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Rainwater composition at two BAPMoN regional stations in SE Australia

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ABSTRACT

Analysis of 5 years of rainwater composition data from two BAPMoN Regional stations in southeastern Australia shows both sites to be relatively little influenced by anthropogenic sulfur and nitrogen emissions. Long-term average depositions of non-sea-salt (nss) sulfate, nitrate and ammonium were all <7.4 mmole m^{-2} yr^{-1} at both sites, which according to Galloway (1985) classifies these sites as "remote continental", or relatively unperturbed. Consistent with this, the long-term mean pH of rainwater at both sites was >5, though it must be acknowledged that the sampling protocols used in the BAPMoN network are such that weak organic acids will be lost from the samples prior to analysis. No secular trends in ion concentration or deposition were discernible over the 5-year data record for any of the species determined.

1. Introduction

The concepts of Baseline and Regional stations developed by the World Meteorological Organisation (WMO) in the early 1970s related to the spatial scales over which pollutants would be transported from anthropogenic sources before being sampled at a given station. At the commencement by WMO of the Baseline Atmospheric Pollution Monitoring Network (BAPMoN), Baseline stations were to be located to "establish global inventories of CO_2 and chemical composition of precipitation on a time scale of more than a year and a space scale in the order of 10,000 km" (Kohler, 1980). Sample air masses were to be devoid of direct contact with anthropogenic sources of pollutants for periods of several days or more. Thus air masses sampled at such stations should have travelled several thousands of km since passing over anthropogenic source regions, and would contain pollutants (primarily the long-lived species) at levels which, at least conceptually, were presumed to represent some sort of zonal mean background.

On the other hand Regional stations, while they were to be located away from the direct impact of anthropogenic source regions (i.e., these were not to act as urban air-quality stations), were supposed to reflect in some way the "regional" air pollution chemistry of continents over the mesoscale (spatial scales of some tens to several hundred km). To again quote Kohler (1980), these stations were "to monitor the atmosphere's composition as influenced by man's activities on a continental or regional scale, excluding however any significant single sources".

These typically rather broad guide-lines have in many countries been interpreted as intrinsically providing sufficient justification for establishment of BAPMoN measurement programs. This has not been a drawback for the few Baseline stations, which generally have clearly focussed scientific objectives for each measurement program, since these objectives are defined by the scientists leading each program who are also the end users of the data produced. In contrast the precipitation composition activities of the quite numerous Regional stations (more than 100 world-wide) are frequently run as a "monitoring" activity by a national meteorological agency, aimed at producing data for the global BAPMoN database, but with little or no internal scientific interest in, or

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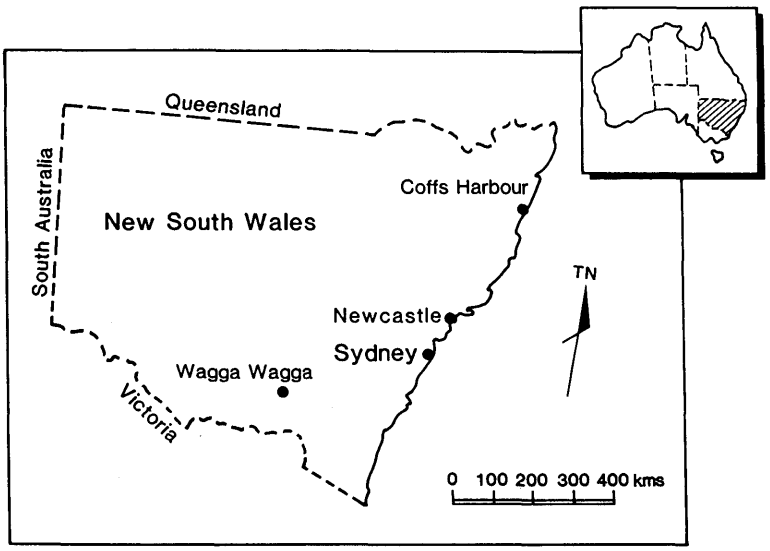

Fig. 1. Map showing locations of Coffs Harbour and Wagga Wagga.

scrutiny of the data. The obvious drawback of this approach is that the scientific usefulness of the data produced might not be routinely (or ever) assessed. There are notable exceptions of course, with the BAPMoN stations in Europe and the US producing data which are regularly scrutinised and used by the national and international "acid rain" communities in these regions.

