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Seasonal variations of dimethylsulfide emissions and atmospheric sulfur and nitrogen species over the western north Atlantic Ocean

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ABSTRACT

Seasonal measurements of atmospheric dimethylsulfide (DMS), sulfur dioxide (SO_2), aerosol methanesulfonate (MSA), non-sea salt sulfate (nss-SO_4^{2-}), ammonium (NH_4^+), nitrate (NO_3^-), and other major ions were made between September 1985–September 1986 in the Western North Atlantic Ocean (WNAO). DMS was also measured in surface seawater. In addition, rainwater samples were collected and analyzed for various trace compounds, including dimethylsulfoxide (DMSO) and carboxylic acids. The DMS flux from the open ocean ranged from 1.3 μmol/m^2/d in winter to 5–10 μmol/m^2/d in late summer and fall. The annual DMS flux from the WNAO area is estimated to be 0.1 Tg S/yr. This is a negligible contribution (3%) compared to the advection of sulfur from North America during westerly wind conditions. However, under easterly wind conditions oceanic DMS emissions may dominate the sulfur budget in the WNAO boundary layer. SO_2 and nss-SO_4^{2-} concentrations varied strongly with wind direction. SO_2 levels were as low as 10 pptv in marine air and reached several ppbv in continentally derived air. No significant differences between MSA levels in polluted and relatively unpolluted air were found. The yield of MSA from DMS oxidation may be similar in both air masses. Relatively weak and statistically not significant seasonal variations were observed for MSA, NO_3^-, and MSA/nss-SO_4^{2-} and NO_3^-/nss-SO_4^{2-} ratios. In contrast, NH_4^+ concentrations showed a clear seasonal variation with a maximum in late summer/early fall and a minimum in winter. Oceanic ammonia emissions may be important for marine background levels of ammonia and NH_4^+ in the WNAO atmosphere. Aerosol particles were predominantly acidic with NH_4^+/nss-SO_4^{2-} ratios of 1–2 mol/mol.

1. Introduction

In recent years, results obtained from major field experiments such as the Western Atlantic Ocean Experiment (WATOX) and the Atmospheric Ocean Chemistry Experiment (AEROCE) have shown that the chemistry of the atmosphere over the North Atlantic Ocean is considerably influenced by long-range transport of anthropogenic pollutants from the eastern United States, Europe, and Africa (Galloway and Whelpdale, 1987; Whelpdale et al., 1988; Prospero et al., 1989). In addition, sporadic outbursts of Saharan dust from Africa contribute to high atmospheric loadings of mineral dust particles in the trade wind region. A comparison of measurements over the Atlantic and Pacific Ocean revealed relatively higher atmospheric "background" concentrations of trace gases and aerosol particles over the North Atlantic, even in regions most distant from continents (Prospero and Savoie, 1989; Savoie and Prospero, 1989; Galloway, 1990). It appears that the anthropogenic imprint is detectable almost everywhere in the North Atlantic atmosphere, particularly with respect to aerosol non-sea salt sulfate concentrations. The question then is to

what extent the atmospheric sulfur cycle over the North Atlantic is impacted by continental pollution relative to natural oceanic sulfur emissions. To answer this question we need to have a quantitative estimate for the sea-to-air flux of sulfur from the North Atlantic Ocean.

The dominant sulfur compound emitted from the oceans is dimethylsulfide (DMS) which is produced in seawater by the metabolism of certain algae, bacteria, and possibly other as yet unknown biological processes (Andreae, 1986; 1990). Other biogenic sulfur compounds are emitted at much lower rates (e.g., Saltzman and Cooper, 1988; Kim and Andreae, 1987). Preliminary estimates of DMS fluxes from the Western North Atlantic Ocean (WNAO) resulted in relatively low values (Van Valin et al., 1987) compared to the input of anthropogenic sulfur from the eastern United States (Galloway and Whelpdale, 1987). These DMS fluxes were derived from atmospheric DMS measurements made in polluted air offshore of Boston, Mass. (Van Valin et al., 1987). They are an order of magnitude lower than estimates based on measurements of DMS in seawater made during the spring and fall seasons (Andreae, 1986). Since all previous flux estimates have been derived from measurements made during spring and fall only (Andreae, 1986), there is no information available about DMS emissions from the WNAO in the winter and summer seasons. Therefore, current estimates of the sea-to-air flux of DMS from the WNAO are very uncertain and need to be improved by systematic seasonal measurements of oceanic DMS emissions. Up to now, the only measurements of this kind have been conducted by Bates et al. (1987) in the North Pacific region, and by Turner et al. (1988) and Leck et al. (1990) in nearshore waters of the North and Baltic Seas, respectively.

We report here seasonal measurements of the distribution of DMS in air and seawater in the Western North Atlantic region. We have also measured atmospheric distributions of related aerosol sulfur and nitrogen compounds to study seasonal changes in the chemical cycles of sulfur and nitrogen in the marine atmosphere. Our measurements were made on four ship cruises between September 1985 and September 1986. The results are used to estimate the contribution of DMS emissions to the atmospheric sulfur budget in the study area. We also discuss the relative importance of the sea-to-air flux of DMS compared to the advection of anthropogenic sulfur from the eastern United States.

2. Experimental

The individual cruise tracks are shown in Fig. 1. Cruises I and II were conducted on the R/V Cape Florida during fall (28 September–17 October 1985) and late winter (3–14 February 1986), respectively. Cruises III and IV were conducted on the R/V Columbus Iselin during spring (22 April–3 May 1986) and late summer/early fall (2–13 September 1986), respectively. Port of departure and return was Miami, Florida. Most measurements were made in the region approximately between 25°N–40°N, 70°W, and the east coast of the United States, including coastal areas, the Gulf Stream region, and the Sargasso Sea.

On 26 September 1985, hurricane "Gloria" had passed through the Sargasso Sea area towards North Carolina. In order to examine possible effects of the hurricane on the distribution of DMS in air and seawater we made a straight transect through the path of the hurricane in the beginning of cruise I, and on 4 October returned to the coast (Savannah, Georgia). The next day the ship moved out again for measurements west of the Sargasso Sea (approximately 30°N, 75°W) but on 9 October had to return into port (Cape Canaveral, Florida) because of tropical storm "Isabel" approaching our study area. The remainder of cruise I was conducted in the vicinity of the Bahamas, with hydrocast stations (S1 and S2; Fig. 1, inset) near Grand Bahama Island and in West Providence Channel.

Some estuarine samples were taken on cruise IV in Delaware Bay and Chesapeake Bay as shown in Fig. 1. The remaining track of this cruise was similar to that of cruises II and III, except that cruise IV started out first to the Sargasso Sea and was concluded by returning along the coast to Miami.

The field program was primarily focused on measurements of the distribution of DMS in air and surface seawater. In addition, we measured atmospheric concentrations of sulfur dioxide (SO_2) and concentrations of methanesulfonate (MSA), non-sea salt sulfate (nss-SO_4^{2-}), ammonium (NH_4^+), nitrate (NO_3^-), sodium, and chloride in

