

NITROGEN AND SULPHUR OVER THE WESTERN ATLANTIC OCEAN

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Abstract—This paper reports new surface and aircraft measurements of sulphur and nitrogen species made during WATOX-85 at Lewes, Delaware and Bermuda. Concentrations of most species measured in this portion of the western Atlantic Ocean atmosphere were higher than those found in remote marine environments, showing clearly the influence of anthropogenic emissions from North America. The experiment was designed such that measurements were made following cold frontal passages in conditions of strong, dry westerly flow, to ensure that measurements at Bermuda were in air masses that had earlier crossed the east coast in the region of Lewes. Boundary-layer SO_2 concentrations decreased by a factor of 20 between the east coast and Bermuda, while sulphate was the same at both locations. First-order decay distances for SO_2 and total S were 340 and 620 km, respectively, under these conditions. The decay distance for total S is substantially shorter than previously determined, indicating that SO_2 in particular is removed in near-coastal environments more quickly than previously supposed. Boundary-layer NO_x and HNO_3 concentrations decreased by close to an order of magnitude between the east coast and Bermuda, whereas for NO_3^- the decrease was a factor of two. Corresponding first-order decay distances of NO_x and total N were 500 and 550 km, respectively.

Key word index: WATOX, Atlantic Ocean, sulphur, nitrogen removal, deposition.

INTRODUCTION

Anthropogenic emissions of S and N species are now known to dominate the tropospheric S and N budgets over North America (Logan, 1983; Galloway and Whelpdale, 1980). Measurements of S and N compounds at the North American east coast and over the western Atlantic Ocean have shown concentrations well in excess of levels in more remote areas (Church *et al.*, 1988; Wolff *et al.*, 1986a,b; Galloway, 1985). A large portion of North American emissions is deposited onto the continent by wet and dry deposition, either in the dioxide forms (SO_2 or NO_2) or, after chemical conversion, in the oxidized SO_4^{2-} and NO_3^- forms including the strong acids H_2SO_4 or HNO_3 . However, budget calculations have shown that a considerable fraction of the S and N emitted is advected eastward over the Atlantic Ocean (Galloway *et al.*, 1984). This has important consequences both on the continent and in the ocean. Material that is advected

away from the continent will not contribute to regional air pollution problems nor have adverse effects on sensitive aquatic and terrestrial ecosystems. On the other hand, this same material may well have a significant impact on marine biogeochemical cycling of these substances, particularly as SO_4^{2-} and NO_3^- are nutrients.

The objective of the Western Atlantic Ocean Experiment (WATOX) is to determine the flux and fate of the S, N, trace metal and synthetic organic compounds that are advected eastward from the North American continent. Whelpdale *et al.* (1984) used several years of meteorological data to determine the average air mass flux leaving the continent in a total of 24 regions (eight latitude by three altitude bands) along the east coast. Galloway *et al.* (1984) used these data and available trace gas and particle concentration data to determine the fluxes of S and N being advected off the East coast. For both species they found that transport at all altitudes from the surface to 5500 m, and at latitudes

from 38° to 52° N was important. They estimated that 34 % of the emitted anthropogenic S and between 24 and 71% of the emitted N were advected eastward away from the continent. The large range for the N estimate indicates the paucity and uncertainties of the concentration measurements used for the calculations.

A WATOX measurement program was begun in 1980 to improve concentration, and thus flux, estimates and to try to determine the fate of the material leaving the continent. The field measurement program has two components, long-term and intensive. The long-term measurements provide continuous data on wet deposition at Lewes, Delaware, Bermuda and Ireland. Intensives are held on an occasional basis to investigate the processes that control the transport, transformation and deposition of materials to the western Atlantic Ocean. A major WATOX intensive was mounted from 15 February to 30 March 1985. During this intensive, measurements of NO, NO_x (nitrogen oxides measured using a FeSO₄ converter), HNO₃, SO₂, O₃, particulate SO₄²⁻ and particulate NO₃⁻ were made at ground stations at Lewes and Bermuda and from an aircraft. Seven groups operating a wide range of instrumentation and using several different analytical techniques were involved. The purpose of this paper is to report the results obtained from the WATOX-1985 intensive measurement period and to use these data to examine the fate of the S and N that leave the North American continent. The use of these data to improve flux estimates is reported in Galloway *et al.* (1988).

EXPERIMENTAL

Experiment design

A specific objective of this experiment was to determine how the chemical character of an air mass changed as it moved across the North American east coast and out over the western Atlantic Ocean. A relatively simple meteorological situation was selected in which to make measurements—viz., following strong, cold frontal passages over the coast and out toward Bermuda. A review of past records determined that the frequency of such events was greatest in the early part of the year (see Galloway *et al.*, 1988). Cold fronts move rapidly down from the northwest, across the coast and in an E direction out over the ocean. Following the frontal passages, winds remain fairly strong and steady from the west, little precipitation occurs, and the humidity is low. Over-ocean transport can be fairly rapid under these conditions, with the air often reaching Bermuda in a few tens of hours. The advantages of this type of situation are that it is easy to forecast, conditions remain steady for 2 or 3 days, and there is little precipitation. One disadvantage is that concentrations of chemical species tend to be low because of the strong flow.

Two sites were used in this study; their locations are shown in Fig. 1. The ground site at Lewes, Delaware was used to characterize the chemical composition of the air leaving the continent. The site at Bermuda (1000 km to the east) was used to characterize the air in mid-ocean. Concentration changes in the vertical were determined near both ground sites using an aircraft.