This situation is changing with the establishment of WMO's Global Atmosphere Watch (GAW), with additional impetus for change coming from a review and scientific assessment by WMO of the global precipitation composition database. However prior to these changes the situation in Australia regarding the BAPMoN precipitation activities was typical of that in many countries: there was a Baseline station (Cape Grim) for which the rainwater composition data were well-scrutinised and used (Ayers and Ivey, 1988; 1990), and two Regional stations for which the data had been routinely collected by the national meteorological agency but never scientifically scrutinised or used. The purpose of this short paper is to review for the first time the quite extensive data sets available from the two Australian Regional stations. These two Regional stations are located at Coffs Harbour and Wagga Wagga in the south-eastern sector of the continent (Fig. 1).

2. Site characteristics

The BAPMoN rainwater samplers are located near other meteorological instruments on open ground at Coffs Harbour airport (30°19′19″S, 153°7′1″E, elevation 5 m) and Wagga Wagga airport (35°9′58″S, 147°27′42″E, elevation 22 m). Coffs Harbour and Wagga Wagga are both small rural cities servicing adjoining regions which are almost entirely rural/agricultural in character, with little regional industrial development. However Coffs Harbour is a coastal city so at this site the coastline forms a natural discontinuity between onshore winds reflecting marine air masses and off-shore winds reflecting continental air masses. Populations at mid-1989 were 48,000 at Coffs Harbour and 52,000 at Wagga Wagga. The long-term mean rainfall at Coffs Harbour (38 years of records) is 1708 mm, with 144 rain-days per year. At Wagga Wagga (45 years of records) the corresponding figures are 570 mm and 103 raindays.

There are no obvious point sources of anthropogenic emissions relevant to rainwater quality at either Coffs Harbour or Wagga Wagga. The nearest major sources of anthropogenic pollutants likely to affect rainwater composition (SO_2 and NO_X) are the city of Sydney (pop.

$>3 \times 10^6$) and the Hunter Valley region to the north of Sydney which contains the steel-making city of Newcastle, but more importantly also contains large coalfields and >5,000 MW of installed coal-fired electricity generating capacity. However both BAPMoN sites are located considerable distances away from Sydney and the Hunter Valley. Coffs Harbour is 325 km NNE of the Hunter Valley, and 450 km NNE of Sydney. Wagga Wagga is 400 km WSW of Sydney and 475 km SW of Newcastle. Coffs Harbour is also about 300 km south of the city of Brisbane (pop. 1×10^6), but persistent northerly winds are not common so Brisbane is an unlikely source of rainwater components.

It is worth adding that Australian coals are low in sulfur, and previous rainwater composition studies in both Sydney (Ayers and Gillett, 1984; Ayers et al., 1987) and Newcastle/Hunter Valley (Avery, 1984; Bridgman et al., 1988) have found elevation of rainwater acidity as a result of anthropogenic emissions to be moderate at worst, and at many sites only slight. Bridgman (1989) provides a convenient review of past studies on rainwater acidity in Australia.

3. Experimental methods

Rainwater sampling is carried out using identical methods at both sites: wet-only samplers (ERNI type ARS721) containing a polyethylene sample bottle into which rainfall is accumulated for each designated sampling period. At the end of the sampling period the sample is shipped to AGAL (Australian Government Analytical Laboratory) in Tasmania, where the samples are analysed within a period of a few weeks for the cations sodium, potassium, magnesium, calcium (flame atomic absorption spectroscopy) and ammonium (indophenol-blue colorimetric method), the anions chloride, nitrate and sulfate (suppressed ion chromatography with conductivity detection), and pH and electrical conductivity (standard electrode methods). Prior to analysis samples are stored in the dark at about 2°C.

The methods employed in these analyses are similar to those used for analysis of the rainwater samples from the Cape Grim Baseline station (Ayers and Ivey, 1988). Detection limits and precision are also similar being, respectively, in the range 0.1–0.5 μmol/l depending on ion and better than ±10% down to about 1 μmol/l for all ions.

The samples are not filtered at any stage, no biocide is used, and no analyses are performed for organic acids in the current program, although at Cape Grim the samples are retrieved on a daily basis and stored in the dark at 2°C until each weekly sample is accumulated. The lack of incorporation of a biocide into the sampling protocol and the lack of analysis for formic and acetic acids can now be seen as a weakness in these current protocols, given recently available information on the importance of organic acids in the atmosphere (Keene and Galloway, 1988) and the fact that these acids are subject to rapid biological consumption in the collected sample if a biocide is not used (Herlihy et al., 1987). Thus in the discussion that follows it must be born in mind that the acid-base balance observed almost certainly does not include any significant influence of organic acids, even if an influence did exist at the time of sample collection.

