Tellus (1989), *41B*, 427–443

Processes controlling the concentrations of $SO_4^=$, NO_3^-, NH_4^+, H^+, $HCOO_T$ and CH_3COO_T in precipitation on Bermuda

By J. N. GALLOWAY, W. C. KEENE, *Clark Hall, Department of Environmental Sciences, University of Virginia, Charlottesville, Virginia 22903, USA*, R. S. ARTZ, JOHN M. MILLER, *NOAA, Air Resources Laboratory, 8060 13th Street, Silver Spring, Maryland 20910, USA*, T. M. CHURCH, *College of Marine Studies, University of Delaware, Newark, Delaware 19711, USA* and A. H. KNAP, *Bermuda Biological Station for Research, Inc., 17 Biological Station Lane, Ferry Reach GE-01, Bermuda*

(Manuscript received 2 November 1987; in final form 16 May 1988)

ABSTRACT

The composition of precipitation on Bermuda can be characterized as a slightly acidic, dilute seawater solution. The acidity of the solution is controlled by H_2SO_4, HNO_3, HCOOH and CH_3COOH in a 67:20:8:3 mixture, respectively. $CaCO_3$ and NH_3 have reduced the potential acidity of the solution by 24% and 13%, respectively.

The concentrations of non-sea-salt (nss) $SO_4^=$ and NO_3^- in precipitation on Bermuda are about a factor of three greater than those in remote marine areas of the world. These differences are attributed in part to anthropogenic activities. NH_4^+, $HCOO_T$ and CH_3COO_T concentrations in Bermuda precipitation more closely resemble remote areas, although there are distinct events where transport from North America is evident. Precipitation associated with air masses from the central Atlantic Ocean is enriched relative to remote marine areas by about a factor of two in nss $SO_4^=$. This appears to be caused by anthropogenic emissions in North America, Europe and Africa. There are higher volume-weighted average concentrations of nss $SO_4^=$ and NO_3^- in storms on Bermuda associated with the NW airflow sector (from North America) compared to the SE airflow sector. These higher concentration are in part due to the influence of North America and in part due to lower amount of precipitation in the NW storms. An analysis of deposition differences between the two sectors confirms that there is at least a factor of two impact of North American anthropogenic activities on nss $SO_4^=$ and NO_3^- in precipitation on Bermuda.

1. Introduction

The composition of precipitation can be used to investigate atmospheric cycles by determining (1) the temporal and spatial trends in atmospheric composition (NRC, 1986), (2) the extent of transport of materials through the atmosphere (Galloway and Gaudry, 1984; Uematsu et al., 1985; Prospero, 1981), (3) the upper limits on the amount of material emitted to the atmosphere (Andreae, 1985), (4) the importance of mechanisms for atmospheric chemical transformations by measuring amounts of reactants and products in atmospheric deposition (Wolff et al., 1987; Hales and Dana, 1979), and (5) new species in atmospheric deposition which can point to potentially important but previously undescribed reactants or transformation sequences (e.g., HCOOH and CH_3COOH; Keene et al., 1983).

Past studies of precipitation chemistry at Bermuda have addressed many of these topics. For example, reports have discussed the influence of continental versus marine sources on precipitation composition (Jickells et al., 1982; Galloway et al., 1983), compared Bermuda precipitation composition to that in the Eastern United States (Church et al., 1982), discussed the sources of acidity in Bermuda precipitation

(Galloway et al., 1982, 1983), evaluated the impact of Bermuda on precipitation composition (Galloway et al., 1988), assessed methods for differentiating sea-salt (ss) and non-sea-salt (nss) components in marine precipitation (Keene et al., 1986), and calculated S and N budgets for the atmosphere of the western Atlantic Ocean (Galloway and Whelpdale, 1987). However, the data sets that these papers evaluated were for short time periods. This paper uses a 50-month record of precipitation composition to re-evaluate some of the above issues and goes beyond previous work on Bermuda by addressing (1) the sources of HCOOH and CH_3COOH and their influence on acidity, (2) the enrichments, relative to remote marine areas, of nss $SO_4^=$, NO_3^-, H^+ and NH_4^+ in the atmosphere of the Western North Atlantic Ocean and (3) the differences in the frequency distributions of species deposition as a function of source region.

2. Methods

2.1. Sample collection

Precipitation was collected on Bermuda at two stations, Harbor Radio Tower (HRT) and High Point (HP), on the NE and SW coasts, respectively. This paper considers bulk and wet-only precipitation collected at HRT from 1 April 1980 to 18 May 1984 and wet-only precipitation collected at HP from 21 August 1982 to 18 May 1984 (see Galloway et al. (1982) for descriptions of collectors). At both locations, samples were collected on an event basis. At HP, all precipitation events were treated with $CHCl_3$ to ensure chemical stability. At HRT, samples from approximately 90% of the precipitation events were either refrigerated until analysis or were treated with $CHCl_3$. When sample volume permitted, samples were split into two aliquots and chloroform was added to one but not to the other.

2.2. Sample analysis

The majority of precipitation samples from HRT were analyzed at the University of Virginia, although from 21 August 1980 to 4 August 1982, samples were analyzed at the Bermuda Biological Station. All samples collected at HP were analyzed at the University of Virginia. H^+, NH_4^+, Na^+, Mg^{++}, Ca^{++}, K^+, SO_4^{2-}, NO_3^- and Cl^- were measured in all samples with sufficient volume. $HCOO_T$ ($HCOOH + HCOO^-$) and CH_3COO_T ($CH_3COOH + CH_3COO^-$) were measured in all samples with sufficient volume collected after 9 March 1983 at HP. Analytical methods included ion chromatography (anions), automated colorimetry (NH_4^+), and atomic absorption spectrophotometry (base cations). Details on the methodologies are described by Galloway et al. (1982) and Keene et al. (1983).

2.3. Meteorological analysis

The source of the air mass associated with each precipitation event was determined by trajectory analysis. The trajectory program used in this study is GAMBIT (Gridded Atmospheric Multilevel Backward Isobaric Trajectory model) and is based upon the Air Resources Laboratory model developed by Heffter and Taylor (1975). GAMBIT trajectories are computed using analyzed winds along constant pressure surfaces and can be run for any receptor on the globe for up to two mandatory levels, twice each day. Input wind data consist of gridded wind components at mandatory pressure levels produced by a global atmospheric model. The model's first estimate is produced by a nine layer prediction model (Stackpole, 1978). Meteorological observations from around the globe are fed into the Optimum Interpolation program which outputs the wind data and other parameters in gridded form. A description of the Optimum Interpolation method can be found in Bergman (1978) and a description of its application to the nine-layer model can be found in McPherson et al. (1979). Sources of input data utilized include rawinsonde and pibal observations as well as aircraft and satellite measurements. Harris (1982) presented a detailed description of the GAMBIT model.

2.3.1. Trajectory limitations. Careful examination of the model physics shows that the trajectory model has several rather serious limitations. Probably the most important is that computation of trajectories on other than mandatory surfaces (1000 mb, 850 mb, 700 mb, etc.), while possible, is not recommended because of the averaging of winds between mandatory levels can yield unrealistic trajectories in regions of strong wind shear. This is particularly a problem in areas of limited observations such as over

oceans, polar areas, and the less-developed continental areas.

A second limitation concerns the use of 1000 mb trajectories. The model will produce trajectories for model points where surface pressure is less than 1000 mb, a clearly unrealistic physical interpretation. Near surface trajectories are also of questionable quality because frictional forces are not considered, yet are likely to be important within the boundary layer.

The GAMBIT model was not designed to track a specific air parcel from one place to another. It can be more appropriately applied in conjunction with other meteorological data to indicate a general pattern of airflow and is a valuable tool in determining an airflow climatology. Trajectories are most reliable when calculated under steady wind regimes over level topography, for areas where large data gaps in time and space do not exist, and on mandatory pressure levels of 850 mb or above. This model is appropriate for backward computations from Bermuda due to the lack of topography, generally well-defined synoptic regimes over the western Atlantic, and a reasonably complete data base. The model is used at the 850 mb level in an area where gridded winds comprise the best available data set for trajectory computations. It should be stressed, however, that while these trajectories are believed to be reliable for the determination of source regions, there is an unknown amount of error incurred due to the neglect of vertical motion and the sparsity of data, both spatially and temporally over the ocean. Trajectories are likely to be least representative over regions of strong frontal development.