On the basis of a forecast for a cold frontal passage by the meteorologists in the group, the field crews were alerted 24 to 36 h in advance. Once a suitable front had passed, 'event' status was declared and measurement systems were operated according to pre-arranged schedules. All the Lewes data cited in this paper were collected during designated events. Subsequent analysis of back trajectories confirmed the event

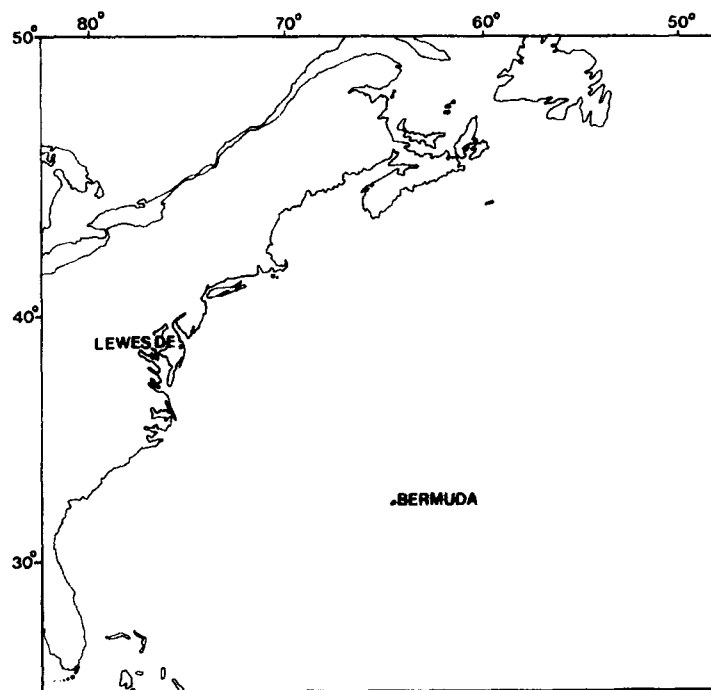


Fig. 1. Map of the east coast of North America and the western Atlantic Ocean showing the location of the two sampling sites.

designation in all cases. Not all fronts reached Bermuda; several dissipated en route over the ocean. As a result, 'event' data from Lewes and Bermuda did not always correspond. The Bermuda data used here were selected on the basis of isobaric back-trajectory analysis. If the air mass being sampled at Bermuda had crossed the east coast in the region of Lewes at all pressure levels no more than 3 days prior to the time of measurement, the data were included. Where available, isentropic trajectories were used to confirm the isobaric assignments. Most of the measurement periods identified on Bermuda followed declared 'events' on the east coast. The aircraft was deployed only under event conditions off the east coast so all data there were used. At Bermuda the aircraft data were selected on the basis of the back trajectories.

Sites and measurement systems

With the involvement of several groups and measuring systems, the quality of the measurements and their compatibility were of primary concern. Hastie *et al.* (1988) have described fully the various measurement systems and techniques, examined the accuracy of the measurements, and carried out detailed intercomparisons between the data sets. A brief description is given below and Table 1 lists the systems, identifying them by group name and species measured.

The east coast ground site was near Lewes, Delaware in an open area approximately 150 m south of the MAP3S site in the Cape Henlopen State Park. This site is within sight of the coast and away from any major urban or industrial centres. It can thus be considered suitable for collecting data on the

chemical character of air which is typical of that leaving the continent, while not being unduly influenced by any local effects. This site is described in more detail in Wolff *et al.* (1986a). The University of Maryland: University of Washington (UMD:UW) and Atmospheric Environment Services (AES) filter pack systems were used to measure particulate SO_4^{2-} and NO_3^- , SO_2 and HNO_3 . York University and Unisearch Associates measured NO and NO_x using a chemiluminescent analyzer with a ferrous sulphate converter, O_3 with a Dasibi model 1003-AH analyzer and HNO_3 and formaldehyde using a tunable diode laser absorption spectrometer (TDLAS).

The ocean site was on the western end of the island of Bermuda at High Point, on a 35 m sea cliff on the south shore. It has been shown to be isolated from local pollution sources, and is described in Wolff *et al.* (1986b). Particulate NO_3^- and SO_4^{2-} , and gas-phase HNO_3 and SO_2 were measured using the same UMD:UW and AES systems as at Lewes. Filter-handling protocols, shipping and analysis routines were kept as similar as possible to minimize the possibility of site-dependent biases in the data collection.

Aircraft measurements were made from the NOAA Air Quality Division's Beechcraft King Air C-90. This aircraft has a payload weight of 1660 kg including fuel, a cruising speed of 112 m s^{-1} , although this was lowered to 55 m s^{-1} for our sampling, and a flight duration of 5 h. NO_x were measured using equipment identical to that at the Lewes site. O_3 was measured with a Dasibi 1003-AH instrument and SO_2 was measured continuously using a Meloy S analyzer. The AES filter pack system, identical to those at Lewes and Bermuda, was used to measure particulate SO_4^{2-} and NO_3^- , HNO_3 and