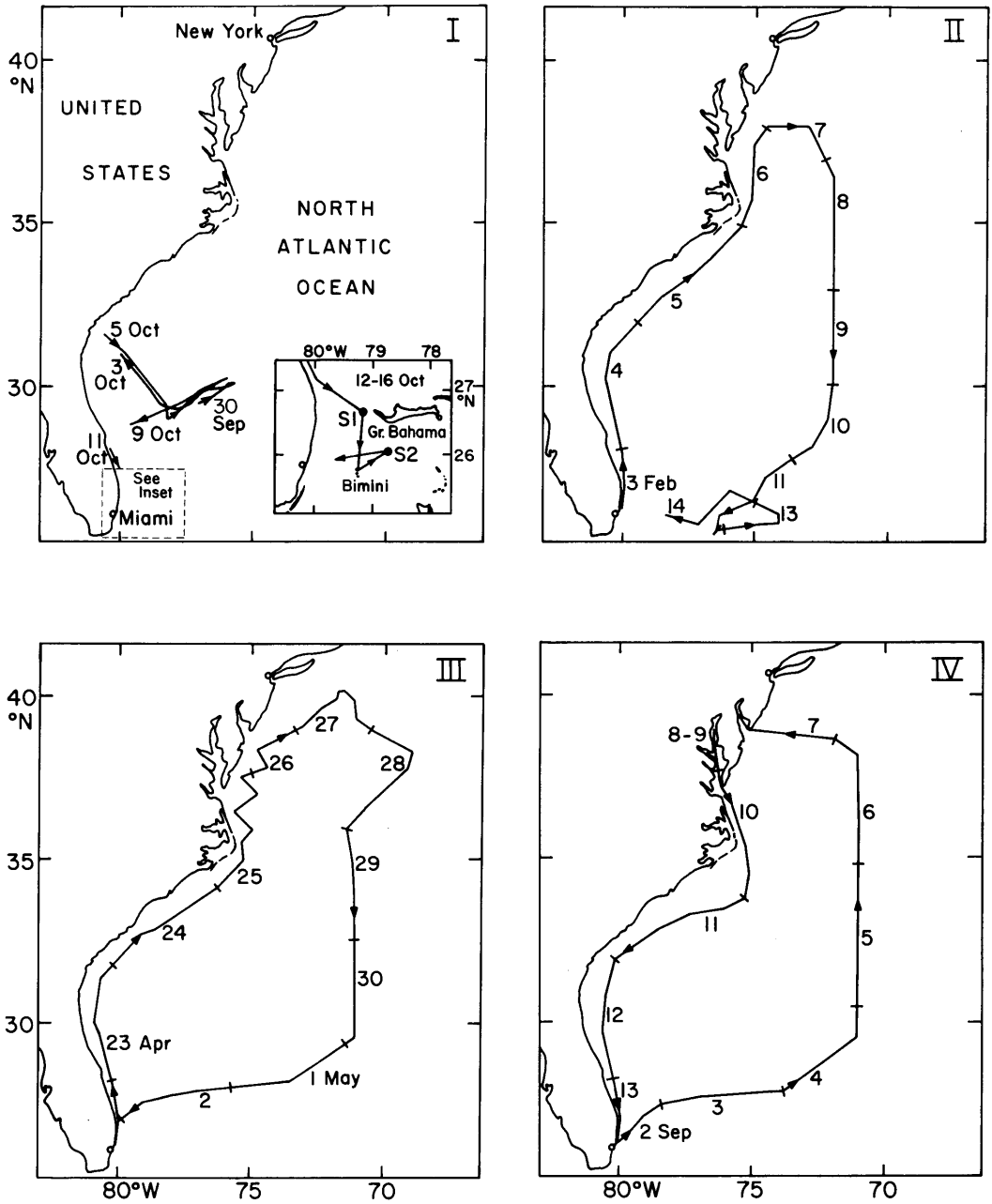

Fig. 1. Map of the study area showing individual cruise tracks and dates indicating the ship's location. Subsequent cruises are ordered by roman numbers (upper right corner of each scheme). The individual cruises took place between 28 Sep.–17 Oct., 1985 (cruise I), 3–4 Feb., 1986 (cruise II), 22 April–3 May, 1986 (cruise III), and 2–13 Sep., 1986 (cruise IV). S1 and S2 indicate two hydrocast stations offshore of the Bahamas Islands.

atmospheric aerosol and rainwater samples. In this study the results obtained for individual compounds measured in the gas phase or in aerosol are reported as mixing ratios in parts per trillion ($ppt = 10^{-12}$). With respect to aerosol compounds, "ppt" means the mixing ratio of each species expressed as "picomole of substance per mole of air"; for gases this unit is equivalent to "pptv". At standard conditions (0°C, 1013 hPa) 22.4 ppt corresponds to 1 nmol/m^3. Aqueous phase concentrations are reported in molar units.

DMS in seawater was sampled and analyzed using a purge-and-trap method described in detail by Andreae and Barnard (1983) and Iverson et al. (1989). Seawater samples were taken from a laboratory flow system with an intake at approximately 3 m below sea level. Aliquots of each sample were filtered into a sample loop (10–15 ml) and then injected into a stripping column where DMS was removed from the water by a continuous flow of helium. DMS was then focused by cryogenic trapping on a column filled with 15% OV3 on Chromosorb W AW-DMCS (60/80 mesh) which was immersed in liquid nitrogen. DMS was separated from other compounds on the same column after removal of the liquid nitrogen and was then determined by flame photometric detection. The detection limit for this method is 0.06 nmol/l for a 15 ml sample. Precision is ±6.2%. Atmospheric DMS samples were taken on the ship's bridge deck approximately 7 m above sea level. DMS was sampled by adsorption on gold "wool" (approximately 2 g of 0.05 mm diameter gold wire) after passing through a scrubber material (5% Na_2CO_3 on Anakrom C22). Sampling flow rates and volumes were between 2–3 l/min and 10–20 l, respectively. Each sample was analyzed within 8 h after sample collection. Previous studies conducted in our home laboratory had shown that DMS is stable on the gold surface for at least 10 days if the samples are stored in the dark. DMS was desorbed from the gold by thermoelectric heating and then trapped and analyzed using the same chromatographic column and detector as described above. The analytical precision of this technique is ±10%. The detection limit is 1 pptv DMS for a 20-l sample. Details of this method have been given by Andreae et al. (1985) and Berresheim (1987).

Aerosol and SO_2 samples were taken from a platform approximately 20 m above sea level. A 3-stage polycarbonate filter unit (Nuclepore) was used containing a 47 mm diameter filter on each stage. The first stage consisted of a Nuclepore filter (nominal pore size: 8 μm; 50% cut-off diameter: ca. 1.5 μm, John et al., 1983), the second stage of a teflon filter (Gelman, nominal pore size: 2 μm). The third stage was used to trap SO_2. It contained a paper filter (Schleicher & Schuell, FF # 2) impregnated with a solution of 25% K_2CO_3 and 10% glycerol. Based on previous laboratory and field tests (see Berresheim et al., 1990; Quinn and Bates, 1989) the SO_2 collection efficiency of the impregnated filters was shown to be >90%. However, these tests did not take into account possible losses of SO_2 which may occur on the first aerosol filter stage due to scavenging by alkaline sea salt particles. In previous intercomparison measurements at shipboard level a good agreement was found between SO_2 samples obtained with high-flow and low-flow filter pack units (Pszenny et al., 1989; Berresheim, 1987). Relative amounts of sea salt collected on aerosol prefilters using the high-flow/high-volume sampling system were typically 1–2 orders of magnitude larger than in corresponding samples taken with the low-flow unit. The results obtained from both types of measurements showed an average difference of less than 10% at typical ambient SO_2 concentrations of 10 pptv, suggesting that SO_2 scavenging on the aerosol prefilters was not significant. In the present study, we used a low-flow filter pack unit similar to that used by Berresheim (1987), with typical sampling flowrates and volumes ranging between 50–70 l/min and 10–50 m^3, respectively. Based on our previous discussion, we estimate that, on the average, 90% of the SO_2 in each air sample was collected on the impregnated filter stage. During sampling a blank filter unit was used side-by-side with the sampling unit. A third stacked filter unit was used at the same location to sample aerosol black (soot) carbon on a 25 mm diameter Nuclepore filter (nominal pore size: 0.8 μm or 1.0 μm). The first stage of this two-stage filter pack contained a 8 μm pore size Nuclepore filter (47 mm diameter) to remove particles of >1.5 μm diameter. The sampling flow rate was between 1–2 l/min. Usually, filter samples were changed at dawn and dusk to provide daytime and nighttime samples. The sampling pumps were operated automatically by a directional air sampling controller (Weathertronics) to avoid contamination

by ship exhausts. Using this device, air was sampled only when the relative wind was blowing from a 180° sector ahead of the ship, at a speed of at least 1 m/s. After sampling, all filters (including blank filters) were placed separately in polycarbonate petri dishes, sealed in polyethylene bags and stored at +4°C. The filters were analyzed in the home laboratory within about 2 weeks after each cruise. Care was taken to minimize uptake of gaseous ammonia from ambient air during handling of the aerosol filters. Exposure of the filters during their analytical preparations we kept to a minimum. Since a glove box was not used for handling, however, and since no control filters preloaded with sulfuric acid were carried through the handling process, the possibility of some uptake of ammonia cannot be rigorously excluded. On the other hand, agreement was found in previous field measurements using the same procedures (Andreae et al., 1988) with results obtained using a very rigorous protocol (Quinn et al., 1988) supporting the validity of our measurements. Nuclepore filters were leached with 10 ml water (deionized; resistivity: 18 megohms-cm), teflon filters with 1 ml methanol and 10 ml water, and impregnated filters were leached with 10 ml of 0.06% H_2O_2 converting all sulfur (IV) to sulfate. The solutions were then analyzed on a Dionex model 2020 ion chromatograph as described by Berresheim (1987). The precision of the aerosol ion measurements was ca. 10%, with the largest uncertainties due to the filter blank corrections. Soot carbon was determined by the reflectance absorption technique of Andreae et al. (1984) in which the decrease of the intensity of light reflected from a loaded filter relative to a blank filter is measured with a differential photometer. The system is calibrated using gravimetrically prepared standard filters loaded with acetylene soot of a particle size similar to the black carbon in atmospheric aerosols. The precision is better than 2% and the accuracy is about 20%. Rainwater samples obtained on cruises I and IV were analyzed by ion chromatography for sulfur, nitrogen, and carboxylic acid ions. Samples were collected on an event basis using polyethylene buckets or bottle/funnel combinations. Chloroform was added immediately after sampling (about 1 ml per 250 ml rainwater) to prevent microbial growth and the resulting loss of organic species in the solution. Dimethylsulfoxide (DMSO) was determined in two rainwater samples using the method described by Andreae (1980).

Wind direction and wind speed, sea surface temperature, and salinity were obtained from each ship's SAIL (Serial ASCII Instrumentation Loop) system. Results from other measurements made in this project have been published elsewhere (Andreae, 1990; Iverson et al., 1989; Kim and Andreae, 1987).

