MEASUREMENTS OF SOₓ, NOₓ AND AEROSOL SPECIES ON BERMUDA

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Abstract—During August 1982 and January and February 1983, General Motors Research Laboratories operated an air monitoring site on the southwest coast of Bermuda. The data show that the levels of the NO_x and SO_x species reaching Bermuda are determined by the direction of the air flow. The highest levels of sulfate (mean = $4.0 \mu g\, m^{-3}$), nitric acid (126 ppt) and other species are observed when air masses arrive from the northeastern United States while the lowest levels (sulfate = $1.1 \mu g\, m^{-3}$; nitric acid = 41 ppt) occur during air flow from the SE direction. With westerly air flow, increases in many anthropogenic constituents such as particulate sulfate, lead, elemental carbon, sulfur dioxide, nitrogen dioxide, nitric acid and ozone are observed. These species are generally the lowest during SE winds which bring high concentrations of soil- and crustal-related aerosol species. The source of this crustal material appears to be the Sahara Desert. On the average, the levels of anthropogenic constituents are higher in winter because of frequent intrusions of N American air masses. Conversely, the levels of crustal materials are higher in summer when the SE flow is more prevalent.

Key word index: Aerosols, Bermuda, carbonaceous aerosols, crustal aerosols, fine particles, long-range transport, nitrogen oxides, sulfur oxides, trace metals.

1. INTRODUCTION

To understand the fate of anthropogenic air pollutants, the atmospheric life cycles or budgets of the various species must be known. This includes understanding the pollutant sources, sinks, transport characteristics, and chemical transformations. Two of the more extensively studied budgets are the SO_x and NO_x budgets for eastern N. America (Galloway and Whelpdale, 1980; Galloway *et al.*, 1984; Logan, 1983). Even these budgets, however, have large uncertainties associated with various terms and they either ignore or inadequately deal with atmospheric transformations. One reason for these uncertainties is the lack of data on the concentrations of key species in certain geographical areas. To obtain some of these data, General Motors Research Laboratories (GMRL) participated in an intensive experiment which was part of the Western Atlantic Ocean Experiment (WATOX). During August 1982 and January–February 1983, GMRL operated sites near the Atlantic Coast in Lewes, DE (Wolff *et al.*, 1986), and on the island of Bermuda. The Lewes site served to obtain data on air masses leaving the eastern United States while the Bermuda site served as a downwind receptor site. The

role of GMRL in the intensive experiment was to collect data on the concentrations of ground-level aerosol and trace gaseous species. Other WATOX participants collected data on precipitation chemistry and certain airborne species aloft.

In this paper we present a unique set of concurrent aerosol and gas measurements made in Bermuda. These measurements were made during 1–31 August, 1982 and 25 January–28 February, 1983. Topics which will be discussed include the sources of these species, the transport of these species from N America and their seasonal behavior. When possible, comparisons will be made with measurements made by others on Bermuda and over the adjacent N Atlantic waters. The pollutant species which were measured and will be discussed include sulfate, nitrate, ammonium, particulate carbon, Si, Cl, K, Ca Ti, V, Mn, Fe, Cu, Zn, Se, Pb, Br and Na, and gaseous species including O_3, SO_2, NO_x and HNO_3.

2. EXPERIMENTAL

2.1. Site description

The sampling site was located on the southwest coast of Bermuda in Southampton Parish at 32°14′52″ N and 64° 51′ 58″ W (see Fig. 1). A trailer, which housed the NO_x and O_3 analyzers as well as the recorders and electronics for the meteorological equipment, was situated on a bluff 30 m above MSL. The site was 25 m inland from the site of the tower used

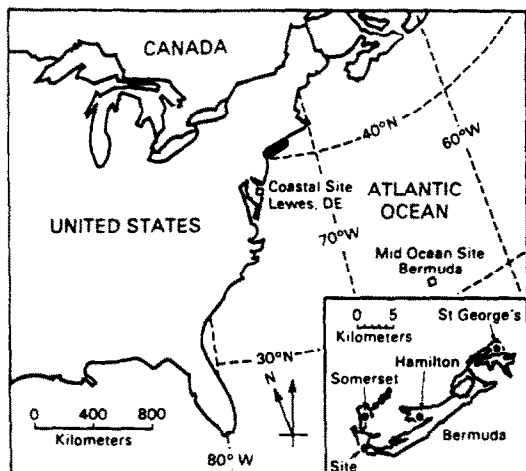*Current Affiliation: Dept. of Chemistry, University of Colorado-Denver, Denver, Colorado, U.S.A.

Fig. 1. Location of Bermuda sampling site.

by Hoffman and Duce (1974) in 1973–74. The sampling tube inlet for the NO_x and O_3 analyzers was located about 7 m above the ground. About 20 m to the N, a second bluff rose sharply to a height of about 5 m above the first bluff. The particulate samplers were located on the second bluff.

2.2. Sampling and analyses

Three types of data were obtained at the Bermuda site: aerosol, gaseous, and meteorological. All filter samples were 24 h samples starting at 0900 h local time. Continuous measurements of some gases and meteorological variables were reduced to hourly averages and then 24-h averages were computed beginning at 0900 h.

Two Sierra manual dichotomous samplers were used to obtain most of the particulate data. Particles from 2.5 to 10 μm were collected on the coarse stage, while on the fine stage, particles < 2.5 μm were collected. Teflon membrane filters (Ghia Tefweb ® Teflo ® 1.0 μm pore size) were used on one dichotomous sampler (Sampler A) while Gelman Microquartz filters (Sampler B) were used on the other. The Teflon filters were assayed for aerosol mass, SO_4^{2-}, NO_3^- and trace elements. The mass was determined gravimetrically while the SO_4^{2-} and NO_3^- were determined by ion chromatography. Data on the following elements were determined by X-ray fluorescence (XRF): Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br and Pb. Data for Al are not reported because of a contamination problem. Other elements usually determined by XRF were at or below the lower detection limit 50% or more of the time. The Microquartz filters were assayed for organic (OC) and elemental (EC) carbon using a combustion method (Cadle et al., 1983).