Table 1. Instrumentation operational during the WATOX-85 intensive

Species	Site	Group	Instrument/ analytical technique
Particulate sulphate	Lewes	AES	Filter pack/I.C.*
		UMD:UW	Filter pack/I.C.
	Bermuda	AES	Filter pack/I.C.
		UMD:UW	Filter pack/I.C.
	Aircraft	AES	Filter pack/I.C.
UMD:UW		Filter pack/I.C.	
Particulate nitrate	Lewes	AES	Filter pack/I.C.
		UMD:UW	Filter pack/I.C.
	Bermuda	AES	Filter pack/I.C.
		UMD:UW	Filter pack/I.C.
	Aircraft	AES	Filter pack/I.C.
UMD:UW		Filter pack/I.C.	
NO_x	Lewes	York/Unisearch	Chemiluminescence
	Bermuda	none	
	Aircraft	York/Unisearch	Chemiluminescence
Nitric acid	Lewes	AES	Filter pack/I.C.
		UMD:UW	Filter pack/I.C.
		York/Unisearch	Tunable diode laser
	Bermuda	AES	Filter pack/I.C.
		UMD:UW	Filter pack/I.C.
Aircraft	AES	Filter pack/I.C.	
Sulphur dioxide	Lewes	AES	Filter pack/I.C.
		UMD:UW	Filter pack/I.C./†PGAA
	Bermuda	AES	Filter pack/I.C.
		UMD:UW	Filter pack/I.C.
	Aircraft	AES	Filter pack/I.C.
		NOAA	Flame photometric
Ozone	Lewes	York/Unisearch	u.v. absorption
	Bermuda	none	
	Aircraft	NOAA	u.v. absorption

* I.C. —ion chromatography.

† PGAA—prompt gamma activation analysis.

SO₂. The UMD:UW filters were analyzed only for particulate SO₄²⁻ and NO₃⁻. Measurements were made at the ground sites from 15 February to 30 March, and from the aircraft on the east coast from 27 February to 26 March, and out of Bermuda from 2 April to 11 April.

RESULTS

Particulate sulphate

Excess particulate SO₄²⁻ was measured by the UMD:UW and AES groups. The SO₄²⁻ intercomparison (Hastie *et al.*, 1988) showed that the ground-based UMD:UW and AES measurements were not significantly different from each other, nor was there a difference between ground sites. The aircraft intercomparison showed a significant difference between the two systems; this is reflected in the lower absolute accuracies assigned to these measurements. The average excess SO₄²⁻ concentrations presented in Table 2 were obtained by averaging all event data points from both groups with all filter measurements equally weighted. The standard deviations of the mean are given, as are the measurement accuracies. For the ground-based samples the measurement accuracy comes from combining the 20% instrumental accuracy of each technique with the precision which is 10% for a single measurement but decreases with the number of individual determinations averaged. The aircraft values were determined in the same way except that the intercomparison results (Hastie *et al.*, 1988) suggested the measurement accuracy was not as good as at the ground sites, consequently a value of 28% was used. When comparing these results with

those of other studies the measurement accuracy should be used. However, when using these data to study concentration variations with time or distance, only the standard deviations need be used, as the same groups are using the same techniques and standards at each site. However, the standard deviation of the average excess particulate SO₄²⁻ exceeds the accuracy of the mean, indicating that the variation in the measured concentrations rather than the measurement accuracy will limit the usefulness of the data.

On the basis of both ground-based and aircraft measurements, the excess particulate-SO₄²⁻ concentrations in the boundary layer at Lewes and Bermuda are the same, with an average value of 42.5 nmol m⁻³. The boundary layer aircraft value at Bermuda, 60 nmol m⁻³, is not significantly different from the Bermuda surface value, as determined by the *t*-test at the 5% level. The decrease in SO₄²⁻ in going from the boundary layer to the free troposphere, both at the east coast and at Bermuda, is significant at the 1% level. The decrease in the free troposphere SO₄²⁻ between the east coast and Bermuda is not significant at the 5% level.

Particulate nitrate

The NO₃⁻ intercomparison (Hastie *et al.*, 1988) showed significant differences between the two groups' data sets and so the assigned measurement accuracies (per cent) are greater than for the SO₄²⁻ data. The particulate NO₃⁻ data for each location given in Table 3 represent the averages of all UMD:UW and AES measurements. The measurement accuracies are

Table 2. Average particulate excess sulphate concentrations (nmol m⁻³)

Location	Mean	Standard deviation	Accuracy	Number of points
East coast				
Lewes, surface	41.1	17	8.2	26
Aircraft, BL	40.0	23	11.2	7
Aircraft, FT	20.0	15	5.6	11
Mid-ocean				
Bermuda, surface	41.2	22	8.2	26
Aircraft, BL	60.1	25	16.8	5
Aircraft, FT	8.4	2.7	2.4	6

Table 3. Average particulate nitrate concentrations (nmol m⁻³)

Location	Mean	Standard deviation	Accuracy	Number of points
East coast				
Lewes, surface	26.7	18	7.5	26
Aircraft, BL	14.3	11	8.6	7
Aircraft, FT	4.1	2.2	2.5	12
Mid-ocean				
Bermuda, surface	14.2	10	4.0	28
Aircraft, BL	9.6	7.3	5.8	5
Aircraft, FT	4.0	1.4	2.4	5

determined as described for the SO_4^{2-} measurements, using instrumental accuracies of 28% for Bermuda data and for Lewes data, and 50% for aircraft data.