4. Data record

The Coffs Harbour site commenced sampling in August 1983, while the Wagga Wagga site commenced in April 1984. Until April 1985 samples at both sites were collected on a monthly basis (on a Tuesday, as per WMO guide-lines). From that date sampling frequency was increased to weekly in accordance with changed WMO recommendations. The data record available for scrutiny here extends to March 1989, giving for Coffs Harbour a total record of almost 6 years comprising 20 monthly samples plus 4 years of weekly data, while for Wagga Wagga the record spans 5 years made up of 12 monthly samples plus 4 years of weekly data. Of course the number of samples at each site is somewhat less than the total number of sampling periods in each case since weeks devoid of rainfall occur at each site. This is more common at Wagga Wagga because of its location inland behind the continental ranges, where rainfall is significantly less than on the coastal strip to the east of the ranges.

5. Results

The prime assessment of data quality carried out here is based on a comparison of the anion sum with the cation sum for each sample. This standard ion balance check is based on the electroneutrality requirement and the assumption that the ions determined by chemical analysis represent all the major contributors to the cation and anion sums, with the sums expressed in μeq/l.

A convenient way of comparing the cation and anion sums for all samples in a given data set is to carry out a regression of cation sum on anion sum. As recommended by Keene et al. (1986) we use here the reduced major axis regression method. Results are presented in Table 1. Included in Table 1 is information based on a parameter representing a percentage "imbalance" for each sample, calculated as

$$\% \text{ imbalance} = \frac{100(\text{cation sum} - \text{anion sum})}{0.5(\text{cation sum} + \text{anion sum})} \quad (1)$$

Also included is the calculated volume-weighted mean cation and anion sum for each data set.

A regression slope of unity and intercept of zero should result if all ions were accounted for and all chemical analyses were without error. The results in Table 1 indicate that both the Coffs Harbour and Wagga Wagga data sets come close to these expectations, with high correlation coefficients. However for both data sets the calculated slope and intercept both just differ from unity and zero at 95% confidence (the 95% confidence interval is approximately equal to twice the standard error). This suggests either that some ions have not been determined, or that the imprecision of the chemical analyses is a limiting factor, or both.

There is some evidence from the Table to suggest that analytical imprecision may be a major contributor to the slight deviations from the expected slope and intercept. The data on volume weighted mean cation and anion sums in the Table reveal that the total dissolved ion content at Wagga Wagga is very low in absolute terms at 44 μeq/l, and is only about a quarter of that at Coffs Harbour. This would place many of the analyses for individual ions in the Wagga Wagga rain at levels not much above the analytical detection limits, which necessarily results in relatively more analytical uncertainty for these samples. Poorer relative analytical precision for the lower concentrations of the major ions at Wagga Wagga would thus explain both the poorer correlation coefficient and the higher frequency of samples with ion imbalances >20% (see Table 1). No other explanation seems plausible given the fact that the chemical analyses for both sites are performed at a single laboratory, during the same

Table 1. *Data quality control parameters*

	Coffs Harbour	Wagga Wagga
Regression results		
number of points	185	133
slope (standard error)	1.034(0.011)	0.945(0.027)
Intercept (standard error)	−13.7(3.5)	6.1(2.3)
correlation coefficient	0.99	0.94
% of samples with imbalance* in range shown		
<10% imbalance	56	35
10%–<20% imbalance	26	19
20%–50% imbalance	16	35
>50% imbalance	2	11
Vol. weighted means		
cation sum, μeq/L	163	44
anion sum, μeq/L	170	44

* "Imbalance" defined in Eq. (1).

Table 2. *Volume-weighted mean ion concentrations and standard errors, μmol/l*

	Coffs Harbour		Wagga Wagga	
ion	mean	stand. error	mean	stand. error
H^+	8.4	1.3	2.5	0.2
Na^+	112	5	10.5	1.0
K^+	3.3	0.2	2.0	0.2
Mg^{2+}	13.3	0.7	2.5	0.2
Ca^{2+}	5.1	0.3	5.6	0.5
NH_4^+	3.0	0.4	13.0	1.0
Cl^-	143	6	17.7	1.4
NO_3^-	4.0	0.4	9.8	0.7
SO_4^{2-}	10.8	0.4	6.8	0.4

work periods, by the same analyst, on the same analytical instruments.

Table 2 contains volume-weighted mean ion concentrations for the two data sets. These data support the above interpretation, since it is clear that the relative variance associated with the major ions is larger in the Wagga Wagga data set for which most ion concentrations are lower. For the major contributions to the ion balance, Na^+, Mg^{2+}, Cl^-, and SO_4^{2-}, the ratio of standard error to mean from Table 2 ranges from 4 to 5% for the Coffs Harbour ions, but is significantly larger at 6 to 10% for the Wagga Wagga ions (this situation is reversed for NH_4^+ and NO_3^- which have higher concentrations at Wagga Wagga).