2.3.2. Method of trajectory assignment. Trajectory assignments of Bermuda precipitation events were made using 10-day 850 mb isobaric back-trajectories. The first 3 to 5 days of trajectory movement were carefully considered, but little weight was given to the last five days of computation. The 850 mb level was chosen as the most representative available level, as the 1000 mb level is too low and subject to the problems discussed above and the 700 mb level is generally considered to be too high to carry large amounts of natural or anthropogenic materials in rainwater. Trajectories were calculated for all days of the study period twice daily at 00Z and 12Z. The influence of trajectory on precipitation composition was determined by assigning each trajectory to a grid based on compass sector. The trajectory grid employed in this analysis (Fig. 1) is based upon a similar grid used by Jickells et al. (1982) and Miller and Harris (1985). It has been suggested that air masses originating in the NW sector contain measurable amounts of anthropogenic material of North American origin and that air masses originating in the SW sector contain materials from predominately natural sources (Jickells et al., 1982). Relative to the NW sector, precipitation associated with air masses from the SW, WSW and NE sectors contain lesser amounts of anthropogenic materials. For some precipitation events, associated trajectories passed through more than one sector during the first five days of calculation. In most cases, residence time was short (less than 12 hours) in all sectors except the one chosen and was not considered to be a factor in our analysis. However, for cases where a dominant sector could not be assigned, especially between the NW, SW, and WSW sectors, the trajectory was not categorized and was dropped from the analysis.

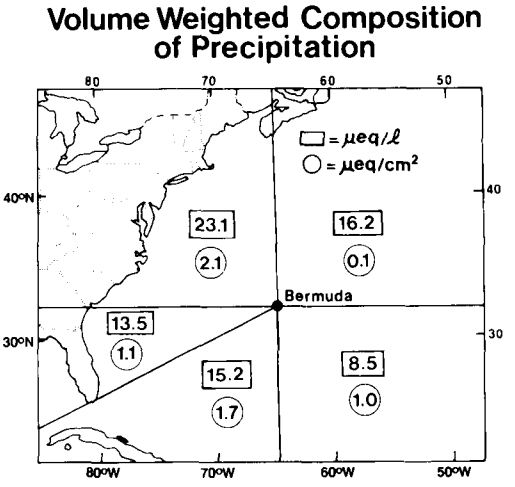

Fig. 1. The VWA concentrations (μeq/l in box) and wet deposition (μeq/cm²/year in circle) of nss $SO_4^=$ as a function of compass sector. The number of samples in each VWA are given in Table 3.

2.3.3. Precipitation record. The amount and timing of precipitation was determined at Harbor Radio Tower, High Point, the Bermuda Botan-

ical Garden and the Bermuda Biological Station. Differences in locations on Bermuda and precipitation timing were insignificant in regard to model application. For each precipitation event, the periods of precipitation were determined from a Belfort 12-inch dual traverse 192-hour Universal Raingauge chart and the 850 mb trajectory best representing the precipitation period was selected. For the situations where an event covered several 12-hour periods or where several discrete events were collected over the period of several days in the same sample bucket, all applicable 12-hour trajectories were examined; if several sectors were identified as source regions during a single precipitation event, the sample was dropped from the trajectory portion of the analysis.

3. Data

The main HRT data set contains 478 precipitation samples. However, many of these samples were from the same storm and differed by either the type of collector used (bulk versus wet) or the type of sample treatment (with or without $CHCl_3$). Bulk collectors were open for a maximum of 24 hours during non-raining periods while wet collectors were open only during precipitation events. The HRT data set was screened to select the most representative sample for each event. The four different types of samples are listed below in decreasing order of preference.

1. Samples, treated with $CHCl_3$, from wet collectors.
2. Samples, treated with $CHCl_3$, from bulk collectors.
3. Samples, not treated with $CHCl_3$, from wet collectors.
4. Samples, not treated with $CHCl_3$, from bulk collectors.

This order is based on the assumptions that samples stabilized with $CHCl_3$ are preferable to unstabilized samples and that samples that excluded dry deposition are better than ones that included dry deposition.

After one sample for each storm was selected, the data were examined to identify samples that had obvious contamination or analytical errors. Questionable data were identified by analyzing anion–cation balances and ss ratios for selected constituents. If the anion–cation ratio was $> \pm 25\%$ away from unity, the sample was discarded. Of the discarded samples, 24 had aberrant Na^+ values due to a suspected short-term analytical problem in the laboratory. One sample was contaminated with HCl and another exhibited aberrant Mg^{++} and K^+ values. In addition, 13 samples were obviously contaminated with NH_4^+ before analysis. The remaining samples (295) comprised the reduced data set. In this data set there were 22 samples collected at HRT that were sent untreated with $CHCl_3$ to the University of Virginia for analysis. Since samples of this type can experience decreases in NO_3^-, NH_4^+ and H^+ (Keene et al., 1983; Muller et al., 1982) the NO_3^-, NH_4^+ and H^+ concentrations may be underestimated. In this data set, 37 samples were collected in bulk collectors. This will cause the sea salt concentrations to be higher, due to dry deposition. However, since only 12% of the samples were collected with bulk collectors, the increase in the volume weighted average (VWA) concentrations of sea-salt constituents was small.

The reduced data set for HRT ($N = 295$) was used to determine (1) the temporal trends in the composition of precipitation, (2) the influence of air mass trajectory on precipitation composition, and (3) wet deposition rates of S and N species. Since the HRT data base did not have organic acid analyses, a second database ($N = 88$) of HP samples included analyses of anions (nss $SO_4^=$, NO_3^-, Cl^-, $HCOO^-$, and CH_3COO^-) of all the major proton donors, and was used to determine the relative importance of the causes of acidity and the sources of $HCOO_T$ and CH_3COO_T in precipitation. The criteria used to determine data quality for HP samples are similar to those described above and have been previously described by Keene et al. (1986).

4. Results and discussions

4.1. VWA composition of precipitation on Bermuda

The composition of precipitation collected on Bermuda reflects the influence of a number of sources for material—ss and nss (biogenic emissions from the ocean, anthropogenic and terrestrial emissions from Bermuda and continen-

tal regions). The relative importance of ss versus nss sources for the species considered in this paper can be evaluated by creating a correlation matrix of the concentration data. Relative to Na^+, there are three clusters of values of correlation coefficients (r). The first group (Cl^-, Mg^{++}) has large r values (>0.99); the second group (Ca^{++}, $SO_4^=$, K^+) has intermediate r values (0.7–0.9). The third group (NH_4^+, NO_3^-, H^+) has low r values (<0.4). The first group has essentially one source—seawater. The second group has a strong seawater influence with a contribution from a nss source(s). The concentrations of materials in the third group are controlled primarily by nss sources.

For the materials that are influenced by both ss and nss sources, (e.g., K^+, Ca^{++}, $SO_4^=$) it is possible to quantify the importance of the two components. Na^+ and Mg^{++} are commonly used as ss tracers to calculate the concentration of the nss components. We chose to use Na^+ as the ss tracer because of a small possible source of Mg^{++} from the carbonate minerals on Bermuda (Keene et al., 1986; Galloway et al., 1988).

The (VWA) composition of precipitation on Bermuda can be described as a slightly acidic (pH 4.86), dilute seawater solution (Table 1). Of the seawater constituents, none of the Na^+ (by definition), 5% of the Mg^{++}, 2% of the Cl^-, 26% of the K^+, 49% of the Ca^{++}, and 50% of the $SO_4^=$ are present in levels higher than that expected from simple seawater dilution (Table 1). These calculated results reflect the grouping of the correlation coefficients—K^+, Ca^{++} and $SO_4^=$ had lower values of r than did constituents with a predominant ss source.

Table 1. *Volume weighted averages of precipitation constituent concentrations at Bermuda ($\mu eq/l$)**

	Sea-salt component	nss component	% nss	Total
Na^+	115.9	—	0	115.9
Mg^+	26.3	1.5	5	27.8
Ca^{++}	5.1	4.9	49	10.0
K^+	2.5	0.9	26	3.4
H^+	—	13.1	100	13.1
NH_4^+	—	2.8	100	2.8
Cl^-	135.1	3.0	2	138.1
$SO_4^=$	14.0	14.1	50	28.1
NO_3^-	—	4.4	100	4.4
$HCOO^-$	—	2.0	100	2.0
CH_3COO^-	—	0.8	100	0.8

* Data on $HCOO^-$ and CH_3COO^- are from HP ($N=88$). Data on all other species are from HRT ($N=295$). For all species collected at HRT, the Σ anions = 170.6 μeq/l and the Σ cation = 173.0 μeq/l).