3. Results and discussion

3.1. DMS in surface seawater

The distributions of all sulfur and aerosol nitrogen compounds measured on cruises I–IV are compiled in Figs. 2a and 2b. The top graph in Fig. 2a shows the DMS concentrations measured in surface seawater. A statistical summary of the DMS data is given in Table 1. We present for the first time DMS surface seawater data obtained during the winter season in the WNAO area. Our results obtained in spring and fall compare reasonably well with mean DMS concentrations previously reported by Andreae (1986) for the Florida Atlantic coast (2.8 nmol/l, fall, 1983), Bahamas coast (3.2 nmol/l, fall, 1983), US NE coast (2.1 nmol/l, spring, 1984), Gulf Stream/Sargasso Sea (2.5 nmol/l, fall, 1981; 2.3 nmol/l, fall, 1983), and the temperate North Atlantic (2.1 nmol/l, fall, 1980). Recently, Church et al. (1990) have reported measurements of various atmospheric compounds and of DMS in North Atlantic seawater made on a ship cruise in spring of 1984. Most of the seawater DMS values reported by these authors fall into the same range as our results obtained in spring of 1986 (cruise III, Table 1). However, in some of the temperate regions of the North Atlantic Ocean springtime DMS concentrations in seawater appear to be significantly higher than in the oligotrophic waters of the Sargasso Sea. Church et al. (1990) measured DMS levels of approximately 12 nmol/l near Newfoundland, and Andreae (1986) reported a mean springtime DMS concentration of 4.4 nmol/l for the temperate North Atlantic. In contrast, significantly lower DMS levels were measured in the Sargasso Sea area during our cruise in spring of 1986 (mean: 2.7 nmol/l, Table 1).

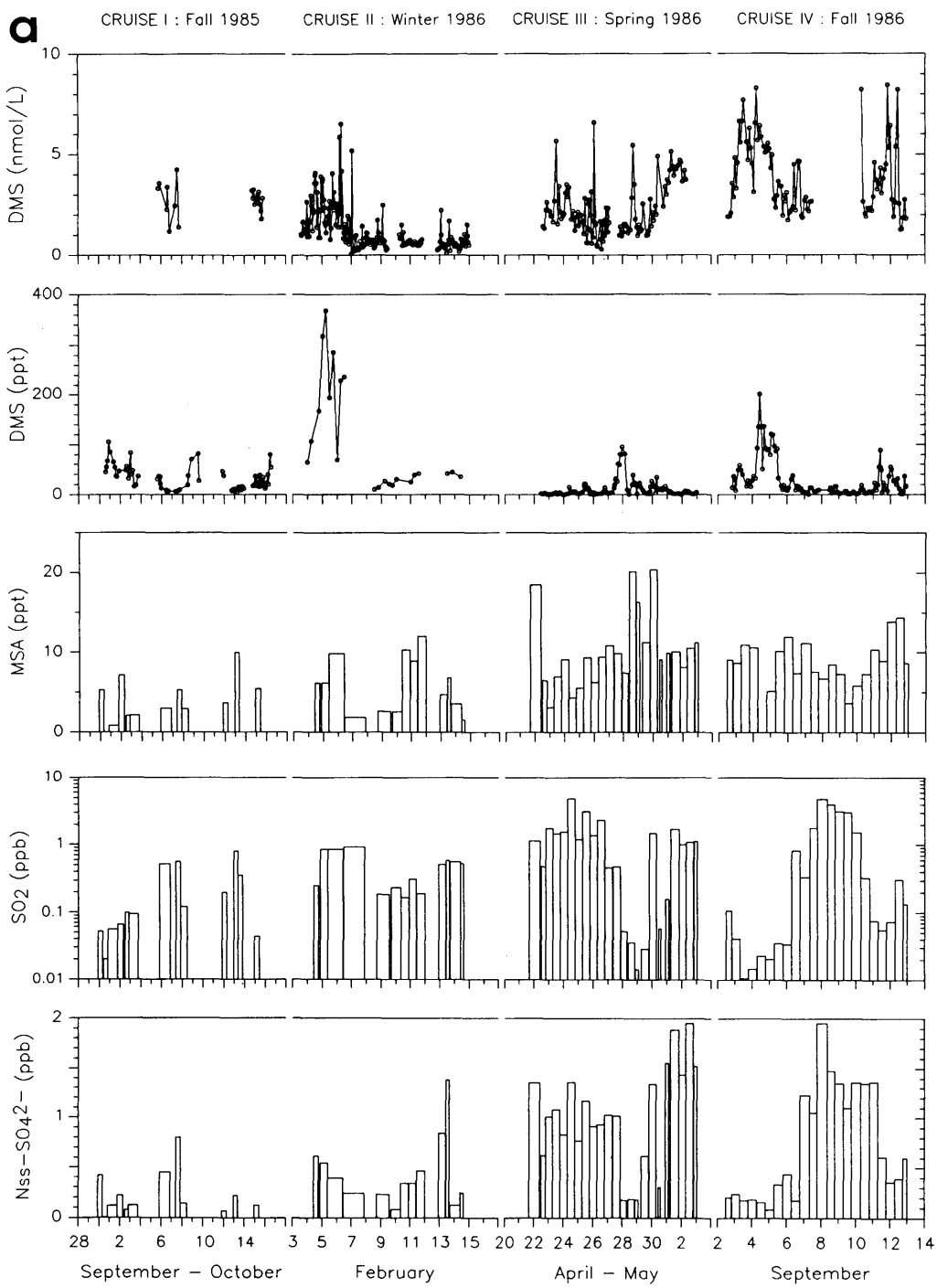

Fig. 2. (a) Distribution of DMS in surface seawater (top graph) and of atmospheric sulfur compounds measured in the WNAO area. Note the logarithmic scale for sulfur dioxide concentrations.

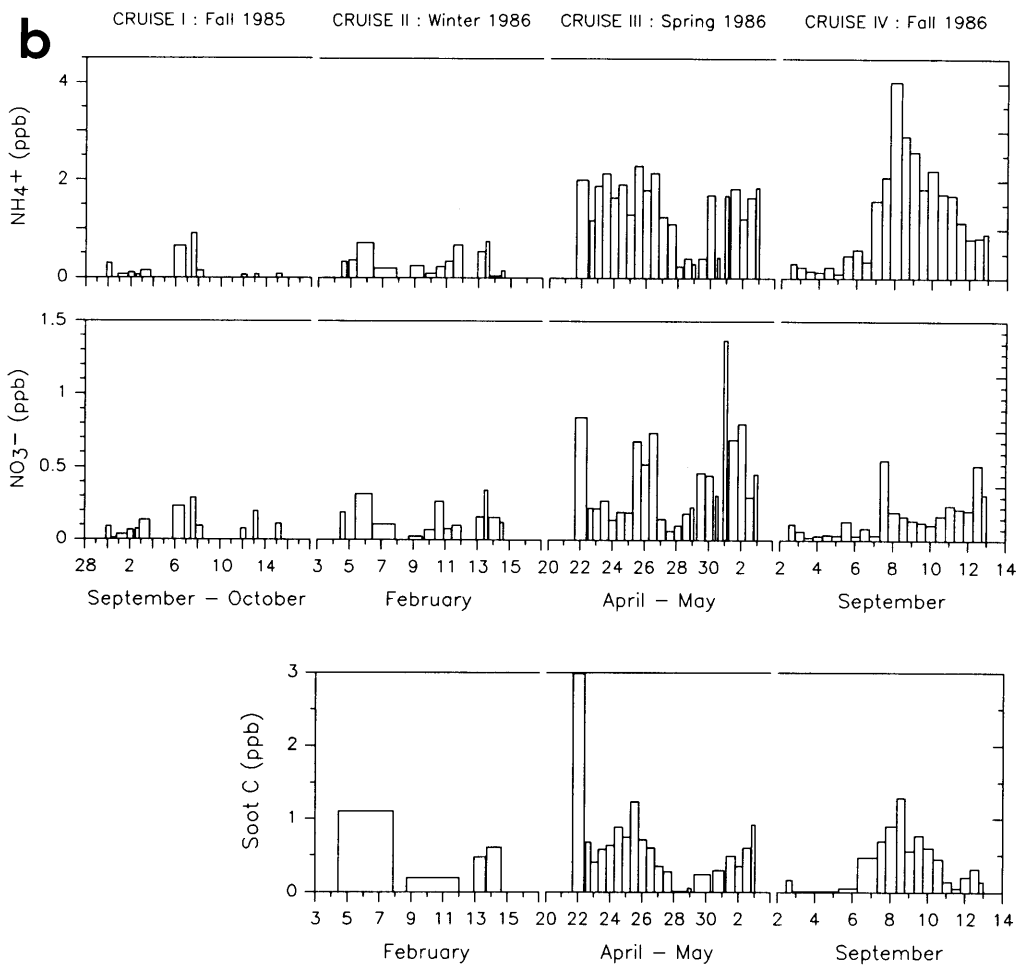

Fig. 2. (b) Distribution of aerosol ammonium, nitrate, and soot carbon measured over the WNAO.

Surprisingly, very few measurements of DMS in WNAO waters have been reported for the summer season. Recently, Cooper and Saltzman (1991) published surface seawater DMS concentrations measured on a cruise between Miami and the Gulf of Maine in the summer of 1987. However, this cruise was conducted only in the coastal shelf region of the WNAO. The individual DMS concentrations ranged from 0.6–2.4 nmol/l, with a mean value of 1.5 nmol/l. These results are similar to our data obtained in coastal waters in spring and early fall of 1986 (Table 1).