The boundary layer particulate NO_3^- data are similar for the Bermuda surface measurements and both the east coast and Bermuda aircraft boundary layer measurements, with an average value of 14 nmol m^{-3} . However, the Lewes surface value is significantly higher at 27 nmol m^{-3} . If only those Lewes event data for days when the aircraft was in the air are selected, the average Lewes surface NO_3^- concentration becomes $18 \pm 11 \text{ nmol m}^{-3}$ which is not significantly different from the above value. This indicates that the particulate NO_3^- in this area is highly variable. (This is not true for SO_4^{2-} . The selection of 'aircraft only' days for the SO_4^{2-} data yields a Lewes value of $37 \pm 16 \text{ nmol m}^{-3}$ which is not significantly different from either the aircraft value or the Lewes value using the full event data set). The free troposphere NO_3^- concentration is significantly lower than any of the boundary layer values, and within the accuracy of these data, appears to be constant at $4 \pm 2 \text{ nmol m}^{-3}$ at the east coast and Bermuda.

Sulphur dioxide

Intercomparison of the filterpack SO_2 measurements from the two systems at Lewes and Bermuda showed no significant differences (Hastie *et al.*, 1988). Consequently the SO_2 filter measurements have been treated in the same way as those of SO_4^{2-} and NO_3^- , by averaging all data together; these values are listed in Table 4. The measurement accuracies are composed of the 20% instrumental accuracy cited by the investigators and an individual measurement precision of 10% which decreases with the number of points averaged. The real-time aircraft SO_2 measurement of Luria *et al.* (1987) did not compare well with the AES filter values. These real-time values are listed in parentheses in Table 4 for completeness. Luria *et al.* (1987) do not quote any accuracy or precision numbers so no measurement accuracy is reported here.

SO_2 concentrations decrease dramatically as we move eastward from the coast. Ground level values

show a 20-fold decrease from 210 nmol m^{-3} at Lewes to only 11 nmol m^{-3} at Bermuda. The aircraft values show the same trend in the boundary layer. At the east coast the free troposphere concentration of 46 nmol m^{-3} is a factor of 3 below the boundary layer value of 146. Both the filter data and the real-time analyzer show a reduction in the free troposphere value from the east coast to Bermuda although there are insufficient data to quantify the decrease.

Nitric acid

The HNO_3 intercomparison (Hastie *et al.*, 1988) showed that the filter systems were not significantly different from each other or from the Tunable Diode Laser System. As the TDLAS was operating only for a small fraction of the measurement time and this time was covered by the filter systems we have not included these data to avoid biasing the data towards that period. The HNO_3 data given in Table 5 are the average of the two filter systems and have a measurement accuracy determined using the cited 20% instrumental accuracy and an individual measurement precision of 10%.

The boundary layer HNO_3 concentration dropped markedly from 33 nmol m^{-3} at Lewes to 3 nmol m^{-3} at Bermuda. The aircraft boundary layer data also show a substantial decrease. There is also a decrease in HNO_3 , by more than a factor of 2, between the boundary layer and the free troposphere at the east coast and although a further drop in the free troposphere concentration from the east coast to Bermuda is indicated this is not statistically significant due to the small number of measurements.

Nitrogen oxides

There was a single nitrogen oxide analyzer at Lewes and a second on the aircraft. NO and NO_x were measured by a chemiluminescent NO monitor with a ferrous sulphate converter. NO_x has been shown to be comprised of NO , NO_2 , and contributions from other nitrates, especially PAN (Fehsenfeld *et al.* (1987)). No intercomparisons were carried out, but the calibration standards were intercompared in the laboratory. The

Table 4. Average gas-phase sulphur dioxide concentrations (nmol m^{-3})

Location	Mean	Standard deviation	Accuracy	Number of points
East coast				
Lewes, surface	209.9	154	42	28
Aircraft, BL	146.5	66	41	4
	(65.1)	35.1		3)
Aircraft, FT	46.3	7.6	13	2
	(32.0)	22.8		4)
Mid-ocean				
Bermuda, surface	10.7	9.7	2.1	21
Aircraft, BL	26.4		7.8	1
Aircraft, FT	28.7		8.5	1
	(15.3)	14.2		3)

Table 5. Average gas phase nitrogen compound concentrations (nmol m^{-3})

Location	Mean	Standard deviation	Accuracy	Number of points
Nitric acid				
East coast				
Lewes, surface	33.1	16	6.6	18
Aircraft, BL	12.8	5	2.6	4
Aircraft, FT	5.1	4	1.0	5
Mid-ocean				
Bermuda, surface	3.0	2.6	0.6	25
Aircraft, BL	3.0	0.4	0.6	3
Aircraft, FT	2.0	0.05	0.4	2
NO				
East coast				
Lewes, surface	79.5	28.1	24	3
Aircraft, BL	145.8		33	1
Aircraft, FT	8.9		2	1
Mid-ocean				
Bermuda, surface				
Aircraft, BL	9.8		2.2	1
Aircraft, FT	23.6	2.8	2.5	1
NO _x				
East coast				
Lewes, surface	318	90	96	3
Aircraft, BL	547	161	122	1
Aircraft, FT	44.2	8.9	9.9	1
Mid-ocean				
Bermuda, surface				
Aircraft, BL	43.6	16.5	8.8	3
Aircraft, FT	23.6	2.8	4.8	3

data from these instruments are presented in Table 5. The measurement accuracies are composed of an individual measurement precision of 10% and instrumental accuracies of 20% on the aircraft and 30% at Lewes (Hastie *et al.*, 1988).

As with SO₂ and HNO₃ there is a marked decrease in the boundary layer NO and NO_x between Lewes and Bermuda and between the boundary layer and the free troposphere at the east coast. The average Lewes concentration was 318 nmol m^{-3} whereas the boundary layer value in the vicinity of Bermuda was only 44 nmol m^{-3} . The aircraft NO_x for the east coast is the result of a single measurement and, when compared to other east coast measurements (e.g. Misanchuk *et al.*, 1987), appears to be anomalously high.

