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Quantifying the relationship between atmospheric transport and the chemical composition of precipitation on Bermuda

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ABSTRACT

In an effort to investigate the influence of different atmospheric flow patterns on the composition of precipitation on the island of Bermuda, a cluster analysis of atmospheric trajectories was performed to identify periods of similar transport. The cluster analysis technique represents a relatively objective alternative to the more subjective method of classifying trajectories according to compass sector. Data were stratified into two broad seasons, defined as a warm (April–September) and a cool (October–March) season. Relative to the cool season, significantly higher per event concentrations of non-seasalt sulfate and nitrate occurred in the warm season on Bermuda. There was no significant difference in the per event precipitation amount between seasons; however, there was significantly higher per event deposition of warm season non-seasalt sulfate, and nitrate. Significant differences in precipitation composition were also identified between flow patterns. It was found that the source regions which contributed the largest fraction of hydrogen ion deposition and non-seasalt sulfate deposition on Bermuda differed by season. During the cool months, 40% of the deposition occurred with transport from the west, off the East Coast of the US, implicating anthropogenic sources. In the warm season, an equally large fraction of deposition was associated with flow from the Bahamas region, suggesting an oceanic source of biogenic sulfur as the precursor.

1. Introduction

The application of atmospheric back trajectories as a tool employed in interpreting atmospheric chemistry data has become a standard practice, as illustrated by the recent review and bibliography prepared by Miller (1987). Several studies have used back trajectories to consider the influence of different source regions on the composition of precipitation on Bermuda (Jickells et al., 1982; Church et al., 1982; Galloway et al., 1983; Galloway et al., 1989). However, all these studies relied on a subjective manual classification of isobaric trajectories into pre-defined source regions or compass sectors. The present study used an objective classification technique, cluster analysis, which considered the wind speed and direction of four years of isobaric back trajectories to identify precipitation events which occurred under conditions of similar transport to Bermuda at 850 mb. This objective classification was used to define dominant flow patterns which deliver precipitation to Bermuda in two broad seasons, warm (April–September) and cool (October–March). Using nonparametric statistical tests, significant differences in precipitation composition among the resulting flow patterns have been identified and related to source region strength.

2. Data

The precipitation chemistry data set included 295 precipitation samples, collected during a 50 month period spanning 1980 to 1984. The creation of this quality checked data set is described in detail in Galloway et al. (1989). For each

precipitation sample, the precipitation amount, laboratory pH, and concentrations of Na^+, Cl^-, $SO_4^=$, NO_3^-, NH_4^+, Ca^{++}, Mg^{++}, and K^+ were recorded. For ions with seasalt sources (Cl^-, $SO_4^=$, Ca^{++}, Mg^{++}, and K^+), the non-seasalt (nss) concentrations have been calculated using Na^+ as the seawater reference species. Both Na^+ and Mg^{++} have been used as seasalt tracers. Na^+ was used in this study because of the potential for a small contribution of Mg^{++} from the carbonate minerals on Bermuda (Keene et al., 1986).

Isobaric trajectories were calculated using the GAMBIT (Gridded Atmospheric Multilevel Backward Isobaric Trajectory) model (Harris, 1982). The model employs a two-step process, with an initial objective analysis of wind data from rawinsondes, pibals, aircraft, and satellites. The objective analysis transforms these irregularly spaced observations into data on a regularly spaced grid. The spatial interpolation procedure which accomplishes this is a dynamic global 9-layer primitive equation model (Stackpole, 1978). Using these analyzed wind fields, ten-day back trajectories were calculated on two different isobaric surfaces, 850 mb and 700 mb.

In this study, only the last three days of transport to Bermuda were considered, for the following reasons. First, only complete trajectories could be used in the cluster analysis. Using 5-day back trajectories, 35% of the events had incomplete trajectories. If 4-day back trajectories were used, 20% would have been incomplete. However, using 3-day back trajectories, only 3% of the trajectories were incomplete. Second, using data three days back reduced the uncertainty, which increases as a function of time upwind, in the location of trajectory endpoints. Finally, 3 days were generally sufficient to determine the relative source regions of these trajectories.

For each precipitation event, the periods of precipitation were determined from Belfort Universal Raingauge charts. The trajectory time which corresponded to the period of precipitation was selected. Back trajectories from Bermuda were calculated at 12 hour intervals. When an event lasted through several 12-h periods, all possible 850 mb trajectories were examined. The sample was dropped if these trajectories were from significantly different directions. If the trajectories were not directionally divergent, one was chosen to represent the event.

30 events occurred during periods when trajectories could not be calculated because of missing gridded wind data. Another 8 events were excluded because they had incomplete trajectories going three days back from Bermuda. This reduced the original 295 precipitation samples to 257 samples with complete chemical and meteorological information.

There are certain aspects of isobaric trajectories which are problematic, for example the assumption that the transport of the chemical constituents of interest is reflected by transport on the 850 mb surface. In the presence of fronts, and during precipitation, there may be substantial vertical motion and considerable wind shear. These can invalidate the assumption that air parcels are advected along the path of the 850 mb wind. However, isentropic trajectories, the best alternative to using isobaric trajectories, are plagued by similar shortcomings. Cloud formation and precipitation are diabatic processes which invalidate the underlying assumption of conservation of potential temperature. Additionally, the selection of a representative isentropic surface is subjective without knowledge of what air was entrained into the precipitating clouds. Finally, the cost of generating a 4-year climatology of isentropic trajectories is prohibitive, they are commonly applied in case study analysis, or over short time periods (Merrill et al., 1985). For the purpose of preparing a climatology of relative patterns of transport to Bermuda, the procedure of calculating isobaric trajectories was determined to be adequate.

3. Method

The hypothesis being tested is that the chemical composition of precipitation sampled on Bermuda is influenced by the transport path of air parcels arriving at the Bermuda receptor. A common method for investigating this type of relationship has been to stratify precipitation events into groups of trajectories which arrive from common wind sectors and compare volume weighted averages. The simple procedure of categorizing trajectories by compass sectors uses only the wind direction data, and is relatively subjective. It requires visual inspection of the

trajectories, and a manual classification method. In the effort to use all available information, and remove the need for tedious visual classification, the multivariate technique of cluster analysis has been applied (Andenberg, 1973). This quantitative computerized classification scheme was used to consider the simultaneous variation of wind speed and direction over the duration of transport.

Cluster analysis has been used in a limited number of applications cited in the literature of atmospheric sciences. One of these applications addressed the problem of acid deposition. Slanina et al. (1983) clustered precipitation composition variables (ionic concentrations) into groups exhibiting similar composition and found that the resulting clusters suggested different source regions (continental versus marine) for the precipitating air masses. The present analysis clustered trajectory data into groups of similar transport and then quantitatively compared the chemical distributions within the resulting transport patterns. A similar procedure was applied to mixed-layer trajectories at two mid-latitude continental sites (Moody, 1986; Samson and Moody, 1986) and successfully explained a significant portion of the chemical variability.

Using trajectory data corresponding to each precipitation sample, the object was to group trajectories into clusters such that those within a cluster would represent similar flow patterns. The cluster variables were trajectory endpoints (i.e., latitude and longitude locations), these parameterized the wind speed and direction at 12-h intervals. 6 endpoints were used representing transport 72 h back in time. At the outset, each trajectory represented a cluster. The spatial variance between two trajectories was measured as the sum of the squared distances between the respective endpoints. The smaller the distance between endpoints within a cluster, the more similar the trajectories. Initially, all possible pairs of trajectories were compared and the two most similar were joined in a cluster. The spatial variance of a cluster containing two or more trajectories was calculated to be the sum of squared distances of respective endpoints from the cluster's mean endpoints (Ward's Method; Gordon, 1981). This step-wise optimal cluster routine continued grouping trajectories into clusters until the increase in variance from joining two clusters was too great to warrant their combination. In the application presented here, there were well-defined discontinuities (increases of 100% or greater in the spatial variance), signalling an optimal number of clusters.