Three other low volume filter samplers designed and built at GMRL were also employed. The first (Sampler C) used a triple stack of 47-mm filters. The top filter was a Ghia Teflon and its purpose was to remove particles. The second stage contained a nylon filter which was analyzed for HNO_3 using ion chromatography. The third stage contained 2 Schleicher and Schuell-2W cellulose filters impregnated with a K_2CO_3–glycerol solution (Daum et al., 1982). According to our field tests, the double filter removed SO_2 with an efficiency of 90%. The sorbed SO_2 was oxidized on the filter to SO_4^{2-} and determined by ion chromatography.

A second low volume sampler (Sampler D) was operated with Teflon and nylon filters preceded by a bank of Na_2CO_3 impregnated denuder tubes. The purpose of the denuder system was to remove HNO_3 so that any HNO_3 on the nylon filter could be assumed to be artifact HNO_3 produced by the

reaction between acidic aerosols and NH_4NO_3. Unfortunately, in the humid Bermuda environment, condensate formed nightly on the inside walls of the tubes causing the wall coating to wash down on the filters. Consequently, we obtained no useful HNO_3 artifact data.

A third low volume sampler (Sampler E) was used to collect samples for NH_3, NH_4^+ and Na analysis. An inverted, single glass tube, impregnated with oxalic acid (Ferm, 1979), was used to collect NH_3. After sampling, the tubes were removed, plugged at both ends with polypropylene caps and placed in bags containing ampoules of oxalic acid to prevent additional exposure to NH_3. When they were returned to GMRL, they were washed and the extract assayed for NH_4^+ using the phenol–hypochlorite colorimetric procedure (Harwood and Kuhn, 1970). Condensate was also frequently noted in these tubes in the early morning so no useful NH_3 data was obtained. Because the tubes were inverted, however, the condensate did not affect the backup filter which was removed daily and placed in a Petri dish inside a plastic bag containing ampoules of oxalic acid. These filters were subsequently analyzed for NH_4^+ using the colorimetric procedure and for Na using atomic absorption.

A Sierra high volume air sampler (Sampler F) was also used to obtain samples for determining total suspended particulate mass. These were operated at a flow of 40 cfm using Gelman Microquartz filters.

An MRI model 1597 integrating nephelometer was also located on the second bluff in a wooden instrument shelter. A heater on the inlet line raised the sample temperature about 10°C above ambient (Groblicki et al., 1981). The instrument was calibrated using F-11 and the procedure recommended by Ruby and Waggoner (1981).

O_3 was measured with a McMillen series No. 1100 chemiluminescent monitor. For the 1982 study a Dasibi 1008-PC ozone generator was used for calibration. For the 1983 study the ozone generator failed and calibrations were done with an improvised gas-phase titration system. O_3 concentrations generated from a u.v. light source were determined by reacting the O_3 with a stream of 200 ppb NO. The product, NO_2, was measured using the NO_2 detection system described below. The uncertainty in this calibration was estimated to be ± 25%.

NO and NO_2 were determined using a luminol-based chemiluminescent detector designed and built by Gregory Wendel and Donald Stedman (Wendel et al., 1983). The detector responds to the NO_2 luminol chemiluminescent reaction. Sample air is alternately passed directly into the reaction chamber or passed first over a CrO_3 catalyst before entering the reaction chamber. The former provides a response to just NO_2 while the latter provides a response to NO + NO_2. The detector does not respond to HNO_3, but PAN is detected as NO_2 and CH_3ONO as NO. The uncertainty is ± 10 ppt for NO_2 and ± 100 ppt for NO.

Wind speed, wind direction, temperature and dew point were measured at the site with a Climatronics modular meteorological system. Additional surface observations were also obtained from the U.S. Naval Base.

2.3. Eliminating local influences

The influences from local emissions were eliminated by not including the concentration of certain species on days when there was evidence of a local influence. Considering the emission sources on Bermuda, we felt the following species could be generated by local sources: OC_f, EC_f, Pb_f, NO, Br_f, NO_2, Zn_f and Cu_f. (The subscript, f, denotes particles < 2.5 μm.) The days on which possible local contamination may have occurred were identified using the following criteria: (1) air parcel trajectories which passed over Bermuda before arriving at the site, (2) surface wind direction measurements which indicated that the air came from over land for

more than 5 min, (3) spikes in either condensation nuclei or in aerosol light-scattering which lasted more than 5 min or occurred repeatedly. This process identified 25 out of the 64 days as having a potential local influence, so the data were deleted. For Zn and Cu, however, deleting these data resulted in no significant change in the mean values or their distributions, so they were retained. Besides OC_f, EC_f, Pb_f, Br_f, NO and NO_2, there were no significant differences for any of the species listed in Table 1.

3. RESULTS

3.1. General

The data are summarized in Table 1 which contains the overall arithmetic means, the mean uncertainties associated with each variable, the range and the arithmetic mean values for both sampling periods. The uncertainties were calculated from classical propagation of error analysis methods (Shoemaker and Garland, 1962) and in many cases were dominated by the uncertainty in the zero or blank values calculated from the method of Gabriels (1970).