Ozone

Ozone data have been included as an indicator of the total oxidant level in the atmosphere. There were O₃ instruments at Lewes for two weeks and full time on the aircraft. These instruments are regularly calibrated against standards by the operating groups but no intercomparisons were performed. The measurements are given in Table 6; the listed accuracies are the 3 ppbv quoted by the manufacturer. The aircraft data have been corrected for altitude. The average Lewes concentration was 1900 nmol m^{-3} (43 ppbv). The aircraft data show significant increases in O₃ over the ocean between Lewes and Bermuda amounting to 24% in the boundary layer and 6% in the free troposphere.

Table 6. Average ozone concentrations (nmol m^{-3})

Location	Mean	Standard deviation	Accuracy	Number of points
East coast				
Lewes, surface	1897	312	134	6
Aircraft, BL	1945	359	134	5
Aircraft, FT	2166	342	134	7
Mid-ocean				
Aircraft, BL	2521	150	134	3
Aircraft, FT	2298	81	134	3

DISCUSSION

Figure 2 shows the average concentrations of the key N and S species measured at Lewes and Bermuda, along with the values for remote areas. The concentrations reported here for Lewes and Bermuda are higher than those in remote continental and marine areas, respectively, showing the effect of the anthropogenic inputs from North America. Also, different chemical forms of the same element show very different behaviour over the ocean. The concentration of excess particulate SO_4^{2-} in the boundary layer is the same at the East coast and Bermuda, whereas that of particulate NO_3^- decreases by almost a factor of 2. The gas

phase species NO_x , HNO_3 and SO_2 all show substantial decreases (factors of 7, 11 and 20, respectively) over this distance. All species (except particulate NO_3^-) show a decrease in their free troposphere concentrations between the east coast and Bermuda, and (except for SO_2 at Bermuda) a decrease in going from the boundary layer to the free troposphere.

Sulphur

The measurements reported here show that SO_4^{2-} concentrations are higher over the western Atlantic than in remote areas while those for SO_2 at Bermuda are comparable. The average boundary layer excess

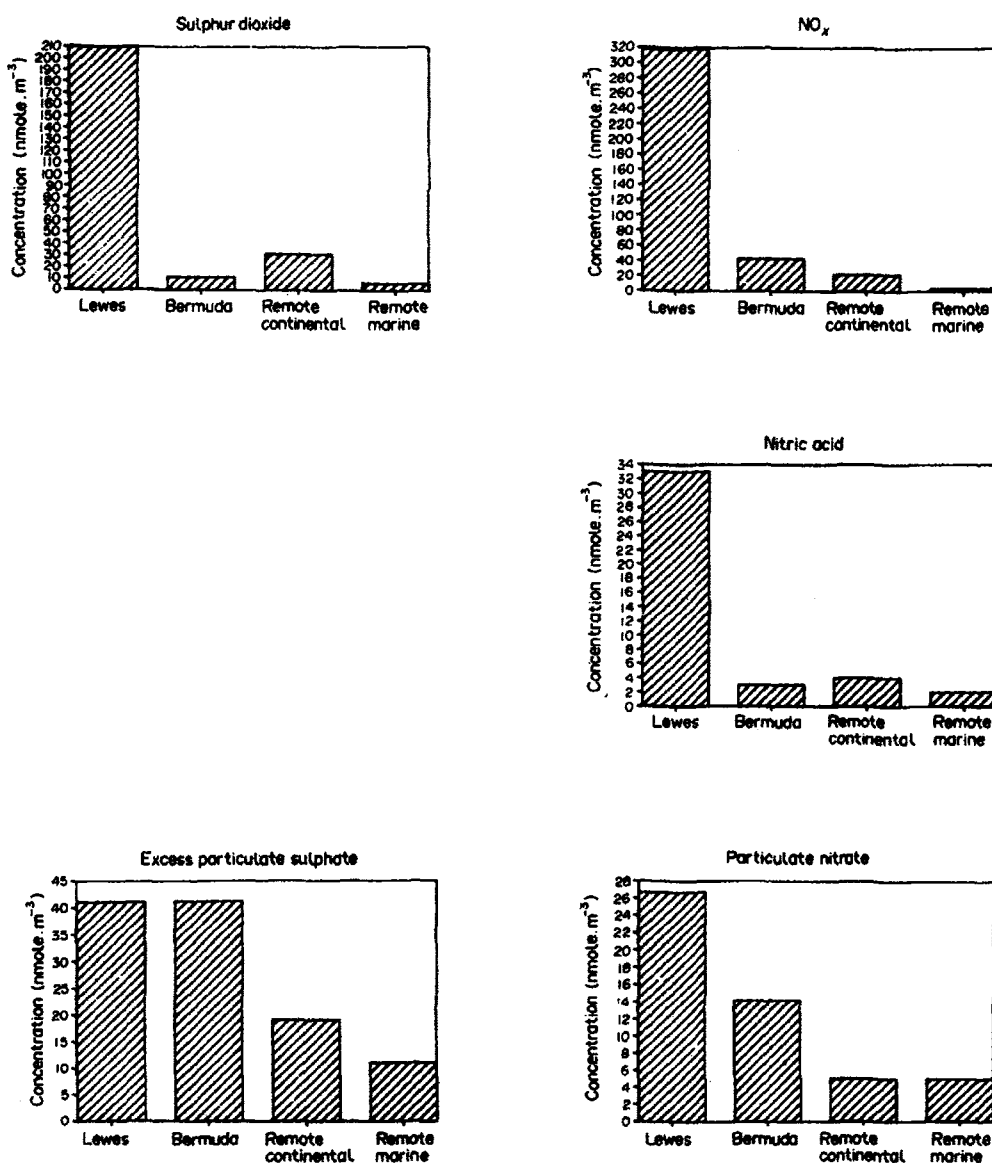


Fig. 2. Average concentrations of S and N species measured at Lewes and Bermuda. Concentrations typical of remote areas are also shown (NO_x from Carroll and Ridley (1984), Kley *et al.* (1981), and Fahey *et al.* (1986); HNO_3 from Logan (1983); nitrate, sulphate and sulphur dioxide from Galloway (1985)).