4. Comparison of chemistry between seasons

A general comparison of the composition of precipitation between seasons was performed. Table 1 contains the volume weighted averages of the major non-seasalt ions in solutions, average precipitation amount per event, and ion ratios for the cool season and warm season respectively. Table 2 contains the average deposition per event

Table 1. *Seasonal volume weighted averages and ion ratios*

	Cool season	Warm season
nss-$SO_4^=$	12.95 (μeq/l)	16.29 (μeq/l)
NO_3^-	4.33 (μeq/l)	4.57 (μeq/l)
H^+	12.67 (μeq/l)	14.52 (μeq/l)
NH_4^+	2.66 (μeq/l)	2.86 (μeq/l)
Average precipitation amount	1.81 (cm)	2.22 (cm)
nss-$SO_4^=/NO_3^-$*	3.9	5.0
nss-$SO_4^=/H^+$	1.5	2.6

* Average per event equivalents ratios.

Table 2. *Seasonal average per event depositions and total deposition for the period 1980–1984*

	Cool season	Warm season	Total
Dnss-$SO_4^=$	2.35 (μeq/m2)	3.61 (μeq/m2)	741.5 (μeq/m2)
DNO_3^-	0.79 (μeq/m2)	1.01 (μeq/m2)	226.7 (μeq/m2)
DH^+	2.30 (μeq/m2)	3.22 (μeq/m2)	691.0 (μeq/m2)
DNH_4^+	0.48 (μeq/m2)	0.64 (μeq/m2)	140.7 (μeq/m2)

for the same ions by season, and the total ion deposition over the entire sampling period. These tables may suggest differences between seasons in concentration and deposition. However, to quantify the variability in chemical composition between seasons, statistical tests were used to distinguish significant differences in the distributions of ion concentration, ion deposition, and precipitation amount.

Nonparametric tests were used throughout this paper for the following reasons. Based on measures of skewness and kurtosis, the distributions of chemical species indicated significant departures from normality and the sample sizes were often too small (20 events or less) to rely on asymptotic normality. The statistical comparison of pairs of distributions was performed using the Mann-Whitney test (Conover, 1980). The null hypothesis states that the pair of distributions tested represent random samples from identical populations. For all tests performed in this paper, significant differences have been reported when the null hypothesis was rejected at the 95% confidence level.

There were no significant differences in the distributions of per event precipitation amount between seasons. However, upon comparing distributions of per event concentrations of nss-$SO_4^=$, NO_3^-, and the ratios of nss-$SO_4^=/NO_3^-$ and nss-$SO_4^=/H^+$, concentrations were significantly higher in the warm season. Additionally, when distributions of per event deposition were compared between seasons, nss-$SO_4^=$ and NO_3^- deposition was greater in the warm season. These differences may result from increased photochemical oxidation of sulfur and nitrogen species in the warm season. They could also suggest a longer lifetime of nitrogen species in the warm season resulting from lower dry deposition velocities and less scavenging by large seasalt aerosols (Savoie and Prospero, 1982). Additionally, biogenic sources of sulfur may be expected to make a contribution to warm season emissions. However, it is also important to consider the influence of different transport patterns in each season. This is addressed in Section 5.

5. Cluster analysis results

Using the cluster method described previously, 7 transport clusters were derived from 148 cool season events. Fig. 1 is a plot of the mean vector for each cluster of trajectories, the caption indicates the number of trajectories combined in each cluster. Each trajectory represents transport three days back, arrowheads mark 6-h intervals. The larger the distance between arrowheads, the greater the wind speed. For example, clusters 5 and 7 both arrive from the north and west, however events in cluster 5 had much lower wind speeds.

The same method was applied to 109 warm season events and 9 clusters were formed. 2 of these clusters were too small, comprising of 2 and 3 events, respectively, to use in the following statistical analysis. Upon inspection, it was found that all of these events occurred in April or early May, and these trajectories were very similar to those with cool season transport from the west and northwest (clusters 2 and 7). This illustrates that these events were likely misclassified as warm season events, being more typical of cool season flow patterns. It points out the difficulty of dividing the year into seasons. However, given significant differences in both precipitation composition and flow climatology, the seasonal division seems justified. These 5 trajectories represent less than 5% of the warm season events. They were very low in volume and accounted for less than 2% of the deposition of any ion (nss-$SO_4^=$, NO_3^-, NH_4^+, and H^+). These events were classified as outliers and excluded from further analysis.

The 7 warm clusters retained have each been represented by their mean trajectory in Fig. 2. Again, the number of trajectories grouped in each cluster is listed in the caption. There was significantly less transport from the west and northwest in the warm season, and wind speeds were lower.

These results are consistent with the Bermuda flow climatology compiled by Miller and Harris (1985) which considered 7 years of transport, 1975–1981. In the present study, using trajectories for rain days only, 1980–1984, transport with a westerly component occurred most frequently in the cool months, with this flow being most common in December, January and March. In the warm season, flow with a southerly component was prevalent, occurring most frequently in June, August and September. Miller and Harris (1985) describe this general climatic situation being

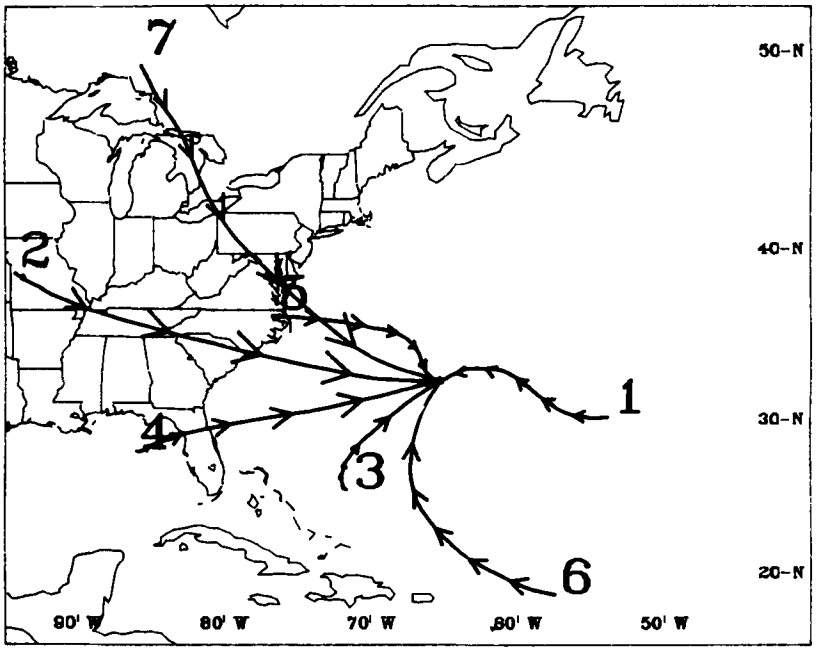

Fig. 1. Mean trajectories for 7 cool season transport clusters formed from 148 trajectories corresponding to precipitation events collected at Harbor Radio Tower, Bermuda. (1 (n = 21), 2 (n = 23), 3 (n = 30), 4 (n = 30), 5 (n = 16), 6 (n = 16), 7 (n = 12).)

