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Local influences on the composition of precipitation on Bermuda

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ABSTRACT

The understanding of atmospheric biogeochemical cycles in marine areas depends heavily on the collection and analysis of precipitation samples. However, collection of marine precipitation is difficult due to constraints on sampling locations. For example, the island of Bermuda has been used to characterize the composition of precipitation over the western north Atlantic Ocean. However, Bermuda is a small, heavily populated island and the possibility exists that local processes can influence the composition of precipitation. Using 2 years of data on the composition of precipitation at 2 locations on Bermuda, this paper documents that enrichments of sea-salt in Bermuda precipitation, relative to open ocean precipitation, can occur due to ocean–island turbulence. Smaller enrichments of non-sea-salt (nss) Ca^{++}, nss $SO_4^=$, NH_4^+ and H^+ are also observed. At present it is not possible to determine whether the enrichments are due to island sources or spatial variability in the precipitation scavenging process. By assuming the latter effect to be negligible, the upper limits of the effect of island sources on the concentrations of the nss components (Ca^{++}, $SO_4^=$, NO_3^-, H^+) are ~5–30%, depending on the species. Precipitation associated with westerly airflow is the least affected by local sources.

1. Introduction

Precipitation to the ocean represents an important sink of atmospheric constituents and an important source for some marine constituents. By necessity, marine precipitation is collected on ships and islands. Both platforms have inherent characteristics that make it difficult to obtain a representative sample in a contamination-free manner. Ships generate products of fossil fuel combustion, sea spray, and have limited locations where precipitation can be collected without contamination. Islands can be densely populated, and can also alter the composition of the marine atmosphere due to local emissions and generation of sea-salt aerosols at the island–ocean boundary. While these factors make it difficult to collect precipitation that is representative of the marine environment, such sampling is critical to advancing our understanding of the role wet deposition plays in the marine biogeochemical cycles of both atmosphere and ocean systems.

In 1979, the Western Atlantic Ocean Experiment (WATOX) was initiated to determine the flux and fate of pollutants advected eastward from North America (Galloway et al., 1987). As part of this program, it was necessary to collect samples that were representative of marine precipitation over the western Atlantic Ocean. A previous paper presented protocols for the collection of precipitation on board ships (Galloway et al., 1983). This paper addresses the impact of Bermuda on the concentration of non-sea-salt (nss) $SO_4^=$, nss Ca^{++}, NH_4^+, NO_3^-, H^+ and Na^+ (as a sea-salt tracer) in precipitation.

Many of these species have been hypothesized to originate with long distance transport from continental regions. Hoffman et al. (1977, 1980)

postulated that nss Ca^{++} in the Bermuda atmosphere originates with long-range transport from Africa. Chen and Duce (1983), Jickells et al. (1982), Church et al. (1982), Wolff et al. (1986) and Galloway et al. (1983) suggested that North American emissions contribute significantly to the concentrations of nss $SO_4^=$, NO_3^-, H^+ and NH_4^+ in the Bermuda atmosphere and precipitation. However the islands also contribute substances to the overlying atmosphere. Sea-salt aerosol is generated at the island–ocean boundary by breaking waves and bursting bubbles. Calcareous aerosol originates with wind turbulence at the atmosphere–island boundary. SO_2 and NO_x ($NO + NO_2$) are emitted by anthropogenic activities on Bermuda (1.1×10^9 g S/yr and 1.8×10^9 g N/yr, respectively; Knap et al., 1981). NH_3 is emitted by biological processes on Bermuda. The following analysis is designed to determine if such local sources make a significant contribution to the composition of precipitation on the island.

2. Methods

2.1. Site description

Bermuda is located at 32° N, 64° W, some 1000 km east of Cape Hatteras. It is a carbonate dune field of islands with relief up to 150 m, situated on the southeast flanks of a submerged volcanic pedestal. It is about 30 km in length, 2 km in width, situated in a northeast, southwest orientation with an extensive shallow lagoon to the northwest (Fig. 1). The island is heavily populated (60,000 people) with extensive tourist activity but no major industrial activity. The main population center is the city of Hamilton (Fig. 1), where the island's main oil-fired power plant is located. St. Georges, the second largest population center is located at the east end. Cruise ships (approximately 3/week) come to both Hamilton and St. Georges from the spring through the fall. A major airport is located west of St. Georges with numerous commercial and military flights, predominately during daylight hours. Diesel buses are the main form of public transport (16,000 cars, 2000 trucks, and 30,000 motorbikes) (Knap, 1981).

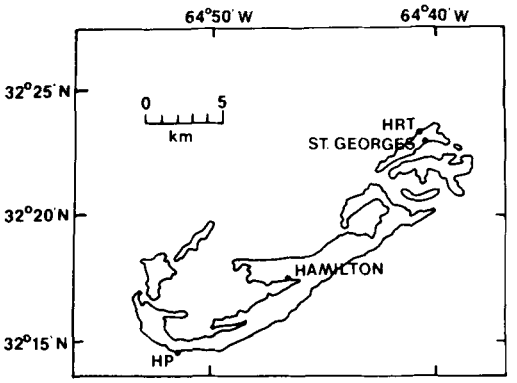

Fig. 1. The island of Bermuda showing the two sampling locations, High Point (HP) and Harbor Radio Tower (HRT).