The chemical constituents of precipitation can be grouped into those with a large nss component (H^+, NH_4^+, Ca^{++}, $SO_4^=$, NO_3^-, $HCOO_T$, CH_3COO_T) and those contributed predominantly by seawater (Cl^-, Na^+, Mg^+, K^+) (Table 1). The remainder of this paper will focus on nss $SO_4^=$, NO_3^-, NH_4^+, H^+, $HCOO_T$ and CH_3COO_T in Bermuda precipitation. The nss Ca^{++} and the sea-salt components have been previously discussed by Galloway et al. (1988) and Keene et al. (1986), respectively.

4.2. *Comparison of Bermuda precipitation to remote areas*

The concentrations of H^+, NO_3^- and nss $SO_4^=$ in precipitation on Bermuda are higher than those in precipitation at more remote marine areas (Table 2). Other nss components (NH_4^+, $HCOO_T$ and CH_3COO_T) have VWA concentrations within the range of remote marine sites (Table 2). If we assume that the arithmetic means for the volume weighted data from remote regions presented in Table 2 are representative of the Sargasso Sea in the absence of anthropogenic impacts, and that atmospheric processes are identical in Bermuda and in remote regions, then approximately 70% of the nss $SO_4^=$ and 40% of the NO_3^- in Bermuda precipitation may originate with anthropogenic sources. Given the large regional variability in data for the Northern and Southern Hemispheres, we recognize that these estimates include a large degree of uncertainty.

4.3. *The composition of Bermuda precipitation as a function of air mass trajectory*

Under periods of westerly flow, Bermuda is downwind of North America. The VWA concentrations of nss $SO_4^=$ (Fig. 1), H^+, NO_3^-, $HCOO^-$, CH_3COO^- and NH_4^+ (Table 3) in Bermuda precipitation associated with NW flow are higher than those associated with SE flow. Previous reports using more limited data bases have stated that the higher concentrations of nss $SO_4^=$, NO_3^-, H^+, and NH_4^+ in precipitation

Table 2. *The composition of precipitation on Bermuda versus remote marine areas (μeq/l)*

	H^+	NH_4^+	NO_3^-	nss $SO_4^=$	$HCOO_T$	CH_3COO_T
Bermuda	13.1	2.8	4.4	14.1	2.2	1.3
*Remote marine areas**						
Amsterdam Island	8.8	1.8	1.3	4.9	2.2	0.6
Samoa	3.0	—	—	2.0	—	—
Discoverer	9.4	2.8	2.2	—	3.4	1.9
New Zealand	3.4	—	0.5	3.3	1.0	1.2
Korolov	7.6	2.9	1.3	—	—	—
Central Tasman Sea	5.3	—	2.2	6.3	—	—
Arithmetic average	6.2	2.5	1.5	4.1	2.2	1.2

* Remote area data for H^+, NH_4^+, NO_3^- and nss $SO_4^=$ are from Galloway (1985). Data for $HCOO_T$ and CH_3COO_T are from Keene and Galloway (1986).

Table 3. *Volume-weighted average concentrations (μeq/l) of precipitation as a function of compass sector**

Sector	nss $SO_4^=$	NO_3^-	$HCOO^-$	CH_3COO^-	NH_4^+	H^+
SE	8.5	2.2	1.3	0.6	1.7	8.6
SSW	15.2	3.8	1.7	0.8	2.2	13.3
WSW	13.5	4.9	2.1	0.9	3.2	11.6
NW	23.1	7.6	3.2	0.9	4.3	22.1
NE	16.2	4.7	0.6	0.6	2.2	9.1

* Data for $HCOO^-$ and CH_3COO^- are from HP; the number of samples were 13, 19, 13, 20 and 1 for the SE, SSW, WSW, NW and NE sectors, respectively. Precipitation amounts were 28.1, 43.1, 23.5, 15.0 and 0.9 cm, respectively. All other data are from HRT; the number of samples were 46, 57, 48, 59 and 6, respectively. Precipitation amounts were 116, 116, 82.5, 93.3 and 5.5 cm, respectively.

associated with NW flow are due to transport from North America (e.g., Church et al., 1982; Jickells et al., 1982). Because the previous reports have been based on only 1–2 years of data, an assessment of the variability of precipitation composition within and among sectors has not been possible. However, with the larger data base presented in this paper it is possible to not only compare VWA concentrations but to also compare the variability of precipitation composition within and among sectors. This analysis is based upon the subjective classification of mass trajectories into compass sectors (Fig. 1). A more objective classification of trajectories by cluster analysis has also been performed by Moody and Galloway (1988). The latter is a potentially powerful approach which provides a more quantitative framework to assess variation of precipitation composition as a function of air mass source.

4.3.1. nss $SO_4^=$. Frequency distributions of the concentrations of nss $SO_4^=$ in the NW and SE sectors show that approximately 40% of the precipitation events associated with the NW sector have nss $SO_4^=$ concentrations greater than any observed for storms from the SE sector (Fig. 2). However, it also shows that there is a wide range of concentrations for precipitation events from the NW sector. Thus, within a given sector there appear to be other factors that influence variability of precipitation composition on Bermuda. One variable is difference in source region within a compass sector. For example, within the NW sector, the trajectories of air masses associated with precipitation events had a wide variety of transport paths (Fig. 3) and therefore may have picked up differing amounts of S emissions. A similar situation exists for trajectories from other sectors. Another within-sector source of variability is the length of transit time for the airmass to reach Bermuda from North America. The longer the time, the greater the opportunity for continental material to be removed from the atmosphere before arrival at Bermuda. To illustrate this relationship, all NW

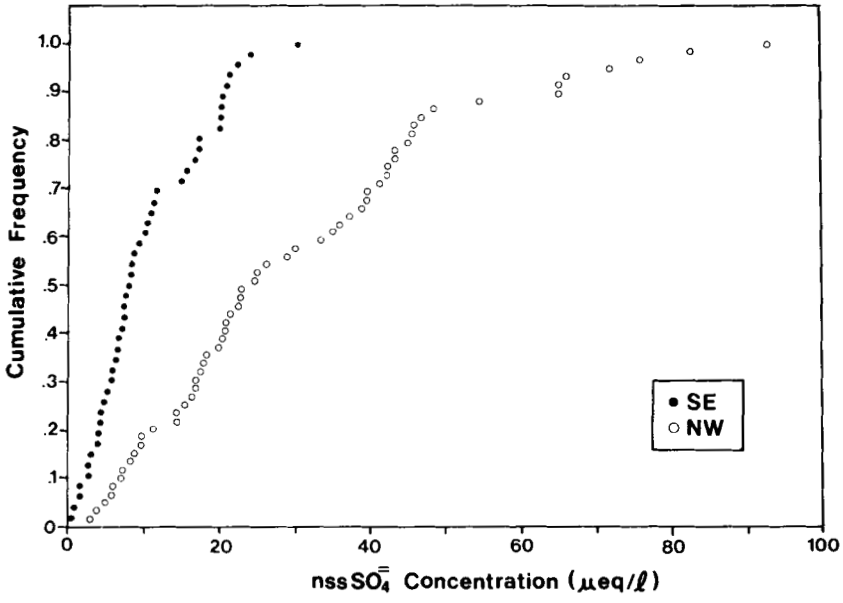

Fig. 2. Frequency diagram of nss $SO_4^=$ concentrations for the NW ($N = 59$) and SE ($N = 46$) sectors.

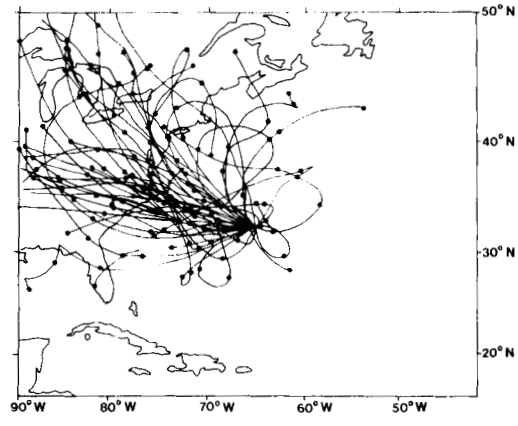

Fig. 3. Air mass back trajectories (3 day) of individual storms associated with the NW sector.

