with the observed mean pH of 6.01. The result thus confirms the conclusion reached earlier that the pH of Cape Grim rainwater is elevated from maritime background values by alkalinity derived from local soil contamination.

A second implication of the calculations is that in the absence of local contamination, the pH of Cape Grim rainwater would not differ greatly from the value of 5.05 reported by Keene et al. (1986) for Amsterdam Island, where soil contributions were minimal. Of course some effect of trace organic acids might exist at Cape Grim, however no data on these species is available. However one major difference between Cape Grim and Amsterdam Island is the contribution made to the acid/base balance by sea-salt. For Amsterdam Island where sodium concentration was reported to range up to only 1467 μeq/l from an average of 225 μeq/l the calculations made above suggest that variations in sea-salt contribution would lead to potential variations in pH of only one or two tenths of a pH unit. On the other

hand monthly average sodium levels ranging from 500 to greater than 5000 μeq/l at Cape Grim imply that variations in salt content could lead to rainwater pH variations of more than 1 pH unit, over the range of about pH 5 to pH 6 or more. While Cape Grim may be unusual in this respect, it is evident that at this site sea-salt can often be the dominant alkaline substance in rainwater and a controlling influence on the pH of uncontaminated rainwater.

8. Conclusions

A major conclusion of this work is that surface level collections of maritime rainwater on the top of Cape Grim are contaminated by the local soil material, which significantly effects the rainwater concentrations of potassium and calcium, and significantly elevates pH. Effects on other ions were not obvious, but cannot be ruled out.

The cause of this local contamination is probably cliff-top erosion resulting from the rather high wind speeds associated with the "roaring forties" which are the prevailing winds at the site. These high wind speeds also lead to unusually high sea-salt loadings in rainwater, with both average sodium and average chloride concentrations in the millimolar range. One consequence of this high sea-salt content is that excess sulfate cannot be adequately estimated against the very high levels of rainwater sulfate derived from the sea-salt. A second consequence is that for uncontaminated rain variations in rainwater alkalinity and pH are probably dominated by variations in sea-salt content, with pH of uncontaminated rain predicted to vary at least over the range 5 to 6.

The lengthy, monthly sampling period in use at Cape Grim prior to 1985 creates an uncertainty about the representativeness of the data for the two labile nitrogen species ammonia and nitrate (as well as pH), although a recent change to event sampling has indicated no systematic change in the average ammonia and nitrate levels. If it is assumed that the ammonia and nitrate contents of the rainwater are representative, then both the concentration and annual deposition values are found to accord well with the few other published southern hemisphere data.

While the change to event sampling instituted in March 1985 will remove one deficiency in the sampling protocol, the problems associated with high sea-salt loading and local contamination cannot be resolved for any surface level collections at this site. For a few species, which are not important components of local soil matter, local contamination is not a problem. Methanesulfonate is one such species for which good data has been obtained (Ayers et al., 1986b). However it is clear that rainwater composition at Cape Grim cannot be accepted at face value as being representative of local maritime rain. Preliminary interpretations of all such BAPMoN data (for example Sequeira, 1981) should not be made until data editing and quality assurance have been carried out and any weaknesses in the data have been revealed.

9. Acknowledgements

REFERENCES

Ayers, G. P. and Gras, J. L. 1983. The concentration of ammonia in Southern Ocean air. *J. Geophys. Res. 88*, 10,655–10,659.

Ayers, G. P., Gillett, R. W. and Cernot, U. 1986a. Chemical composition of rainwater at New Plymouth, NZ, in 1981–82. *Clean Air (Aust.) 20*, 89–93.

Ayers, G. P., Ivey, J. P. and Goodman, H. S. 1986b. Sulfate and methanesulfonate in the maritime aerosol at Cape Grim, Tasmania. *J. Atmos. Chem. 4*, 173–185.

DOS, 1986. Baseline 83–84, Baseline Atmospheric Program (Australia) 1983–1984. Australian Department of Science/Bureau of Meteorology, 84 pp.

Erickson, D. J., Merrill, J. T. and Duce, R. A. 1986. Seasonal estimates of global atmospheric sea-salt distributions. *J. Geophys. Res. 91*, 1067–1072.

Galloway, J. N. 1985. The deposition of sulfur and nitrogen from the remote atmosphere. In: *The biogeochemical cycling of sulfur and nitrogen in the remote atmosphere.* J. N. Galloway, R. J. Charlson, M. O. Andreae and H. Rodhe, eds., D. Reidel Publishing Company, 143–175.

Galloway, J. N. and Gaudry, A. 1984. The composition of precipitation on Amsterdam Island, Indian Ocean. *Atmos. Environment 18*, 2649–2656.

Huebert, B. J. and Lazrus, A. L. 1980a. Tropospheric gas-phase and particulate nitrate measurements. *J. Geophys. Res. 85*, 7322–7328.

Huebert, B. J. and Lazrus, A. L. 1980b. Bulk composition of aerosols in the remote troposphere. *J. Geophys. Res. 85*, 7337–7344.

Keene, W. C., Pzenny, A. A. P., Galloway, J. N. and Hawley, M. E. 1986. Sea-salt corrections and interpretation of constituent ratios in marine precipitation. *J. Geophys. Res. 91*, 6647–6658.

Millero, F. J. 1974. The physical chemistry of seawater. *Ann. Rev. Earth Plan. Sci. 2*, 101–150.

Mopper, K. and Zika, R. G. 1987. Free amino acids in marine rains: evidence for oxidation and potential role in nitrogen cycling. *Nature 235*, 246–249.

Pzenny, A. A. P., MacIntyre, F. and Duce, R. A. 1982. Sea-salt and the acidity of marine rain on the windward coast of Samoa. *Geophys. Res. Lett. 9*, 751–754.

Rodhe, H. and Granat, L. 1984. An evaluation of sulfate in European precipitation 1955–1982. *Atmos. Environment 12*, 2627–2639.

Sequiera, R. 1981. Acid rain: some preliminary results from global data analysis. *Geophys. Res. Lett. 8*, 147–150.

Varhelyi, G. and Gravenhorst, G. 1983. Production rate of airborne sea-salt sulfur deduced from chemical analysis of marine aerosols and precipitation. *J. Geophys. Res. 88*, 6737–6751.

WMO, 1974. WMO operations manual for sampling and analysis techniques for chemical constituents in rain and air. *World Meteorological organisation publication WMO-No. 299*, 56 pp.

WMO, 1978. International operations handbook for measurement of background atmospheric pollution. *World Meteorological Organisation publication WMO-No. 491*, 110 pp.

WMO, 1987. *BAPMoN Newsletter No. 2*, March 1987. World Meteorological Organisation, 8 pp.