6. Discussion

6.1. Major sources of rainwater ions

Factor analysis with varimax rotation provides a convenient method of scrutinising rainwater composition data for patterns in variance which may be used to identify major sources of rainwater ions (Crawley and Sievering, 1986). Certainly factor analysis has some problems when applied as a means of quantitative source apportionment (for example see Henry, 1987). However, it is applied here only as a qualitative tool for identifying groupings of ions which show commonality in variance.

Factor analysis seeks linear combinations of variables within the data set to produce a small number of "factors" to explain the overall variance in the dataset. Each of these factors has a certain "loading" for each of the individual variables which in combination go into making up that factor. For the Coffs Harbour and Wagga Wagga data a majority of the variance (>90%) was explained by 2 and 3 factors respectively, as detailed in Table 3. Factor loadings exceeding about ± 0.5 generally are considered to be significant, although Crawley and Sievering (1986) attributed significance to loadings down to ± 0.4. We have arbitrarily taken a value of ± 0.44 as the cut-off, thus including Ca^{2+} in factor 2 for Coffs Harbour (Table 3). Loadings below this value are omitted from the Table.

The pattern of factor loadings in Table 3 clearly identifies 2 major sources of rainwater ions at both sites. Factor 1 in each case is a "sea-salt" source, dominated at both sites by the major sea-salt ions Na^+, Mg^{2+}, Cl^- and SO_4^{2-}. At the near-coastal site of Coffs Harbour where the absolute concentrations of sea-salt are higher (see Table 2) K^+ and Ca^{2+}, which also are significant sea-salt ions (Millero, 1974), are included in the factor 1. The higher sea-salt influence at Coffs Harbour is also reflected in the fact that at this site the sea-salt factor, factor 1, accounts for 75% of total variance, compared with 64% at Wagga Wagga.

Independent confirmation that sea-salt is the source of the major ions at Coffs Harbour is provided by a clear dependence of "sea-salt" ion

Table 3. *Results from application of factor analysis with varimax rotation to the Coffs Harbour and Wagga Wagga rainwater composition data*

Variable	Coffs Harbour		Wagga Wagga		
	factor 1	factor 2	factor 1	factor 2	factor 3
% variance explained	74.9	17.4	63.6	16.6	11.4
H^+					
Na^+	0.97		0.87		
K^+	0.61	0.49		0.67	
Mg^{2+}	0.87		0.56		
Ca^{2+}	0.53	0.44		0.54	
NH_4^+		0.76			0.71
Cl^-	0.97		0.93		
NO_3^-		0.89		0.68	
SO_4^{2-}	0.68	0.64	0.72		

concentrations on wind direction. Scalar mean wind direction at 900 hPa was calculated from twice-daily sondes at Coffs Harbour, using only days within each sampling period on which rainfall was non-zero. Since the coastline at Coffs Harbour runs close to north-south, a simple stratification of data into onshore 900 hPa wind direction (0°–180°) and off-shore wind direction (180°–360°) shows clearly the influence of the oceanic source: arithmetic mean sodium concentration was 269 μmol/l for the onshore wind category but was significantly lower at 92 μmol/l for the off-shore wind category.

Factor 2 in each case contains ions characteristic of continental sources, ions such as K^+ and Ca^{2+} (soil dust), SO_4^{2-} (oxidation product of anthropogenic emissions), NO_3^- (oxidation product of anthropogenic emissions or soil emissions) and NH_4^+ (soil and plant emissions of NH_3). Thus factor 2 in each case can be considered to be a "continental" factor. In the case of Wagga Wagga the continental sources of rainwater solutes is actually split into two separate factors, with NH_4^+ appearing as the single significant component of factor 3. This separation of NH_4^+ into a separate factor is perhaps not surprising, since NH_4^+ is the dominant cation at Wagga Wagga, and the biological sources of this ion may well have different emission characteristics than the sources of other continental emissions, such as the soil/dust source of K^+ and Ca^{2+} and anthropogenic sources of NO_3^- and SO_4^{2-}.

Our results accord very well with the findings of Crawley and Sievering (1986) based on factor analysis of the MAP3S/RAINE precipitation chemistry data from 8 sites in the northeastern US. Their analysis identified 3 factors, a sea-salt factor, an "ammonium/dust/soil" factor containing typically NH_4^+, Ca^{2+} and K^+, and an "acid" factor comprised of H^+, NO_3^- and SO_4^{2-}. The only difference is that at Coffs Harbour and Wagga Wagga our "continental" factor, factor 2, is essentially equivalent to a combination of the "ammonium/dust/soil" and "acid" factors of Crawley and Sievering (1986), but without the strong H^+ component. It is entirely reasonable that separate factors would emerge in the northeastern US where acidic deposition is a severe regional problem and the ionic loading in precipitation is dominated by sulfuric and nitric acids. At Coffs Harbour and Wagga Wagga the sulfuric and nitric acid components are low, by US standards, and may have quite significant continental sources other than anthropogenic industrial emissions, in the form of soil/biological emissions and biomass burning emissions, for example.