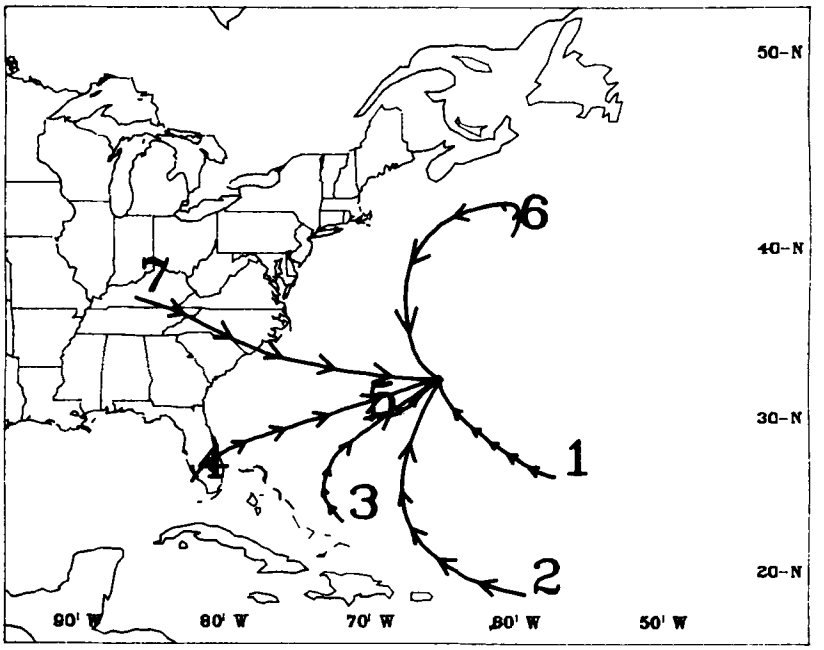

Fig. 2. Mean trajectories for 7 warm season transport clusters retained from clustering 109 trajectories corresponding to precipitation events collected at Harbor Radio Tower, Bermuda. (1 (n = 22), 2 (n = 14), 3 (n = 19), 4 (n = 15), 5 (n = 20), 6 (n = 6), 7 (n = 8).)

controlled by the seasonal movement of the Bermuda High. This semi-permanent synoptic feature favors southerly flow in the warm months, and moves south during cool months, allowing strong westerly flow to reach Bermuda. The fact that southerly flow was more common in the warm season when nss-$SO_4^=$ and NO_3^- concentrations and depositions were significantly higher supports the concept of a longer residence time for these species over the Southern Atlantic Ocean in the warm season.

The volume weighted averages of the ions in each cluster have been calculated and are used to summarize the chemical behavior of each transport pattern. In order to illustrate the volume weighted averages of the ions on the same scale, the values were normalized. Relative concentration factors were calculated as the ratio of the volume weighted average (VWA) of a species in a cluster to the VWA of that species for the entire season (detailed in Appendix A.) A relative concentration of 1 indicates the VWA of an ion was the same for the cluster and the season. The x-axis has been labeled by both cluster number, and a general description of transport direction (E, W, NW, etc.) and relative speed (Low, Moderate, High).

Fig. 3 is a plot of the relative concentration factors for the cool season transport clusters formed. This figure readily illustrates that high speed transport from the W and NW (clusters 2 and 7) resulted in VWA's 60% to 100% greater than the cool season average, while transport with an easterly component (clusters 1 and 6) had VWA's 40 to 60% below the season average. The normalized average precipitation amount, and % of seasonal water deposition occurring in each cluster were also plotted on this graph. Comparing transport from the E and W (clusters 1 and 2), both contributed similar amounts of total water deposition, and both had below average per event precipitation amount. However, low speed E winds (cluster 1) had concentrations 40% below average while high speed W winds (cluster 2) had concentrations 60 to 100% above average. This illustrates that there was no simple dilution explanation for the observed differences in concentration.

Fig. 4 is a plot of the relative concentration factors for the seven warm season clusters. The highest factors occurred with high speed transport form the NNE (cluster 6), with VWA concentrations 60% to 180% above the warm season average. However, the average precipitation

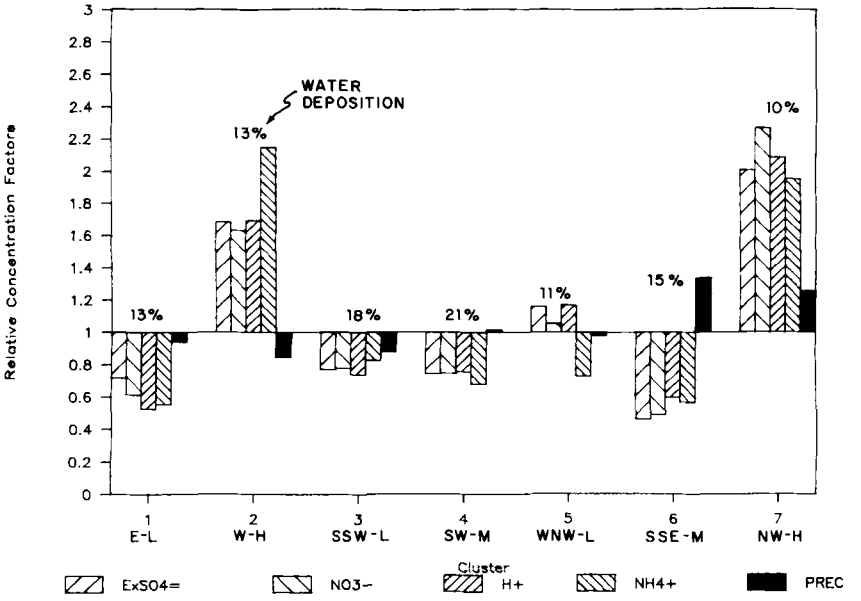

Fig. 3. Relative concentration factors (normalized volume weighted averages) of the major non-sea-salt ions by cool season cluster. The normalized average per-event precipitation amounts have also been plotted, along with the percentage of cool season water deposition occurring in each cluster.

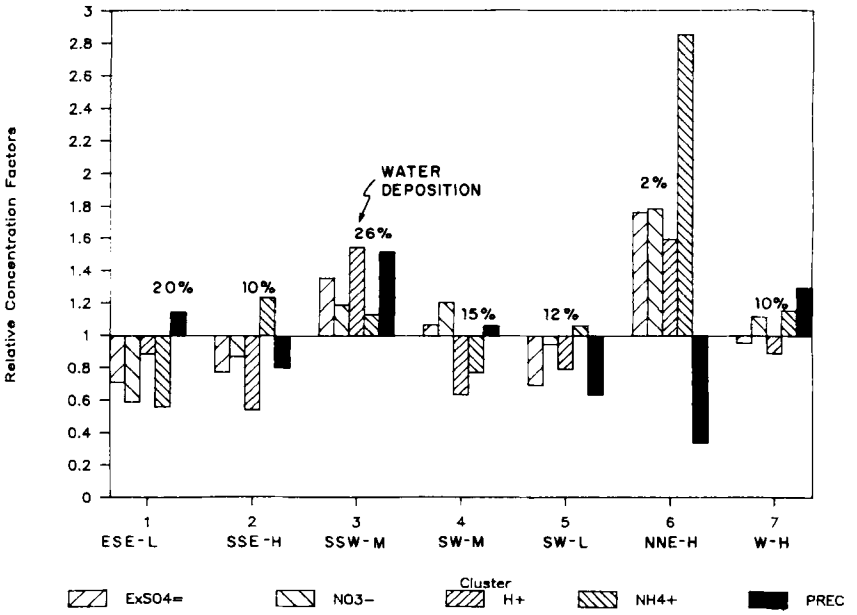

Fig. 4. Relative concentration factors (normalized volume weighted averages) of the major non-sea-salt ions by warm season cluster. The normalized average per-event precipitation amounts have also been plotted, along with the percentage of warm season water deposition occurring in each cluster.