Using *t*-tests, we have examined the difference between the mean seawater DMS concentrations listed in Table 1 with respect to (a) season, and (b) biogeographic region (coastal versus open ocean). Results from cruise I were omitted from the calculations because of the low number of DMS data obtained on this cruise. The *t*-tests revealed that seasonal differences between mean DMS concentrations in both coastal and open ocean areas are significant at the 95% confidence level. This agrees with previous studies (Bates et al. 1987, Turner et al., 1988, Leck et al., 1990) reporting a significant annual variation of surface seawater DMS concentrations in other coastal and open ocean regions of the world. This variation appears to be most pronounced in temperate

Table 1. *Statistical summary of DMS data from cruises I–IV; concentration units are nmol/l for DMS (sea) and pptv for DMS (air)*

			Coastal shelf*				Open ocean			
Compound	Cruise	Season	Median	Mean	Concentration range	Number of samples	Median	Mean	Concentration range	Number of samples
DMS (sea)	I**	fall	3.5	3.5	3.3–3.6	2	2.4	2.5	1.2–4.3	6
	II	winter	1.8	2.1	0.1–6.5	81	0.6	0.7	0.1–2.5	141
	III	spring	1.7	1.9	0.3–6.6	67	2.4	2.7	1.0–5.5	47
	IV***	fall	2.8	3.4	1.3–8.3	37	4.4	4.1	1.8–8.3	50
DMS (air)	I**	fall	36.6	40.3	17.1–81.9	13	44.4	42.3	4.0–105.5	27
	II	winter	211.5	203.9	64.0–368.0	10	26.2	27.9	10.2–44.1	13
	III	spring	3.2	5.9	<0.3–30.9	74	6.5	16.4	0.4–94.4	65
	IV	fall	16.5	23.1	1.3–89.2	32	30.3	46.4	<0.3–201.1	51

* Average extension of coastal shelf from eastern US shoreline: ca. 150 km.
** Bahamas coast data not included (mean values: 2.6 nmol/l, 21.5 pptv, respectively).
*** Estuary data for DMS (sea) published by Iverson et al. (1989) are not included.

latitudes showing a maximum in both coastal and open ocean regions in mid-summer. Our results from this study (Fig. 2a) show that DMS concentrations in the WNAO area in late summer/early fall are relatively high and comparable to the mid-summer values reported by the aforementioned authors for other oceanic regions. Spring and wintertime concentrations observed in coastal waters were found to be not significantly different from each other (based on the 95% confidence level). The data indicate a relatively early development of biological activity in coastal waters producing elevated DMS concentrations already before the beginning of the spring season. On the other hand, concentrations in the open ocean waters of the Gulf Stream region and the Sargasso Sea are significantly lower in late winter than in the spring season.

Regional (coastal versus open ocean) differences in mean DMS concentrations were found to be significant at the 95% level for the winter and spring season. However, the data show no consistent annual differences between DMS concentrations in both regions. In winter, average DMS concentrations were higher in coastal relative to open ocean waters whereas reverse conditions were observed in spring. No significant differences were found between DMS concentrations in these areas for the late summer/early fall season (cruise IV). As mentioned previously, at that time of the year DMS production in seawater appears to be still near its mid-summer maximum in both regions.

In summary, our results from cruises II–IV (Table 1) indicate the following: 1. Mean sea surface DMS concentrations increase from late winter through early fall. This increase is rather moderate in coastal waters (factor 1.7) and more pronounced in open ocean waters (Sargasso Sea; factor 2.9). 2. DMS concentrations in open ocean waters show a relatively higher seasonal amplitude. They are lower in late winter and higher in late summer/early fall compared to the concentrations in coastal waters. 3. On a yearly average basis, no significant regional differences were found between DMS concentrations in coastal and open ocean waters.

3.2. DMS in the atmosphere

Atmospheric DMS distributions are shown in Fig. 2a and a data summary is given in Table 1. The concentrations were strongly dependent on wind direction indicating different origins of air masses advected to the sampling area. Isobaric ten-day back trajectories were calculated for 1000 hPa, 850 hPa, and 700 hPa levels (J. Harris, personal communication, 1990) to determine the source regions of the individual air masses. Both trajectory analyses and results obtained from aerosol soot carbon measurements (Fig. 2b) made it possible to roughly classify individual air

masses into two major source categories: (a) air masses with *predominantly continental* origin (soot carbon level >10 ppt), and (b) air masses with *predominantly marine* origin (soot carbon level $\leqslant 10$ ppt). It was frequently observed that DMS levels dropped sharply when the surface wind turned to a westerly direction and predominantly continental air was advected. A clear example are the measurements made between 6–8 October, 1985 (cruise I; Fig. 2). The passage of a cold front on 5 October brought abrupt changes in surface wind speed and direction from light easterly (1–5 m/s) to relatively gusty WNW (5–13 m/s) wind. Atmospheric DMS levels dropped immediately. It cannot be excluded that enhanced vertical mixing processes may have partially contributed to this decrease in DMS concentrations. Unfortunately, no soot carbon data are available from this cruise. However, corresponding trajectories and the significant increase in nss-SO_4^{2-}, NH_4^+, and NO_3^- levels observed during the same period (Figs. 2a, 2b) clearly indicate the continental character of the associated air mass. Much higher DMS levels and, conversely, lower levels of nss-SO_4^{2-}, NH_4^+, and NO_3^- were again measured on 8–9 October when the ship was near the Florida coast and strong winds were blowing from ESE due to the approach of tropical storm "Isabel". Andreae et al. (1985) reported similar dramatic effects on atmospheric DMS levels observed on a cruise in the Bahamas area which were caused by the passage of a front and corresponding changes in air mass character. Clearly, atmospheric DMS concentrations over the WNAO area are very low when air is advected from the U.S. continent. This has been observed previously by Andreae and coworkers, Van Valin et al. (1987), Church et al. (1990), and Cooper and Saltzman (1991). Another clear example from our present data set are the measurements made during cruise III (Fig. 2a). Throughout most of the cruise, with the exception of 27–28 April, predominantly continental air was advected to the sampling region at fairly constant speed (3–5 m/s). Median atmospheric DMS levels near the U.S. east coast and over the open ocean were 3.2 and 6.5 pptv, respectively (Table 1). Excluding the high values from 27–28 April mean DMS levels in both regions were 5.9 and 9.2 pptv, respectively. The difference between the two means is statistically significant (95% confidence level). As one might expect, this suggests that the impact of continental air on marine atmospheric DMS levels decreases with transport time and distance from the coast. The only measurements on this cruise showing relatively high DMS concentrations in the air were made on 27–28 April when the ship was located southwest of the center of a low pressure system (Fig. 3). As suggested by the isobars and wind data shown in Fig. 3 air masses advected to this region were predominantly from open ocean areas east of the low pressure system. This conclusion is strongly supported by the corresponding 1000 hPa level trajectories and the very low concentrations observed for soot carbon during the same period (Fig. 2b) and is also consistent with simultaneously low SO_2, nss-SO_4^{2-}, NH_4^+, and NO_3^- concentrations (Figs. 2a, 2b). Only the free troposphere trajectories (700 hPa level) indicated advection of continental air from North America. In summary, the results from cruises I and III clearly show that atmospheric DMS levels over the WNAO are highly dependent on air mass charac-

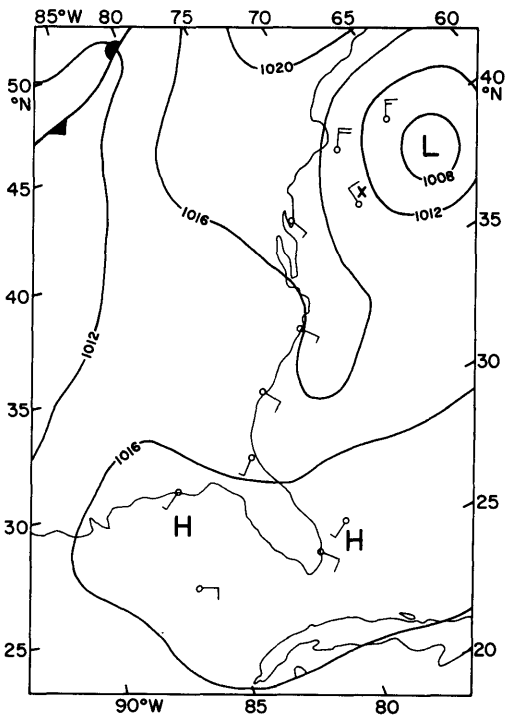

Fig. 3. Surface weather map for 27 April, 1986, 20.00 EST. The X marks the ship's location at that time.

ter and can increase just as sharply as they can drop due to changes in wind direction and corresponding type of air mass. Such conditions make it extremely difficult to distinguish between the relative contributions of chemical and meteorological processes to the observed atmospheric distributions and diel cycles of DMS. Atmospheric DMS levels over the WNAO strongly depend on the degree of mixing of continental air with marine air. Continental air from eastern North America usually contains relatively high concentrations of ozone and radical species (OH, NO_3) or their corresponding precursors causing rapid photooxidation of DMS in the marine atmosphere. Despite significant DMS concentrations in surface seawater the overlying atmosphere can be almost completely depleted of DMS in relatively polluted air, as shown, e.g., by the estuarine (Delaware/Chesapeake Bay) measurements made on cruise IV (Figs. 1 and 2a; see also Iverson et al., (1989)). Similar observations and conclusions have been reported by Cooper and Saltzman (1991).