Bermuda has some advantages and disadvantages for precipitation sampling. Advantages are a small island with little orographic effects on precipitation, some elevation above moderate reef surf conditions, relatively easy access and logistics, and a fully equipped marine and atmospheric laboratory facility at the Bermuda Biological Station. Disadvantages include substantial human and traffic activity, and a meteorology which is alternatively under easterly and westerly wind conditions during different seasons (Nemkosky, 1980).

As part of WATOX, precipitation was collected at two sites on Bermuda, Harbor Radio Tower (HRT) and High Point (HP) (Fig. 1). HP is a US Navy parcel on a 20 m sea cliff which faces due south to the ocean with about a 220° open marine sector from east-northeast through west. There is moderate surf and boating activity to seaward. HRT is on a 100 m hill 1.5 km northwest of St. Georges. It is on a rising slope over a golf course and has new condominium construction on surrounding low ground. A pilot navigation tower and cruise ship anchorage are nearby to the southeast.

2.2. Sample collection

This paper discusses precipitation collected at HRT from 1 April 1980 to 18 May 1984 using bulk (wet plus dry deposition) and wet-only (excluding dry deposition) collectors and precipitation collected at HP from 21 August 1982 to 18 May 1984 using wet-only collectors. At both locations all samples were collected on a daily basis. At HP all precipitation samples were treated with $CHCl_3$ to prevent biological uptake or transformation of chemical species. At HRT,

samples from 91% of the precipitation events were either refrigerated until analysis or were treated with $CHCl_3$.

2.3. Sample analysis

Most of the samples were analyzed at the University of Virginia, although samples collected between 14 January 1981 and 3 August 1982 were analyzed at the Bermuda Biological Station. Samples were analyzed for H^+, NH_4^+, Na^+, Mg^{++}, Ca^{++}, K^+, $SO_4^=$, NO_3^- and Cl^-. Analytical methods are described by Galloway et al. (1982). Sea-salt and nss components were differentiated using Na^+ as a reference species according to the procedure of Keene et al. (1986).

3. Data

3.1. Precipitation

The first data set analyzed included all samples that met quality control criteria (Keene et al., 1986) collected at HRT ($N = 127$) and HP ($N = 126$) between 21 August 1982 and 18 May 1984. Volume-weighted average (VWA) concentrations for each data set were compared to determine if an average significant difference existed between the composition of precipitation at the two sites (Table 1).

The second data set ($N = 66$) was a subset of the first which included only those paired samples from the two sites that fell within 12 h of each other (Table 2). In an attempt to quantify the magnitude of island effects, we analyzed this second data set as a function of surface wind direction. These data were stratified into 3 classes—(1) W: winds from the west (225° to 315°), (2) S: winds from the south (90° to 225°), and (3) N: winds from the north (315° to 90°). HP and HRT are situated such that during westerly surface winds both sites should be upwind of Bermuda and thereby impacted by only surf zone processes (Fig. 1). HRT is on the northwest coast and as such could be influenced by inland sources during periods of southerly flow and surf zone processes during northerly flow. HP is on the southern coast (Fig. 1) and would be influenced by inland sources during periods of northerly flow and surf zone processes during southerly flow (Fig. 1). For each of the three classes, the concentrations of constituents in precipitation at HP and HRT were compared (Table 3) (Figs. 2–6).

Table 1. *A comparison of the VWA composition of precipitation for all storms at HRT ($N = 127$) and HP ($N = 126$) over the period 21 August 1982 to 18 May 1984 ($\mu eq/l$)*

	HRT	HP
Total		
Cl^-	125 ± 13.6	194 ± 18
$SO_4^=$	26.2 ± 2.1	33.7 ± 2.6
Na^+	105 ± 11.6	168 ± 15.6
Mg^{++}	23.8 ± 2.6	37.2 ± 3.5
Ca^{++}	8.5 ± 0.8	11.1 ± 1.4
K^+	3.0 ± 0.3	3.5 ± 0.3
nss		
$SO_4^=$	13.6 ± 1.2	13.5 ± 1.6
NO_3^-	4.0 ± 0.4	4.1 ± 0.4
H^+	11.3 ± 1.2	11.4 ± 1.1
NH_4^+	2.9 ± 0.3	3.3 ± 0.4
Ca^{++}	4.0 ± 0.6	4.2 ± 1.0

Table 2. *A comparison of the VWA composition of precipitation for concurrent storms ($N = 66$) at HRT and HP over the period 21 August 1982 to 18 May 1984 ($\mu eq/l$)*

	HRT	HP
Na^+	101 ± 14	169 ± 20
nss $SO_4^=$	11.8 ± 1.3	10.4 ± 1.1
NO_3^-	3.6 ± 0.4	3.1 ± 0.4
H^+	10.5 ± 1.5	9.0 ± 0.7
NH_4^+	2.6 ± 0.3	2.8 ± 0.4
nss Ca^{++}	3.5 ± 0.6	3.7 ± 1.2

The last data set ($N = 62$) comprises all precipitation events sampled simultaneously at HRT with bulk and wet-only collectors. The nss Ca^{++} and H^+ data from the precipitation sampled in bulk collectors were compared to the corresponding data from wet-only collectors to determine if the nss Ca^{++} resulted in a neutralization of acidity.