A mass balance for the major fine and coarse particulate species for both seasons is presented in Table 2. The data in Table 2 indicate that 88% of the

fine and 76% of the coarse aerosol mass can be accounted for by the major aerosol species. For the fine aerosol budget several assumptions were made. The fine sea salt component is the sum of Cl_f^-, Na_f^+ and fine sea salt sulfate ($SO_{4_{fss}}^{2-}$), but only Cl_f was measured directly. $SO_{4_{fss}}^{2-}$ was assumed to be equal to Cl_f times 0.140 while the Na_f^+ was assumed to be equal to Cl_f times 0.555 (C. Culberson, University of Delaware, Personal Communication). The crustal component was calculated by assuming that Si accounted for 20% of the crustal aerosol (Rahn, 1976). The excess or nonsea salt sulfate $SO_{4_{fss}}^{2-}$ was assumed to be equal to $SO_{4_f}^{2-} - SO_{4_{fss}}^{2-}$. As it turned out this correction was negligible. All of the NH_4^+ was assumed to be fine since it is probably all associated with the $SO_{4_{fss}}^{2-}$. OC_f was multiplied by 1.5 to estimate the mass of the organic compounds (Daisey et al., 1984).

For the coarse fraction, Na_c^+ was assumed to be equal to the total measured Na minus Na_f^+. The concentrations of Cl_c and SO_4^{2-} were measured. This results in $Na_c^+/Cl_c^- = 0.696$ and $SO_{4_c}^{2-}/Cl_c^- = 0.149$. The latter is in excellent agreement with the literature value of 0.140, but the former is considerably higher than the literature value of 0.555. This 'excess' Na is probably

Table 1. Summary of measurements

Species	Units	Sampler*	Overall mean	Mean uncertainty (±)	Range	Mean Aug. 82	Mean Jan.–Feb. 83
FPM	$\mu g\,m^{-3}$	A	9.4	1.2	1.2–22.4	11.2	8.1
CPM	$\mu m\,m^{-3}$	A	11.4	3.2	1.2–35.8	8.1	17.4
TSP	$\mu g\,m^{-3}$	F	32.8	2.9	12.5–95.3	30.0	35.0
$SO_{4_f}^{2-}$	$\mu g\,m^{-3}$	A	1.95	0.11	0.12–7.73	1.76	2.09
$SO_{4_c}^{2-}$	$\mu g\,m^{-3}$	A	0.50	0.11	< 0.01–1.48	0.32	0.63
$NO_{3_f}^-$	$\mu g\,m^{-3}$	A	0.15	0.03	0.00–0.63	0.20	0.12
$NO_{3_c}^-$	$\mu g\,m^{-3}$	A	0.28	0.06	0.00–1.58	0.15	0.38
EC_f	$\mu g\,m^{-3}$	B	0.03	0.03	0.00–0.09	0.04	0.03
OC_f	$\mu g\,m^{-3}$	B	0.67	0.25	0.09–1.65	0.77	0.57
Si_f	$ng\,m^{-3}$	A	699	17	0–5959	1390	165
Cl_f	$ng\,m^{-3}$	A	531	13	0–2634	508	548
K_f	$ng\,m^{-3}$	A	62	2	1–302	94	38
Ca_f	$ng\,m^{-3}$	A	79	2	4–370	128	41
Ti_f	$ng\,m^{-3}$	A	14.0	0.4	0.0–113	30	2
V_f	$ng\,m^{-3}$	A	1.9	0.1	0.0–13.0	2.9	1.1
Mn_f	$ng\,m^{-3}$	A	2.5	0.1	0.0–17.0	5.0	0.5
Fe_f	$ng\,m^{-3}$	A	109	3	3–904	224	20
Cu_f	$ng\,m^{-3}$	A	5.7	0.1	0.0–29.0	10.6	2.0
Zn_f	$ng\,m^{-3}$	A	10.7	0.3	0.6–133.0	11.1	10.3
Se_f	$ng\,m^{-3}$	A	0.20	0.04	0.00–1.00	0.17	0.23
Pb_f	$ng\,m^{-3}$	A	3.6	0.2	< 0.1–8.7	2.5	5.5
Br_f	$ng\,m^{-3}$	A	4.7	0.4	0.1–17.7	3.9	6.1
NH_4^+	$\mu g\,m^{-3}$	E	0.40	0.08	0.00–1.50	0.34	0.44
Na	$\mu g\,m^{-3}$	E	2.64	0.20	0.35–11.79	1.90	3.14
$O_{3\,max}$†	ppb	—	29	‡	14–44	24	31
HNO_3	ppt	C	66	28	< 30–700	101	43
NO	ppt	—	< 100	20%	< 100	< 100	< 100
NO_2	ppt	—	623	7%	289–1252	573	764
SO_2	ppt	C	230	80	0–1670	320	200
b_s	$10^{-4}\,m^{-1}$	—	0.37	0.03	0.16–1.36	0.34	0.39

*A—dichotomous sampler with Teflon filter; B—dichotomous sampler with quartz filter; C—low volume sampler with triple stack; E—low volume sampler with NH_3 denuder; F—high volume sampler.
†O_3 is mean of daily 1 h maximum values.
‡For 82 it was ± 5 ppb; for 83 it was ± 25%.

Table 2. Mass balance

Fraction	Component	Species	Concentration ($\mu g\,m^{-3}$)	Comment (sampler)*
Fine	Sea salt	Cl_f^-	0.53	Measured Cl_f (A)
		$SO_{4_{fss}}^{2-}$	0.07	$Cl_f \times 0.14$
		Na_f^+	0.29	$Cl_f \times 0.555$
		Sea salt total	0.89	
	Crustal		3.50	$Si \times 5$ (A)
	Nonsea salt SO_4^{2-}	$SO_{4_{fex}}^{2-}$	1.88	$SO_{4_f}^{2-} - SO_{4_{fss}}^{2-}$ (A)
	$NH_{4_f}^+$		0.40	Measured NH_4^+ (A)
	$NO_{3_f}^-$		0.15	Measured (A)
	EC_f		0.04	(B)
	Organic aerosol		1.37	$OC_f \times 1.5$ (B)
	Σ of measured fine species		8.23	
	Measured FPM		9.4	
Coarse	Sea salt	Na_c^+	2.34	Measured $Na-Na_f^+$(E)
		Cl_c^-	3.36	Measured Cl_c (A)
		$SO_{4_c}^{2-}$	0.50	Measured $SO_{4_c}^{2-}$ (A)
		$Mg_{c_{ss}}^+$	0.24	$SO_{4_c}^{2-} \times 0.471$
		Sea salt total	6.44	
	Crustal		1.89	$Si_c \times 5$ (A)
	$NO_{3_c}^-$		0.28	Measured (A)
	Σ of measured coarse species		8.61	
	Measured CPM		11.4	