Because of the important role of different air masses and their corresponding effects on atmospheric DMS chemistry we found very little correlation between atmospheric and seawater DMS levels in all of the four different measurement periods. Church et al. (1990) reported a similar weak correlation for springtime based on their measurements in 1984. A qualitative correlation between both DMS data sets is indicated in our Bahamas data from cruise I, the data obtained from cruise II, and the data obtained from the first part of cruise IV (Fig. 2a). Atmospheric and seawater DMS concentrations measured on cruise I did not indicate a major influence caused by the hurricane conditions preceding this cruise. However, our measurements were made approximately four days after the storm had passed through the area. Four days may have been a sufficient time for pre-storm DMS concentrations to be reestablished in this region. Short-term dramatic changes both in seawater and atmospheric DMS levels may have occurred during the passage of the storm. Atmospheric DMS concentrations measured in the late winter season (cruise II) were extremely different over coastal and open ocean areas (Fig. 2a). Very high DMS concentrations (the highest with respect to all cruises) were measured off the Georgia and South Carolina coastlines (maximum: 370 pptv). This is consistent with the average DMS emission rate calculated for this part of the cruise (see next section) and with high pressure weather conditions in the area indicating relatively little vertical mixing of the air. The DMS flux from coastal waters was found to be more than a factor of 2 higher for this cruise than corresponding fluxes calculated for all other cruises (Table 2). DMS levels over the open ocean were quite low, during both easterly and westerly wind conditions (8–10 February and 11–14 February, respectively). This is consistent with relatively low seawater DMS concentrations in the Sargasso Sea during late winter (Fig. 2a).

3.3. *Seasonal and annual emission of DMS from the western North Atlantic Ocean*

Following the stagnant film algorithm described by Berresheim (1987) we have calculated indi-

Table 2. *Calculation of seasonal DMS fluxes from the Western North Atlantic Ocean*

Cruise	Season	Coastal shelf				Open ocean			
		u (ms^{-1})	T (sea) (°C)	D ($10^{-5}\,cm^{-2}\,s^{-1}$)	DMS flux ($\mu mol\,m^{-2}\,d^{-1}$)	u (ms^{-1})	T (sea) (°C)	D ($10^{-5}\,cm^{-2}\,s^{-1}$)	DMS flux ($\mu mol\,m^{-2}\,d^{-1}$)
I*	fall	4.4	26.6	1.14	3.3	8.7	26.8	1.14	10.0
II	winter	8.5	24.5	1.09	7.6	6.0	23.8	1.06	1.3
III	spring	7.1	10.0	0.71	3.1	5.1	21.5	1.00	3.4
IV	fall	3.9	27.0	1.16	2.2	4.5	29.0	1.22	4.7

* Bahamas coast data not included (mean DMS flux in fall: 2.7 $\mu mol\,m^{-2}\,d^{-1}$).
The symbols u, T (sea), and D denote mean wind speed, mean surface seawater temperature, and mean molecular diffusivity of DMS in seawater, respectively.

vidual DMS fluxes from the WNAO for each season of the year (except for summer). Mean values of the model parameters, i.e., wind speed, u, and surface seawater temperature, T (sea), and DMS concentration in surface seawater, DMS (sea), are shown in Tables 1 and 2, respectively. The results are given in Table 2. The calculated fluxes are uncertain by at least a factor of two. The major uncertainties arise from 1. basic model assumptions, 2. the relative standard deviations of the individual model parameters, and 3. values used for the molecular diffusivity, D, of DMS in seawater as a function of T (sea). Nevertheless, the calculated fluxes are useful for at least a rough assessment of the seasonal variation of DMS emissions to the WNAO atmosphere and the relative importance of these emissions compared to continentally derived sulfur exported from the eastern United States. Despite the inherent uncertainties in the calculations we believe that our present estimates represent a significant improvement relative to previously reported DMS fluxes for the WNAO area. Previous flux estimates were either inferred indirectly from atmospheric DMS measurements (Van Valin et al., 1987) or from DMS (sea) data representing spring and fall conditions only, and pertained mostly to regions with relatively high primary productivity (Andreae, 1986). In addition, in our study we obtained a much larger data set for the WNAO area compared to previous more area-expansive studies over the Atlantic Ocean.

Our calculations for the open ocean WNAO region (Table 2) indicate a significant increase of mean DMS emissions from winter through spring and early fall. The relatively high flux in late summer/early fall results from a combination of relatively high values of all major flux parameters—DMS (sea), T (sea), and mean wind speed, u—in this season. DMS emissions during mid-summer are presumably lower due to low wind speeds caused by the Bermuda high pressure system which dominates the weather in most of the WNAO area during this season.

Based on the results given in Table 2 we may now estimate the mean annual sea-to-air flux of DMS from the WNAO area (defined by 30°N, 60°W, and the U.S. east coast; see Galloway and Whelpdale, (1987)). We neglect the coastal shelf data in our estimate because of the relatively small area of the coastal region compared to the open ocean area of the WNAO. Also, data obtained from cruise I are not included in the following discussion because of the relatively low number of samples obtained on that cruise. In order to estimate a mean annual DMS emission rate we have assumed the individual fluxes obtained from cruises II, III, and IV to represent typical winter, spring, and fall conditions, respectively. Each season has been assumed to have a duration of 3 months. Simple linear interpolation of the data yields a mean summertime DMS flux of 4.1 μmol/m^2/d. From this estimate and the flux values calculated for the other three seasons (Table 2), we obtain a mean annual DMS emission from the WNAO of approximately 3.4 μmol/m^2/d. This rate agrees remarkably well with previous gross estimates by Galloway and Whelpdale (1987; 3.4 μmol/m^2/d) and Warneck (1988; 3.6 μmol/m^2/d) which were based on only very few available data. Most of our open ocean measurements have been made in oligotrophic regions of the WNAO where surface seawater DMS concentrations are often lower than in temperate regions, especially during springtime (see Andreae (1986)). Therefore, the average DMS flux derived in this study should be considered as a minimum estimate. Galloway et al. (1990) and Pszenny et al. (1990) adopted a range of 2–10 μmol/m^2/d for the DMS flux from the WNAO. Based on our flux estimate derived in this study and an estimated area of the WNAO of 2.3×10^{12} m^2 (Galloway and Whelpdale, 1987), the total biogenic sulfur flux from the WNAO is approximately 0.1 Tg S/yr. Since this is a minimum estimate, we assume it may range as high as 0.3 Tg S/yr. This flux represents about 3–10% of the average sulfur flux from the eastern U.S. continent to the WNAO atmosphere (3–4 Tg S/yr) estimated by Galloway and Whelpdale (1987). Therefore, it appears that the atmospheric sulfur budget over the WNAO area is clearly dominated by the continental sulfur input from North America. This is consistent with recent calculations by Cooper and Saltzman (1991) who estimate that the total flux of natural sulfur (including biogenic DMS, SO_2, and nss-SO_4^{2-}) from the WNAO atmosphere to the United States during easterly flow is less than 10% of the transport of anthropogenic sulfur in the reverse direction during westerly flow. On the other hand, our atmospheric DMS measurements indicate that biogenic sulfur emissions from the ocean may be

an important source for sulfur in the WNAO atmosphere during easterly wind conditions. Similarly, Church et al. (1990) conclude from their measurements that levels of biogenic DMS are high enough to account for most of the non-sea salt sulfate in marine "background" air over the North Atlantic in spring. Based on atmospheric measurements in summer of 1988, Galloway et al. (1990) calculated a total sulfur deposition flux of 14 μmol/m^2/d to the WNAO for easterly wind conditions. Therefore, similar to Galloway et al. (1990) we conclude that under easterly flow conditions DMS emissions may contribute up to 75% to the sulfur budget over the WNAO. The remaining 25% (or higher) may be contributed from continental sources due to large-scale mixing of continental air with marine background air in the North Atlantic boundary layer.

3.4. *Sulfur dioxide, and aerosol sulfur and nitrogen compounds*

The distributions of sulfur and nitrogen compounds measured in the study area are shown in Figs. 2a and 2b, respectively. Tables 3 and 4 present a statistical overview of the results obtained from SO_2 and aerosol sulfur and nitrogen measurements, including concentration ratios. As previously discussed the data have been classified by air mass based on shipboard measurements of wind direction, wind speed, and soot carbon concentrations. In the following sections the data are discussed in detail with respect to the corresponding air mass category, as well as seasonal, diel, and regional variations, and particle size distributions of individual aerosol compounds.

3.4.1. Advection of continental air: Impact on sulfur and nitrogen concentrations in the marine atmosphere. Above, we discussed the impact of continental air on DMS concentrations in the marine atmosphere. We estimated that under westerly wind conditions approximately 97% of the amount of sulfur in the WNAO atmosphere is contributed from the eastern United States, mainly in the form of SO_2 and nss-SO_4^{2-}. As shown in Table 3, the average concentrations of both compounds in predominantly continental air were clearly higher than in marine air advected from the open ocean. Mean nss-SO_4^{2-} to total sulfate fractions in both air categories were 92 ± 10% and 76 ± 15%, respectively. These concentration differences in both air masses were observed in each season, particularly in spring (cruise III). The late summer/early fall median SO_2 and nss-SO_4^{2-} concentrations obtained in marine "background" air (Table 3, cruise IV) are similar to corresponding values measured by Galloway et al. (1990) in summer of 1988 in air masses advected from the central and tropical North Atlantic (72 ppt and 246 ppt, respectively). As discussed in several recent articles (e.g., Pszenny et al., 1990; Galloway et al., 1990; Church et al., 1990) these "background" levels are still significantly higher than over other remote ocean areas (e.g., Savoie and Prospero, 1989; Berresheim et al., 1990) indicating a ubiquitous anthropogenic SO_2 and nss-SO_4^{2-} signal in the North Atlantic atmosphere. Previous measurements of SO_2 and nss-SO_4^{2-} concentrations over the WNAO were mostly made in continental air advected from North America. Median values were found to be 490 ppt and 560 ppt, respectively (Galloway and Whelpdale, 1987). Church et al. (1990) measured similar nss-SO_4^{2-} concentrations (ca. 200–1000 ppt) in continental air over the WNAO during spring of 1984. As shown in Table 3, our seasonally corresponding results agree well with the previously published data. Concentrations reported by Galloway and Whelpdale (1987) for the eastern shoreline of North America between 28°–47°N (1.5–5.9 ppb and 1.2–1.5 ppb, respectively) are comparable to our results obtained in polluted air in the Delaware and Chesapeake Bay area (cruise IV).