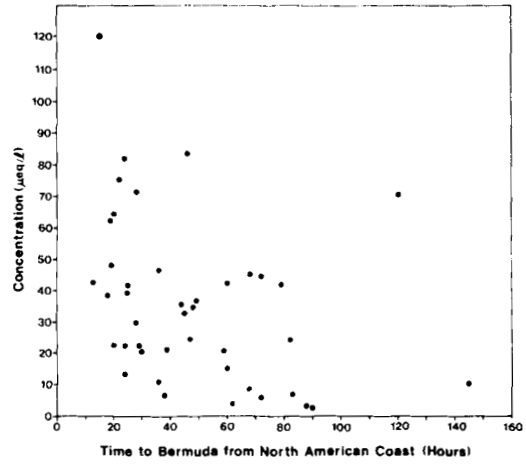

Fig. 4. The concentration of nss $SO_4^=$ in Bermuda precipitation as a function of transit time of airmass between North America and Bermuda.

back trajectories were analyzed to determine the period of time elapsed between the air parcels leaving North America to the time they reached Bermuda. Multiple trajectory events were averaged to determine a mean transport time. Fig. 4 shows a plot of concentration versus transport time from North America for all NW storms which were characterized. It is apparent that while events with quicker transport times generally had higher concentrations, a simple relationship does not exist. A larger NW trajectory data set might allow further refining of this relationship.

The amount of precipitation associated with each storm may also account for some of the

concentration differences between storms within each sector. Within each sector, concentration–volume effects can be normalized by the calculation of VWA. However, when VWA concentrations are compared between sectors (e.g., Table 3), differences in the distribution of storm volumes between sectors can affect the differences in VWA concentration.

For example, the amount of precipitation for storms associated with the NW sector is lower relative to the SE sector. The median values are 1.7 and 0.7 cm for the SE and NW sectors, respectively. This could result in higher concentrations in precipitation associated with the NW sector if there is a dilution effect on the nss $SO_4^=$ concentrations due to increasing precipitation amounts. This possible relationship is graphically examined by plotting the concentration of nss $SO_4^=$ versus the amount of precipitation for each storm associated with the NW and SE trajectories (Fig. 5). There is a dilution effect in the sense that high volume storms from the NW and SE sectors have lower concentrations of nss $SO_4^=$ than low volume storms (<4 cm), but the magnitude of the effect is different for the two sectors. The SE sector's low volume storms have concentrations that are on average about a factor of two higher than high volume storms. But for the NW sector, low volume storms exhibit concentrations that are substantially larger (a factor of 3–5) than those of high-volume storms. Indeed, the NW low volume storms have concentrations several times larger (Fig. 4) than the SE low volume storms. It is this subset of storms where the influence of North American emissions is most evident.

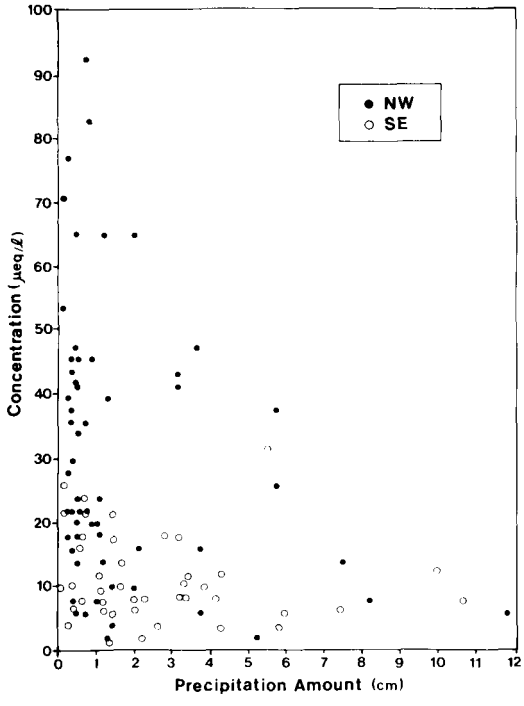

Fig. 5. Concentration of nss $SO_4^=$ in precipitation associated with air masses from the NW and SE sectors as a function of precipitation amount.

The confounding influence of precipitation amount on the interpretation of the differences in the frequency distribution of nss $SO_4^=$ concentrations (Fig. 2) can be avoided by analyzing deposition. Over the 50-month period, the precipitation rate on Bermuda was 140 cm/year. This compares to the climatological average of 146 cm/year based on 99 years of data (Macky, 1957). Using the VWA concentration for nss $SO_4^=$ of 14.1 μeq/l (Table 2) and appropriate conversion factors, an annual deposition rate of 0.23 g S m^{-2} $year^{-1}$ is calculated. This rate is about twice the mean of that observed in remote marine regions (0.1 g S m^{-2} $year^{-1}$; Galloway, 1985) and reflects the influence of anthropogenic sulfur.

To further quantify the influence that North America has on nss S deposition to Bermuda, deposition associated with NW trajectories is compared to deposition associated with the SE trajectories. The frequency diagrams of the per-event deposition (left vertical axis, Fig. 6) for the NW and SE sectors are similar over most of the distributions. Differences between the distributions are only evident in about the top 28% of the events, i.e., for most storms there are few differences between the deposition frequencies. However, a comparison between the cumulative deposition frequencies (right vertical axis, Fig. 6) of the NW and SE sectors shows that those small number of NW storms that have higher depositions, relative to the SE storms, result in over a factor of two difference in total deposition when the NW and SE sectors are compared. Another related point is that for both sectors, a small % of storms accounts for most of the deposition. Specifically, 12 and 17% of the storms, respect-

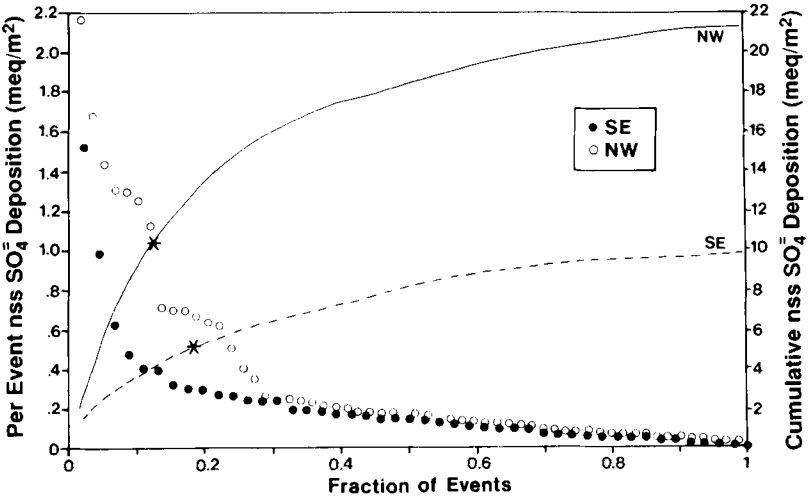

Fig. 6. Per-event deposition as a function of cumulative deposition for nss $SO_4^=$ for storms associated with the NW and SE sectors.

ively, account for half of the deposition for storms associated with NW and SE flow (noted by asterisks, Fig. 6).

The deposition of nss $SO_4^=$ from NW storms is about twice that deposited from SE storms (Fig. 6), even though there was more precipitation associated with SE storms than with NW storms (116.5 cm versus 93.5 cm, respectively). This difference between the two sectors is associated with the 16 highest deposition storms from the NW sector (Fig. 6). The factor of two difference in nss $SO_4^=$ deposition between NW and SE storms is attributed to anthropogenic influences. However, we postulate that it represents a lower limit of the difference for two reasons. First, over the 50-month period that this data-base spans, there was less precipitation associated with NW air masses and more with SE air masses relative to a 7-year average (Miller and Harris, 1985). For the 50-month database, of the precipitation that was assigned trajectories (71%), 28% and 23% was associated with SE and NW trajectories, respectively. However, based on seven years of data, the average is 21% and 33%, respectively (Miller and Harris, 1985). Thus, the 50-month period used in this analysis may not be representative of a larger time period.