*See explanation at the bottom of Table 1.

due to either that some of the Na particles collected by the GMRL low volume sampler were greater than $10\,\mu m$ in diameter, while the Cl_c and $SO_{4_c}^{2-}$ collected on the dichotomous samplers were $10\,\mu m$ and less, or that the Na_f is underestimated due to Cl_f loss from acidified sea salt particles. Mg_c^{2+} was assumed to be equal to $SO_{4_c}^{2-}$ times 0.471 (C. Culberson, Personal Communication).

3.2. *Classification by trajectory direction*

Five-day backward air parcel trajectories, which terminated in Bermuda, were calculated using the Canadian Atmospheric Environment Service trajectory model described by Voldner *et al.* (1981) and Olson *et al.* (1979). This gridded model calculates back trajectories twice a day (0000 and 1200 GMT) using wind data and height analyses supplied by the Canadian Meteorological Center. For this study, trajectories, calculated at the 850-mb level at 0000 GMT time, were selected because they corresponded approximately to the midpoint of the filter sampling period. The direction categories as well as the number of sampling days within each category are shown in Fig. 2 and Table 3. Direction 1 corresponds to air masses which travelled from the northeastern United States between the N Carolina/Virginia and Maine/Canadian borders. Direction 2 extends from the N Carolina/Virginia border to the southern tip of Florida. Direction 3 is from the Caribbean Sea. Direction 4 is the SE quadrant. Direction 5 includes the NE quadrant while 6 extends from due north to the U.S./Canadian border. These directional sectors were chosen because each sector represents a different source area and they correspond to the sectors used by
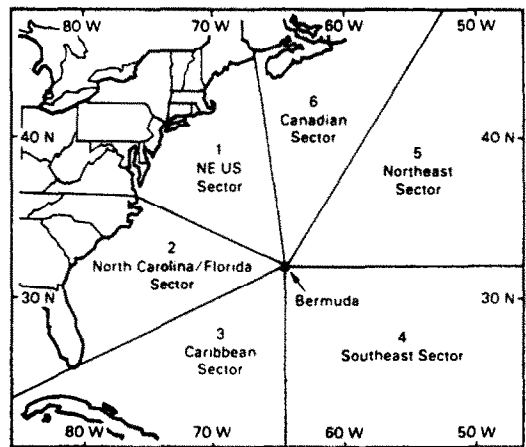

Fig. 2. Sectors used in air parcel trajectory analysis.

Table 3. Distribution of trajectories arriving in Bermuda by sector

Sector	Number of trajectories (% of total)		
	Aug. 82	Jan.–Feb. 83	Total
1. Northeastern U.S.	3 (11)	10 (29)	13 (21)
2. U.S.; Florida to N Carolina	8 (29)	11 (31)	19 (30)
3. Caribbean	2 (7)	5 (14)	7 (11)
4. SE Quadrant	15 (54)	2 (6)	15 (24)
5. NE Quadrant	0 (0)	3 (9)	3 (5)
6. Canada	0 (0)	4 (11)	4 (6)
Total days	28	35	63

other investigators (Duce et al., 1976; Jickells et al., 1982).

Many of the trajectories curved so some of them passed through two sectors. For these trajectories, the starting point of the trajectory was used for classification purposes unless the trajectory passed over an area of higher emissions. For example, a trajectory which originated in sector 2 but passed through the Northeastern States would be classified in sector 1. Similarly a trajectory which originated in sector 4 but passed over some Caribbean islands would be classified in sector 3. However, if it only passed over open ocean not near the islands, it would be classified in sector 4.

The mean concentrations of the FPM species, the gaseous constituents and several other parameters as a function of trajectory direction are presented in Table 4. Data for sectors 5 and 6 are not included because these trajectories had to pass over the island of Bermuda. Also presented in Table 4 are the enrichment factors (EF) for appropriate species. These were calculated using Fe as the reference element and Mason's (1966) crustal reference material. The EF is computed from:

$$EF = \frac{X_f/Fe_f}{X_{cr}/Fe_{cr}}$$

where X_f is the concentration of element X in the fine aerosol, Fe_f is the concentration of Fe in the fine aerosol, and X_{cr}/Fe_{cr} is the ratio of element X to Fe in

Mason's crustal reference material. An EF close to unity indicates that the source of the material is crustal while an EF much greater than unity indicates noncrustal sources.

4. DISCUSSION

4.1. General

The major fine aerosol species in Bermuda were crustal, 37% (by mass), nonsea salt sulfate, 20%, organic material, 15%, and sea salt, 10%. On an equivalent basis, $SO_{4_{fea}}^{2-}/NH_4^+ = 1.76$, which indicates that the $SO_{4_{fea}}^{2-}$ is only 57% neutralized. If we associate the NH_4^+ mass with $SO_{4_{fea}}^{2-}$ and assume the unneutralized $SO_{4_{fea}}^{2-}$ is H_2SO_4, the mass of $SO_{4_{fea}}^{2-}$ compounds account for 24.5% of the FPM.

In the coarse fraction, the dominant species are sea salt, 57%, and crustal material, 17%. The unaccounted fraction, 25%, is probably dominated by water associated with the hygroscopic sea salt aerosol.