As discussed in Subsection 3.2 relatively abrupt changes from polluted to "clean" air conditions can occur in the WNAO boundary layer in connection with low pressure systems moving over the ocean. This was observed, for example, on 27 April when the ship was located on the backside of a low pressure system (Fig. 3). On the same day soot carbon concentrations decreased sharply from 12.5 ppt to less than 0.8 ppt, and SO_2 and nss-SO_4^{2-} levels dropped from 456 to 48 ppt and from 1030 to 168 ppt, respectively. On the other hand, DMS concentrations increased significantly to a maximum of 94 ppt on 27 April (Fig. 2a). Both vertical mixing processes and advection of marine air from the frontside of the system may have contributed to these results. Late on 29 April relatively polluted air was dominant again, DMS levels were low, the soot carbon concentration increased to 11 ppt, and SO_2 and nss-SO_4^{2-} levels

Table 3. *Statistical summary of SO_2 and aerosol sulfur, nitrogen, and soot carbon data (ppt)*

Cruise	Season	Statistic	Soot carbon	N	MSA	SO_2	Nss-$SO_4^=$	NH_4^+	NO_3^-	100 * MSA/ Nss-$SO_4^=$	NH_4^+/ Nss-$SO_4^=$	NO_3^-/ Nss-$SO_4^=$
Dominant air mass: MARINE												
I	fall	mean	NA	10	3.7	110.0	142.9	119.6	75.9	2.7	0.8	0.8
		SD	NA		2.0	94.1	111.9	75.4	35.1	1.5	0.2	0.5
		median	NA		3.3	79.5	120.0	90.6	75.7	2.4	0.8	0.9
II	winter	mean	8.7	4	6.1	225.7	324.1	221.1	144.7	1.8	0.7	0.5
		SD	···		3.5	56.7	123.2	88.1	124.0	0.5	0.1	0.3
		median	···		5.8	210.7	356.4	232.1	96.7	1.9	0.7	0.4
III	spring	mean	<2.5	5	12.9	37.9	293.2	349.9	256.0	5.8	1.4	0.9
		SD	···		4.7	15.8	168.7	72.3	123.7	3.5	0.5	0.2
		median	···		11.3	36.0	186.0	398.4	226.3	4.2	1.4	1.0
IV	fall	mean	4.1	16	9.9	150.7	491.1	701.1	186.9	3.3	1.4	0.5
		SD	3.2		2.4	205.4	421.2	552.8	175.2	1.9	0.4	0.4
		median	2.5		10.1	63.9	343.7	528.3	128.0	3.6	1.4	0.4
Total*		mean	3.8	35	8.3	131.5	350.2	448.8	162.7	3.3	1.2	0.6
		SD	3.5		4.4	157.4	337.7	465.0	149.7	2.4	0.5	0.4
		median	2.5		8.8	65.0	211.6	289.0	99.7	2.9	1.2	0.6
Total, DAYTIME		mean		15	10.1	163.2	333.6	514.6	222.4	3.7	1.4	0.8
		SD			4.1	210.3	326.5	446.0	181.8	2.6	0.5	0.5
Total, NIGHTTIME		mean		17	8.2	107.1	375.3	450.9	130.7	3.5	1.1	0.5
		SD			3.8	99.5	365.9	497.7	107.6	2.2	0.4	0.3
Dominant air mass: CONTINENTAL												
I	fall	mean	NA	3	6.1	626.4	488.8	541.0	237.6	2.0	1.0	0.6
		SD	NA		2.9	123.3	238.8	347.7	37.9	1.9	0.5	0.2
		median	NA		5.3	559.1	451.4	642.2	230.2	0.7	1.1	0.5
II	winter	mean	32.5	9	5.8	583.1	649.0	414.0	247.8	1.1	0.7	0.5
		SD	14.7		3.3	242.0	371.4	246.9	117.0	0.7	0.4	0.3
		median	27.1		6.1	557.8	563.5	355.9	207.8	0.8	0.5	0.3
III	spring	mean	34.7	18	9.4	1475.9	1210.2	1700.1	459.6	0.8	1.5	0.4
		SD	27.5		4.2	1050.9	359.6	350.5	330.0	0.3	0.4	0.2
		median	27.5		9.4	1274.4	1125.8	1749.5	371.3	0.7	1.4	0.3
IV	fall	mean	29.8	5	6.4	3316.6	1447.9	2714.4	194.8	0.4	1.8	0.1
		SD	13.0		1.6	1101.0	281.1	748.4	41.0	0.1	0.2	0.0
		median	25.9		6.7	3154.3	1357.2	2581.7	183.0	0.4	1.9	0.1
Total*		mean	32.2	30	8.0	1123.1	969.7	1198.4	378.2	1.0	1.2	0.4
		SD	24.5		4.2	931.9	461.9	694.9	287.0	0.8	0.6	0.3
		median	26.7		7.6	886.2	934.3	1227.4	251.5	0.7	1.2	0.4
Total, DAYTIME		mean		13	7.6	1343.3	1068.4	1312.9	341.4	0.8	1.2	0.3
		SD			2.8	1298.5	481.4	700.5	217.4	0.4	0.6	0.2
Total, NIGHTTIME		mean		14	9.1	995.5	988.3	1238.5	441.2	1.2	1.2	0.5
		SD			4.9	447.2	419.4	673.6	353.5	1.0	0.6	0.3

NA = Data not available; N = number of aerosol/SO_2 samples; SD = standard deviation.
* Estuary data from cruise IV are not included.

Table 4. *Regional variation of annual mean aerosol sulfur, nitrogen, and sea salt concentrations (ppt)*

Category	Statistic	N	MSA	SO_2	Nss-$SO_4^=$	NH_4^+	NO_3^-	SO_2/ Nss-$SO_4^=$	100 * MSA/ Nss-$SO_4^=$	NH_4^+/ Nss-$SO_4^=$	NO_3^-/ Nss-$SO_4^=$	Na^+	EF(Cl)
Continental Air/	mean	6	6.6	3060.3	1382.4	2607.2	285.2	2.2	0.5	1.9	0.2	195.3	0.28
Estuaries	SD		1.5	1157.0	295.4	724.0	205.6	0.6	0.1	0.2	0.2	267.4	0.19
	median		7.0	3105.6	1352.6	2401.1	201.0	2.4	0.5	1.9	0.1	86.6	0.26
Continental Air/	mean	17	7.9	1430.9	891.6	1357.6	361.5	1.7	1.1	1.4	0.4	999.4	0.44
Coastal	SD		3.7	1077.5	340.3	735.1	227.9	0.9	1.0	0.6	0.3	1116.3	0.26
	median		7.0	1149.6	911.5	1645.6	251.5	1.6	0.8	1.5	0.3	524.0	0.53
Continental Air/	mean	13	8.1	720.6	1071.9	990.2	411.5	0.9	0.9	0.9	0.4	1327.8	0.43
Open Ocean	SD		4.7	447.3	567.8	575.6	346.1	0.8	0.6	0.3	0.3	734.1	0.24
	median		8.1	557.8	1019.2	907.2	287.3	0.7	0.6	1.0	0.4	1055.7	0.51
Marine Air/	mean	11	8.4	160.5	517.2	769.4	268.6	0.6	2.8	1.5	0.8	769.5	0.57
Coastal	SD		3.8	110.8	454.5	594.0	174.0	0.8	1.7	0.5	0.4	332.0	0.30
	median		8.8	107.2	374.1	815.1	249.6	0.3	2.7	1.4	0.2	759.9	0.66
Marine Air/	mean	24	8.3	118.2	280.6	309.4	118.6	0.7	3.6	1.1	0.6	1373.9	0.78
Open Ocean	SD		4.6	173.1	243.0	304.4	111.8	1.1	2.6	0.5	0.4	958.5	0.19
	median		8.9	52.8	186.0	238.9	85.8	0.3	2.7	1.0	0.5	1032.1	0.84

N = number of samples; SD = standard deviation.
EF(Cl) = chloride enrichment factor (see text).

increased from 25 to 1490 ppt and 192 to 1340 ppt, respectively.

Both the MSA concentration and the MSA/nss-SO_4^{2-} ratio showed maximum values on 28 April (20 ppt and 0.11, respectively). These values were reached approximately half a day later than the DMS maximum suggesting in situ production of MSA from atmospheric DMS oxidation. However, another strong increase of the MSA concentration occurred between 29–30 April. Our data do not lend an obvious explanation for this case since DMS levels were considerably lower than during the previous days whereas SO_2 and nss-SO_4^{2-} levels were high due to prevalent continental air over the study area. Overall, the total MSA data obtained from cruises I–IV were not significantly correlated or anticorrelated with the results obtained for any of the other measured compounds, including DMS. One exception are perhaps the MSA values from cruise II obtained in marine air which indicate a weak correlation with nss-SO_4^{2-} ($r^2 = 0.82$, $n = 4$). Previously, Church et al. (1990) also reported a weak, but significant correlation with nss-SO_4^{2-} ($r^2 = 0.62$, $n = 8$) observed on their spring cruise. We found no significant differences between total average MSA concentrations in marine and continental air masses (Table 3). However, MSA/nss-SO_4^{2-} ratios were clearly higher in marine air masses because of relatively lower nss-SO_4^{2-} levels. These results suggest that the yield of MSA from DMS oxidation is similar in both types of air masses over the WNAO.