6.2. *Sulfate and nitrate and acidity*

A major impetus for establishment of the BAP-MoN Regional Stations was the aim of observing perturbations to the biogeochemical cycles of sulfur and nitrogen, as well as to atmospheric acidity in regions impacted by sulfuric and nitric acids of anthropogenic origin.

Table 4 contains data on annual wet deposition fluxes of nss-SO_4^{2-}, NO_3^- and NH_4^+ at Coffs Harbour and Wagga Wagga and compares these with values from the Cape Grim baseline station in Tasmania, values proposed by Galloway (1985) as representative for remote, unpolluted continental regions (based on his extensive review of available data world-wide), values from Likens et al. (1987) for Katherine in tropical Australia, and values

Table 4. *Annual average wet deposition of sulfate, nitrate and ammonium at Coffs Harbour and Wagga Wagga, values from Cape Grim (Ayers and Ivey, 1988), median values estimated for remote continental regions by Galloway (1985), average values for 1980–1984 for Katherine in tropical Australia given by Likens et al. (1987), and 95 percentile values for polluted regions in the eastern US (NAPAP, 1990); all values in mmole* m^{-2} yr^{-1}

	Coffs Harbour	Wagga Wagga	remote continent	Katherine, NT	Cape Grim	eastern US
nss-SO_4^{2-}	7.0	3.5	6.3	2.2	n.a.	33¶
NO_3^-	6.8	5.6	7.1	4.3	2.1	34¶
NH_4^+	5.0	7.4	5.7	3.0	1.2	—

¶ 5% of the area of the Eastern US had wet deposition in 1985–87 above this value.

typical of regions in the eastern US heavily influenced by anthropogenic emissions of SO_2 and NO_x. The term nss-SO_4^{2-} refers to "non-sea-salt-sulfate", which is estimated from total sulfate by subtracting an estimated sea-salt component. That component is estimated by assuming that Na^+ serves as a quantitative tracer for sea-salt, and that the sea-salt ratio of SO_4^{2-} to Na^+, 0.02927/0.48534 mole/mole (Millero, 1974), is preserved in the rainwater samples.

The Table makes it immediately clear that in annual-averaged terms the two Australian BAP-MoN sites can be considered to be free of large anthropogenic perturbations to the wet deposition parts of the atmospheric S and N cycles. The values for Coffs Harbour and Wagga Wagga fit