3.2. Wind direction

Data on surface winds used in the analysis of the 66 events that occurred concurrently (within 12 h) at HP and HRT are from site operator readings and from the records of the Harbor Radio Tower office, respectively. Of these events, 56% were associated with southerly flow, 24%

Table 3. *A comparison of the VWA composition of precipitation at HP and HRT as a function of surface wind direction (μeq/l)*

	Na^+	nss $SO_4^=$	NO_3^-	H^+	NH_4^+	nss Ca^{++}
Westerly winds; neither HP or HRT downwind of Bermuda ($N = 13$)						
HRT	72.9 ± 17.4	13.0 ± 2.8	3.7 ± 0.9	12.0 ± 2.0	3.3 ± 0.4	2.7 ± 1.1
HP	150 ± 46	14.3 ± 3.0	4.4 ± 1.0	14.7 ± 2.6	3.3 ± 0.5	1.8 ± 0.7
Northerly winds; HP downwind of Bermuda ($N = 16$)						
HRT	112 ± 32	9.2 ± 1.6	3.0 ± 0.6	8.1 ± 1.0	2.3 ± 0.3	2.7 ± 1.0
HP	101 ± 42	11.4 ± 2.4	2.2 ± 0.5	10.5 ± 1.9	2.0 ± 0.3	0.8 ± 0.2
Southerly winds; HRT downwind of Bermuda ($N = 37$)						
HRT	103 ± 19	12.5 ± 1.9	3.8 ± 0.6	11.1 ± 2.4	2.5 ± 0.4	4.0 ± 0.9
HP	206 ± 22	9.0 ± 1.6	3.3 ± 0.5	6.9 ± 0.7	3.0 ± 0.6	5.6 ± 2.1

with northerly flow and 20% with westerly flow. Surface wind climatology over a 22 year period shows that southerly, northerly and westerly flows were 49, 34 and 14%, respectively (Macky, 1956).

3.3. Data analysis

We used three data analysis techniques to determine the effect of Bermuda on precipitation composition. First, a comparison of the average composition of precipitation at the four sites was performed by the calculation of the standard deviations for the VWA concentrations (Hawley, 1985) at HP and HRT (Tables 2, 3). We assume that if the standard deviations of two VWM concentrations overlap, that the means are not significantly different. Second, we used scatter plots of the concentrations at HP and HRT as a function of surface wind direction (Figs. 2–5). We did not use linear regression analysis because of the small data set and the unrepresentative influence of outliers on the regression statistics. Third, we assumed that the differences between the higher concentration and the lower concentration of a given constituent in precipitation samples from the same storm collected at HP and HRT corresponded to the influence of Bermuda sources. Therefore, to calculate the VWA composition of precipitation on Bermuda that was not influenced by such sources (the "marine background"), we used the lowest value of the two (HP versus HRT), and then calculated a new VWA concentration and standard deviation with the usual method (Hawley, 1985). This estimate of the marine background was then compared to the observed VWA concentrations from HP and HRT to estimate the influence of island sources on precipitation composition.

Our estimate of the "marine background" is exactly that—an estimate. Our estimate of the marine background can be too large if there is an impact of Bermuda sources on the lowest concentration (this would overestimate the "marine background") and/or if there are spatial differences in the composition of precipitation that are unrelated to Bermuda sources (e.g., difference in precipitation scavenging rates) then an estimate of the marine background can be too small.

4. Results and discussion

4.1. Comparison of average precipitation composition at HRT and HP

The VWA composition of precipitation at HP is identical, within statistical uncertainty, to that at HRT for nss Ca^{++}, nss $SO_4^=$, NO_3^-, NH_4^+ and H^+ but significantly greater at HP than at HRT for the total (sea-salt plus non-sea-salt) components due to the higher concentrations of sea-salt species at HP. This is true for the data set that encompasses the entire 2-year collection period (Table 1) and the data set that includes only those storms where precipitation was collected at HP and HRT within the same 12-h period (Table 2). As previously mentioned, HP is located on a cliff nearer the surf zone than is HRT and thus is more influenced by sea-salt generated by surf and wind turbulence. The larger sea-salt component in precipitation at HP is confirmed by taking the difference between ion