4.2. Comparison with other data

Data collected in Bermuda or in the N Atlantic Ocean by previous investigators are summarized in Table 5. There is excellent agreement between the data in Table 5 and our data for Mn_f, V_f, Na, Cl (total), Pb_f, SO_{4f}^{2-} and Se_f. The averages of ten samples reported by Minert and Winchester (1977) for K_f, Ca_f, Fe_f and Zn_f are somewhat lower, but well within the range of our

Table 4. Mean concentrations and enrichment factors (EF) as a function of trajectory direction

Species	Conc. units	1-Northeastern U.S. Conc.	EF	2-Florida-N.C. Conc.	EF	3-Caribbean Conc.	EF	4 SE Conc.	EF
Si_f	$ng\,m^{-3}$	160	1.1	445	1.3	274	1.1	1635	1.3
Cl_f	$ng\,m^{-3}$	304	4700	549	3440	614	5430	611	1020
K_f	$ng\,m^{-3}$	58	5.6	51	2.0	38	2.1	98	1.0
Ca_f	$ng\,m^{-3}$	65	3.2	63	1.2	50	1.4	133	0.7
Ti_f	$ng\,m^{-3}$	4.2	1.5	8.6	1.2	5.2	1.0	34	1.3
V_f	$ng\,m^{-3}$	2.5	37	1.8	11	1.2	10	2.2	3
Mn_f	$ng\,m^{-3}$	1.1	2.3	1.7	1.5	1.1	1.3	5.4	1.2
Fe_f	$ng\,m^{-3}$	28	1.0	69	1.0	49	1.0	259	1.0
Cu_f	$ng\,m^{-3}$	5.6	200	4.0	59			9.8	39
Zn_f	$ng\,m^{-3}$	19.8	570	5.6	65			9.6	30
Se_f	$ng\,m^{-3}$	0.36	14480	0.21	3430	0.06	1420	0.15	650
Br_f	$ng\,m^{-3}$	7.4	5950	4.5	1470			2.6	230
Pb_f	$ng\,m^{-3}$	9.3	1500	3.4	220			5.0	90
SO_4^{2-}	$\mu g\,m^{-3}$	4.01	10300	1.98	2070	1.25	1840	1.07	300
Nonsea salt SO_4^{2-}	$\mu g\,m^{-3}$	3.97	10200	1.90	1990	1.16	1710	0.98	270
OC_f	$\mu g\,m^{-3}$	0.47		0.51				0.98	
EC_f	$\mu g\,m^{-3}$	0.06		0.02				0.03	
$OC_f + EC_f$	$\mu g\,m^{-3}$	0.53	4730	0.53	1750			1.01	950
NO_{3_f}	$\mu g\,m^{-3}$	0.16		0.14		0.11		0.20	
NH_4^+	$\mu g\,m^{-3}$	0.58		0.36		0.53		0.33	
FPM	$\mu g\,m^{-3}$	10.8		8.6		10.0		10.4	
Na	$\mu g\,m^{-3}$	2.12		2.66		3.94		2.62	
b_s	$10^{-4}\,m^{-1}$	0.50		0.39		0.42		0.23	
SO_2	ppt	391		254		80		156	
HNO_3	ppt	126		66		26		41	
NO_2	ppt	716		676				527	
$O_{3\,max}$	ppb	33		31		32		22	

Table 5. Aerosol data from Bermuda and the N Atlantic

Species	Mean conc.	Range	EF	Site*	Reference†
Mn	3.5 ng m^{-3}	0.17–20	0.73–2.3	B	1
		0.05–5.4	2.6	NA	2
V	1.2 ng m^{-3}	0.37–6.6		B	1
		0.6–14	17	NA	2
Na	2.4 μg m^{-3}	0.38–9.0		B	1
Cl	3.9 μg m^{-3}	0.25–16.6		B	1
SO$_4^{2-}$	1.5 μg m^{-3}	0.05–9.5		B	1
S	0.5 μg m^{-3}			B	3
K$_f$‡	12.5 ng m^{-3}			B	3
Ca$_f$‡	20.1 ng m^{-3}			B	3
Fe$_f$‡	14.4 ng m^{-3}	2.4–40		B	3
OC	0.29 μg m^{-3}	0.15–0.47		B	4
	0.57 μg m^{-3} §			NA	5
	1.84 μg m^{-3} ‖			NA	5
	0.44 μg m^{-3}			SS	6
Pb		0.1–64	2200	NA	2
	3.4 ng m^{-3}	0.1–71	175	B	7
Cu		0.12–10	120	NA	2
	1.0 ng m^{-3}	0.7–24	11	B	7
Zn	2.6 ng m^{-3}	0.1–32	22	B	7
		0.3–27	110	NA	2
Zn$_f$‡	6.2 ng m^{-3}			B	3
Cr		0.07–1.1	11	NA	2
	0.28 ng m^{-3}	0.04–3.3	1.7	B	7
Se	0.13 ng m^{-3}	< 0.02–0.62	2600	B	7
Ni	0.08 ng m^{-3}	0.02–1.5	1.1	B	7
EC	μg m^{-3}	0.02–0.5		NA	8

*B, Bermuda; NA, North Atlantic; SS, Sargasso Sea.

†1, Chen and Duce (1983), 2, Duce et al. (1975), 3, Meinert and Winchester (1977), 4, Hoffman and Duce (1974), 5, Eichmann et al. (1979), 6, Chesselet et al. (1981), 7, Duce et al. (1976), 8, Andreae (1983), Andreae et al. (1984).

‡Fine aerosol-diameter ≤ 2.0 μm.

§Based on six air samples collected in pure marine air arriving on the West Coast of Ireland.

‖Based on ten marine air samples which had some continental influence.

numbers. Our mean Cu$_f$ values are somewhat higher than Duce et al.'s (1975), but they fall within the ranges of values observed both at Bermuda and in the N Atlantic. In addition, the mean EF of 48 falls within the range reported by Duce et al. of 11–120 observed at the same respective locations.

Our OC data from Bermuda fall within the range of values presented in Table 5. However, comparisons between OC and EC data collected by various groups who use different methods should be done cautiously because the methods give different results (Wolff and Klimisch, 1982; Cadle et al., 1983; Wolff, 1985). The lowest OC values were reported by Hoffman and Duce (1974) who state that the OC recovery efficiency of their method has been estimated to be 50–90%.