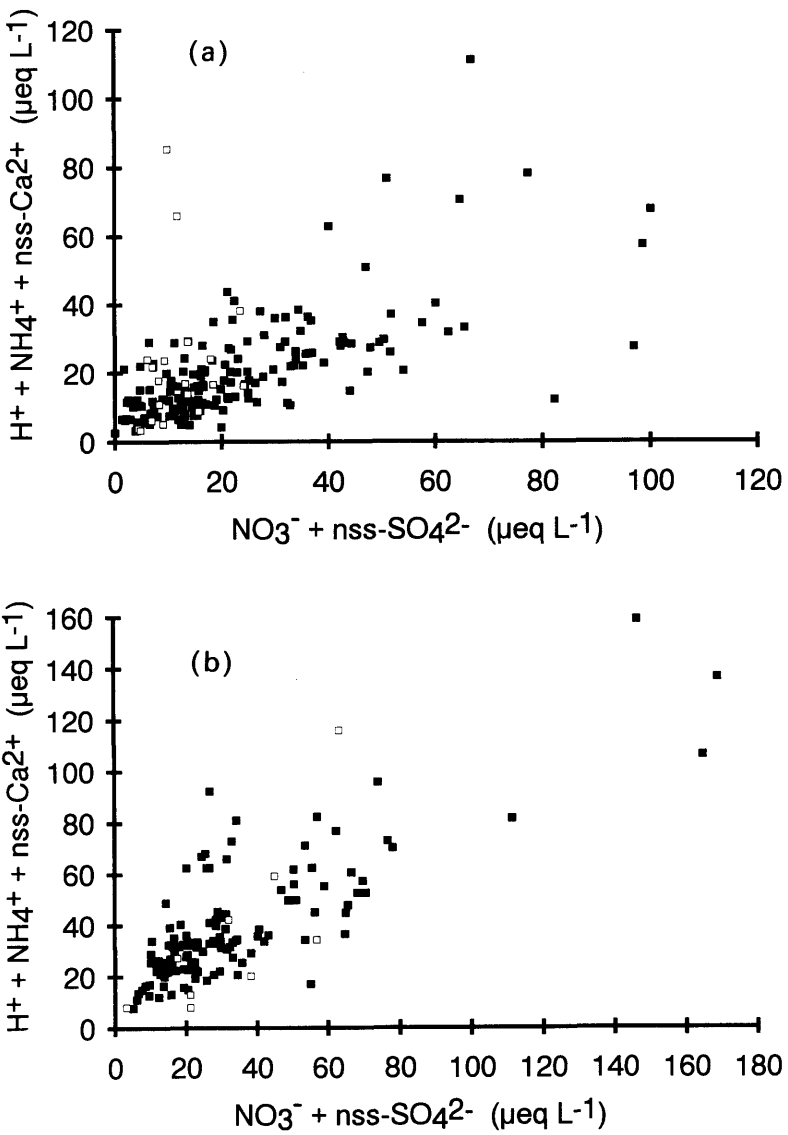

Fig. 2. Partial acid-base balance, upper plot Coffs Harbour, lower plot Wagga Wagga. Open squares are points derived from monthly samples, filled squares derived from weekly samples.

well with the values derived by Galloway (1985) as representing median values for "remote continental", in other words largely unpolluted, continental sites. The very low deposition values for Cape Grim reflect the sampling strategy at this site which restricts sampling of rainwater only two occasions with onshore flow of very clean, Southern Ocean air.

Comparison with values from Katherine in the Northern Territory of Australia perhaps suggests some small anthropogenic contributions to the Coffs Harbour and Wagga Wagga samples. However in comparison with the typical north American data shown in the final column of the Table it is clear that any such contributions at Coffs Harbour and Wagga Wagga are small by northern hemisphere standards. It must also be acknowledged that the Katherine data come from

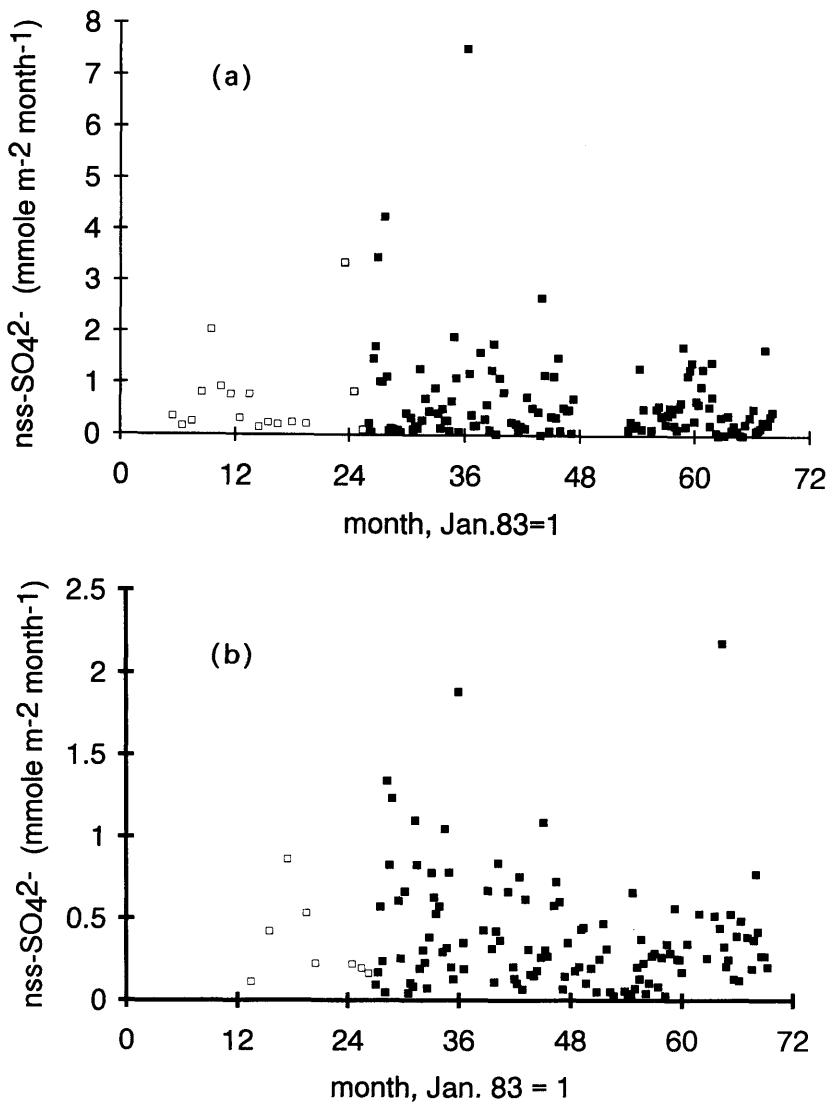

Fig. 3. Time series plot of nss-SO_4^{2-} wet deposition at Coffs Harbour (upper) and Wagga Wagga (lower), in units of mmole m^{-2} $month^{-1}$. Open squares are points derived from monthly samples, filled squares derived from weekly samples.