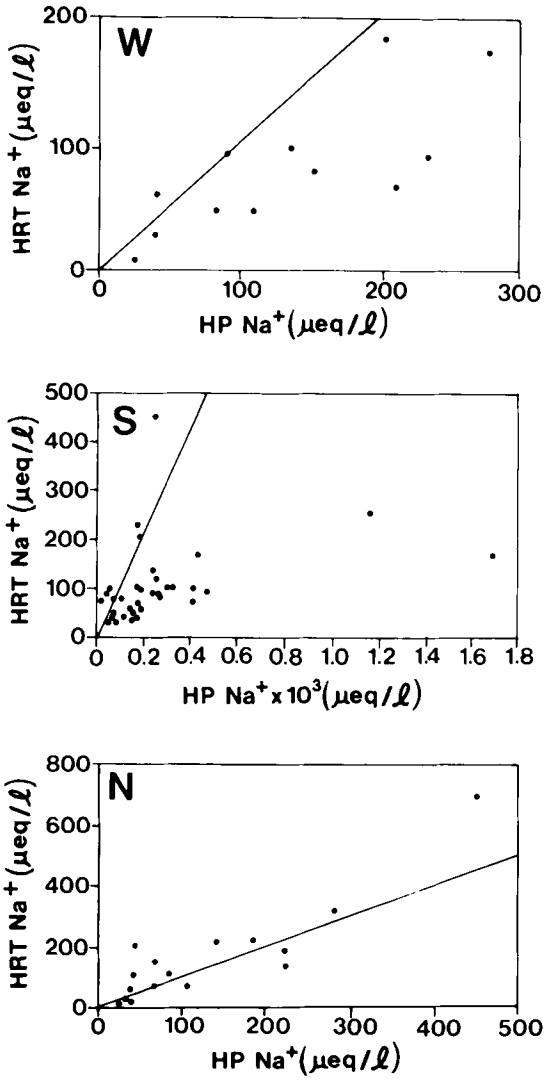

Fig. 2. The concentration of Na^+ (μeq/l) in precipitation collected at High Point (HP) versus Harbor Radio Tower (HRT) as a function of surface winds. W: westerly winds; S: southerly winds; N: northerly winds. For graphical reasons, one pair of Na^+ data was not plotted on these graphs because of very high (>2000 μeq/l) concentrations at HP. The 1:1 line is shown.

concentrations at the two sites, and comparing their ratios to that of bulk seawater. As examples, the ratios of Na^+/Cl^- and Mg^{++}/Cl^- in bulk seawater on a μeq l^{-1} basis are 0.87 and 0.20, respectively. The additional salts at HP yield ratios of 0.91 and 0.19, respectively.

For the nss components, the similarity of the VWA composition between the two sites over each of the two time periods indicates that both sites provide the same information on the average composition of the nss components of precipitation on Bermuda. However, this analysis

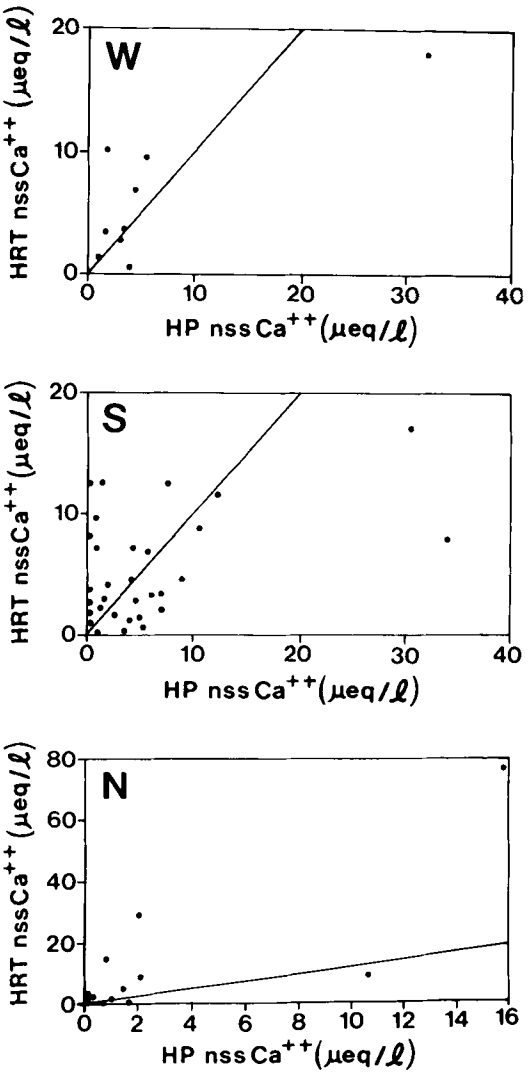

Fig. 3. The concentration of nss Ca^{++} (μeq/l) in precipitation collected at High Point (HP) versus Harbor Radio Tower (HRT) as a function of surface winds. W, S and N designations are as in Fig. 2. For graphical reasons, one pair of Ca^{++} data was not plotted on these graphs because of very high (<190 μeq/l) concentrations at HP. The 1:1 line is shown.