Table 3. *% of Bermuda cool season (Oct–Mar) deposition by transport pattern*

Cluster	*n*	% precipitation	% nss-$SO_4^=$	% NO_3^-	% H^+	% NH_4^+
1 E-L	21	13.2	9.6	8.1	7.0	7.4
2 W-H	23	13.1	22.1	21.4	22.3	28.2
3 SSW-L	30	17.8	13.7	13.9	13.1	14.7
4 SW-M	30	20.6	15.3	15.4	15.5	14.0
5 WNW-L	16	10.6	12.2	11.1	12.3	7.7
6 SSE-M	16	14.5	6.6	7.0	8.6	8.2
7 NW-H	12	10.2	20.4	23.0	21.2	19.8

Table 4. *% of Bermuda warm season (Apr–Sep) deposition by transport pattern*

Cluster	*n*	% precipitation	% nss-$SO_4^=$	% NO_3^-	% H^+	% NH_4^+
1 ESE-L	22	23.1	16.5	13.7	20.5	12.9
2 SSE-H	14	10.3	8.0	9.0	5.6	12.7
3 SSW-M	19	26.4	35.8	31.4	40.8	29.8
4 SW-M	15	14.6	15.5	17.5	9.4	11.2
5 SW-L	20	11.7	8.1	11.0	9.3	12.4
6 NNE-H	6	1.9	3.3	3.4	3.0	5.4
7 W-H	8	9.5	9.1	10.6	8.5	11.0

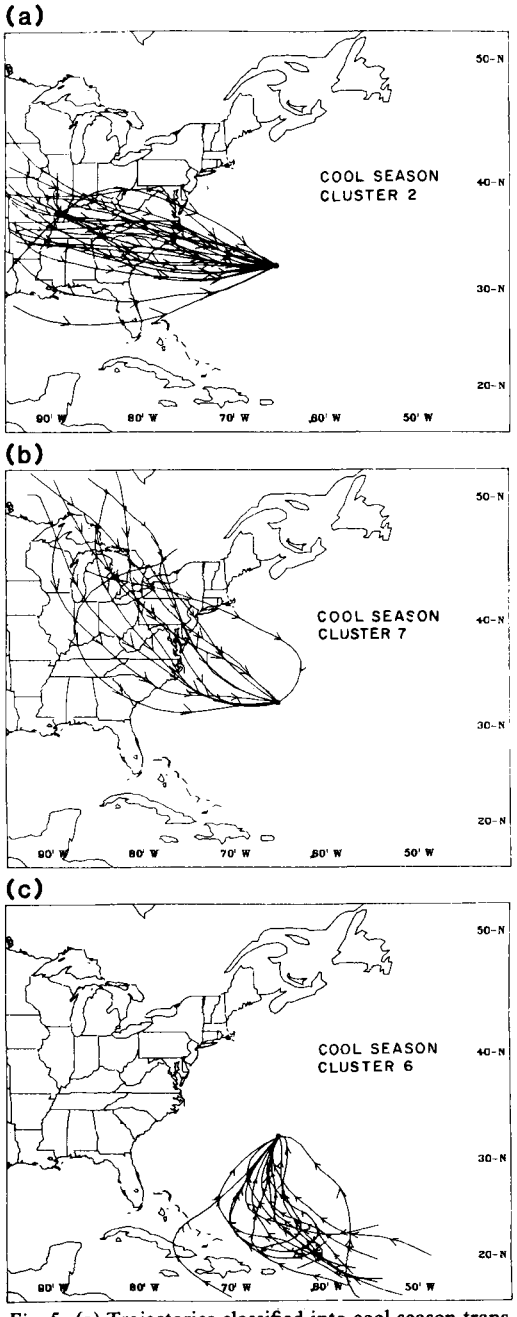

Fig. 5. (a) Trajectories classified into cool season transport cluster 2, depicting rapid transport from the southeastern US, and the lower Ohio River Valley. (b) Trajectories classified into cool season transport cluster 7, depicting rapid transport from the northeast and southeast US, and the Great Lakes region. (c) Trajectories classified into cool season transport cluster 6, depicting transport from the south out of the southern north Atlantic.

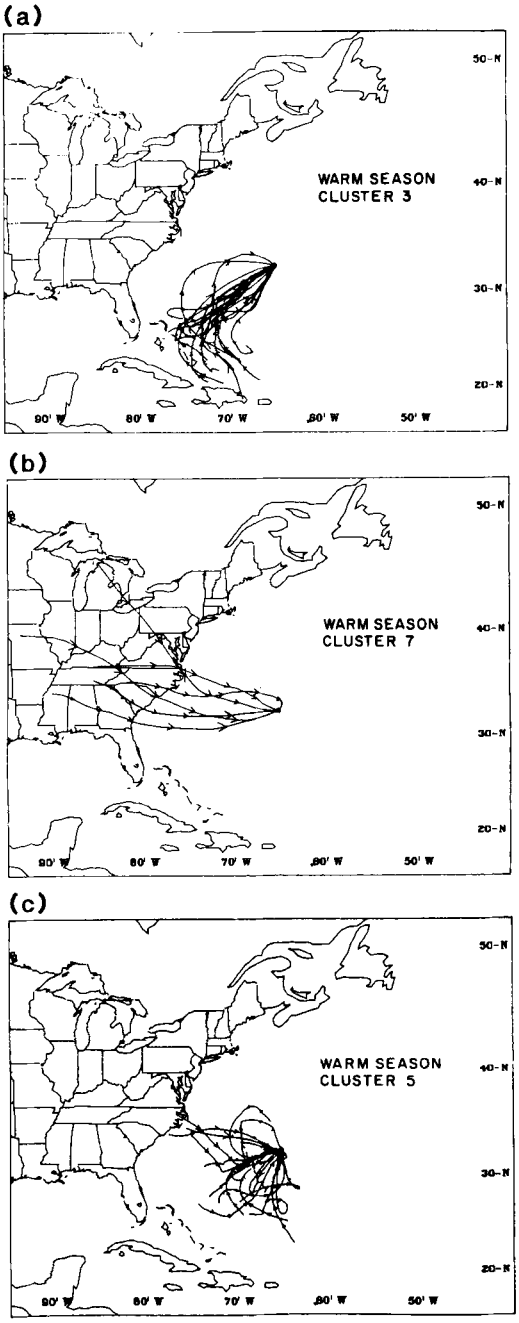

Fig. 6. (a) Trajectories classified into warm season transport cluster 3, depicting transport form the Bahamas region. (b) Trajectories classified into warm season transport cluster 7, depicting slower (relative to cool season) transport from the southeastern US. (c) Trajectories classified into warm season transport cluster 5, depicting very low speed transport with variable direction averaging southwest.

amount per event for these 6 events was 60% below the season average, and less than 2% of the water deposition occurred in this cluster. Therefore, even though NH_4^+ concentrations were relatively high in this cluster, these events only accounted for about 5% of the total NH_4^+ deposition. In contrast, events with moderate wind speeds and transport from the SSW (cluster 3) had both high relative concentration factors and occurred with large precipitation amounts.