a region in the wet-dry tropics of Australia which has a quite different regional climate/environment from that of Coffs Harbour and Wagga Wagga, so it cannot be assumed a priori that variations in the "natural" deposition between the tropical and southeast regions may not be responsible for part of the small differences shown in Table 4.

It is no surprise then that the long-term volume-weighted mean pH values at Coffs Harbour and Wagga are both above 5, at 5.08 and 5.60 respectively. Again these figures can be contrasted with mean values of 4.5 and below at polluted northern hemisphere sites (e.g., NAPAP, 1990 and references therein). The obvious conclusion suggested by these data is that both Coffs Harbour and Wagga Wagga are sites which may be considered to be relatively free from major anthropogenic pollution.

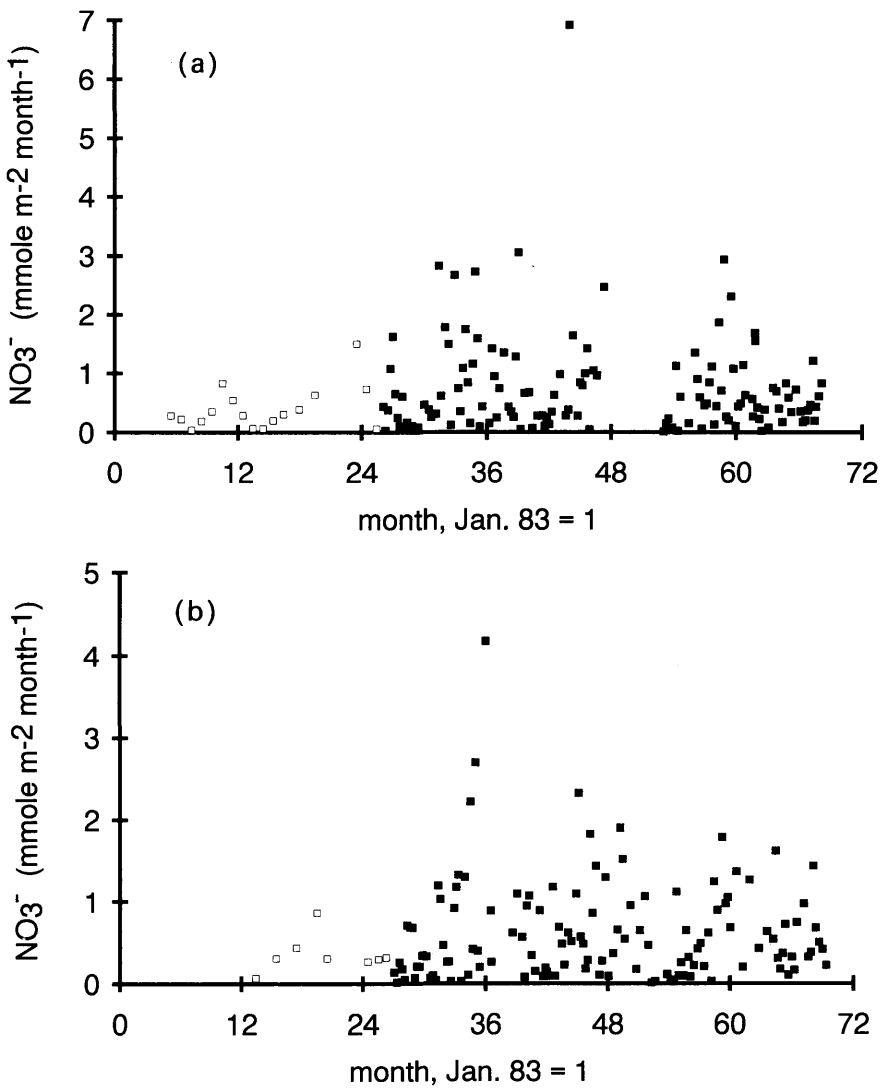

Fig. 4. Time series plot of NO_3^- wet deposition at Coffs Harbour (upper) and Wagga Wagga (lower), in units of mmole m^{-2} $month^{-1}$. Open squares are points derived from monthly samples, filled squares derived from weekly samples.