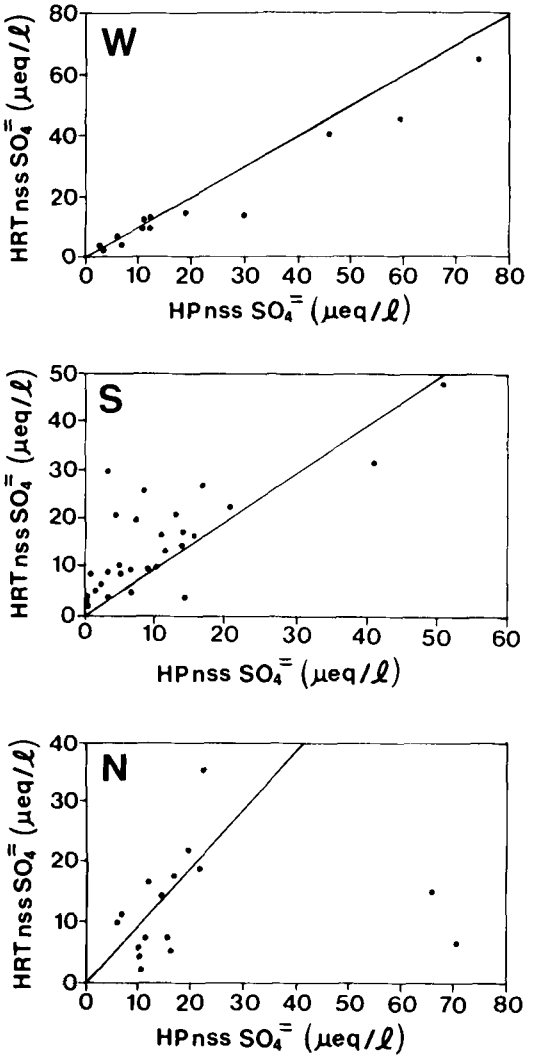

Fig. 4. The concentration of nss $SO_4^=$ (μeq/l) in precipitation collected at High Point (HP) versus Harbor Radio Tower (HRT) as a function of surface winds. W, S and N designations are as in Fig. 2. The 1:1 line is shown.

cannot determine whether, on average, there is either no effect or an equal effect of Bermuda on the concentration of nss components in precipitation.

4.2. *Impact of Bermuda on precipitation: Na^+, nss Ca^{++}, nss $SO_4^=$, NO_3^-, and NH_4^+*

To address the possibility that the precipitation at both sites is impacted by local sources on Bermuda, we use the data that are stratified by wind direction (Table 3; Figs. 2–6).

In the case of Na^+, the VWA concentrations (Table 3) and the plots (Figs. 2W and 2S) illustrate the large enrichment of sea-salt in the HP samples relative to HRT when winds are southerly and westerly and HP is downwind of the ocean and the surf zone (Figs. 2S and 2W). Sea-salt is generally not enriched in HP precipi-

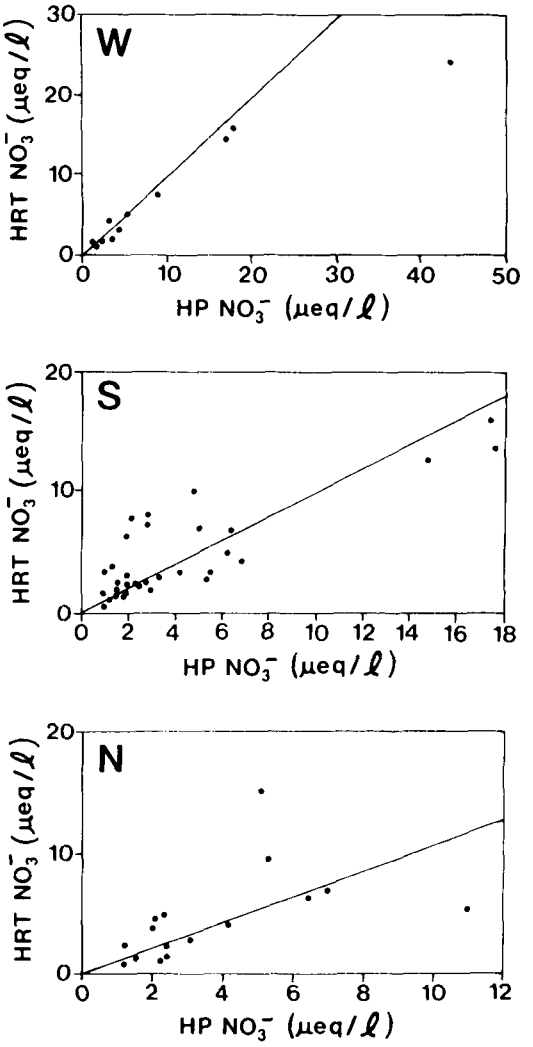

Fig. 5. The concentration of NO_3^- (μeq/l) in precipitation collected at High Point (HP) versus Harbor Radio Tower (HRT) as a function of surface winds. W, S and N designations are as in Fig. 2. The 1:1 line is shown.

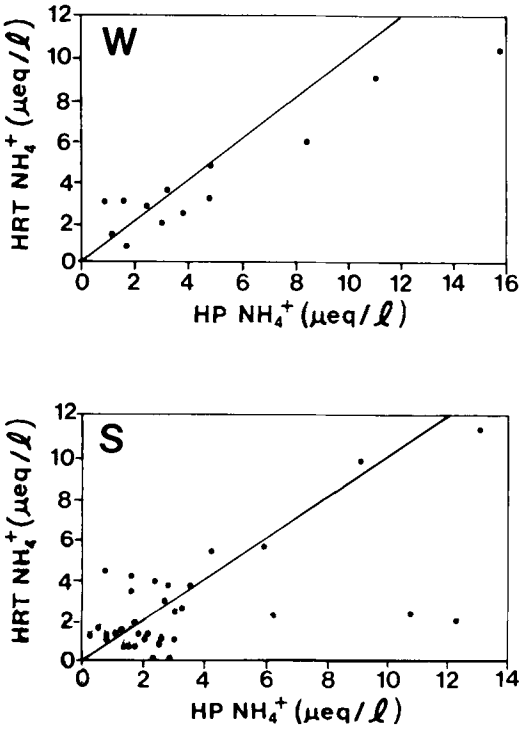

Fig. 6. The concentration of NH_4^+ (μeq/l) in precipitation collected at High Point (HP) versus Harbor Radio Tower (HRT) as a function of surface winds. W, S and N designations are as in Fig. 2. The 1:1 line is shown.