For EC, a comparable data set was collected in the eastern N Atlantic (Andreae, 1983; Andreae et al., 1984). On a cruise from England to the equator, EC in seven samples ranged from 0.02 to 0.5 μg m^{-3}. The highest concentrations occurred in air masses which passed over Europe while the lowest occurred off the coast of Spain with W winds. Air masses which passed over S America and Tropical Africa had EC concentrations of 0.07–0.20 μg m^{-3}. These relatively higher

concentrations were attributed to biomass combustion emissions in the tropics.

The mean SO$_2$ concentrations were 320 and 200 ppt for 1982 and 1983, respectively, and an overall mean of 230 ppt. Unfortunately, there is no directly comparable data from other investigations. Georgii (1970) reports on aircraft measurements made with an unspecified SO$_2$ measurement technique over an undefined part of the E Atlantic between 30 and 40°N. The SO$_2$ concentrations were 700–1230 ppt. Maroulis et al. (1980) report SO$_2$ values of 89 ± 69 ppt collected in the boundary layer over the eastern N Pacific from one of the Gametag flights. Since lower SO$_2$ concentrations would be expected over the Pacific, our SO$_2$ values for Bermuda seem reasonable.

O$_3$ values reported here are consistent with the aircraft data reported by Browell et al. (1983) and Harriss et al. (1984). Flights made by NASA in August 1982 over Bermuda, while we were sampling on the surface, indicate that O$_3$ was 30–40 ppb from the surface up to 500 m. Above 500 m, the O$_3$ increased to 60 ppb and remained fairly constant up to 5 km.

Measurements of NO$_x$ and HNO$_3$ species are also in reasonable agreement with data from other remote

areas. At a coastal location in W Ireland, Cox (1977) reported mean concentrations of $\leqslant 200$ ppt and 400 ppt for NO and NO_2, respectively. In remote marine atmospheres in the N Hemisphere boundary layer, Huebert and Lazrus (1980) reported concentrations of HNO_3 between 10 and 270 ppt with a mean of 70 ppt. At Niwot Ridge, Colorado, Kelly et al. (1980) report 'clean air' concentrations of NO_x and HNO_3 to be ≈ 400 ppt and 40 ppt, respectively. On occasions when air was advected from Denver, NO_x would exceed 1000 ppt and HNO_3 would exceed 400 ppt.

As mentioned earlier, an unsuccessful attempt was made to determine the magnitude of artifact HNO_3 formed when acid aerosols, primarily H_2SO_4, react with NH_4NO_3 on the Teflon prefilter. We feel, however, that any HNO_3 formed in this manner was probably small. With an acid sulfate aerosol around, the existence of pure NH_4NO_3 is unlikely to be based on equilibrium considerations (Cadle et al., 1982). On the other hand, we became concerned that high loadings of sea salt on the Teflon prefilter might have scrubbed out some of the HNO_3. Consequently we conducted a series of experiments in our laboratory. Teflon prefilters used in Bermuda were selected from several days with high Na^+ concentrations and placed in a filter holder in front of an unused nylon filter. Known HNO_3 concentrations as low as 800 ppt were then passed through the filters for 1–2 h. The nylon filters were then removed and analyzed for NO_3^-. In all of the experiments, there was no loss of HNO_3 by the prefilter. Consequently we feel that our HNO_3 data are reasonable.

4.3. Seasonal variations

The mean concentrations for August 1982 and January–February 1983 are shown in the last two columns of Table 1. Concentrations for CPM, TSP, Na, Cl_f, SO_4^{2-}, Se_f, Br_f, Pb_f, NH_4^+, NO_2, and b_s were all higher in the winter of 1983. In contrast, the fine crustal-related species, Si_f, K_f, Ca_f, Ti_f, and Fe_f as well as V_f, Mn_f, Cu_f, HNO_3 and SO_2, were all higher during the summer of 1982. Most of these differences can be explained by the distribution of trajectories during the two periods.

During the summer of 1982, trajectories from the SE occurred on 54% of the days while trajectories from the U.S. occurred on only 40% of the days. In contrast, during the winter of 1983, 60% of the trajectories came from the U.S. with only 6% arriving from the SE sector. These frequencies are consistent with previous flow climatologies conducted in the W Atlantic (Nemcosky, 1980; Miller and Harris, 1986; Chen and Duce, 1983). The data in Table 4 show that the highest concentrations of fine crustal material occurred when the flow was from the SE quadrant. We suspect that this is Saharan dust and this will be discussed later. On the other hand, the highest levels of many species that are dominated by anthropogenic emissions occurred when the air flow was from the U.S. Thus, the high frequency of SE-sector trajectories explains the higher

1982 concentrations of Si_f, K_f, Ca_f, Ti_f and Fe_f. The higher concentrations of V_f and Mn_f also appear to be of crustal origin as the EF for both species during SE quadrant trajectories are very low. The explanation for Cu_f is probably the same, though its enrichment factor on SE days is 34. However, this EF is considerably lower than on non-SE days and it compares well with Cu EFs calculated from data collected at other remote sites (Rahn, 1976).

The higher wintertime values of SO_4^{2-}, EC_f, Se_f, Br_f, Pb_f, NH_4^+, NO_2, and b_s are consistent with the hypothesis that the U.S. is the source of these species during periods of westerly flow. The higher winter concentration of CPM, TSP, Cl_f and Na indicates that there was more sea salt aerosol during the winter. Since sea salt aerosol is a function of wind speed (Blanchard and Woodcock, 1980), the higher wintertime wind speeds in Bermuda support this hypothesis (Nemcosky, 1980).