Tables 3 and 4 summarize the amount of deposition of each of the major ions by cluster for each season. The largest fraction of cool season deposition occurred with high speed transport off the east coast of the United States, in clusters 2 and 7. Fig. 5a and b illustrate the trajectories which comprise these clusters. Together these two transport patterns account for over 40% of the seasons nss-$SO_4^=$ and H^+. Transport of moderate speed from the SE of Bermuda (cluster 6, Fig. 5c) contributed least to major ion deposition in the cool season.

The largest fraction of warm season deposition occurred with moderate speed transport out of the SSW, from the Bahamas region (cluster 3), as shown in Fig. 6a. This single transport pattern accounted for more than 40% of the warm season hydrogen ion deposition, and 36% of the nss-sulfate. Relatively high speed transport off the east coast (cluster 7), which was so important in the cool season (Fig. 6b), made a relatively small contribution to warm season ion deposition, contributing 9% of the total nss-$SO_4^=$ and H^+ and 11% of the NO_3^- and NH_4^+ deposition. Low speed transport from the SW generally describes cluster 5 (Fig. 6c). These events exhibited variability in direction, but were characterized by very low wind speeds. Events in this cluster also deposited a relatively small fraction (8–9%) of the nss-$SO_4^=$ and H^+ deposition.

Differences in relative concentration factors and % deposition by transport pattern have been shown, however, to test the significance of these differences it was necessary to look at the distributions of per event concentration and per event deposition by cluster. Fig. 7 is a plot of cumulative frequency distributions of nss-$SO_4^=$ concentrations for several cool season transport clusters. In the following analyses, only the distributions representative of concentration and deposition extremes have been plotted. Clusters not shown on these plots had concentration and deposition values which fell within the range of clusters discussed below.

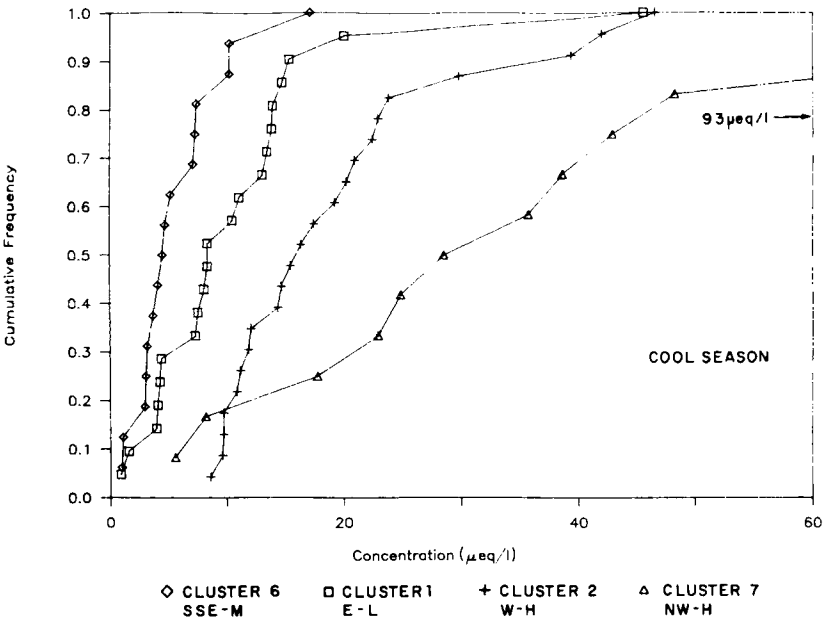

Fig. 7. Cumulative frequency distributions for nss-$SO_4^=$ concentration by cool season transport clusters 2 (mean transport from the west, high speed), 7 (northwest, high speed), 1 (east, low speed), 6 (south southeast, low speed).

Using nonparametric pairwise comparisons of distributions, cool season results indicate that per event nss-$SO_4^=$ concentrations were significantly higher with rapid transport from the NW (cluster 7) relative to transport from the W, E and SSE (clusters 1, 2 and 6). Additionally, in events with rapid transport from the W (cluster 2) nss-$SO_4^=$ was significantly more concentrated than per event concentrations from the E and SSE (clusters 1 and 6). Again, this illustrates the highest concentrations were associated with high speed flow off the US coast in the cool season.

A similar comparison was made of the distributions of per event nss-$SO_4^=$ deposition (Fig. 8). A statistical comparison of these distributions reveals that only high-speed transport from the NW (cluster 7) deposited significantly more nss-$SO_4^=$ per event.

Fig. 9 is a plot of cumulative frequency distributions for nss-$SO_4^=$ concentration by selected warm season transport clusters. Relative to the cool season (Fig. 7), all clusters had relatively high concentrations, and the variability was not as great. For example, cool season clusters had median values ranging from 5 μeq/l to 30 μeq/l. In the warm season, no cluster had a median value below 10 μeq/l or above 25 μeq/l. Again, this is evidence of a higher background of nss-$SO_4^=$ in the warm season relative to the cool season.

Within the warm season, the nss-$SO_4^=$ concentrations associated with moderate speed SSW winds (cluster 3) and relatively high speed W winds (cluster 7) were significantly greater than concentrations associated with low speed ESE and SW winds (clusters 1 and 5). Comparing deposition distributions (Fig. 10), per event nss-$SO_4^=$ deposition was significantly greater in moderate speed SSW flow (cluster 3) relative to low speed flow from the ESE and SW (clusters 1 and 5).

Fig. 11 and 12 summarize the results of the pairwise statistical comparisons of all ion distributions by transport cluster for each season. These figures are matrix representations of the concentration and deposition distribution comparisons. For example, the first element of the concentration matrix in Fig. 11 compared the ion concentration distributions associated with high speed transport from the W (cluster 2) versus the

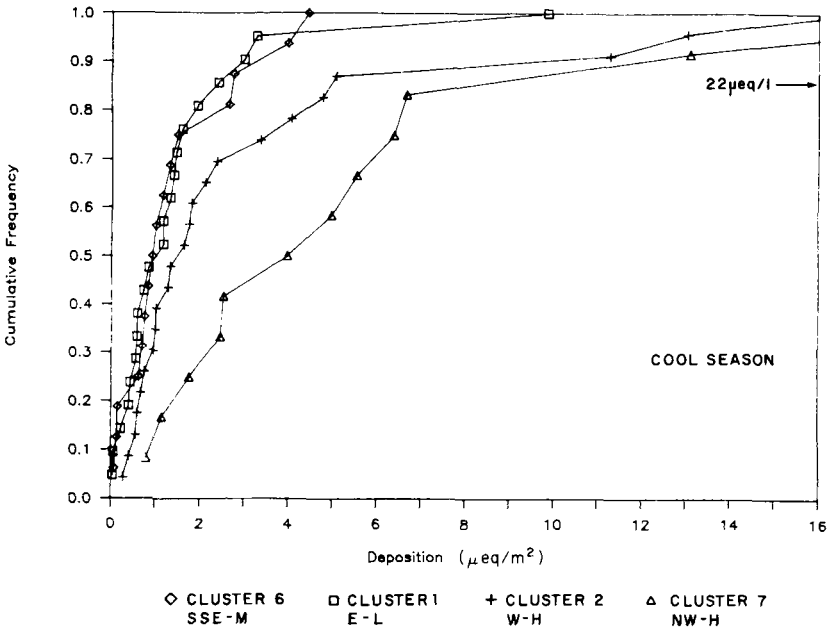

Fig. 8. Cumulative frequency distributions for nss-$SO_4^=$ deposition by cool season transport clusters 2 (mean transport from the west, high speed), 7 (northwest, high speed), 1 (east, low speed), 6 (south southeast, low speed).