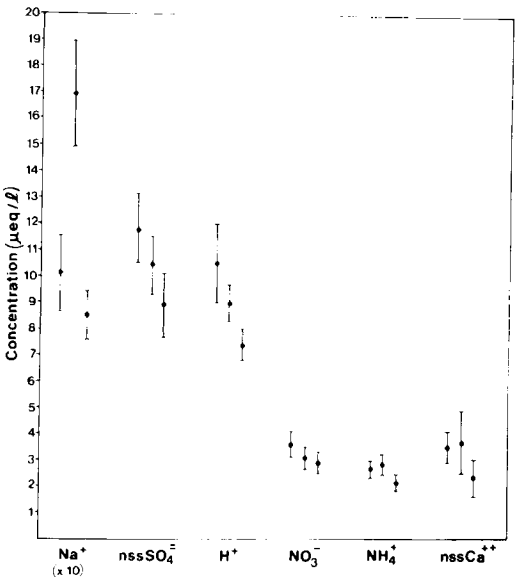

Fig. 7. The volume weighted composition (μeq/l) of precipitation from samples collected at HRT, HP and from a data set composed of minimum values of paired samples collected at HP and HRT within 12 h of each other.

tation relative to HRT when HP is downwind of the island (Fig. 2N). Under northerly winds, the small difference between Na^+ concentrations at HRT and HP are presumably because HRT is further removed from the surf zone than is HP. Our estimated value of the "marine background" concentration of Na^+ is about half of that at HP and close to the value at HRT (Fig. 7). Thus, precipitation collected at HP is less representative of the sea-salt composition of marine precipitation. In addition, due to an increase in the error of calculation of nss components with increasing sea-salt concentrations, there will be a greater uncertainty in the nss concentrations in precipitation collected at HP relative to HRT.

It appears that Bermuda does contribute nss Ca^{++} to precipitation collected on the island (the concentrations are different at the two sites), but that it does so in a complex fashion (Table 3; Fig. 3). There is substantial variability of nss Ca^{++} at HP and HRT as a function of wind direction and thus the enrichment of nss Ca^{++} at HP or HRT appears to be a function of local activities as well as wind direction. HRT is located on a carbonate hill and has, over the collection period, been the site of construction activities. The enrichments of nss Ca^{++} at HP, relative to HRT, during periods of southerly flow could be the result of local wind turbulence generating calcareous dust at the base of the cliff where the collection site is located. In addition to these local sources, other possible sources are long distance transport from Africa (Hoffman et al., 1977; Hoffman et al., 1980) and North America (Chen and Duce, 1983). Based on

our estimate of the "marine background" it appears that on the average, Bermuda sources account for about one-third of the nss Ca^{++} in Bermuda precipitation, with HRT slightly more influenced than HP (Fig. 7).

For nss Ca^{++} and sea-salt species, precipitation has been impacted by large particles injected into the atmosphere by turbulence at the island edge and surface. However, for nss $SO_4^=$, NO_3^-, and NH_4^+, there are other local processes that could affect the composition of Bermuda precipitation. Specifically, fossil fuel combustion can produce SO_2 and NO_x, while agricultural and natural biological activities can result in the emission of NH_3 to the atmosphere.

In the case of nss $SO_4^=$, when the surface winds are westerly, there appears to be only a slight, bias towards higher concentrations at HP (Fig. 4W). Under southerly surface winds, the data exhibit a large amount of variability and the concentrations at HRT (site downwind of Bermuda) are generally higher than at HP (Fig. 4S). When the surface winds are northerly (HP downwind of the island) there is again scatter to the data and there appears to be an episodic nature to the impact of Bermuda activities on the amount of nss $SO_4^=$ in precipitation (Fig. 4N). The local source of the nss $SO_4^=$ in Bermuda precipitation originates primarily with SO_2 emissions from the Bermuda Electric Company (Knap, 1981). Using our estimate of the marine background, on the average the local contributions of nss $SO_4^=$ to precipitation at HRT and HP are about 30% and 10% of the VWA concentrations, respectively (Fig. 7). As we will discuss later, these are maximum effects due to other sources of spatial variability in precipitation composition on Bermuda.