Our expectations that the differences in cumulative deposition (Fig. 6) represent the lower limit of the influence of anthropogenic activities is supported by a second line of reasoning. We assume that the nss $SO_4^=$ concentrations of storms associated with SE air masses are not significantly affected by anthropogenic activities. This may not be true. The VWA concentration of nss $SO_4^=$ of SE storms is 8.1 μeq/l, about double the mean found in remote marine areas (Table 2). It is not unexpected to find the influence of anthropogenic activities on the atmosphere of the central Atlantic Ocean. The source strengths of S to the North Atlantic atmosphere from North America and the North Atlantic Ocean are similar. Andreae (1985) estimated that the emission of biogenic S to the North Atlantic Ocean atmosphere from 0–60°N is 4.3 Tg S/year. Estimates of the amount of S advected eastward from North America to the North Atlantic Ocean atmosphere are 2.2 Tg S/year (Fay et al., 1986), 3.0 Tg S/year (Bischoff et al., 1984), 4.3 Tg S/year (Galloway et al., 1984), and 5.8 Tg S/year (Shannon and Lesht, 1986). The similarity of the biogenic and anthropogenic fluxes to the atmosphere over the North Atlantic Ocean supports the hypothesis that the apparent enrichments of nss $SO_4^=$ in SE sector storms, relative to remote marine areas in the Southern Hemisphere, are due to the anthropogenic source. This observation is further supported by the earlier work of Meszaros (1978) and the more recent results of Savoie (1984) and Whelpdale et al. (1988) who

indicate that the entire atmosphere of the North Atlantic Ocean is impacted by anthropogenic emissions.

Based on this 50-month database of precipitation composition, the distribution of precipitation as a function of compass sector and the contribution of anthropogenic sulfur sources to SE storms, we estimate that the deposition of nss $SO_4^=$ in precipitation associated with the NW sector is a minimum of 2 and possibly several times greater than would exist in the absence of anthropogenic activities.

4.3.2. NO_3^-. The average deposition of NO_3^- to Bermuda is 0.086 g N m^{-2} $year^{-1}$. This is over twice the mean wet deposition rate to remote marine areas (0.03 g N m^{-2} $year^{-1}$; Galloway, 1985). As with nss $SO_4^=$, the difference is ascribed to anthropogenic activities. The influence of these activities is also illustrated in the frequency distributions of per-event and cumulative deposition of NO_3^- in the NW and SE sectors (Fig. 7). Distribution of NO_3^- deposition in the SE sector is similar to the NW sector for the low-deposition storms, but in the top 40% of the deposition frequency there are substantial differences. These differences manifest themselves in the cumulative frequency distributions (right hand vertical axis, Fig. 7), where NW NO_3^- deposition is over 2.5 times that of SE deposition. As with nss $SO_4^=$, a small % of the storms for both sectors account for much of the deposition. 14 and 22% of the storms provide half of the NO_3^- deposition for the NW and SE sectors, respectively.

The conclusion that the higher deposition of nss $SO_4^=$ and NO_3^- in Bermuda precipitation associated with NW air mass trajectories (relative to SE trajectories) is primarily due to North American sources is supported by studies on the influence of air mass sources on atmospheric concentrations. Wolff et al. (1986) found that the concentrations and composition of fine aerosol and trace gaseous species on Bermuda in August, 1982 and February, 1983 were governed by the type of air mass influencing the island. During incursions of air from the northeastern United States, which were most frequent during the winter, higher concentrations of the anthropogenically-derived species, such as $SO_4^=$, HNO_3, SO_2, O_3, Pb, Se, and elemental carbon were observed relative to air originating in the SE sector. Higher nss $SO_4^=$ concentrations in fine aerosols were associated with higher concentrations of the coal-burning tracer, Se, and higher concentrations of HNO_3 and O_3. SO_2 was strongly associated with the oil-burning tracer, V.

Chen and Duce (1983) collected 78 atmospheric samples from April to October, 1974. They found that most of the sulfate in excess of that from sea spray and V in excess of that from weathered crustal material in the particles at

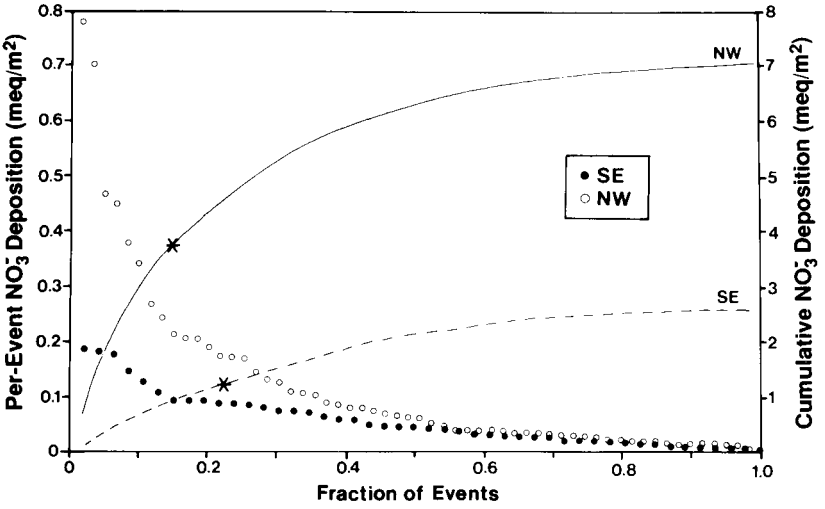

Fig. 7. Per-event deposition as a function of cumulative deposition for NO_3^- for storms associated with the NW and SE sectors.

Bermuda was pollution derived, primarily from North America. They concluded that relatively direct transport of aerosol particles from North America to Bermuda apparently occurs 35–40% of the time each year.

4.3.3. NH_4^+. The average deposition of NH_4^+ to remote marine areas is 0.04 g N m^{-2} $year^{-1}$ (Galloway, 1985). This is compared to 0.055 g N m^{-2} $year^{-1}$ for Bermuda. The VWA concentration of NH_4^+ in precipitation on Bermuda is within the range of that in remote marine areas (Table 2). However, the VWA concentrations of NH_4^+ in the NW and SE sector are substantially different, 4.3 versus 1.7 μeq/l, respectively, indicating a possible impact of North America on precipitation composition that is not apparent in the comparison of Bermuda with remote areas. This is illustrated by examining the per-event and cumulative deposition frequency distributions of NH_4^+ (Fig. 8). The NW and Se distributions are more similar for HN_4^+ than for nss $SO_4^=$ and NO_3^- (Figs. 6 and 7). However, there are several events associated with NW trajectories that fall outside of the SE distribution. These high deposition events may reflect the influence of North American sources.

4.3.4. $HCOO_T$ (and CH_3COO_T). $HCOO_T$ (and CH_3COO_T) are highly correlated ($r = 0.95$) in precipitation on Bermuda (Keene and Galloway, 1986). Therefore, since the behavior of $HCOO_T$ is representative of that for CH_3COO_T, only data for $HCOO_T$ were analyzed in detail. Data for $HCOO_T$ measured in precipitation collected at High Point, Bermuda were evaluated using the methods previously described in this paper to assess the relative importance of terrestrial versus marine sources. A plot of concentrations as a function of normalized frequency for events originating in the NW and SE sectors indicates significant differences for the medians and distributions of the two data sets (Fig. 9). In addition to possible long distance transport of terrestrial material, these differences may, as previously discussed for nss SO_4^{2-}, originate with a number of processes including storm size and transit time over the ocean. For the data subset depicted in Fig. 9, the mean water deposition of SE storms was 1.9 cm compared with 1.0 cm for NW storms. The larger water content of storms associated with the SE sector may have diluted scavenged material contributing to the observed differences in concentration. To assess this possibility, concentrations for $HCOO_T$ for storms from both sectors were plotted as a function of water deposition (Fig. 10). When all data for both sectors are considered, a general trend of decreasing concentration with increasing storm size is evident. When viewed as a function of source region, however, different distributions are observed for