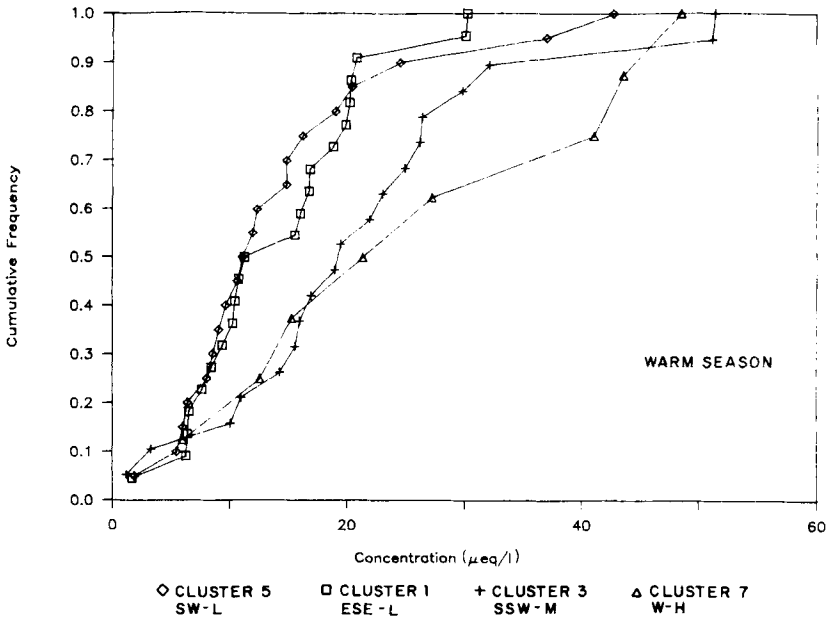

Fig. 9. Cumulative frequency distributions for nss-$SO_4^=$ concentration by warm season transport clusters 3 (mean transport from the south-southwest, moderate speed), 5 (southwest, low speed), 7 (west, high speed), 1 (east southeast, low speed).

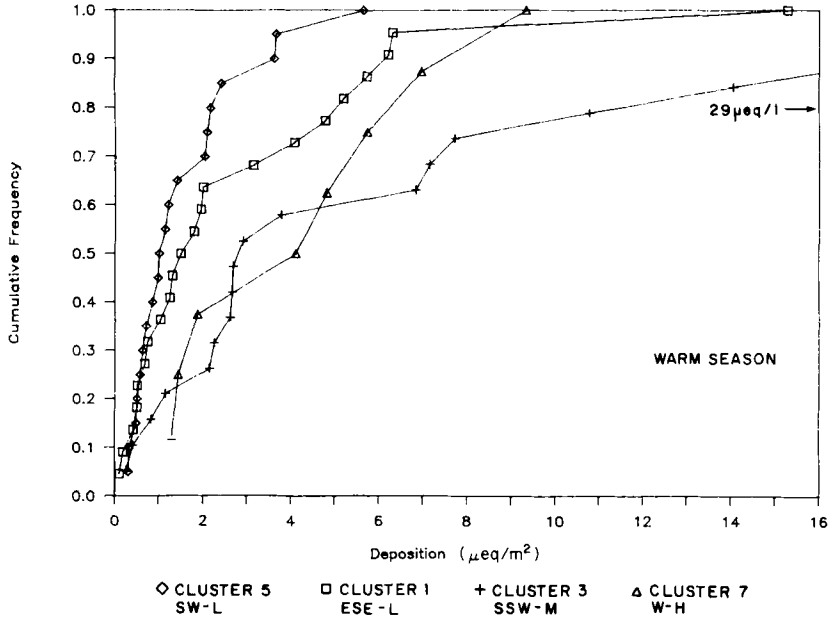

Fig. 10. Cumulative frequency distributions for nss-$SO_4^=$ deposition by warm season transport clusters 3 (mean transport from the south-southwest, moderate speed), 5 (southwest, low speed), 7 (west, high speed), 1 (east southeast, low speed).

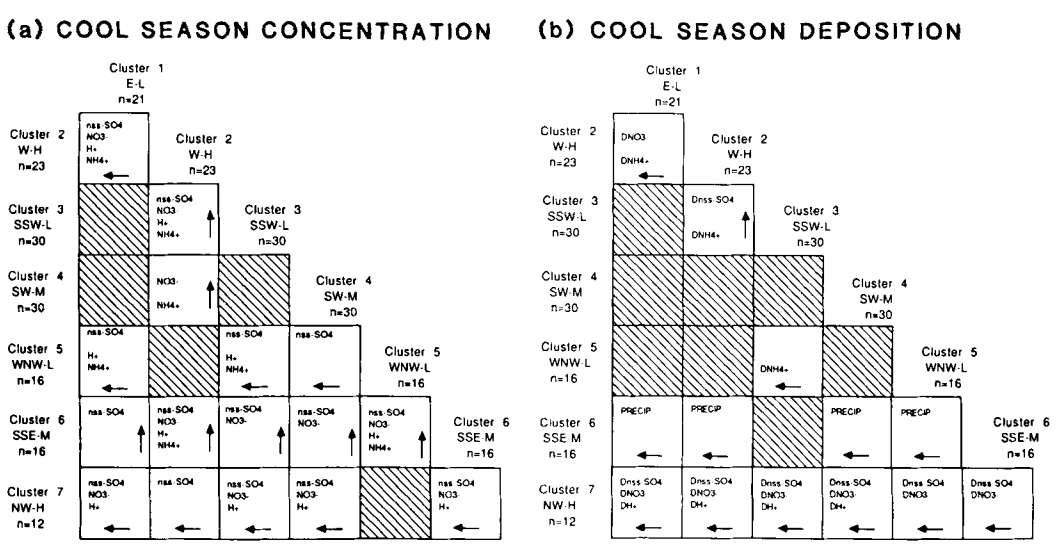

Fig. 11. Pairwise statistical comparison of (a) concentration and (b) deposition between cool season transport clusters. Species listed in each box represent those with significantly different distributions. The arrow points to the cluster with higher concentrations or deposition of these ions. Cross-hatched squares indicate no statistically significant differences were identified.

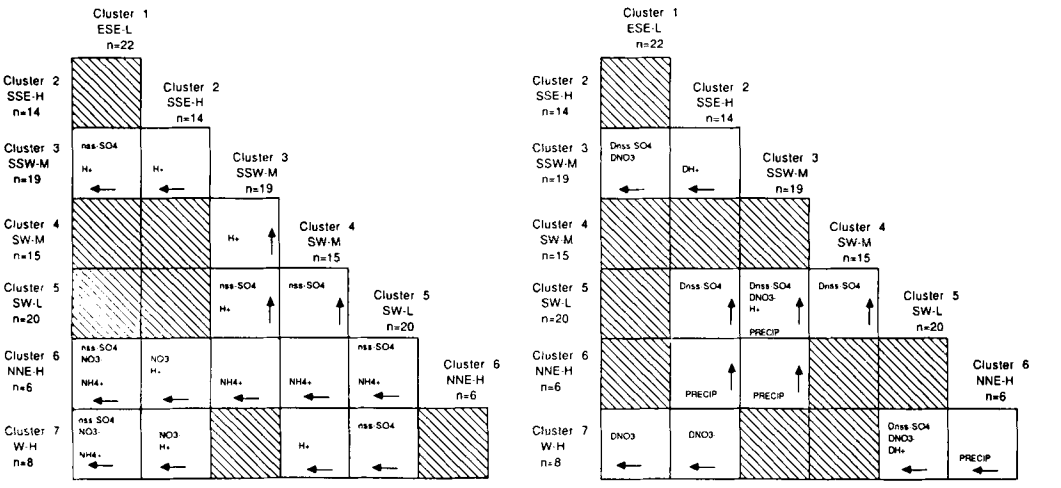

Fig. 12. Pairwise statistical comparison of (a) concentration and (b) deposition between warm season transport clusters. Species listed in each box represent those with significantly different distributions. The arrow points to the cluster with higher concentrations or deposition of these ions. Cross-hatched squares indicate no statistically significant differences were identified.

concentration distributions associated with low speed transport from the E (cluster 1). The species listed (nss-$SO_4^=$, NO_3^-, H^+ and NH_4^+) had significantly different distributions in these two transport clusters. The arrow, pointing toward cluster 2, indicates that for all of these ions, significantly higher concentrations were observed in transport from the W (cluster 2). When the same cluster comparisons of per event deposition distributions were made, only NO_3^- and NH_4^+ deposition were significantly higher with transport from the W (cluster 2).