The behavior of two species, SO_2 and HNO_3, cannot be explained by any of the above mechanisms. It would seem logical that they would be higher in winter when Bermuda is dominated by U.S. trajectories and when the other anthropogenic species such as SO_4^{2-}, NO_2, and Pb_f were higher, but this is not observed. Higher photochemical activity during the summer may partially explain the higher HNO_3 but it would also be expected to enhance the conversion of SO_2 to SO_4^{2-}. Higher summertime temperatures would be expected to produce higher biological activity which would increase biogenic S emissions which are precursors to SO_2 (Westberg and Lamb, 1984). In addition, two sinks for these species may be more important in the winter. HNO_3 is readily scavenged by coarse sea salt (Savoie and Prospero, 1982) and coarse crustal (Wolff, 1984) aerosols. Thus, the higher winter concentrations of sea salt aerosol near Bermuda may contribute to the lower HNO_3. This is consistent with the higher NO_3^- concentration in winter and the good HNO_3/NO_{3c}^- correlation ($r = 0.69$, $p = 0.0001$) in winter and an insignificant correlation in summer. Other possible processes include both in-cloud and below-cloud scavenging and reactions of SO_2 and NO_2 and their products. Thus, the greater frequency of precipitation in the winter over the W Atlantic could contribute to the observed seasonal behavior of these water soluble species. For example in August of 1982, precipitation was recorded on 10 of 31 days while in January and February 1983, precipitation was measured on 25 of 35 days in Bermuda.

4.4. Dependence upon trajectory direction

The data in Table 4 show that for most anthropogenically derived species the highest concentrations and enrichments occur when the trajectories arrive from the NE United States and the lowest occur on SE winds. This is consistent with previous analyses (Jickells et al., 1982; Church et al., 1982; Chen and Duce, 1983). In contrast, the crustal species are highest on SE winds. For V_f, Zn_f, Se_f, Pb_f, Br_f, SO_4^{2-}, EC_f,

SO_2 and HNO_3, the northeastern United States is the major source area for these species in Bermuda. Se and SO_4^{2-} are the most highly enriched species. In general, trajectories from the Southern states result in intermediate concentrations and enrichments.

The enrichment factors for the crustal species, Si_f, Ca_f, Ti_f, Mn_f, and Fe_f are similar regardless of wind direction. This strongly suggests a crustal source for all directions. However, one commonly considered crustal species, K_f, is an exception. It is considerably enriched when NE United States (type 1) trajectories occur. Furthermore, for type 1 trajectories, the wintertime EF for K_f is 6.5 while in the summer it is only 2.5. This enhanced wintertime enrichment of K_f is consistent with wood combustion in the NE U.S. being the source of K_f (Wolff et al., 1981).

The behavior of OC_f is somewhat confusing. Though the highest total C EFs occur on type 1 trajectories, the highest concentrations occur on SE trajectories. Whether this OC is crustal in origin, generated from the ocean (Hoffman and Duce, 1976), produced from biomass burning in the tropics (Andreae, 1983) or gas phase reaction products (Hoffman and Duce, 1977) is unknown. Because our routine OC method cannot discriminate between C as OC and CO_3^{2-}, six samples obtained during SE trajectories were acidified to remove CO_3^{2-} and reanalyzed for OC. The results indicated that the CO_3^{2-} accounted for 13% of the reported OC (range 0–19%). Consequently CO_3^{2-} cannot explain the observed levels of OC on days with SE trajectories.

The interrelationships between the various parameters can be further examined by employing multivariate statistical techniques. Duce et al. (1976) employed factor analysis using elemental data from Bermuda. In the present analysis, we employ a type of factor analysis used previously to aid in the analysis of data from Virginia (Wolff et al., 1984) and from

Detroit (Wolff et al., 1985). It employs principal component analysis (PCA) followed by a varimax orthogonal rotation. The resulting factor pattern, based on 62 observations, is shown in Table 6.

The strong association of Si and Fe in factor 1 suggests that this is the crustal factor, while the high loadings in factor 3 for Na and Cl indicate that this is the sea salt factor. The high loading in factor 1 for Mn indicates that this element is also dominated by crustal species. This is consistent with the EFs shown in Table 4 which indicate only a slight enrichment in Mn_f with type 1 trajectories. The moderate association of $NO_{3_f}^{-}$ in this factor is consistent with crustal aerosol being a sink for HNO_3 (Wolff, 1984). The significant loading for OC_f suggests that there is some OC associated with this factor. As discussed earlier, this does not necessarily mean that the OC is of crustal origin because the highest concentrations occur with the same trajectory as the highest crustal concentrations. A weak loading for V suggests that there is some crustal V. This is consistent with the low EF for V on SE winds.

The second factor has moderate loadings for Se_f, Pb_f, SO_4^{2-}, O_{3max} and HNO_3. These associations suggest that this factor represents aged N American air masses. However, the coal combustion emissions, represented by Se, and the fuel oil combustion emissions, represented by V, appear in separate factors. Factor 2 contains the coal emissions while factor 4 contains the fuel oil emission. Since fuel oil combustion occurs primarily in the NE U.S., factor 4 appears to be specific for that area, while factor 2, which also contains Pb, a ubiquitous species, appears to be of less specific geographic origin. It is also interesting to note that SO_4^{2-} is more strongly associated with the coal factor while SO_2 is more strongly associated with the oil factor. Consequently it appears that the fuel oil emissions impacting Bermuda are less aged than the coal combustion emissions. This is consistent with the

Table 6. Rotated factor pattern

Species	Factor number 1	2	3	4	5	Communality
Fe_f	0.94					0.98
Si_f	0.94					0.97
Mn_f	0.94					0.96
K_f	0.92					0.94
$NO_{3_f}^{-}$	0.65					0.57
OC_f	0.51		−0.35		0.30	0.57
Se_f		0.69				0.55
Pb_f		0.68	−0.30			0.67
$SO_{4_f}^{2-}$		0.67		0.30	0.51	0.81
O_{3max}		0.67				0.60
HNO_3		0.65	−0.38			0.67
Na			0.77			0.72
Cl_f			0.75		−0.41	0.77
EC_f			−0.64		−0.40	0.61
SO_2				0.91		0.92
V_f	0.41			0.80		0.87
NO_2					0.80	0.78
% of Variance	26.9	14.3	13.8	11.8	9.3	

NE U. S. being closer to Bermuda than the prime coal burning areas of the midwestern and interior SE states.