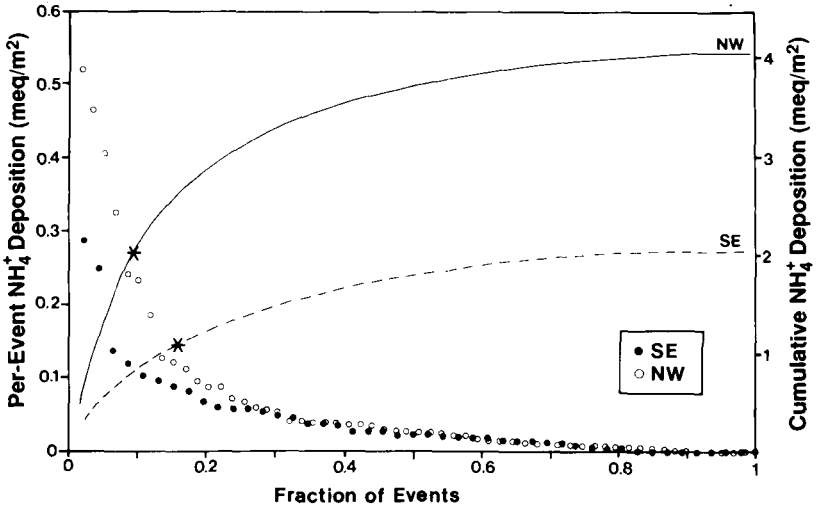

Fig. 8. Per-event deposition as a function of cumulative deposition for NH_4^+ for storms associated with the NW and SE sectors.

the two data sets. With one exception, SE sector storms exhibit little variability in concentrations over a wide range of storm sizes whereas NW sector storms show a large amount of variability in concentrations for small volume events (<1.5 cm) (Fig. 10). Sixty-one percent of NW sector storms contained concentrations of $HCOO_T$ which were higher than all but one such observation for SE sector storms. This suggests that there may be $HCOO_T$ of continental origin in precipitation generated by NW sector airflow.

A second method of assessing the influence of storm size on associated concentrations is to compare the per-event and cumulative deposition for the NW and SE sectors (Fig. 11). Unlike the situation for nss $SO_4^=$, NO_3^- and NH_4^+, the differ-

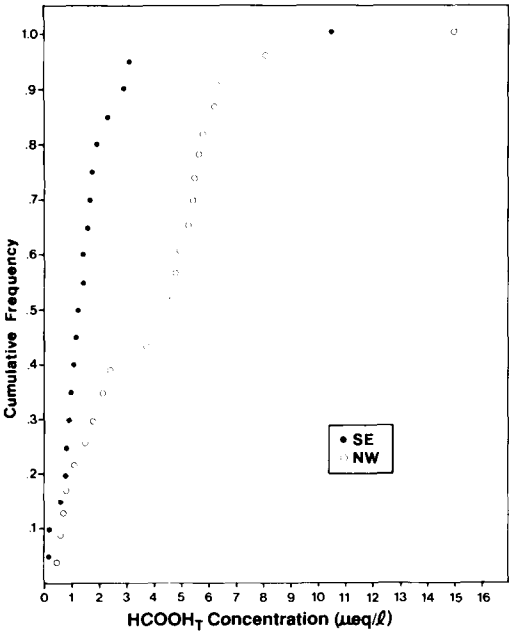

Fig. 9. Frequency diagram of $HCOO_T$ concentrations for the NW and SE sectors.

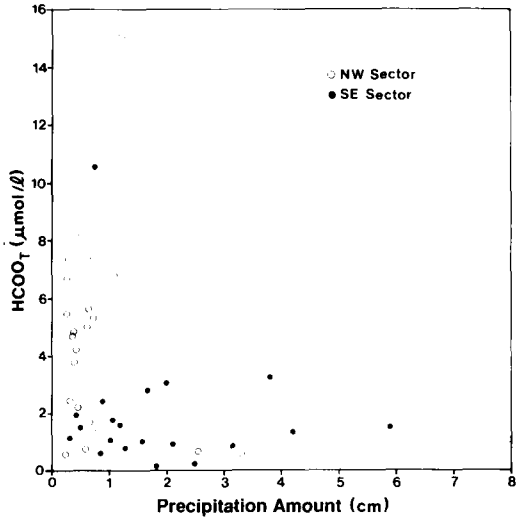

Fig. 10. Concentration of $HCOO_T$ in precipitation associated with air masses from the NW ($N = 20$) and SE ($N = 13$) sectors as a function of precipitation amount.

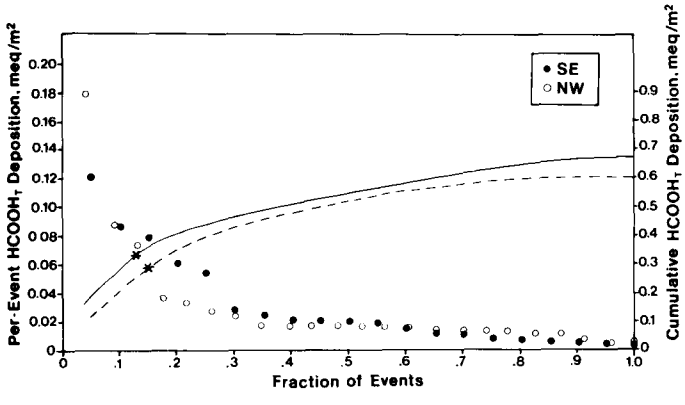

Fig. 11. Per-event deposition as a function of cumulative deposition for $HCOO_T$ for storms associated with the NW and SE sectors.

ences are slight between the distributions of depositions for the two sectors. This observation indicates that if there is a North American effect, it may only be apparent in low volume storms that account for a small amount of the deposition. The observation also suggests that there may be similar source strength for $HCOO_T$ (and CH_3COO_T) in both sectors.

Indirect estimates and quantitative measurements reveal a distinct seasonality in aqueous and vapor phase concentrations and depositions of HCOOH and CH_3COOH in the eastern North America with the highest values observed during the terrestrial growing season (Keene and Galloway, 1984, 1986; Talbot et al., 1987). This and other evidence (Keene and Galloway, 1986) supports the hypothesis of a strong terrestrial vegetative source for these constituents between April and September. Although, relative to other seasons, higher event depositions were also observed on Bermuda during the spring and early summer, these higher values were not restricted to NW sector storms, but were also associated with those from the SW sector. Of the upper 27% of the storms from both sectors (Fig. 11), 10 of 11 were collected during this period. This suggests that the higher depositions measured during the spring and summer on Bermuda may originate with a seasonally varying source in the marine atmosphere rather than with transport of terrestrial material. This hypothesis is consistent with seasonal variations in the strength of atmospheric transport off the continent. During the summer when continental concentrations of $HCOO_T$ and CH_3COO_T are high, offshore flow is weak and therefore a large continental signal is not evident in precipitation on Bermuda. During the winter when continental concentrations are low, offshore flow is well-developed, but even if there was significant transport of continental $HCOO_T$ and CH_3COO_T to Bermuda, it is difficult to discern from the marine background. Taken together, this analysis supports the hypothesis of a significant seasonally varying source for $HCOO_T$ and CH_3COO_T in the marine atmosphere. Such a source would be consistent with a biogenic precursor such as alpha-olefins which are emitted by marine microorganisms, volatilized to the atmosphere, and subsequently photooxidized as suggested by G. R. Harvey and R. F. Lang (personal communication).

4.4. Control on precipitation pH

The previous sections have discussed the distribution and the relative magnitude of the major proton donors in precipitation. These proton donors, in conjunction with the bases NH_3 and $CaCO_3$, control the concentration of the free acidity of precipitation on Bermuda. This section of the paper discusses the acids responsible for precipitation acidity on Bermuda using a database generated from samples collected at HP ($N = 88$) which included analyses of all major acids and bases.

The VWA concentrations of nss $SO_4^=$, NO_3^-, $HCOO^-$, CH_3COO^-, H^+, NH_4^+ and nss Ca^{++} are presented in Table 4. The sum of anions is greater than the H^+ concentration (and the sum of the cations). This imbalance between cations and anions is due to the exclusion of two nss components (nss K^+ and nss Mg^{++}) because of their trace quantities (<1.5 μeq/l). We believe that the sum of the anions is about twice the H^+ because of the neutralization of the potential acidity by basic material. It has been postulated that the primary bases are $CaCO_3$ and NH_3 (Galloway et al., 1988).