The bottom row of the concentration matrix contains the comparison of ion distributions with high speed transport from the NW (cluster 7) with each other cluster. It indicates nss-$SO_4^=$, NO_3^-, and H^+ concentrations were significantly higher in rapid transport from the NW relative to most other flow patterns. Only low speed trajectories from the WNW showed no significant chemical concentration differences. However, when deposition distributions were compared, even these low speed WNW events (along with every other cluster) deposited significantly less nss-$SO_4^=$ and NO_3^- relative to events from the NW.

This highlights the complex relationship between concentration and deposition. There were no significant differences in the distributions of per event concentration or per event precipitation amount between cool season low speed WNW flow (cluster 5) and high speed NW flow (cluster 7), however the distributions of the product of these two (deposition) was significantly different. This information could not be obtained by simply comparing the RCF's for these clusters in Fig. 3.

In the comparison of moderate speed SSE transport (cluster 6) with other transport clusters (Figs. 11a and b), it appears that in some instances, significantly lower concentrations were influenced by higher per event precipitation amounts. These examples underscore the importance of considering distributional differences in concentration, deposition and precipitation amount when describing the chemical climatology of a site. This type of analysis provides considerably more information than can be accounted for by simply tabulating volume weighted averages.

Similar summaries of warm season concentration and deposition distributions are presented in Figs. 12a and b. Transport from the SSW out of the Bahamas (cluster 3) was significantly more concentrated in H^+ than any other cluster with a southerly wind component (clusters 1, 2, 4 and 5). However, when deposition distributions were compared only two of these clusters (2 and 5), with high speed transport from the SSE and low speed transport from the SW, deposited significantly less H^+ than transport from the Bahamas.

These events depicting transport from the SSW out of the Bahamas region (cluster 3) are interesting because there is no obvious anthropogenic source for the high H^+ and relatively high nss-$SO_4^=$ concentrations. In both seasons, there were clusters describing similar low to moderate speed transport from the SSW, they were each labeled cluster 3 (see Figs. 1 and 2). Comparing the chemistry associated with these SSW trajectories between seasons, the warm season cluster 3 events had significantly higher concentrations of nss-$SO_4^=$, H^+, NO_3^- and NH_4^+.

In each season, there were also clusters describing high speed transport from the W (cluster 2 in the cool season, cluster 7 in the warm season), and moderate speed transport from the SW (cluster 4 in both seasons). Comparing these trajectories, W versus W and SW versus SW, between seasons, there were no significant chemical differences. Therefore, chemical concentrations and depositions were not uniformly higher in the warm season for all transport situations. This suggests that a source of ions was present in the warm season SSW flow (cluster 3) which was not present during the cool season.

One possible explanation of this source is simply a regional distribution of pollution during the warm season, when anthropogenic material transported over the southern Atlantic Ocean may have a longer residence time. However, the low concentrations associated with low speed SW transport (cluster 5) do not support this explanation. Furthermore, even considering a higher regional background concentration of sulfate in the warm season, the events with SSW flow from the Bahamas were chemically enhanced in nss-$SO_4^=$ and H^+ relative to other transport clusters (see Fig. 4).

Another possible explanation for higher nss-$SO_4^=$ and H^+ concentrations associated with cluster 3 warm season events is transport at levels about 850 mb. Most of the clusters formed did not show significant wind shear between 850 and 700 mb, i.e., trajectory clusters described similar transport at both levels. This is similar to the flow climatology results of Miller and Harris (1985). In warm season transport from the SSW (cluster 3), about 50% of the events did have 700 mb trajectories with a more westerly component, arriving off the coast of Florida. However, when the events were stratified into those with westerly flow at 700 mb verus those with southerly flow at

700 mb, there were no significant chemical differences.

A third possible explanation for the relatively high concentrations of nss-$SO_4^=$ and acidity in SSW flow during the warm season is a biogenic source on sulfur. Andreae et al. (1985) found very high atmospheric concentrations of dimethyl sulfide (DMS) during two Atlantic cruises, one in the vicinity of the Bahamas and the other between the east coast of the US and Bermuda going south to 30°. DMS production is expected to be greatest during maximum phytoplankton

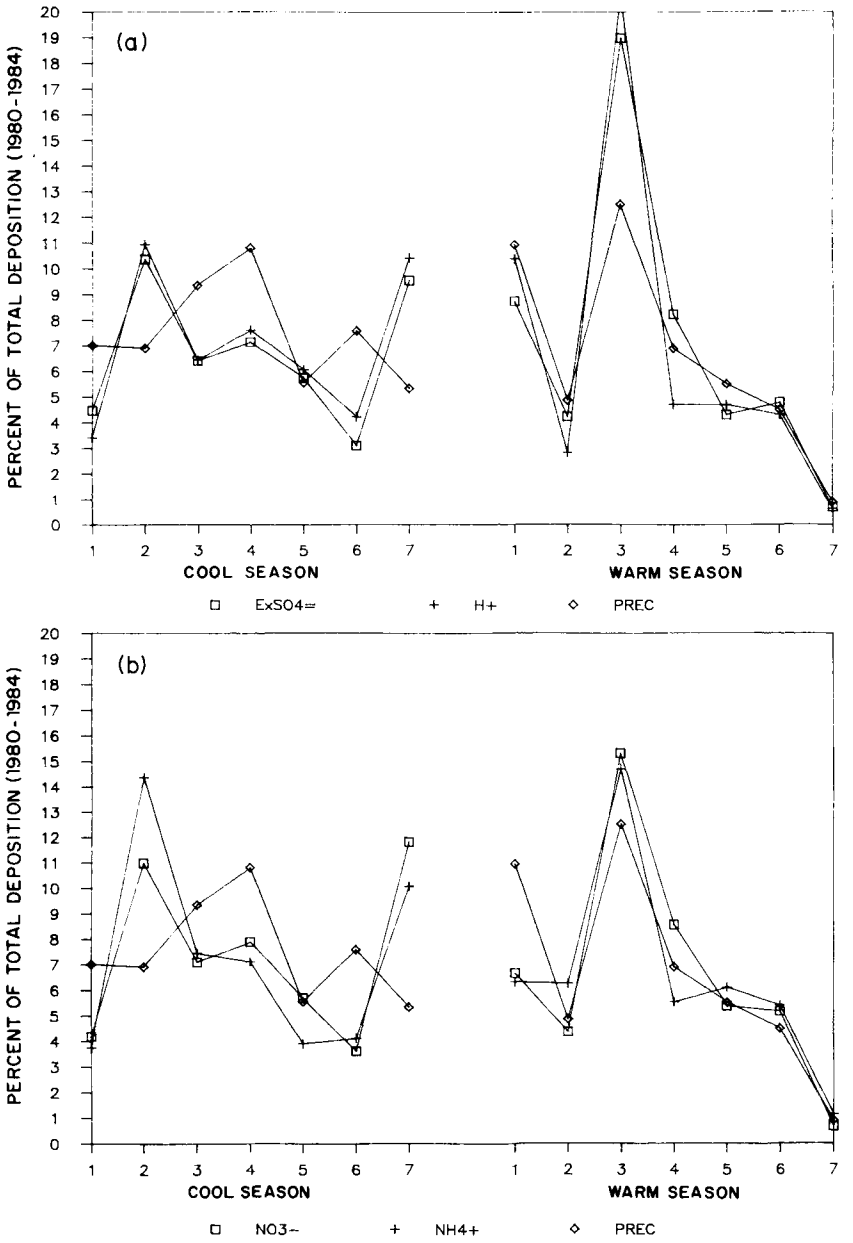

Fig. 13. (a) % of total water deposition, nss-$SO_4^=$ and H^+ deposition by cluster and season. (b) % of total water deposition, NO_3^- and NH_4^+ deposition by cluster and season.