For NO_3^-, under the influence of westerly winds, the concentrations in precipitation collected at HP are similar to those at HRT, suggesting that under such conditions Bermuda has little effect on these sites (Fig. 5W). When the surface winds are from the south and the north, the data are more variable and thus show no clear enrichment at either site relative to the other (Figs. 5S, 5N and Table 3). In these circumstances, there may be some local influence (vehicles, airport) of Bermuda on the NO_3^- concentrations in precipitation collected at HRT and HP. The local source of NO_3^- in Bermuda precipitation is not only the result of NO_x emissions from the Bermuda Electric Company but also an additional large source of NO_x from combustion of gasoline in vehicles (Knap, 1981). The VWA concentration of NO_3^- at HRT and HP are a maximum of 25% and 8% higher than the "marine background" respectively, due to local sources (Fig. 7).

In the case of NH_4^+, when the winds are westerly, there appears to be a slight bias towards higher concentrations at HP (Fig. 6W). When the winds are southerly, the data exhibit a large amount of variability with occasional higher concentrations at HP and HRT (Fig. 6S). When the winds are northerly, the downwind site, HP, can have higher concentrations although a large number of storms have very similar concentrations at HP and HRT (Fig. 6N). For all three surface wind classes, these slight differences disappear when the VWA concentrations and their standard deviations are examined. Thus if the differences between the sites exist, they are slight indeed. Relative to our estimate of the "marine background", NH_4^+ concentrations in precipitation at HP and HRT are about 25% higher due to Bermuda sources (Fig. 7).

4.3. Impact of Bermuda on precipitation acidity

It is likely that if there are increased concentrations of nss $SO_4^=$, NH_4^+, NO_3^- and nss Ca^{++} due to local sources, there will be an effect on the acidity of Bermuda precipitation. Presumably, nss $SO_4^=$ and NO_3^- originated primarily from SO_2 and NO_x, given the absence of other major Bermuda sources. Thus, increased concentrations should result in increased acidity. Conversely, if the nss Ca^{++} and NH_4^+ in precipitation from Bermuda sources were from $CaCO_3$ and NH_3, a decrease in the acidity of precipitation should result. To estimate the impact of Bermuda sources on the acidity of precipitation, we use our calculated value of the marine background. It appears that on the average, precipitation on Bermuda has a maximum of about 2–3 μeq/l more H^+ due to local sources (Fig. 7).

This calculation assumes that nss Ca^{++} from Bermuda is present as $CaCO_3$. This hypothesis can be tested by examining the relationship between the concentrations of nss Ca^{++} and H^+ in precipitation sampled in the bulk versus the wet-only collectors. If Ca^{++} is deposited from the

atmosphere as $CaCO_3$, then the sample in the bulk collector should have higher concentrations of nss Ca^{++} and equivalent lower concentrations of H^+ due to neutralization, relative to the samples from the wet collectors. To determine if there was an equivalent relationship between the Ca^{++} and the H^+ differences between the samples from the wet and bulk collectors, a plot of $[(Ca^{++})_{bulk} - (Ca^{++})_{wet}]$ versus $[(H^+)_{wet} - (H^+)_{bulk}]$ was constructed. The plot shows that with the exception of a few outliers, $CaCO_3$ results in the neutralization of H^+ in bulk collectors and (presumably) in wet collectors (Fig. 8).

Based on these analyses, there does appear to be an impact of Bermuda on the concentrations of sea-salt, nss $SO_4^=$, nss Ca^{++}, NO_3^-, H^+ and NH_4^+ in precipitation. The effect is at times related to wind direction but at other times appears to be controlled by other factors. The magnitude of the maximum effect varies from ~5–30% of the VWA concentration, depending on the species.

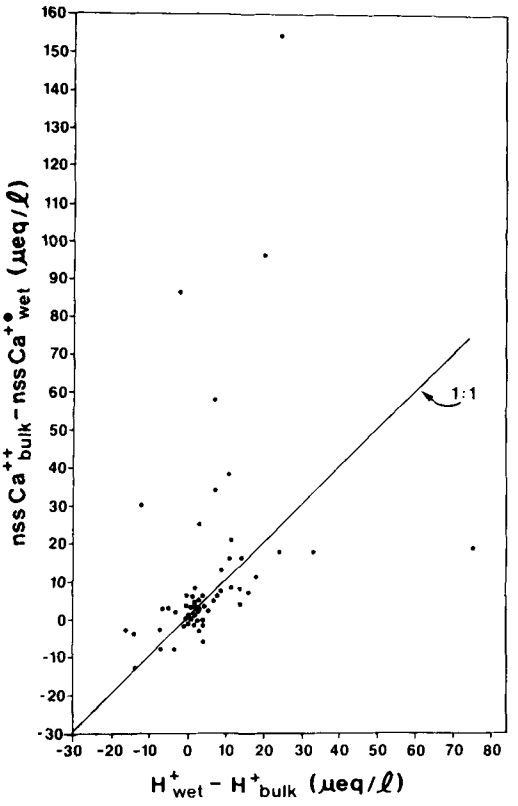

Fig. 8. The relationship between [nss $Ca^{++}_{(bulk)}$ – nss $Ca^{++}_{(wet)}$] and [$H^+_{(wet)} - H^+_{(bulk)}$]. The units are μeq/l; the line is the 1:1 relationship.