Using the data from the 50-month record of precipitation composition on Bermuda (Table 1), we estimate that a maximum of 24% of precipitation acidity on Bermuda is neutralized by $CaCO_3$ and a maximum of 13% by NH_3. There is also neutralization of H^+ by the ss alkalinity. However, we estimate that it is $<5\%$ of the original acidity (Galloway et al., 1983).

If there are no direct sources for salts of $SO_4^=$, NO_3^-, etc., and if we have measured all the acid anions, the maximum contribution of the proton donors to the free acidity of Bermuda precipi-

Table 4. *Volume weighted average concentrations of protons, possible proton donors and neutralizing substances in Bermuda precipitation* ($\mu eq/l$)

Cations			Anions		
H^+		11.9	nss $SO_4^=$		15.1
nss Ca^{++}		4.3	NO_3^-		4.6
NH_4^+		3.7	$HCOO^-$		2.0
	total	19.9	CH_3COO^-		0.8
				total	22.5

tation is determined by summing the concentration of the acid anions and dividing the sum into the individual acid anion concentrations. Using this method, the maximum contribution of H_2SO_4, HNO_3, HCOOH and CH_3COOH to the free acidity is 67, 20, 8 and 3%, respectively.

As mentioned, all storm events were assigned a trajectory classification (e.g., Fig. 1). To determine if the relative contribution of these acids to free acidity was dependent on air mass source, we have calculated VWA as a function of trajectory sector. These VWA concentrations for each anion have been normalized by the VWA of the total acid anion concentration for each trajectory sector. The results show that in storms associated with SE air flow, the organic acids (Fig. 12) are increased in importance relative to storms associated with NW air flow. However, even with this increased importance, the order of importance of the acids in contributing to the free acidity is still $H_2SO_4 \gg HNO_3 > HCOOH > CH_3COOH$. Thus, air mass source has only a small effect on the relative importance of the acids in controlling the pH of precipitation.

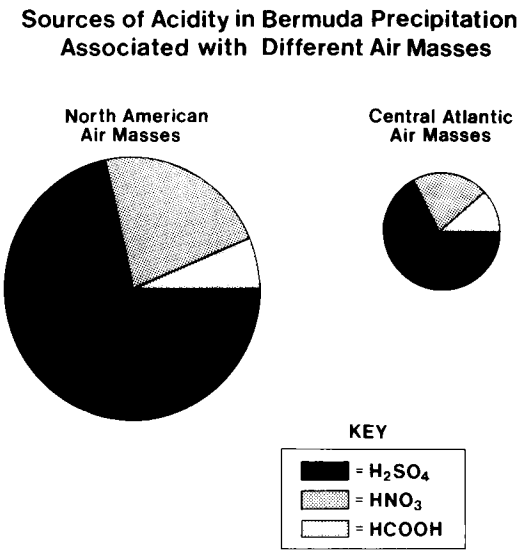

Fig. 12. Sources of acidity in Bermuda precipitation associated with different air masses. The size of the circle reflects the VWA H^+ concentration over a two year period.

4.5. Temporal variability of trends in composition of precipitation on Bermuda

4.5.1. Monthly variability. The monthly VWA's of Na^+ and nss $SO_4^=$ are plotted to illustrate seasonal variability (Fig. 13). For Na^+ (and Mg^{++}, K^+, Cl^-), there is a strong seasonal pattern with low values in summer months and higher (factor of 2–3), more variable values in the winter months. Na^+ has a strong seasonal signal because its concentration in precipitation results almost exclusively from scavenging of ss aerosol generated by wind turbulence. Highest wind velocities are observed primarily during the winter months (Erickson et al., 1986). nss $SO_4^=$ (and NO_3^-, H^+, and NH_4^+) have a less well-defined pattern (Fig. 13) because the concentrations of these parameters in precipitation are controlled by several processes occurring at some distance from Bermuda: air–sea exchange, air–land (North America) exchange, atmospheric transport and atmospheric transformations.

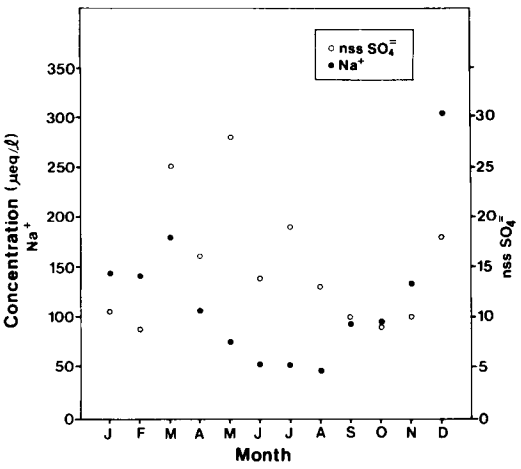

Fig. 13. Monthly VWA concentration of Na^+ and nss $SO_4^=$ at Bermuda.

4.5.2. Annual variability. The ss and nss components of precipitation both show large degrees of variability over the 4-year period (Table 5). Since one of the primary sources of variability could be year-to-year differences in airflow path, we plot the annual VWA concentrations for the entire data set and for only those precipitation events associated with air flow from the NW and SE sectors (Fig. 14). As is evident, even after classifying by trajectory, there is still

Table 5. *The volume weighted average composition of precipitation over four one-year periods (μeq/l)*

	1 April 1980 to 31 March 1981	1 April 1981 to 31 March 1982	1 April 1982 to 31 March 1983	1 April 1983 to 31 March 1984	Coefficient of variation
ss components					
Cl^-	128.9	183.1	141.8	102.5	0.24
$SO_4^=$	13.3	18.9	14.7	10.6	0.24
Na^+	110.6	157.1	121.7	88.0	0.24
Mg^{++}	25.1	35.6	27.6	19.9	0.24
Ca^{++}	4.9	6.9	5.3	3.9	0.24
K^+	2.4	3.4	2.7	1.9	0.24
nss components					
H^+	15.4	16.0	8.8	11.9	0.25
$SO_4^=$	16.0	14.6	9.0	15.1	0.24
NO_3^-	4.3	5.4	3.6	4.1	0.18
NH_4^+	2.5	3.0	2.6	2.9	0.07

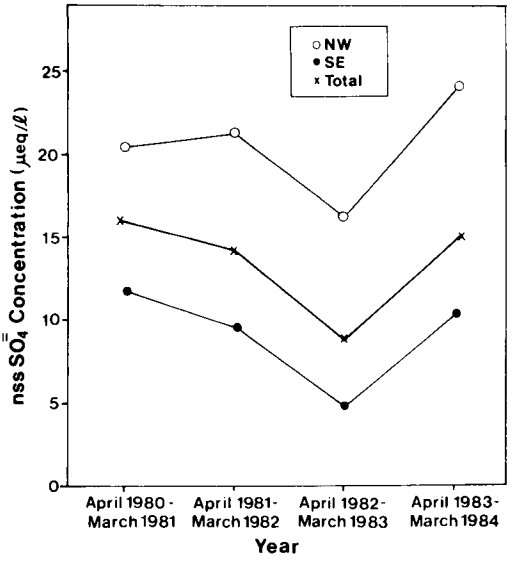

Fig. 14. Annual VWA concentration of nss $SO_4^=$ at Bermuda and annual VWA concentrations for the SE and NW trajectory sectors.

substantial and remarkably consistent annual variability. This variability is not controlled by differences in precipitation amount. The years with the lowest VWA concentrations do not have the highest total precipitation amount or the highest precipitation amount per event. The data in Fig. 14 suggest that similar synoptic-scale processes may control the variability.

5. Summary

The composition of precipitation on Bermuda can be characterized as a slightly acidic, dilute seawater solution. The acidity of the solution is controlled by H_2SO_4, HNO_3, HCOOH and CH_3COOH in a 67 : 20 : 8 : 3 mixture, respectively. $CaCO_3$ and NH_3 have reduced the potential acidity of the solution by 24% and 13%, respectively.

The composition of precipitation on Bermuda is different from remote areas. nss $SO_4^=$ and NO_3^- have concentrations 70% and 40% greater, respectively. NH_4^+, $HCOO_T$ and CH_3COO_T concentrations in precipitation on Bermuda are more similar to remote areas, however there are distinct events where transport from North America is evident. Precipitation associated with air masses from the central Atlantic Ocean is enriched by about a factor of two in nss $SO_4^=$, relative to remote marine areas. This appears to be caused by anthropogenic emissions in North America, Europe and Africa.