The acid-base balance at both Coffs Harbour and Wagga Wagga seems adequately described by a balance between acidity provided by sulfuric and nitric acids on the one hand, and alkalinity provided by ammonia and soil dust (the calcium carbonate component) on the other hand. Plots of $H^+ + NH_4^+ + \text{nss-}Ca^{2+}$ versus $\text{nss-}SO_4^{2-} + NO_3^-$ representing this balance are shown in Fig. 2. However it must also be noted that the contributions from organic acids cannot be assessed here because the sampling protocols do not include a biocide to prevent the biological consumption of organic acids which has been readily apparent in other studies (Herlihy et al., 1987; Likens et al., 1987).

Finally we consider another role assigned initially to the stations in the BAPMoN network, that of providing long-term records for detection of secular trends in important atmospheric species (especially S and N species in precipitation samples). Fig. 3 contains time-series plots of sulfate deposition, while Fig. 4 contains similar plots for nitrate. No obvious secular trend is evident in either figure. Clearly, with the amount of variability evident in both plots a 5-year record would be inadequate for detection of a secular trend unless the trend were very substantial.

6.3. Additional remarks

This short analysis of the data available from Coffs Harbour and Wagga Wagga indicates that the data quality at both sites is satisfactory: the ion balance results in Table 1 are acceptable, the factor analysis results in Table 2 appear reasonable, as does the simple bivariate acid-base relationship shown in Fig. 2. There is some indication, however, that data quality could be improved especially at Wagga Wagga if analytical precision at low ion concentrations were to be improved.

One other aspect of the Coffs Harbour and Wagga Wagga operations which applies to all BAPMoN stations globally is the question of the role played by organic acids in rainwater composition and acidity, since to date no BAPMoN stations have measured organic acids. Yet it is now abundantly clear (Likens et al., 1987; Keene and Galloway, 1988) that organic acids, principally formic and acetic acids, can have a profound influence on the composition and acidity of precipitation. Thus the operators of all BAPMoN sites, including Coffs Harbour and Wagga Wagga should consider changing the sampling protocols to include a method of preserving the samples from biological degradation of the organic acids (Herlihy et al., 1987) prior to the time of chemical analysis.

It would also be useful to enlarge the suite of species determined in precipitation from BAPMoN stations to include the ion methanesulfonate (MSA), an important tracer for atmospheric sulfur species derived from oxidation of dimethyl sulfide emitted biologically from the global oceans (Berresheim et al., 1989). A major removal path for these species is via wet deposition (Berresheim et al., 1989), so measurements of MSA as well as $\text{nss-}SO_4^{2-}$ at coastal BAPMoN sites, such as Coffs Harbour, can make a major contribution in this area. An example of the usefulness of this type of MSA data is the work of Ayers and Ivey (1990), where the data were obtained from the Cape Grim BAPMoN site.

Finally we note that the major difference in wet deposition at Coffs Harbour and Wagga Wagga is in sea-salt loading. The calculated deposition of S and N species reveals little difference in anthropogenic contributions, in comparison with the large difference between the two Australian sites and a northeastern US site. This finding raises a question about the scientific need to maintain the only two Australian Regional stations within the same southeastern corner of the continent. Given the large size of the Australian continent and the wide variety of climatic regimes it encompasses it seems highly likely that considerable value could be achieved by moving one of the current stations to a different region of the continent.

7. Conclusions

The Australian regional BAPMoN stations at Coffs Harbour and Wagga Wagga have produced respectively 6 years and 5 years of wet-only rainwater composition data which has been assessed subjectively to be of "good" quality.

The major influences on rainwater composition at both sites are sea-salt, and continental sources such as soil dust, ammonia, and low levels of sulfate and nitrate which presumably have both natural and anthropogenic components.

The data show both sites to be relatively free of anthropogenic influence when compared with

precipitation composition data typical of sites in the northeastern US. Indeed the wet deposition of nss-sulfate and nitrogen species at Coffs Harbour and Wagga Wagga is at such low levels (<7 mmole m^{-2} yr^{-1}) that it falls in the range characterised by Galloway (1985) as "remote continental". Long-term mean pH values at both sites are >5, with no secular trend discernible at this stage in any rainwater components.

We can conclude that the atmospheric nitrogen and sulfur cycles and atmospheric acidity are not greatly perturbed by human activities in the southeast region of the Australian continent represented by rainwater composition at Coffs Harbour and Wagga Wagga.

Finally, we suggest that the scientific value of data from the global precipitation composition network would be significantly improved by use of a biocide to prevent biological degradation of the samples, and addition of formic acid, acetic acid and methanesulfonate to the suite of analytes determined.

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