The fifth factor also contains secondary SO$_4^{2-}$ and NO$_x$ species as well as a weak loading for OC. Although the interpretation of this factor is uncertain, it could reflect secondary photochemical formation processes.

This analysis was also conducted without the sector 4 (SE Atlantic) data, and the results were somewhat similar. Factor 1 contained moderate to high loadings for only the crustal species, Fe, Si, Mn and K and explained 21.2% of the variance. Factor 2 was moderately loaded in Pb$_f$, OC$_f$ and EC$_f$ and explained 15.1% of the variance. Factors 3 and 4, explaining 14.5% and 14.0% of the variance, respectively, were similar to factors 3 and 4 in Table 6 except that Pb did not appear in the term with the Se$_f$, SO$_{4f}^{2-}$, O$_{3max}$ and HNO$_3$.

4.5. *Estimation of* SO$_x$ *and* NO$_x$ *budgets*

Eventually, when the WATOX data bases are merged, SO$_x$ and NO$_x$ budgets for the W Atlantic will be calculated. Using the data presented here, however, some aspects of the budget can be crudely examined. An estimation of the transport terms for SO$_x$ and NO$_x$ from the U.S. to the Atlantic Ocean at Bermuda can be made and compared to the flux of these species from the U.S. as estimated by Galloway, Whelpdale and Wolff (1984) (GWW). In GWW, the fluxes of SO$_x$ and NO$_x$ species, as S and N, from the U.S. exiting between the S tip of Florida and S Maine between the surface and 1500 m are 1.39 Tg a^{-1} and 0.73 Tg a^{-1}, respectively. The total air flux from the same region into the Atlantic is 3.82×10^{17} m^3 a^{-1} (Whelpdale *et al.*, 1984).

The region examined by GWW roughly corresponds to trajectory sectors 1 and 2. The difference is that the State of Maine is excluded in GWW. However, it has a negligible impact on the eastern United States SO$_x$ and NO$_x$ budgets since Maine emissions are small and airflow from Maine to Bermuda is rare. As a first approximation, we assume that the average concentrations of the species observed in Bermuda on days with trajectories from sectors 1 and 2 represent the mean concentration of all air masses which travelled from the U.S. to anywhere 1250 km offshore. (From anywhere on the E Coast from N Carolina to Cape Cod, the distance to Bermuda is between 1150 and 1350 km.) Averaging the sectors, converting to μg S and N bases and summing the species, one calculates mean values of 1.46 μg m^{-3} S and 0.58 μg m^{-3} N. These numbers are then multiplied (with the appropriate unit conversions) by Whelpdale *et al.*'s (1984) air flux estimate to get the total S and N fluxes across the line 1250 km offshore of the U.S. They are 0.56 Tg a^{-1} S and 0.20 Tg a^{-1} N which represent 40% and 29% of the respective S and N fluxes calculated by GWW below 1500 m. This means that 40% of the SO$_x$ and 29% of the NO$_x$ species which exit the U.S. between 0 and 1500 m reach the line 1250 km downwind. The losses are due to deposition, venting to

higher layers and horizontal dispersion. Horizontal dispersion, however, has probably been accounted for by our averaging techniques.

GWW estimated that 34% of the S emissions in eastern N America are advected off the East Coast. Most of the S emissions occur in an area bounded on the east by the Atlantic Ocean and the west by a line 1250 km W of the Atlantic Ocean. Consequently, it seems consistent that of the 34% of the S emissions which are advected out of the 1250 km source area into the Atlantic, 40% make it an additional 1250 km.

GWW's calculated N flux from N America in the lowest 1500 m is 22% of the total N emissions. Despite the large uncertainty, our 29% advection value for N at least appears to be the correct order of magnitude.

5. SUMMARY AND CONCLUSIONS

The concentrations and composition of fine aerosol and trace gaseous species on Bermuda are governed by the type of air mass influencing the island. During incursions of air from the NE U.S., which are most frequent during the winter, higher concentrations of the anthropogenically-derived species, such as SO$_{4f}^{2-}$, HNO$_3$, SO$_2$, Pb$_f$ and Se$_f$ are observed. Higher SO$_4^{2-}$ concentrations are associated with higher concentrations of the coal burning tracer, Se$_f$, and higher concentrations of Pb, HNO$_3$ and O$_3$. SO$_2$ is strongly associated with the oil burning tracer, V$_f$.

Although most of the intrusions of NE U.S. air occurred during the winter campaign, they also occurred during the summer. However, the summer was dominated by a SE flow which was associated with high concentrations of fine crustal material which probably originated in the Sahara Desert. Again these occurred most frequently during the summer, but wintertime intrusions still occurred. Days with SE air flow were associated with high levels of Si$_f$, Ti$_f$, K$_f$, Fe$_f$, Ca$_f$ and Mn$_f$ as well as the lowest *EFs* for all anthropogenic species. The *EFs* for the crustal species were generally independent of wind direction with the exception of K$_f$. The higher K$_f$ *EF* from the NE U.S. during the winter suggests woodburning as the source of the excess K$_f$.

The Bermuda NO$_x$ and SO$_x$ data were used to make a rough estimate of the fluxes of these species in the lowest 1500 m from N America to a N/S line which is 1250 km E of the U.S. and passes through Bermuda. In both cases, significant amounts of the material advected off the East Coast made it to Bermuda and the fluxes appear to be consistent with fluxes calculated by Galloway, Whelpdale and Wolff (1984).

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