6. Acknowledgements

This is a contribution to the Western Atlantic Ocean Experiment (WATOX) and the Bermuda Biological Station for Research, Inc. (contribution number 1183). WATOX is funded by the

US National Oceanic and Atmospheric Administration. We acknowledge and appreciate the technical support of Tim Jickells, Rachel Dow and Joe Tokos. We also appreciate the data reduction skills of Dan Smith and the hours that Brenda W. Morris spent typing yet another version. This paper benefited by the numerous discussions that the authors had with Doug Whelpdale and the review comments of Jennie Moody and Alex Pszenny.

REFERENCES

Andreae, M. O. 1985. The emission of sulfur and nitrogen to the remote atmosphere. Background paper: sulfur emission. In *Biogeochemical cycling of sulfur and nitrogen in the remote atmosphere* (eds. J. N. Galloway, R. J. Charlson, J. O. Andreae and H. Rodhe). NATO ASI Series, Dordrecht, Holland: D. Reidel Publ. Co., 249 pp.

Bergman, K. H. 1978. Multivariate analysis of temperatures and winds using optimum interpolation. *Mon. Wea. Rev. 107*, 1423–1444.

Bischoff, W. D., Patterson, V. L. and MacKenzie, F. T. 1984. Geochemical mass balance for sulfur- and nitrogen-bearing components: Eastern United States. In *Geological aspects of acid deposition* (ed. O. P. Bricker). Acid Precipitation Series, Vol. 7. Boston: Butterworth, 1-20.

Chen, L. and Duce, R. A. 1983. The sources of sulfate, vanadium and mineral matter in aerosol particles over Bermuda. *Atmos. Environ. 17*, 2055–2064.

Church, T. M., Galloway, J. N., Jickells, T. D. and Knap, A. H. 1982. The chemistry of western Atlantic precipitation at the mid-Atlantic coast and on Bermuda. *J. Geophys. Res. 87*, 11013–11018.

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.

Fay, J. A., Kumar, S. and Golomb, D. 1986. Annual and semi-annual anthropogenic sulfur budgets for eastern North America. *Atmos. Environ. 20*, 1497–1500.

Galloway, J. N., Likens, G. E., Keene, W. C. and Miller, J. M. 1982. The composition of precipitation in remote areas of the world. *J. Geophys. Res. 87*, 8771–8786.

Galloway, J. N. 1985. The deposition of sulfur and nitrogen from the remote atmosphere. In *Biogeochemical cycling of sulfur and nitrogen in the remote atmosphere* (eds. J. N. Galloway, R. J. Charlson, M. O. Andreae and H. Rodhe). NATO ASI Series. Dordrecht, Holland: D. Reidel Publ. Co., 249 pp.

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

Galloway, J. N. and Whelpdale, D. M. 1987. WATOX-86 Overview and western North Atlantic Ocean S and N atmospheric budgets. *Global Biogeochemical Cycles 1*, 261–282.

Galloway, J. N., Likens, G. E., Keene, W. C. and Miller, J. M. 1982. The composition of precipitation in remote areas of the world. *J. Geophys. Res. 87*, 8771–8786.

Galloway, J. N., Knap, A. H. and Church, T. M. 1983. The composition of western Atlantic precipitation using shipboard collectors. *J. Geophys. Res. 88*, 10859–10864.

Galloway, J. N., Whelpdale, D. M. and Wolff, G. T. 1984. The flux of S and N eastward from North America. *Atmos. Environ. 18*, 2595-2607.

Galloway, J. N., Tokos, J. J., Jr., Knap, A. H. and Keene, W. C. 1988. Local influences of the composition of precipitation on Bermuda. *Tellus 40B*, 178–189.

Hales, J. M. and Dana, T. M. 1979. Regional-scale deposition of sulfur dioxide by precipitation scavenging. *Atmos. Environ. 13*, 1121–1132.

Harris, J. M. 1982. The GMCC Atmospheric Trajectory Program. NOAA Tech. Memo., *ERL ARL-116*.

Heffter, J. L. and Taylor, A. D. 1975. Trajectory Model—Part 1. A Regional Continental Scale Transport, Diffusion, and Deposition Model. NOAA Tech. Memo. *ERL ARL-50*, 28 pp.

Jickells, T., Knap, A., Church, T., Galloway, J. and Miller, J. 1982. Acid Rain on Bermuda. *Nature 297*, 55–57.

Keene, W. C. and Galloway, J. N. 1984. Organic acidity in precipitation of North America. *Atmos. Environ. 18*, 2491–2497.

Keene, W. C. and Galloway, J. N. 1986. Considerations regarding sources for formic and acetic acids in the troposphere. *J. Geophys. Res. 91*, 14466–14474.

Keene, W. C., Galloway, J. N. and Holden, J. D., Jr. 1983. Measurement of weak organic acidity in precipitation from remote areas of the world. *J. Geophys. Res. 88*, 5122–5130.

Keene, W. C., Pszenny, 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.

Macky, W. A. 1957. The rainfall of Bermuda. Bermuda Meteorological Office. Technical note *no. 8*, 59 pp.

McPherson, R. D., Bergman, K. H., Kistler, R. E., Rasch, G. E. and Gordon, D. S. 1979. The NMC operational global data assimilation system. *Mon. Wea. Rev. 107*. 1445–1461.

Mészáros, E. 1978. Concentration of sulfur compounds in remote continental and oceanic regions. *Atmos. Environ. 12*, 699–705.

Miller, J. M. and Harris, J. M. 1985. The flow climatology to Bermuda and its implication for long-range transport. *Atmos. Environ. 19*, 409–414.

Moody, J. L. and Galloway, J. N. 1988. Quantifying the relationship between atmospheric transport and the chemical composition of precipitation on Bermuda. *Tellus 40B*, 463–479.

Muller, K. P., Aheimer, A. and Gravenhorst, G. 1982. The influence of immediate freezing on the chemical composition of rain samples. In *Deposition of atmospheric pollutants* (eds. H.-W. Georgii and J. Pankrath). Dordrecht, Holland: D. Reidel Publ. Co., pp. 125–132.

National Research Council. 1986. *Acid deposition: Long-term trends*. Washington, DC: National Academy Press, 506 pp.

Prospero, J. M. 1981. Eolian transport to the world ocean. In *The Sea 7* (ed. C. Emiliani), 801–874.

Savoie, D. F. 1984. Nitrate and non-seasalt sulfate aerosols over major regions of the world ocean: Concentrations, sources and fluxes. PhD thesis, University of Miami, Miami, FL, USA.

Shannon, J. D. and Lesht, B. M. 1986. Modeled trends and climatological variability of the net transboundary mass flux of airborne sulfur between the United States and Canada. *Proceedings of Air Pollution Control Association Speciality Conference on Meteorology of Acidic Deposition*, Albany, NY, USA, 18 March.

Stackpole, J. 1978. The NMC 9-Layer Global Primitive Equation Model on a Latitude–Longitude Grid, *NMC Office Note 178*, National Meteorological Center, Suitland, MD, USA, 31 pp.

Talbot, R. W., Stein, K. M., Harriss, R. C. and Cofer III, W. R. 1988. Atmospheric geochemistry of formic and acetic acids at a mid-latitude temperate site. *J. Geophys. Res. 93*, 1638–1652.

Uematsu, M., Duce, R. A. and Prospero, J. M. 1985. Deposition of atmospheric mineral particles to the north Pacific Ocean. *J. Atmos. Chem. 3*, 123–138.

Whelpdale, D. M., Eliassen, A., Galloway, J. N., Dovland, H. and Miller, J. M. 1987. The transatlantic transport of sulfur. *Tellus 40B*, 1–15.

Wolff, G. T., Ruthkosky, M. S., Stroup, D. P., Korsog, P. E., Ferman, M. A., Wendel, G. J. and Stedman, D. H. 1986. Measurements of SO_x, NO_x, and aerosol species on Bermuda. *Atmos. Environ. 20*, 1229–1239.

Wolff, G. T., Church, T. M., Galloway, J. N. and Knap, A. H. 1987. An examination of SO_x, NO_x, and trace metals washout ratios over the Western Atlantic Ocean. *Atmos. Environ. 21*, 2623–2628.