NH_4^+ and NO_3^- concentrations were generally higher in continental air with the exception of nitrate levels in spring (Table 3). On the other hand, NH_4^+/nss-SO_4^{2-} ratios were similar in both air masses due to a positive correlation between both compounds (marine air: $r^2 = 0.87$, $n = 32$, slope: 0.7; continental air: $r^2 = 0.48$, $n = 30$, slope: 1.0). The mean molar ratio of 1.2 (Table 3) indicates that aerosol particles were moderately acidic with both compounds mainly associated as ammonium bisulfate. The differences between nitrate levels in both air masses were much smaller compared to ammonium. NO_3^-/nss-SO_4^{2-} ratios were essentially the same in both air masses. Correlations between nitrate and nss-sulfate were weak (marine air: $r^2 = 0.11$, $n = 25$, slope: 1.0; continental air: $r^2 = 0.26$, $n = 26$, slope: 0.8). Nitrate concentrations in marine air were about a factor of 4–5 higher than over the remote South Pacific (Prospero and Savoie, 1989). This suggests that an anthropogenic (or continental) signal exists not only for nss-SO_4^{2-} but also for NO_3^- in North Atlantic "background" air.

3.4.2. Seasonal variation. As shown in Table 3, SO_2 and aerosol data have been categorized primarily by air mass character. A secondary classification was made by season. Since the number of data assigned to each seasonal sub-category is relatively small the discussion of the data in this section implies relatively large uncertainties and the conclusions should be regarded as preliminary. We have performed *t*-tests for the individual mean concentrations and concentration ratios listed in Table 3 to test if the corresponding seasonal differences are significant. The differences were considered to be significant if the confidence level was 95% or higher. In this and the next two sections all aerosol data are reported as total (fine + coarse mode) concentrations. Our results can be summarized as follows:

MSA concentrations in predominantly marine air decreased significantly to a minimum in mid-fall (cruise I). On the average, maximum concentrations were observed in spring (cruise III). However, *t*-tests showed that spring values were not significantly different from corresponding results obtained in winter (cruise II) and late summer/early fall (cruise IV). This lack of statistical significance is probably due to the low number of data available from the spring and winter cruises. MSA concentrations also showed a springtime maximum in predominantly continental air. Corresponding MSA levels during the other seasons were significantly lower and showed no clear variation.

SO_2 concentrations in predominantly marine air increased from late summer/early fall to a maximum in late winter and showed a minimum in spring. Since marine "background" SO_2 levels over the Atlantic possibly include an anthropogenic signal (as discussed earlier) the observed maximum of SO_2 levels in winter may be linked to elevated use of fossil fuels for heating. No wintertime maximum was found for SO_2 in predominantly continental air. In this category, SO_2 concentrations measured in spring were significantly higher than in winter. However, in spring most of the SO_2 samples collected from this

type of air mass had been obtained over coastal waters (67%; 12 samples). The corresponding fraction of samples obtained over coastal waters during the winter cruise was only 44% (4 samples). Since SO_2 concentrations in this air mass category were significantly higher over coastal than open ocean areas (see next section) the springtime SO_2 data for this category appear to be overweighted in Table 3 relative to the winter data.

Nss-SO_4^{2-} concentrations in predominantly marine air showed a more complex seasonal variation than the corresponding SO_2 data. No correlation was found between individual SO_2 and nss-SO_4^{2-} concentrations measured in this air category ($r^2 = 0.00$). On the other hand, the corresponding median concentrations given in Table 3 suggest that both compounds show a significant decrease from winter to spring. There was also virtually no correlation between individual nss-SO_4^{2-} and SO_2 levels in predominantly continental air ($r^2 = 0.22$). However, the corresponding statistical data in Table 3 suggest that both compounds follow a similar seasonal pattern in this air category. Again, the lack of statistical evidence for a correlation between both compounds may be due to the relatively low number of data available.

MSA/nss-SO_4^{2-} molar ratios did not show a significant seasonal variation in predominantly marine air. Corresponding ratios showed a total range over all measurement periods between 0.005–0.11 bracketing springtime values reported by Church et al. (1990) for the WNAO (0.02–0.03). This is further evidence that in marine "background" air biogenic sulfur emissions make a significant contribution to the atmospheric sulfur budget in the WNAO boundary layer. On the other hand, since the mean MSA/nss-SO_4^{2-} ratio obtained in this study (0.033) is approximately two times lower than the corresponding mean ratio (0.067) reported by Saltzman et al. (1983) for the North Pacific Ocean it also indicates the relatively higher impact of anthropogenic emissions on marine "background" nss-SO_4^{2-} levels over the Atlantic compared to the Pacific Ocean. No significant seasonal trend in MSA/nss-SO_4^{2-} ratios was observed in predominantly continental air.

NH_4^+ concentrations in predominantly marine air showed a clear maximum in late summer/early fall and a significant decline in mid-fall and late winter consistent with the mostly biogenic origin of ammonia. Since ammonia is believed to be mainly emitted from continents the observed seasonal variation illustrates the relative importance of continental contributions to marine "background" air over the WNAO. However, ammonia is also emitted from oceans (Quinn et al., 1988; Andreae et al., 1988). Our results do not permit a distinction between the relative contributions of continental and oceanic sources to the observed seasonal cycle of NH_4^+ in marine "background" air. NH_4^+/nss-SO_4^{2-} ratios generally followed the seasonal cycle of NH_4^+ in both air mass categories. (It should be emphasized here that in Table 3 the mean annual NH_4^+/nss-SO_4^{2-} ratio calculated for the "continental" air category represents a lower limit since data obtained from cruise IV were not included in the calculation; see footnote, Table 3).

Both aerosol nitrate and NO_3^-/nss-SO_4^{2-} ratios showed a weak seasonal trend in predominantly marine air. As indicated by the data in Table 3 the highest values and a maximum correlation between both compounds were observed in spring ($r^2 = 0.86$, $n = 5$). Prospero et al. (1989) also observed only a weak seasonality in nitrate and nss-sulfate concentrations on Bermuda during easterly wind conditions. Our results show a relative concentration maximum in spring for predominantly continental air. Based on data by Prospero et al. (1989) it can be assumed that for this air category mid-summer nitrate levels over the WNAO may even be higher than the springtime values measured in this study.

3.4.3. Regional variation. Table 4 shows annual average statistics for aerosol sulfur and nitrogen species categorized by air mass and biogeographical region (estuaries, coastal waters, and open ocean waters). Mean MSA values showed no significant variation between these regions. SO_2, nss-SO_4^{2-}, and NH_4^+ levels were significantly lower during easterly wind conditions than during advection of predominantly continental air by westerly winds. For the latter air category the data in Table 4 show a strong negative concentration gradient for SO_2 between estuary, coastal, and open ocean areas indicating progressive SO_2 oxidation and/or deposition during air mass transport. This is also illustrated by the corresponding decrease of SO_2/nss-SO_4^{2-} ratios given in Table 4. SO_2 and SO_2/nss-SO_4^{2-} ratios decreased further in

predominantly marine air reaching open ocean "background" levels.

Table 4 shows similar spatial gradients for NH_4^+ and $NH_4^+/nss\text{-}SO_4^{2-}$ ratios in both air mass categories illustrating the progressive acidification of sulfate particles due to SO_2 oxidation and decreasing ammonia levels. It can be noticed from Table 4 that even during easterly wind conditions the concentrations of SO_2, $nss\text{-}SO_4^{2-}$, NH_4^+, and NO_3^- were significantly higher over coastal areas than over the open ocean. This indicates a relatively stronger continental signal in marine "background" levels of these compounds over coastal areas, probably because of the importance of regional (land/sea breeze system) and mesoscale wind circulations near the coast.

NO_3^-, unlike NH_4^+ and sulfur compounds listed in Table 4, showed a slightly positive concentration gradient in predominantly continental air between estuary, coastal, and open ocean areas. Church et al. (1990) also found relatively higher nitrate levels over the open North Atlantic than near the US east coast. Our Na^+ data in Table 4 further indicate a positive gradient for sea salt particle concentrations between these regions. Since aerosol NO_3^- occurred predominantly in coarse size ($>1.5\ \mu m$ diameter) sea salt particles, one explanation for the observed increase in nitrate levels may be the progressive uptake of nitric acid vapor by alkaline sea salt and the overall increase of sea salt particle concentrations with distance from the coastline. Previously, it has been hypothesized that this absorption process causes a loss of chloride from sea salt particles due to volatilization of hydrogen chloride (e.g., Brimblecombe and Clegg, 1988). Consistent with this hypothesis, the chloride enrichment factor EF(Cl), defined as the quotient between the concentration ratio $(Cl^-)/(Na^+)$ in aerosol and the same ratio in seawater, was found to be significantly lower in air advected from the continent compared to predominantly marine air over the study area (Table 4).