particulate SO_4^{2-} concentration of 42.5 nmol m^{-3} is much higher than the $0.63\text{--}11 \text{ nmol m}^{-3}$ measured in the remote marine environment (Galloway, 1985; Varhelyi and Gravenhorst, 1983; Ryaboshapko, 1983; Mészáros, 1982; Savoie, 1984). It is also higher than the 19 nmol m^{-3} reported by Ryaboshapko (1983) and Möller (1983) for remote continental areas but in the same order of magnitude as the $31 \pm 15 \text{ nmol m}^{-3}$ reported by Janssen-Schmidt *et al.* (1981) for remote continental areas.

SO_2 concentrations in remote marine environments are reportedly $1.6\text{--}6.3 \text{ nmol m}^{-3}$ (Galloway, 1985; Varhelyi and Gravenhorst, 1983; Ryaboshapko, 1983; Mészáros, 1982; Granat *et al.*, 1976) and in remote continental areas up to 31 nmol m^{-3} (Galloway, 1985; Ryaboshapko, 1983; Granat, 1976; Möller, 1983; Janssen-Schmidt *et al.*, 1981). While the 210 nmol m^{-3} average concentration measured at the east coast is much larger than the remote marine or remote continental values, the mean SO_2 concentration of 11 nmol m^{-3} measured on Bermuda is close to values found in remote areas.

Sulphur is emitted into the atmosphere from the ocean largely in the form of dimethyl sulphide (DMS, $(\text{CH}_3)_2\text{S}$) (NAS, 1984). Grab samples were taken from the aircraft and subsequently analyzed for DMS. Van Valin *et al.* (1987) reported boundary layer DMS concentrations of 1.2 nmol m^{-3} at the east coast and 2.5 nmol m^{-3} at Bermuda. These values are low compared to the boundary layer SO_2 and SO_4^{2-} concentrations, which total 251 and 51 nmol m^{-3} at the east coast and Bermuda, respectively. Close to the east coast, where both SO_2 and SO_4^{2-} greatly exceed DMS, it appears as if S input from the ocean is small in comparison with anthropogenic inputs. With the SO_2 concentration at Bermuda being close to the remote marine value it is possible that at distances of 1000 km or so from the coast, oceanic sources may contribute noticeably to the measured SO_2 concentrations; however, this is not so for SO_4^{2-} .

Wolff *et al.* (1986a,b) report summer and winter SO_2 and particulate SO_4^{2-} measurements from the same sites as this study. Their winter measurements were taken during January and February and so can be

compared directly to those reported here. A comparison of the two data sets (Table 7) shows that the SO_2 , SO_4^{2-} and total S concentrations are not significantly different at Lewes, nor, with the possible exception of SO_4^{2-} , at Bermuda. The design of the two experiments probably contributes to the differences that do appear. Wolff *et al.* sampled in all flow conditions, while our sampling was confined to strong, dry westerly flow following cold frontal passages. The Wolff *et al.* data show a slightly higher loss of total S in going from Lewes to Bermuda, 86% compared to our 79%, consistent with this difference in design (i.e. slower transport and possible wet deposition in the former case). However, we find that the oxidation of SO_2 to SO_4^{2-} is more rapid in our case: the fraction of S as SO_2 in going from Lewes to Bermuda changes from 84% to 21% in this experiment, whereas for Wolff *et al.* it went from 77% to 24%. We cannot tell if these differences are significant.

The concentration of total S shows a large decrease between Lewes and Bermuda—approximately 80% in the boundary layer and 56% in the free troposphere. Although horizontal and vertical diffusion will serve to reduce concentrations on this scale, deposition to the ocean is also likely to be very important. The rapid decrease in SO_2 , particularly in the boundary layer, likely results primarily from dry deposition and oxidation to SO_4^{2-} (since the experiment ruled out wet deposition). The approximately equal values of boundary layer SO_4^{2-} indicate that production and loss terms balance (at least at the distance of Bermuda). Mixing between the boundary layer and free troposphere occurs, but decreasing concentrations with distance in both reservoirs suggests this is not the dominant process. The efficiency of dry deposition over the ocean is uncertain, both because of a paucity of *in situ* measurements and because of an incomplete understanding of all the important processes (e.g. the role of scavenging by sea-salt aerosol (Sievering *et al.*, 1987)). Deposition velocity values summarized by Galloway (1985), viz., 0.7 cm s^{-1} for SO_2 and 0.2 cm s^{-1} for SO_4^{2-} , for open-ocean deposition would indicate that SO_2 removal is more efficient than that of SO_4^{2-} —and our data are consistent with this.