However, three lines of reasoning suggest that these calculations may overestimate the impact of Bermuda sources on concentration of nss components of Bermuda precipitation. First, there is substantial variation about the VWA concentrations shown in Fig. 7 and Table 2. Second, for the analyses presented in Fig. 7 it was assumed that all differences in the composition of concurrent storms collected at HP and HRT resulted from local sources. This assumption ignores the fact that the spatial variability of the composition of individual storms can be large due to spatial differences in the precipitation scavenging processes. Past research has shown that spatial variability over scales of 10–20 km is of the same magnitude (5–30%) as found in this study (Galloway and Likens, 1978; Slanina et al., 1979). Thus most of the variability between HP and HRT could be due to differences in precipitation scavenging and not to local sources.

The third factor relates to analytical uncertainties. Replicate analyses of a given constituent are normally distributed around a sample mean. In the absence of any island effects, such analytical uncertainties would still contribute to real variability between sets of paired observations at the two sites. If it is assumed that the absolute differences between each pair of observations originates only with island sources, then the influence of such sources will, on average, be overestimated. The magnitude of this bias would be a function of the analytical uncertainties for each species of interest. This type of error is greatest for nss constituents because of the proportionately greater uncertainties relative to data from which they are calculated (Keene et al., 1986). Given these points, while we estimate that the maximum impact of Bermuda on the concentrations of nss $SO_4^=$, NO_3^-, NH_4^+, H^+ and nss Ca^{++} is 5–30%, depending on the species, the actual value is probably much less.

This impact of Bermuda on the average composition of precipitation raises the question of how this affects past publications that have used precipitation collected on Bermuda to estimate the impact of North America on the precipitation over the western Atlantic Ocean. There have been several publications that have suggested

that when the composition of Bermuda precipitation is stratified by air mass trajectory, that the higher concentrations of nss $SO_4^=$, NO_3^-, and H^+ associated with air flow from North America are due to long-range transport of North American material, primarily anthropogenic (e.g., Jickells et al., 1982; Galloway et al., 1983). We do not believe that the results reported in this paper affect these past conclusions because the possible impact of Bermuda on precipitation composition is primarily evident when surface winds are from the north or south. When they are westerly, the impact of Bermuda is substantially reduced (Figs. 2–6).

5. Conclusions

This analysis of data for the chemistry of Bermuda precipitation has shown that the island appears to influence precipitation composition in three ways. First, breaking waves along the island's perimeter increases the sea-salt component of precipitation. The increase in sea-salt is the most obvious local input on the composition of Bermuda precipitation. Second, the island contributes nss Ca^{++} to precipitation, probably as $CaCO_3$, which results in neutralization of precipitation acidity. Third, the island may be a small source of nss $SO_4^=$, NO_3^-, and NH_4^+ in precipitation. We estimate that the maximum increase in precipitation composition of Bermuda due to local sources is 5–30%. The actual value is probably substantially lower due to other causes of the observed spatial variability in precipitation composition (e.g., variation in precipitation scavenging processes).

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REFERENCES

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*, 11,013–11,018.

Galloway, J. N. and Likens, G. E. 1978. The collection of precipitation for chemical analysis. *Tellus 30*, 71–82.

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*, 10,859–10,864.

Galloway, J. N., Church, T. M., Knap, A. H. and Whelpdale, D. M. 1987. The Western Atlantic Ocean Experiment. In: *Chemistry of acid rain* (eds. R. W. Johnson and G. E. Gordon). Amer. Chem. Soc. Special Symposium, Vol. No. 349.

Hawley, M. E. 1985. Comparison of volume-weighted mean concentrations in precipitation chemistry. *Proceedings*, 9th Conference on Probability and Statistics in the Atmospheric Sciences, American Meteorology Society, Boston.

Hoffman, E. J., Fletcher, I. S. and Duce, R. A. 1977. Further consideration of alkali and alkaline earth geochemistry of marine aerosols: Results of a study of marine aerosols collected on Bermuda. *Atmos. Environ. 11*, 373–377.

Hoffman, E. J., Hoffman, G. L. and Duce, R. A. 1980. Particle size dependence of alkali and alkaline earth metal enrichment in marine aerosols from Bermuda. *J. Geophys. Res. 85*, 5499–5502.

Jickells, T. D., Knap, A. H., Church, T. M., Galloway, J. N. and Miller, J. M. 1982. Acid rain on Bermuda. *Nature 297*, 55–57.

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

Knap, A. H. 1981. Pollution. In *Bermudas delicate balance*, Ch. 22 (eds. Hayward, Gomez and Sterrer). Bermuda National Trust, Hamilton, Bermuda, 239–255.

Macky, W. A. 1956. The surface wind in Bermuda. Bermuda Meteorological Office. Technical Note No. 7, 31 pp.

Nemkosky, M. J., Jr. 1980. Local area forecasters handbook. 42, Naval Oceanographic Command Detachments, Bermuda.

Slanina, J., Van Raaphorst, J. G., Zijp, W. L., Vermentenard, A. T. and Roet, C. A. 1979. An evaluation of the chemical composition of precipitation sampled with 21 identified collectors on a limited area. *Int. J. Environ. Anal. Chem. 6*, 67–81.

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.