3.4.4. Diel variation. Separate aerosol samples were taken during daytime and nighttime. The respective sampling integration times were typically on the order of eight hours. The corresponding data were grouped accordingly into daytime and nighttime data, and the respective mean values and standard deviations for each aerosol compound were calculated for each of the two major air mass categories. The results are shown in Table 3. On the average, in neither of the two categories did any of the measured compounds and concentration ratios show a significant diel variation. This does not mean that corresponding diel variations did not exist, however, they may have been mostly obscured by atmospheric transport phenomena, e.g., advection of air masses from different marine or continental source regions. Also, the relatively long sampling integration times used in our study may have prevented the detection of such variations.

3.4.5. Size distribution of aerosol compounds. Both aerosol MSA and NO_3^- showed a significantly different size distribution in the two air mass categories considered in this study. In predominantly continental air, on the average $74 \pm 11\%$ of the MSA and $13 \pm 12\%$ of the nitrate was found in particles with less than $1.5\ \mu m$ diameter (fine particle mode). The corresponding fractions in marine "background" air were $57 \pm 16\%$ and $5 \pm 5\%$, respectively. $Nss\text{-}SO_4^{2-}$ size distributions were similar in both types of air mass. The same similarity was observed for corresponding NH_4^+ size distributions. The average fine particle fractions for both compounds were $77 \pm 17\%$ and $78 \pm 22\%$, respectively. Our conclusions are: 1. Aerosol MSA, $nss\text{-}SO_4^{2-}$, and NH_4^+ occurred predominantly in fine particles. NO_3^- occurred predominantly in coarse particles. 2. The fine particle fraction of MSA and NO_3^- was higher in the "continental" than in the "marine" air category. This was probably due to higher scavenging rates of gaseous MSA and HNO_3 in marine air containing relatively higher concentrations of coarse, alkaline sea salt particles. In contrast, $nss\text{-}SO_4^{2-}$ and NH_4^+ showed similar size distributions in both types of air mass, respectively. 3. The fine particle fraction of MSA in marine "background" air was significantly lower than that of $nss\text{-}SO_4^{2-}$. This difference was not found in predominantly continental air.

3.5. DMSO, MSA, and other species in rainwater

Rainwater was sampled on an event basis during cruises I and IV. The samples were analyzed for sulfur, nitrogen, and carboxylic acid species. The results are shown in Table 5. The data set is

relatively small. Therefore, our discussion will be mainly focussed on one interesting case study based on the results obtained for DMSO and MSA between 3–4 September, 1986 (cruise IV, samples IV–1 through IV–4), and simultaneous observations of DMS in the atmosphere (Fig. 2a). The corresponding rain samples were taken during light to moderate precipitation which started on 3 September and continued until late afternoon of the following day. The rain was caused by a squall line passing through the sampling area in connection with a low pressure system centered over the Sargasso Sea. The mean wind direction changed from east to southwest during this period. A study of the corresponding rainwater data (Table 5) shows that the concentrations of all measured compounds (except for NH_4^+) increased significantly from the onset of the rain in the early afternoon (sample IV–1) until late at night (sample IV–2) and, in the case of pyruvate, the following morning (sample IV–3). Thereafter concentrations dropped sharply, and relatively low values were measured again during the final phase of the rain event (sample IV–4). DMSO was not determined in the last two samples. However, it can be assumed with reasonable certainty that DMSO concentrations in rain continued to follow the pattern observed for MSA and the carboxylic acids during this particular event. There are at least three seasons to support this assumption: (1) All of the measured compounds, including DMSO, are predominantly biogenic compounds. (2) The general time pattern of the results obtained for this rainfall event does not reflect a simple decrease of concentrations in subsequent samples due to continuous wet removal of the individual compounds from the atmosphere. Instead, maximum values were reached *during* the rain event suggesting changes in the source function of the individual compounds. This is consistent with the described changes in wind direction and corresponding advection of air from different source regions (possibly the Gulf Stream area) containing higher concentrations of the individual species. (3) Both DMSO and MSA are oxidation products of DMS. The time pattern for both compounds during 3–4 September was very similar (although somewhat out of phase) to that of atmospheric DMS concentrations (Fig. 2a). DMS levels increased by a factor of five from approximately 40 pptv at 1000 EST (3 September) to a maximum of 205 pptv at 1000 EST (4 September). DMSO levels in rainwater also increased by a factor of five, MSA levels increased by a factor of two. After reaching the corresponding maximum values both DMS and rainwater MSA concentrations decreased relatively smoothly (Fig. 2a; Table 5). DMSO and MSA concentrations measured in rainwater were generally consistent with the results reported by Pszenny et al. (1990).

Table 5. *Concentrations (in μmol/l) of various compounds in rainwater samples*

Sample	Sampling time	DMSO	MSA	Nss-$SO_4^=$	NH_4^+	NO_3^-	100 * MSA/ Nss-$SO_4^=$	NH_4^+/ Nss-$SO_4^=$	NO_3^-/ Nss-$SO_4^=$	Fo	Ac	Py	Fo/Ac
I–1	2 Oct., 1640–1850	NA	0.08	1.5	1.9	7.1	5.4	1.3	4.7	2.4	0.9	NA	2.7
I–2	3 Oct., 1545–1600	NA	0.02	4.8	3.6	7.2	0.4	0.7	1.5	1.4	NA	NA	—
I–3	8 Oct., 1100	NA	0.09	2.4	DL	DL	3.9	—	—	0.7	0.3	NA	2.4
IV–1	3 Sep., 1430	0.005	0.10	0.5	1.2	5.6	19.2	2.4	11.2	1.5	1.3	0.04	1.2
IV–2	4 Sep., 0200	0.021	0.19	2.2	1.2	36.1	8.7	0.5	16.4	2.3	1.7	0.08	1.4
IV–3	4 Sep., 1100	NA	0.19	1.9	DL	DL	9.8	—	—	2.0	1.7	0.12	1.2
IV–4	4 Sep., 1730	NA	0.07	−0.8	DL	DL	—	—	—	0.4	0.5	0.01	0.8
IV–5	6 Sep., 1040	NA	0.17	6.1	2.7	7.2	2.7	0.4	1.2	2.7	2.6	0.12	1.0
IV–6	6 Sep., 1245–1500	NA	0.12	3.4	1.7	7.1	3.6	0.5	2.1	3.0	2.3	0.04	1.3
IV–7	6 Sep., 1715–1750	NA	0.06	2.8	1.6	4.7	2.2	0.6	1.7	1.4	2.3	0.04	0.6
IV–8	8 Sep., 0300–0900	NA	0.08	33.2	11.1	38.3	0.2	0.3	1.2	8.6	6.8	0.40	1.3
IV–9	11 Sep., 1030	NA	0.22	8.6	9.8	6.0	2.6	1.1	0.7	3.0	2.9	0.37	1.0

NA = no data available; Fo = formate, Ac = acetate, Py = pyruvate.
DL = detection limit (= 0.1 μmol/l for NH_4^+ and NO_3^-, respectively).
Times are approximate.

4. Conclusions

(1) The boundary layer atmosphere over the WNAO is impacted by continental air during all seasons.

(2) We estimate the biogenic DMS/sulfur flux to the WNAO atmosphere to be approximately 0.1 Tg S/yr (upper limit: 0.3 Tg S/yr). Under prevailing westerly wind conditions this makes up only 3% of the continental input of sulfur from North America. However, oceanic DMS emissions may dominate the sulfur budget over the WNAO during easterly wind conditions.

(3) DMS concentrations in surface seawater increased from late winter through late summer/early fall with a relatively stronger amplitude in open ocean than coastal waters. The DMS flux from the open ocean WNAO area showed a similar seasonal variation with low values in winter (1 μmol/m^2/d) and high values in late summer/early fall (5–10 μmol/m^2/d). The annual average flux was estimated to be 3.4 μmol/m^2/d. DMS emissions from coastal waters peaked between winter and spring.

(4) SO_2 and nss-SO_4^{2-} concentrations varied strongly with air mass origin (lower pptv to lower ppbv range in predominantly marine and continental air, respectively). No correlation was found between SO_2 and nss-SO_4^{2-} concentrations. On the other hand, a strong SO_2 gradient between estuary, coastal, and open ocean areas was observed indicating progressive oxidation and/or deposition of SO_2 during transport from North America over the WNAO.

(5) The MSA data indicated a slight maximum in spring. Overall, however, MSA concentrations showed little seasonal variation. Also, no significant differences were observed between mean MSA levels in polluted and relatively unpolluted air. The yield of MSA from DMS oxidation may be similar in both types of air over the WNAO. MSA/nss-SO_4^{2-} ratios were relatively higher in marine "background" air (max.: 0.11) than in predominantly continental air.

(6) NH_4^+ concentrations and NH_4^+/nss-SO_4^{2-} ratios showed a clear seasonal variation with a maximum in late summer/early fall and a minimum in late winter. Oceanic ammonia emissions may be important for marine "background" levels of ammonia and NH_4^+ over the WNAO. NO_3^- concentrations showed a relatively weak seasonal variation with the highest values observed in spring. Even higher levels may prevail in midsummer.

(7) The fine particle (<1.5 μm diameter) fractions of MSA, nss-SO_4^{2-}, NH_4^+, and NO_3^- in predominantly marine air were 57%, 77%, 78%, and 5%, respectively. Aerosol particles were moderately acidic, based on NH_4^+/nss-SO_4^{2-} ratios between 1–2 mol/mol.

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