productivity which occurs in the spring and summer. This could account for the seasonal difference in the composition of precipitation from this source region. The highest concentrations of nss-$SO_4^=$ and H^+ in warm season SSW transport occurred during the months of June, July, and August. Additionally, Andreae et al. (1985) found the emission of DMS increased with increasing low-level windspeeds. This could explain the significantly lower concentrations of nss-$SO_4^=$ and H^+ in low speed SW transport (cluster 5). These events passed over potentially productive waters, but they occurred under relatively stagnant conditions were less DMS would be transferred to the atmosphere.

Fig. 13 summarizes the ion deposition on Bermuda in both seasons. Fig. 13a illustrates the percent of total water deposition, nss-$SO_4^=$ deposition, and H^+ deposition over the five year study period which occurred in each transport cluster. Fig. 13b shows the deposition of NO_3^- and NH_4^+ by transport cluster. Note that the general pattern of ion deposition did not follow the pattern of water deposition in the cool season, where concentration had a large influence on the total deposition. However, in the warm season, there was a general correspondence between total water deposition and ion deposition. The exception was the cluster of moderate speed transport from the SSW (cluster 3) where ion deposition was enhanced by relatively high concentrations.

Over the 5-year period, high speed cool season transport from the west and northwest (clusters 2 and 7) delivered a total of 20% of the nss-$SO_4^=$ and H^+ deposition to Bermuda. These events clearly represent an anthropogenic contribution from sources in the eastern half of the United States. In the warm season, precipitation events with transport from the south southwest, out of the Bahamas region (cluster 3) accounted for an additional 20% of the acidity and nss-$SO_4^=$ deposited on Bermuda over the five year study period. The potential exists for at least a portion of this to have been derived from biogenic sources.

6. Conclusions

Significantly higher per event concentrations of NO_3^-, nss-$SO_4^=$ and per event ratios of nss-$SO_4^=/NO_3^-$ and nss-$SO_4^=/H^+$ occurred in the warm season (April–September) on Bermuda. There were no significant differences of per event precipitation amount between seasons, however, per event deposition of nss-$SO_4^=$ and NO_3^- was greater during the warm season.

Cluster analysis identified dominant flow patterns by season. Nonparametric tests of concentration, deposition and precipitation amount distributions were used to quantify chemical differences related to transport. Influenced by different source regions, the transport patterns which contributed the largest fractions of nss-$SO_4^=$ and H^+ deposition were observed to differ between seasons. During the cool season months of December through March, significantly higher concentrations of nss-$SO_4^=$ and H^+, and the greatest deposition of these ions, occurred with transport from the west and northwest, off the east coast of US, indicating an anthropogenic source.

During the warm season, relatively high concentrations and the greatest deposition of nss-$SO_4^=$ and H^+ occurred in the months of June, July, and August, with transport from the Bahamas region. This suggests a contribution from sources of biogenic sulfur emissions. Transport from this region showed considerably more seasonal variability in chemical composition than was observed in transport off the east coast of the US.

This work confirms the general results of earlier studies which indicated high concentrations of nss-$SO_4^=$ on Bermuda were associated with anthropogenic sources in the eastern US. However, this paper illustrates that this results primarily from rapidly advancing cool season storms. An equally important contribution to the total deposition of nss-$SO_4^=$ and H^+ occurred during the warm season with transport from a region with no obvious anthropogenic sources.

There was good qualitative agreement between the results of this analysis and the sector classification scheme of Galloway et al. (1989). However, the objective classification resulting from cluster analysis was more quantitative, defining transport patterns in greater detail. The multivariate capacity of clustering produced groups of trajectories which were similar over their entire length, in speed as well as direction. Differences in wind speed explained some of the warm season chemical variability. In addition,

the sector definition employed in earlier work would have split the warm season events which contributed 20% of the five year total nss-$SO_4^=$ and H^+ between two sectors. For this dataset, the cluster analysis method represents an improvement over the more subjective technique of sector classification.

This paper addressed the influence of transport on precipitation composition. In reality many other physical conditions could affect the resulting composition of precipitation, including wet and dry deposition enroute to the island of Bermuda, and the scavenging characteristics of the precipitation process. Ignoring these other factors limits the amount of chemical variability which can be explained by simply considering transport path. However, this chemical climatology illustrates that both flow patterns and precipitation composition vary seasonally, and within a season, significant differences in composition appear to be related to transport pattern. Cluster analysis has proven to be a useful way of identifying these patterns.

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8. Appendix

Relative concentration factors have been calculated from the concentration distributions of the major ions as a concise way to represent both concentration and deposition information. First two terms must be defined:

$$\frac{\sum_{i=1}^{n_k} c_i p_i}{\sum_{k=1}^{m}\sum_{i=1}^{n_k} c_i p_i}, \quad (A.1) \qquad \frac{\sum_{i=1}^{n_k} p_i}{\sum_{k=1}^{m}\sum_{i=1}^{n_k} p_i}, \quad (A.2)$$

where m is the number of clusters in a season, and n_k is the number of precipitation events in cluster k. Eq. (A.1) represents the fraction of the season total deposition for ion c which occurred in cluster k. Similarly, eq. (A.2) represents the fraction of the season total water deposition which was delivered in cluster k. Taking the ratio of these two equations we get the fraction of ion c deposition relative to the fraction of water deposition in each cluster. When the terms in this ratio are rearranged, we get the following:

$$\frac{\sum_{i=1}^{n_k} c_i p_i}{\sum_{i=1}^{n_k} p_i} \frac{\sum_{k=1}^{m}\sum_{i=1}^{n_k} p_i}{\sum_{k=1}^{m}\sum_{i=1}^{n_k} c_i p_i}, \quad (A.3)$$

The first term is the volume weighted average (VWA) of the ion c in cluster k. The second term is the VWA^{-1} of the ion c for the entire season. Therefore, the relative concentration factor (RCF) of ion c in any cluster is described by the following equation:

$$\frac{VWA(c)_{\text{cluster}}}{VWA(c)_{\text{season}}}. \quad (A.4)$$

When an RCF for ion c is greater than 1 (e.g., 1.5) the VWA for the cluster is enhanced (e.g., 50% greater) relative to the season average. Conversely, when the RCF is less than 1 (e.g., 0.7), the VWA for the cluster is depleted (e.g., 30% less) relative to the season average. Additionally, the % contribution of individual clusters to the total deposition of ion c can be easily determined by multiplying the RCF by the percentage of the seasons water deposition delivered by the cluster of interest.

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