Table 7. Comparison with Wolff *et al.* (1986a, b) data (nmol m^{-3})

Data Source	East coast (Lewes)				Mid-ocean (Bermuda)			
	SO_2	SO_4^{2-}	S	N	SO_2	SO_4^{2-}	S	N
Wolff <i>et al.</i> (1986a,b)	200	59	259		9	28	37	
This paper	± 116	± 38			11	41	52	
	± 43	± 8	251		± 2	± 8		
Wolff <i>et al.</i> (1986a,b)	491	14.3		505	< 39	1.9	8.1	49
This paper	± 240	± 7.1			43.6	3.0	14.2	61
	± 318	± 33.1	26.7	378	± 16.5	± 2.6	± 10	
	± 90	± 16	± 18		(aircraft)			

The behaviour of SO_2 and SO_4^{2-} may be modelled using the following two simplified equations (e.g. Eliassen and Saltbones, 1983):

$$\frac{d[\text{SO}_2]}{dt} = -k[\text{SO}_2] - \frac{v_d}{H}[\text{SO}_2]$$

$$\frac{d[\text{SO}_4^{2-}]}{dt} = +k[\text{SO}_2] - \frac{v_p}{H}[\text{SO}_4^{2-}].$$

The concentrations of $[\text{SO}_2]$ and $[\text{SO}_4^{2-}]$, as a function of time (or distance) are very sensitive to the choice of values for the parameters: k , the transformation rate of SO_2 to SO_4^{2-} ; v_d and v_p , deposition velocities for SO_2 and SO_4^{2-} , respectively; and H , mixing height. Nevertheless, using our measured concentrations from Lewes and Bermuda, along with reasonable values for v_d ($0.5\text{--}1.0\text{ cm s}^{-1}$), v_p ($0.1\text{--}1.0\text{ cm s}^{-1}$) and H ($500\text{--}1500\text{ m}$), provides the following insights:

— SO_4^{2-} concentrations probably reach a maximum somewhere between Lewes and Bermuda;

—rather high values of k ($1\text{--}6\% \text{ h}^{-1}$), v_d ($0.5\text{--}>1\text{ cm s}^{-1}$) and v_p ($>0.3\text{ cm s}^{-1}$) seem necessary to achieve the rapid concentration decay with distance (e.g. a value of $k=3.4\% \text{ h}^{-1}$, and values of $v_d=0.7\text{ cm s}^{-1}$ and $v_p=0.2\text{ cm s}^{-1}$, described as typical by Galloway (1985), do not achieve the observed concentration decrease with distance);

—a value of $v_d > v_p$ seems necessary (e.g. if $v_d = v_p$, a value of 0.64 results, for $H=500\text{ m}$ and $k=4\% \text{ h}^{-1}$).

—the first-order decay distance for SO_2 $\bar{u}(k + v_d/H)^{-1}$, is 340 km, corresponding to a decay time of 12 h for an average wind speed of 8 m s^{-1}

—the first-order decay distance for total S, is 630 km, corresponding to a decay time of 22 h.

We wish to emphasize that the application of such a model is exploratory only; a greatly expanded data set would be required to establish the parameters with confidence.

Previous estimates of decay distances for S over the Atlantic are substantially longer than those calculated above. Whelpdale *et al.* (1987) have used available precipitation SO_4^{2-} concentrations from the North Atlantic as a measure of S in the atmosphere. They find that the concentration decreases with increasing distance from North America consistent with a distance constant of 2400 km and a residence time of 80 h. Church *et al.* (1982) examined precipitation SO_4^{2-} concentrations at Lewes and Bermuda and found less than a factor of 2 decrease in SO_4^{2-} . From this they concluded that of the S leaving North America less than half was lost to the Atlantic Ocean compared to the 80% loss we observe.

The difference between these values based on precipitation measurements, and those calculated here is due to the explicit inclusion of gas-phase SO_2 , which is not well represented by precipitation measurements. The use of precipitation SO_4^{2-} measurements as a

measure of atmospheric S should be restricted to regions containing low SO_2 concentrations. These results suggest a more rapid depletion of atmospheric S in near-coastal regions (i.e. within several hundred kilometers) than previously supposed for the Atlantic Ocean. The SO_2 decay time of 12 h is consistent with published values for other ocean areas (Bonsang *et al.*, 1980, 1987; Nguyen *et al.*, 1975; Prahm *et al.*, 1976; Kritz, 1982; Ito *et al.*, 1986).

Nitrogen

The concentrations of all the N species measured at Lewes were substantially greater than those found in remote marine and continental atmospheres. At Bermuda, particulate NO_3^- and NO_x still show anthropogenic influence, but the HNO_3 values were comparable to those from remote regions.

The average NO concentrations measured were 80 nmol m^{-3} at Lewes and 10 nmol m^{-3} in the boundary layer near Bermuda. These values are very high compared to the marine boundary layer values of 0.04 nmol m^{-3} measured off the coasts of California and Hawaii (Ridley *et al.*, 1987; Davis *et al.*, 1987). The average NO_x at Lewes is 318 nmol m^{-3} and in the boundary layer near Bermuda, 44 nmol m^{-3} . These are also much larger than the boundary layer and free troposphere NO_x concentrations, 0.4 and 4 nmol m^{-3} , respectively, reported by Carroll and Ridley (1984) from measurements off the coasts of California and Hawaii. They also exceed the clean-air, mid-continental NO_x concentrations of 22 nmol m^{-3} (Kley *et al.*, 1981; Fahey *et al.*, 1986; and references therein). Both the Lewes and Bermuda particulate NO_3^- concentrations of 27 and 14 nmol m^{-3} exceed the average remote continental and marine concentrations of 5 nmol m^{-3} (Galloway, 1985). The Lewes HNO_3 concentration of 33 nmol m^{-3} greatly exceeds the 4.3 nmol m^{-3} remote continental estimate of Logan (1983), but the Bermuda concentration of 3 nmol m^{-3} is very close to the marine estimate of 2.1 nmol m^{-3} .

We see less NO_x , comparable NO, but more HNO_3 at Lewes than did Wolff *et al.* (1986a,b) at the same time of year (Table 7). The similarity in the NO concentrations suggests the odd N concentrations are similar for the two missions. Wolff *et al.* used a heated molybdenum converter for their NO_x measurements. This converts N species in addition to NO_2 and PAN and so the measured concentrations would be expected to be higher. A large variability in the N measurements was noted by Hastie *et al.* (1987), so that a comparison based on different measurement periods may well be unreliable. For example there are only three daily averaged HNO_3 data concentrations measured simultaneously with the NO_x (actually from the diode laser system). The average HNO_3 concentration for these 3 days was 21 nmol m^{-3} , i.e. only 64% of the longer term average and within the accuracy of the value of Wolff *et al.* It thus appears that N

concentrations at Lewes are similar to those of Wolff *et al.* (1986a) but different measurement techniques and the large day-to-day variability makes detailed comparisons difficult.

Wolff *et al.* (1986b) quote winter particulate NO_3^- concentrations at Bermuda of 8.1 nmol m^{-3} , significantly lower than our concentration of 14.2 nmol m^{-3} . Their HNO_3 concentration of 1.9 nmol m^{-3} is slightly lower than ours, although both are within the range of remote marine values indicating that all the anthropogenic HNO_3 has been removed. The lower HNO_3 and NO_3^- concentrations of Wolff *et al.* can be explained, at least partially, as with SO_4^{2-} , by the longer time for the air masses to reach Bermuda, and by wet deposition during Wolff *et al.*'s sampling period.

As with S, there is a large decrease in the concentration of total N over the Western Atlantic—by 84% in the boundary layer and 45% in the free troposphere. In the boundary layer NO_x decreases by a factor of 7, HNO_3 by a factor 11 and particulate NO_3^- by a factor of 2; for the free troposphere the values are 2, 2.5 and 1, respectively.

NO_x is lost by dry deposition and oxidation. The deposition velocity for NO_x is less than for SO_2 because of a higher surface resistance to water (e.g. Voldner *et al.*, 1986), with the result that loss by oxidation is probably more important than deposition, and more important for NO_x than SO_2 . The most likely product is HNO_3 through the reaction of NO_2 with OH radicals. The O_3 concentration does not decrease over the ocean so the capacity of the atmosphere to oxidize reduced species does not decrease with distance from the coast. It appears that no additional NO_x is converted to PAN as the NO to NO_x ratio in the boundary layer remains constant. The smaller concentration decrease, relative to SO_2 , is partially a result of less efficient dry deposition.

HNO_3 is lost by deposition to the ocean surface and by conversion to particulate NO_3^- . The fact that HNO_3 concentrations are reduced to remote values at Bermuda despite production from NO_x indicates that this combination of these processes is efficient. The deposition velocity for HNO_3 probably exceeds that for SO_2 , making dry deposition the more efficient sink. Particulate NO_3^- is also lost by dry deposition, possibly more rapidly than SO_4^{2-} because of its larger particle size. In contrast to SO_4^{2-} , particulate NO_3^- decreases by a factor of 2 between the east coast and Bermuda. This is the result of the combination of less efficient production and more efficient removal.

As for S compounds, apparent decay distances and time scales can be derived under the assumption of first-order processes. For NO_x and total N the distance constants are 500 and 550 km, respectively. Assuming a mean wind speed of 8 m s^{-1} gives time constants of 18 and 19 h, respectively. Within the limitations of this first-order assumption and the uncertainty in the measurements, total N is removed slightly more efficiently than total S (19 h cf. 21.5 h)

and SO_2 more efficiently than NO_x (12 h cf. 18 h). Again these values only apply for the conditions of the experiment—viz, in the winter, with a strong westerly flow and the absence of wet deposition.

CONCLUSIONS

The WATOX-85 intensive measurement period produced concentrations of S and N species at Lewes, Delaware, Bermuda and from an aircraft above each of these sites. We examined only those measurements taken behind a cold front, where the air motion was westerly. In this way we could be sure that the air mass sampled at Bermuda was representative of the air-masses being sampled at the E coast.

Over the Western Atlantic Ocean the concentrations of most S and N species are higher than in remote areas, showing the effect of anthropogenic inputs from the North American continent.

For S, we found that the boundary-layer SO_2 concentration decreases by a factor of 20 between the E coast and Bermuda whereas the particulate SO_4^{2-} concentration was the same at both sites. From the decrease in SO_2 and total S concentrations, first-order decay distances of 340 and 620 km, respectively, were determined for dry processes only.

This relatively rapid depletion of S over the Atlantic ocean suggests fairly efficient processes for transformation of SO_2 to SO_4^{2-} and for depletion of SO_2 and SO_4^{2-} by dry deposition. It appears that SO_2 in particular is removed in near coastal environments more quickly than previously supposed.

For nitrogen, NO_x and HNO_3 decrease by close to an order of magnitude between the east coast and Bermuda whereas particulate NO_3^- decreased by only a factor of 2. From the decrease in NO_x and total N concentrations first-order decay distances of 500 and 550 km, respectively were determined. The loss of N over the ocean is consistent with current understanding of atmospheric N chemistry.

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